Physical and chemical methods of soil and water analysis

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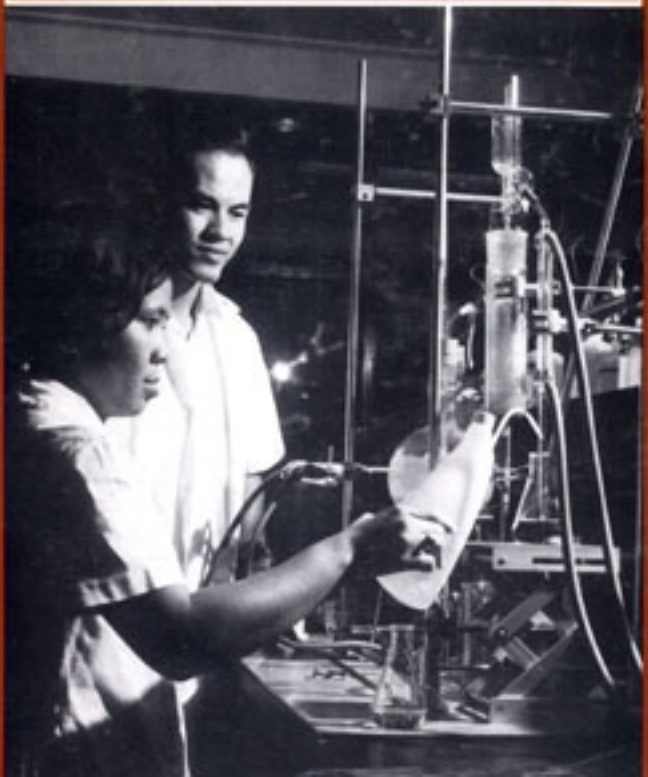
SOILS
BULLETIN

10



FOOD
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CORRIGENDA

Page viii: In Note 2, insert fullstop after "report papers"; continue "Full details of these books, bibliographies and journal or report papers are given in..."

Page 6: Lines 15-16, insert fullstop after "deionization"; continue "A high degree of hardness affects both distillation and deionization, producing deposits...."

Page 7: Line 31, for "tape" read "taps".

Page 29: Line 31, for "II.3.D.", read "II (p.255)".

Page 30: Line 36-37; insert fullstop after "table"; continue "In general, the number of columns of results in a table should not exceed 10-12."

Page 33: Line 9, for "Unland", read "Uhland".

Page 34: Line 21, for "B", read "V".

Page 42: Line 21, for "hera-" read "hexa-"
Line 33, for "to (remove cabonates)" read "(to remove carbonates)".
Line 37-38, delete "thus the solution is 0.5 N as sodium carbonate."
Exchange the last two paragraphs.

Page 43: Line 48, "Brush" and "Small porcelain basins" are separate items.

Page 45: Lines 27-28, for "to regard" read "regard to".

Page 50: Line 37, insert "(ii)" before "Calculate..".

Page 54: Equation (3) should read "$X = \frac{Q}{\sqrt{T}}$ "
Line 20, for "(put to 50)" read "(up to 50)".

Page 55: Line 10, should be "T = 2.5 C if 40 g oven-dry soil is used".

Page 59: Line 9, for "iin" read "tin".

Page 62: Line 37, delete "these".

Page 67: Line 7, insert after "... 1 N potassium chloride" the words "to soil is altered; but, with 0.01 M calcium chloride, the pH value.."

Page 69: Line 4, for "$\frac{KKV}{100}$" read "$\frac{KV}{100}$"

Page 72: Line 11, should read: "or $\frac{5(25 - T)}{Q}$ per cent"

Page 76: Line 14, for "3.3" read "3.53".

Page 80: Line 16, for "See" read "Set".
Line 43, after "(i)" insert the heading "After Macro Digestion"

Page 81: Line 4, should read "...to the neutral point of the mixed indicator".

.../...

XI/A2060/2

Page 91: Line 22, for "ration" read "ratio".

Page 109: Line 34, for "10" read "to"

Page 132: Line 47, insert "ml" between "10" and "ammonium".

Page 135: Line 4, for "and" read "an".

Page 149: Line 3, insert "to" at end of line.

Page 166: Insert "(2)" before the second paragraph under 13-2.F. NOTES.

Page 167: Line 25, delete "neutral".
Line 32, delete "netural".

Page 168: Line 3, delete "neutral".
Line 34, delete "pH 7.0"
Line 35, delete "Check the pH"
Line 38, change "1N" to "0.5N"
Line 39, change "42" to "21"

Page 169: Line 23, change "10 ml of 1 N" to "20 ml of 0.5 N".

Page 185: Line 19, for "must be" read "becomes".
Line 25, for $Na_3H_2IO_6$" read "$Na_3H_2IO_6$".

Page 196: Line 28, for "if" read "of".

Page 197: Line 12, for "any" read "either".

Page 206: Line 19, for "500 ml to 600 ml beaker" read "500 ml to a 600 ml beaker".

Page 212: Line 39, for "or" read "of".

Page 222: Line 17, for "or" read "of".

Page 238: Line 1, for "sulpahte and sample", read "sulphate and samples".

Page 243: Line 4, for "k_2HgI_4" read "K_2HgI_4".

Page 250: Line 7, for "or" read "of".

Page 260: Lines 3 and 10, for Phathalate" read "Phthalate".

Page 265: Line 31, insert "and" between "M" and "allow".

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AUTHORS' PREFACE

An analyst asked to determine a particular constituent in a soil or water sample or to evaluate a precise property, such as cation exchange capacity, usually has a variety of methods from which to choose. Published collections of soil and water analyses offer the most common and popular techniques; while scientific journals contain alternative procedures which individual analysts or groups of analysts have found more suited to certain soil types or more accurate or more rapid in operation without loss of accuracy. Furthermore, the science of soil and water analysis is being continually advanced by the work of Agricultural Research Stations, Soil Institutes, Government Laboratories, University Departments of Agriculture and private firms in many countries. Thus the variety of methods available to an analyst for any one determination is often quite wide and choice of which technique to use difficult.

In this Guide we have included methods of analysis which we consider suited to soil and water laboratories recently or presently established in developing countries. We suggest that the majority of the determinations could form the initial basic routine of such a laboratory, with selection where necessary to suit particular classes of soils. In choosing methods and procedures we have been influenced by some years' experience in various countries, under different working conditions. We have assumed that present-day soil and water laboratories in most developing countries are equipped with modern instruments for weighing, shaking, heating, providing suction or pressure under controlled conditions, measuring the spectral absorption properties of solutions and the emission properties of flames and so on; but we have not included methods based on the use of instruments which are, now, relatively more expensive. This state of affairs will undoubtedly change and, for instance, atomic absorption spectrophotometry will soon be used in routine work, particularly for elements like magnesium.. It is hoped, however, that the techniques presented are neither too advanced for laboratories established some years ago nor too out-of-date for laboratories now being planned.

The Guide has been written on the assumption that its readers have a basic knowledge of soil science and related fields in analytical chemistry and practical physics. No doubt the principles involved will need more explanations in some cases, but this is left to individual soil chemists in charge of training who can adjust their instructions to the needs of their staff.

We shall be grateful if readers will send us suggestions for improvement or comments on their experience with any of the techniques advocated, particularly on the soils of developing countries.

INTRODUCTION

In all the 117 member countries of FAO agricultural and other research is being carried out and the field activities of FAO and UN Agencies and of many national organizations are designed to facilitate, strengthen and make more effective the practical application of our knowledge in the general process of development. This work involves a large number of institutes and laboratories which use, for similar purposes, very different methods of investigation and analysis, the results of which cannot normally be compared directly and easily. Coordination and standardization would obviously facilitate matters, save precious time and make results and conclusions useful for much larger regions of the world than is the case now. To take steps in this direction is obviously one of the functions of international organizations.

Soil research and soil testing laboratories spread all over the world are typical of the situation described. Their purpose is practically the same everywhere but the analytical methods employed vary widely and direct comparison of results from one laboratory to another or from one country to another is often difficult or even impossible. In order to obtain basic information on the actual situation concerning types of soil laboratories and analytical methods, FAO made a world-wide survey and the results are published in Soil Bulletin No. 2, entitled "A Survey of Soil Laboratories in Sixty-Four FAO Member Countries". Among much useful information, this survey brought out clearly which of the analytical methods are being used on the widest scale. Methods varied with climatic regions and, therefore, with soil groups, as was expected; and it is recognized that variations in analytical procedures of this type are inevitable and fully justified. Related information from the survey also showed how a greater uniformity of analytical methods and more standardization and coordination is practically feasible in the future.

The present publication is a practical guide in soil and water analysis which includes all those methods which, according to the FAO survey, are employed most widely. Laboratories following these methods will, in the end, belong to a large group "talking the same language" and comparing their results directly. Explanations, descriptions, procedures and calculations of results are arranged systematically in easy language so that this guide can be used by laboratory personnel with a wide range of educational level. Also basic values and factors needed for calculating results are given in each method so that no extra books and tables are normally required, although some exceptions could not be avoided.

This Guide, together with FAO Soil Bulletin No. 3 ("Guide on General and Specialized Equipment for Soil Laboratories"), should be valuable for budgeting, designing and operating a modern soil and water analytical laboratory with up-to-date methods suitable for most developing countries.

GENERAL NOTES

1. Throughout this Guide, the word "water" has the meaning "distilled or deionized water of low conductivity, in equilibrium with clean air".

   (see Section I.3-1.B.)

2. At the end of Section I and at the end of each method in Sections II, III and IV, references are listed, quoting books (by the name of the author(s) or editor) and bibliographies and journal or report papers are given in the "List of References" at the end of the Guide.

I. I. LABORATORY FACILITIES

1-1. GENERAL DESIGN - AIR CONDITIONING.

Laboratories for soil and water analysis do not usually conform to a standard design because requirements vary from place to place throughout the world. Nevertheless, it is possible to offer recommendations to soil scientists and architects who are cooperating to create a laboratory fitted for all the physical and chemical analyses described in this Guide. These recommendations can be modified for smaller laboratories of limited scope but the main principles involved should not be ignored.

1. The general building lay-out should normally consist of two separate blocks -

   (a) A Scientific Block, for analytical determinations, staff training and administration.

   (b) A Storage Block, for receipt, preparation and storage of samples, which, in case of soils, inevitably involves the danger of contamination of other material.

   Transport of prepared soil samples to the scientific block should be through a passage or buffer room or, if the blocks are on two levels, by means of a service elevator. There should not be direct connection (simply through a door) between a room in which soils are being ground and a room in which analyses are being done.

2. The scientific block may take various forms but an ideal building would contain separate groups of laboratories as follows -

   (a) Laboratories for preliminary operations on soils, involving (say)

      i. weighing of samples for analysis, including sub-sampling an and fine grinding where necessary (in a separat room),

      ii. oven drying,

      iii. extraction, ignition or oxidation for some analyses.

   (b) Laboratories for the physical examination of soils by the methods of Section II.

   (c) Laboratories for general chemical processes involving the use of concentrated acids or alkalies or ammonia, where fumes may be evolved, even if these operations are conducted (as they should be) under fume hoods and the room is air-conditioned.

   (d) "Clean" Laboratories where instruments can be used without danger of being affected by fumes or adverse atmospheric conditions (see (see I.2-4.); this includes the traditional "balance room" (which need not be restricted to balances) and rooms for specialized purposes such as ammonia micro-distillation and certain processes in minor element analysis.

(e) Rooms for preparation and storage of distilled and/or deionized water on a large scale, for general washing and drying of laboratory ware, for repair of instruments and for glass-blowing and construction of apparatus.

The groups of laboratories (c) and (d) should be so arranged and equipped that no soil samples need be taken into them, except those already weighed for analysis and contained in covered vessels (see I.4-3). Although it may be convenient to carry out all the stages of an individual analysis in one room, this often conflicts with the need to keep delicate instruments away from dust, fumes and vibration and frequently leads to unnecessary duplication of equipment.

A separate group of rooms should also be provided for office administration, filing of records, staff meetings and theoretical training, reception of visitors, medical treatment and so on.

3. The storage block should consist of a minimum of three rooms for -

(a) receipt and registration of all samples (soil and water), with areas of bench and shelf space sufficient to deal with the expected input,

(b) grinding and sieving of soil samples, with measures to remove dust from the air,

(c) storage, both before and after analysis, with adequate shelf space.

In addition, in many countries some form of accelerated drying of soil samples may be required and a suitable room should be provided.

4. Rooms should be set aside for the unpacking and the systematic and orderly storage of maintenance supplies of apparatus and chemicals, with the special precautions usually demanded by law for poisons and inflammable material. These storage rooms may either be located in the scientific block or the storage block, although it is usually more convenient to site them together with rooms for soil preparation and storage. In this case, high grade chemicals must be adequately protected from contamination.

5. The design of laboratory benches and the arrangement of fittings for water and drainage, electricity and gas (and vacuum and compressed air in large laboratories) should be standardized throughout the scientific block. The materials used in construction should be immune to attack by chemicals as far as possible (see I.2-2 and 2-3).

6. The whole building should be equipped with fire extinguishers for the control of small fires. The advice of the local fire prevention authorities should be sought in the choice and siting of equipment and all staff should know how to use the extinguishers in emergency.

7. First aid equipment should be available for dealing with minor injuries to staff through cuts, burns, skin damage from chemicals, electrical shock, asphyxiation and so on. One or two staff members should have some knowledge of first aid and be held responsible for maintaining medical supplies in good order. The addresses and telephone numbers of doctors and hospitals should be displayed or be easily accessible for emergency calls on their services.

8. The air temperature of the laboratory and working rooms should ideally be maintained at a constant level (usually between 18 and 25°C.) and the humidity should also be kept reasonably steady at about 50 per cent. In many tropical countries air conditioning of the whole building is virtually as essential as central heating in cold and temperate countries; while, in countries having a continental climate of hot summers and co cold winters, both air cooling and central heating are necessary.

The importance of supplying clean air, at a constant favourable temperature and humidity, to all parts of a scientific laboratory building is too often neglected in the interests of economy, particularly in tropical countries where the seduction of temperature and humidity on a large scale during hot seasons may be costly. However, if some form of central air-conditioning control is not provided, the efficiency of the work done is bound to be reduced and other expenses incurred through the following factors -

(a) Analytical processes normally carried out at room temperature can be affected by differences in this temperature so that an analysis performed in a "cold" room can give a different result to one performed in a "hot" room. For example, the extraction of soils is often so affected (see Section III.12-1.). Control of temperature is possible on a small scale by the use of thermostatic water baths but this is usually impracticable for large scale routine operations. Temperature corrections can, of course, be applied in some cases but these may be inaccurate for wide differences.

(b) Many chemicals are affected by the temperature and humidity conditions under which they are stored, particularly if these condition fluctuate. Thus, a substance may absorb water from humid air or effloresce in dry air or decompose at high temperatures, becoming either useless or needing purification. (see I.3-1.).

(c) Modern scientific instruments can be quickly and permanently damaged by changes in temperature and humidity, which often cause condensation, tarnishing and short-circuits (see I.3-1.).

(d) The efficiency of all laboratory workers is undoubtedly reduced by abnormally high or low temperatures or high humidity and by the presence of even moderate amounts of dust or chemical fumes in the air, thus affecting output both in quantity and quality.

(e) The use of apparently cheaper alternatives to central control of air conditions, such as individual cooling units or heaters in each room or - to reduce temperature - fans or blinds on windows facing the sun or ingenious use of natural breezes by careful architectural design is only partially effective and may even aggravate the disadvantages of absence of control. Almost inevitably, corridors, storerooms, little-used rooms and, often, soil preparation rooms are ignored and this may lead to wide differences of temperature and humidity between such places and analytical laboratories, which is most undesirable. For instance, the air-dry moisture in a soil sample taken straight from a hot and humid storeroom (or a very cold one) may be quite different from that in a similar sample kept in an air-conditioned laboratory; yet both may be weighed for analysis at the same time as "air-dry" samples. Again, the literature often speaks of the effects of storage on the results of analysis of soil samples (see Sections I.4-3 and III.11.); this "storage effect" may vary with temperature and humidity.

1-2. ELECTRICITY - WATER AND DRAINAGE - GAS SUPPLY

A constant supply of electricity at a steady voltage is essential in any modern laboratory employing electronic instruments, electric heating devices and apparatus for shaking and stirring and supplying compressed air and suction based on the lectric motor. Small field laboratories of limited (but nevertheless useful) scope can be designed to operate from a portable gas supply (for heating) and from battery-driven transistorized instruments; but a laboratory for the methods of analysis given in this Guide needs mains electricity.

The design of the mains wiring depends on local arrangements but a safe and reliable system should conform to the following regulations -

1. The main cable should be capable of carrying the full current needed to run all the electrical apparatus at the same time and have the appropriate size of main switch and fuse, with an ample safety margin to allow for the introduction of further apparatus.

2. Rooms or groups of rooms should have their own subsidiary switches and fuses so that a fault in one place does not affect the whole building.

3. An adequate number of points should be provided in strategic positions throughout the laboratories so that apparatus can be used there it is wanted without having to be connected to the electricity supply by long lengths of flex. Ideally, each piece of electrical apparatus should be individually fused at the point, even if a fuse is provided in the instrument itself.

4. Two or three pieces of apparatus (particularly those using large currents) should not be connected to one electric point by means of two- or three-way adapters unless it is certain that the cable to that point (and its fuse) can deal safely with the combined current.

5. Earthing or grounding of all electrical apparatus is advisable for safety and this practice often leads to more efficient operation of electronic equipment. Some mains supply circuits contain a third wire for this purpose and this is adequate in most cases, although delicate instruments may still need a direct connection to earth. Apparatus connected to a two-wire system of electricity supply should be earthed separately. When apparatus is supplied with a three-wire cable, the colour coding of the insulation should be checked before attaching to the mains supply, as different countries may employ different colour systems.

6. All electric wiring should be reliably protected from chemical liquids and fumes, particular attention being paid to the maintenance of flexible cables (from apparatus to point) in good condition.

7. If the mains electricity supply normally fluctuates, a voltage stabilizer should be included in the circuits to electronic instruments and other apparatus which might give inaccurate performances through voltage variation.

The tap water supplied to a laboratory for soil and water analysis should be entirely free of pollution, as free as possible from insoluble matter and under a good and steady hydrostatic pressure. It may be necessary to

filter the supply to certain pieces of equipment (see deionization below). A main stopcock should be provided at the entry point of the water supply, insulated against freezing in countries with cold seasons; and a number of subsidiary stopcocks should be fitted to control supplies to individual rooms or groups of rooms (see point (2) above, on electricity). The positions of all these stopcocks should be easily accessible and known to the laboratory staff so that water can be turned off quickly if there is danger of flooding, an important consideration in buildings with more than one floor.

Drainage should be to a main drain if possible or to good-sized "soakaways". Effluents from soil laboratories contain considerable quantities of waste soil in addition to acid and alkaline liquids; this, not only should acid and alkali proof fittings be employed but also facilities should be provided in the design of the drainage system for periodic cleaning and removal of solid matter.

The supply of gas for heating or for specific pieces of apparatus such as a flame photometer or a blowpipe for glass working can be either from a central generating plant or from individual gas bottles or cylinders (assuming that there is no town gas supply). Selection depends on the requirements of each laboratory and on the availability of supplies. Where a central generating plant is set up, main and subsidiary stopcocks should be provided, in addition to the bench gas taps, for adequate safety control.

1-3. DISTILLED AND DEIONIZED WATER.

Present-day laboratories have the choice of making "pure" water for analytical purposes either by the traditional distillation process or by the modern technique of deionization (or demineralization) with cation and anion exchange resins. Both processes, when efficiently operated, can produce water of very low conductivity, virtually free from salts or any of the elements for which soils and waters may be analysed. However, the production of this high quality water may not be necessary for general purposes and usually two or three grades may be provided in differing amounts.

The following factors govern the choice of apparatus for making "pure" water in a laboratory -

1. Distillation consumes electricity or fuel for heating in large quantities and needs much cooling water, which usually runs to waste. Economic operation of water stills is only possible if the supply of electricity (or other fuel) and water is plentiful and cheap. The large-scale production of distilled water in arid countries or countries with seasonal shortages of water should only be undertaken if the cooling water can be used for other purposes.

2. Deionization involves no loss of water and no fuel is used. Exhausted resins can be either replaced by new stocks purchased from laboratory suppliers or regenerated by treatment with acid and alkali, at little cost.

3. Distillation, which involves heating, means that the water produced may contain traces of the metals or other substances used in the manufacture of the apparatus. Thus distilled water from metal stills often contains copper or zinc and that from borosilicate glass stills may contain borate ion; both may have conductivities near 5 micromhos. This grade of water may, however, be quite suitable for general laboratory purposes (e.g. rinsing glassware) and for certain analyses (e.g. physical determinations on soil). Double or triple distillation in all-glass stills produces higher quality water, free of metals and

with a conductivity of about 1 micromho; but this water may contain traces of borate.

4. Deionization mostly produces water of low conductivity (1-2 micromhos) and a second deionization can reduce the conductivity to below 1 micromho (but see 1.3-1B). "Heavy" metals (copper, zinc, etc.) are effectively removed. Some resins can also eliminate carbon dioxide, if this is desired. However, deionization is entirely an ionic process and it does not affect non-electrolytes. Thus deionized water made from a water supply contaminated with soluble organic matter or bacteria and other micro-organisms will still contain the contaminants: and then distillation must be used for purification. The distillate may, of course be further purified by deionization.

5. Apart from pollution, the tap water supply may contain insoluble matter; this does not affect distillation but it must be removed (usually by means of a porous ceramic filter) before deionization, producing deposits of calcium and magnesium carbonates in the boiling chamber of a still and exhausting a resin more quickly.

The storage, testing and use of "pure" water is discussed in 1.3

I. 2. LABORATORY EQUIPMENT

2-1. PURCHASE.

The equipment needed for most of the determinations described in this Guide has been reviewed and listed in FAO Soils Bulletin No.3. In choosing individual items for purchase, advantage should be taken of recent developments in the design and construction of apparatus so that an analytical operation can be performed as efficiently as present-day techniques and equipment allow having due regard to the degree of accuracy appropriate to a particular operation. Because of the rapid progress in development of scientific apparatus, equipment must be continually reviewed and new items brought into use as they become more suitable than existing ones. However, care must be taken to guard against indiscriminate purchase of newly available apparatus just for the sake of being up-to-date; a new kind of apparatus is only justified if it will increase the accuracy or efficiency or speed of an analysis.

2-2. GLASSWARE AND GENERAL APPARATUS.

Laboratory glassware is almost universally made from some form of borosilicate glass because of its low coefficient of expansion when heated. It is suitable for all purposes except the accurate determination of traces of boron; however, borosilicate glass is attacked slightly by alkaline solutions and it is unwise to use it for storage of such solutions (see 1.3-4.).

Soda glass is cheaper than borosilicate glass and is used for the manufacture of simple apparatus (e.g. bottles, watch-glasses, tubing) which may be quite suitable for some purposes. It is important that soda glassware is not mixed with borosilicate glassware in analytical operations; borosilicate glass is usually stamped with the maker's trade-mark, although this is not always possible (e.g. on glass tubing).

Volumetric glass ware is normally made in various grades, according to

the accuracy of the graduation marks as guaranteed by the manufacturer or by a central testing establishment (e.g. the National Physical Laboratory in U.K.). Supplies of at least two grades should be available and the appropriate grade used for an analytical operation. Thus, preparation and dilution of standard solutions for titrimetry, colorimetry and flame photometry should be done with high grade (usually "Grade A") volumetric flasks and pipettes; and high grade burettes should be used for titrimetric standardizations. But a less accurate grade (usually "Grade B") is suitable for routine dilutions, taking of aliquots and titrations. Since graduated cylinders are mainly used for rough measurements of volume, high grade ones are rarely needed.

All glassware should be kept clean and free from grease, which tends to cover the surfaces in a thin film. There is a tendency to use detergents in the form of washing powders or liquids to remove grease; these are effective but they are usually alkaline and may contain substances difficult to remove from the glass surfaces before the apparatus is used for analytical determinations. Such washing materials should always be used with care and excluded completely in connection with some analyses (see Section III.12.); after use, it is a good practice to wash the glass well with water and then with dilute acid (say, 1:1 hydrochloric acid) before giving a final wash and rinse with distilled or deionized water.

The removal of grease by the traditional method of soaking in "chromic acid" solution (1 litre of commercial concentrated sulphuric acid added carefully to 35 ml of saturated sodium dichromate solution) is very effective and the glass surfaces are not attacked. The liquid should be used with care and the facts that it is a strong oxidant and will become hot in contact with water remembered at all times. Glass-ware cleaned with chromic acid should be thoroughly washed and rinsed to remove all traces of acid.

Grease films are especially troublesome in volumetric ware and such apparatus should be kept scrupulously clean. In general, silicone greases should not be used on the tape of burettes or automatic pipettes, plain vaseline being much the best lubricant; if this does creep on to the inner surface of the pipette or on to the burette scale, it can be easily oxidised with chromic acid but silicone grease must be removed by more drastic measures which may be harmful to the apparatus.

The nature of materials contaminating glassware should be borne in mind when choosing the method of cleaning, which need not always be with chromic acid. Deposits of chalk are most easily dissolved with dilute hydrochloric acid; the tin compounds which tend to stain glassware in the molybdenum blue reaction for phosphorus (using stannous chloride as reductant) can only be effectively removed with hot, nearly concentrated hydrochloric acid; permanganate stains can be destroyed with warm oxalic acid; and so on.

Although borosilicate glass is resistant to fairly sudden changes of temperature, it should not be subjected to thermal shock unless this is necessary to control the violence of a chemical reaction. Also, it is not good practice to use the same vessels for concentrated acid and concentrated alkali solutions successively or alternately, the life of the vessels being shortened by such treatment. Thus the common Kjeldahl method of digestion with concentrated sulphuric acid, followed by distillation with a highly alkaline solution in the same flask is not to be recommended; the acid acid digest should be transferred to a second flask for distillation and the two sets of flasks (one for digestion and one for distillation) should be clearly labelled and kept apart (see Section III.4.).

Apparatus which has to be heated to high temperatures is made of porcelain

or silica (quartz) or platinum, the use of platinum being reserved, because of its expense, to fusions with sodium carbonate, which would attack the surfaces of porcelain or silica vessels (see Section III.9.). Because of the high temperatures used, the surfaces of porcelain and silica ware can soon become stained. Cleaning should follow immediately after completion of an analysis; use of abrasive cleaning powders should be avoided if possible as these will damage the glaze in time.

Other laboratory apparatus for which metals are used in manufacture has been greatly improved by the use of corrosion resistant alloys and stainless steel and treatment of metallic surfaces with plastic films or paints. Thus the dangers of contamination of analytical solutions by metals has been largely reduced, although some care still has to be taken.

2-3. PLASTIC WARE.

Most plastic materials are unaffected by acids and alkalies and salt solutions; and thus they are very suitable for the manufacture of some laboratory vessels. This apparatus is also unbreakable, although it may sometimes split; but it cannot be directly heated. However, hot solutions can be poured into vessels made of some types of plastic without softening the material. The general properties of the different types of synthetic plastic are given in manufacturers' catalogues.

The use of plastic bottles for storage of distilled or deionized water is recommended and nearly all standard solutions, especially those containing alkali, should be stored in plastic reagent bottles (see I.3-4) Plastic centrifuge tubes, made from rigid material, do not break. Plastic wash bottles, made from flexible material, are easy to handle and ensure that the solutions in them are not contaminated with carbon dioxide, as is the case with glass wash bottles; however, glass wash bottles must be used for washing with hot liquids. Plastic tubing tends to last longer than rubber tubing under hot conditions.

The use of beakers, funnels, cylinders and similar apparatus made of plastic for routine operations reduces the breakage rate, as compared with the use of glassware; but plastic ware is rarely transparent and if it is when new, it soon becomes scratched and opaque. It also stains rather easily. In analytical operations it is usually desirable to see solutions clearly and glass remains at present the best material for most analytical vessels.

2-4. LABORATORY INSTRUMENTS.

A modern physical and chemical laboratory for soil and water analysis uses techniques which rely extensively on electronic and other electrical instruments. The methods in this Guide are dependent on pH meters, conductivity meters, flame photometers and spectrophotometers or other instruments for measuring the relative colours of solutions. In addition, the more traditional analytical processes of weighing, stirring, shaking, filtering under suction, heating, drying, incubating and centrifuging are done almost exclusively with the aid of electrical machines and devices.

Electronic equipment and balances are expensive and often delicate and must be maintained in good condition for lasting and efficient performance, which simply means organizing the laboratory rooms in such a way that the equipment is not exposed to dust, fumes and wide changes of temperature and humidity. It is not always convenient to place such apparatus in separate rooms but this is normally the best way to maintain it in a clean and efficient condition, especially if general air conditioning is not

installed. Where electronic or weighing apparatus is isolated in a special room at a reasonably steady temperature and humidity, the machines controlling the air condition should be kept running at all times. Switching them off during the night or at holiday periods causes fluctuations in temperature and humidity which may have serious damaging effects on electronic circuits and the accuracy of delicate balances. When instruments are kept under good, clean conditions, it is unnecessary to cover them with the plastic covers usually provided. Being impervious to water vapour, plastic films may give rise to increased condensation on the instrument; indeed, it could be said that if a plastic cover is needed to keep contamination off an instrument, then this instrument is being housed in unsuitable surroundings.

Electric motors should be examined at frequent intervals and commutator brushes replaced when worn. Many motors are supplied permanently greased; others need periodic attention. The moving parts of shakers, stirrers, suction pumps and centrifuges should be kept greased or oiled and free of abrasive dust. Heating appliances, which are necessarily exposed to fumes and steam, should be examined frequently and particular attention paid to the state of electrical insulation. All electrical apparatus should be efficiently earthed. (see I.I-2.)

Most laboratory instruments are supplied by manufacturers with instruction booklets which include descriptions and diagrams of the apparatus, the recommended method of use, the measures necessary to maintain the equipment in good order and how to find out what is wrong if a fault develops. These booklets should be preserved and the instructions followed carefully. In addition, a special meter should be available for testing voltages, current consumption and resistances of electronic circuits, so that faults can be detected and repaired in the laboratory.

Large-scale routine operations such as shaking, filtering, dispensing measured volumes of liquid and so on can be carried out quickly by using, in conjunction with standard apparatus, various labour-saving devices which usually have to be made especially in the laboratory workshop to suit individual requirements. They are very useful once an analytical method has been proved suitable for the soil types received by the laboratory.

Automatic analysers are worth installing when very large numbers of samples are involved and methods of analysis have been standardised. The equipment is expensive and needs expert maintenance. Also, the output of results may become so great that computers are necessary to handle the interpretation of analytical figures and provide the information needed by the farmers, growers, soil surveyors or agronomists who submitted the soil samples in the first place.

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I. 3. CHEMICALS AND SOLUTIONS

3-1. QUALITY.

3-1.A. CHEMICALS.

Most chemicals are supplied in two or more grades and the appropiate quality should be selected for purchase, according to the proposed use of the chemicals in analysis. Generally, a high grade, guaranteed by the manufacturer to conform to a stated quality, is advisable for all analytical operations; and, in most cases, this chemical may be used confidently without further purification. Lower grades of chemicals (which are, of course, cheaper) should be available for cleaning purposes and for certain analytical processes where the lower grade, although generally less pure, may still contain negligible amounts of the element being determined (e.g. the concentrated sodium hydroxide solution used for ammonia distillation may be prepared from a low grade solid sodium hydroxide which is still nitrogen-free). On the other hand, for special analyses (e.g. minor element determinations in soil) some chemicals may need extra purification in the laboratory.

Certain chemicals absorb water from the air or lose water of crystallization and, if possible, their purchase and use should be avoided, especially if air conditioning is not installed. Often there are better alternatives; for example, an anhydrous salt may be more stable than one containing water of crystallization. When a substance does change through loss or gain of water, it may have to be purified before use if new stocks cannot be obtained quickly (e.g. old samples of sodium borate decahydrate should be recrystallized). Anhydrous substances can usually be safely cleared of water by heating at 105° C for a few hours (see I.3-3.A.).

Quality is, of course, closely associated with economy. Since high grade chemicals are more expensive, their purchase and maintenance in good condition is an important part of laboratory organization. The use of chemicals should be studied in relation to their cost and the possibility of employing alternatives. Not all salt solutions need be made by simply dissolving the salt in water. Thus, ammonium acetate solution made from ammonia and acetic acid costs about half that made from solid ammonium acetate; and, since stannous chloride crystals oxidize quite rapidly, stannous chloride solution is best made by dissolving tin in hydrochloric acid.

3-1.B. WATER.

The distilled or deionized water used for making solutions should be of a quality commensurate with that of the chemicals being dissolved in or mixed with it. Continual checking of quality is advisable and usually this involves a daily measurement of conductivity and an occasional check of pH value. Deionization equipment usually includes a conductivity meter in line, so that continuous control of the effluent is easy; but the contents of the laboratory storage vessels still need checking.

Either distilled or deionized water of good quality in contact with air of average carbon dioxide content has a pH value of 5.8 – 6.0. It is sometimes called "air-equilibrium" water. When testing the pH of such water, the electrodes must be well washed a number of times after the meter calibration with buffer solutions. It is best to calibrate the pH meter first with a solution near pH 7 (see Section III.1.) and secondly with a solution of pH 4 (potassium hydrogen phthalate) before thoroughly

washing the electrodes and reading the pH of a sample of distilled or deionized water.

Distilled water usually has a conductivity of 3-5 micromhos (at 25°C) depending on the apparatus used. A second or third distillation (preferably from slightly alkaline potassium permanganate) can reduce this to about 1 micromho. Deionized water has a conductivity of 1-2 micromhos, which may be reduced to less than 1 micromho by a second deionization treatment. However, both waters in contact with air of average carbon dioxide content have a conductivity of about 1 micrombo.

Once-distilled water is pure enough for the preparation of reagent solutions but water used for the preparation of standard solutions should have a conductivity of less than 2 micromhos. For certain purposes, pure water free from carbon dioxide is needed; this may be prepared by boiling ("boiled-out" water) or by aeration with carbon dioxide free air. The product should have a pH value of 6.8 - 7.2 and will probably have a conductivity a little under 1 micromho, although there is a danger that boiling may dissolve traces of salts from the glass. Once prepared, this water should be used for making the solution required and the remainder (only a little, usually) discarded or used for rinsing glassware. (see I.3-4.)

3-2. PREPARATION OF REAGENT SOLUTIONS.

In the methods of analysis in Sections II, III and IV, "Reagents' includes all solids and solutions needed, whether bought directly or prepared in the laboratory. This account deals with the laboratory preparation of all reagent solutions other than standard solutions (see I.3-3.), which need special consideration.

The care and accuracy required for the preparation of a particular reagent solution should be clear from the context, after a short study of the procedure advocated for the analysis involved. In general, weighing of solids need only be carried out to an accuracy of 0.1 - 0.5 per cent of the weight taken; the weights given are recorded mostly to this degree of accuracy and sometimes the word "about" or "approximately" is used to denote a rough weighing, when a variation of 1-2 per cent in the weight is unimportant. An appropriate balance should be used, capable of supporting the total weight of container and solid and of weighing to the required degree of accuracy; it is generally unnecessary to use an analytical balance of high sensitivity (0.1 mg) although one accurate to 1 mg may be useful for small weights (e.g. of indicator solids).

Measurement of volumes of liquids is always done with graduated cylinders. After dissolving a solid or diluting a liquid, the final adjustment of total volume is usually done in a routine grade volumetric flask, when the temperature of the solution has become equal to that of the laboratory room. Sometimes, however, a solid may be simply dissolved in a measured volume of liquid (e.g. indicator solutions); or two volumes of liquids may be mixed (e.g. preparation of an approximate dilute acid solution).

A salt with water of crystallization which dissolves easily in water may conveniently be weighed in a beaker and dissolved in this vessel before being transferred to a volumetric flask for volume adjustment. Anhydrous salts which also form crystals containing water of crystallization (e.g. sodium sulphate) should preferably be added slowly to water (after weighing on a watch glass or scoop) because some tend to "cake" on the addition of water; however, anhydrous salts which do not form salts containing water of crystallization (e.g. potassium chloride) may be dissolved easily

by the addition of water. Some chemicals need special care in dissolution; thus, if water is added to sodium hexametaphosphate, a glassy mass is produced which is very difficult to dissolve - but solution is rapid if the powdered chemical is added slowly to well stirred water.

It is convenient to make large quantities (i.e. 5 or 10 litres) of some reagent solutions used in routine soil analysis. If volumetric flasks of these capacities are not available (they exist but are uncommon), a boiling flask of appropriate size may be calibrated at a volume which brings the level of solution into the neck of the flask - e.g. a "5-litre" boiling flask may hold 5,500 ml of liquid to a mark on the neck. The weight of salt needed is adjusted proportionately, together with the solution is to be stored. It must be remembered that temperature changes affect large volumes of liquid quite considerably and solutions should be given ample time to attain room temperature before the adjustment of final volume.

3-3. PREPARATION OF STANDARD SOLUTIONS.

A standard solution in analytical chemistry is one which has an exact and known concentration. The accuracy of all the titrimetric, colorimetric and flame photometric analyses described in this Guide and all pH and conductivity measurements depends ultimately on the reliability of the standard solutions used in them. These must therefore be prepared with great care from the purest chemicals and high grade distilled or deionized water, using accurate analytical balances (sensitivity 0.1 - 0.05 mg) and guaranteed volumetric glassware.

It may be mentioned here that it is possible to buy certain volumetric solutions already prepared for use and guaranteed to be correctly standardized; it is also possible to buy sealed ampoules containing accurate weights of solids or liquids for the preparation of standard solutions by dissolving in or diluting to a definite volume with water. These ready prepared products are, of course, more expensive but they may be convenient in some circumstances. However, it is assumed in this account that standard solutions are prepared in the soil and water laboratory as they are required.

3-3.A. VOLUMETRIC SOLUTIONS FOR TITRIMETRY.

These are prepared so that the final solution has a known normality or molarity. In this Guide, the solutions advocated are an exact fraction or multiple of "Normal" or "Molar" because this makes calculation of results easier and less liable to error than employment of a factor (e.g. 0.1027 N instead of 0.1000 N). Having standardized a solution, it is only a little extra trouble to dilute it to an exact fraction or multiple of N or M and restandardize as a check (see below).

Where very pure chemicals of exact composition can be used (e.g. potassium dichromate and ethylenediaminetetraacetic acid, disodium salt), calculated weights accurate to about 0.01 per cent are dissolved to an exact volume at a temperature near 20°C (the usual temperature at which volumetric flasks are calibrated). In humid conditions, anhydrous salts should be dried at 105°C for a few hours - or at higher temperatures in individual cases (e.g. potassium dichromate at 150°C) - or salts containing water of crystallization may be heated at specified temperatures (e.g. ethylenediaminetetraacetic acid, disodium salt at 80°C) to ensure that the chemical composition is correct; and then the salts are cooled in dry air before weighing. Since an exact weight is required, the use of weighing bottles is awkward; but the salt may be quickly and conveniently weighed

on a watch glass with a rapid automatic balance. (Substances which absorb or lose water in the minute or two required for weighing on an open watch glass are unsuitable for the preparation of standard solutions in this way). After weighing, the salt is transferred carefully with water to an appropriately sized beaker, dissolved and the solution then transferred quantitatively to a volumetric flask and made to the required volume.

Substances which cannot be weighed accurately because of deliquescence must be weighed roughly, using a slight excess to allow for absorbed water, and then dissolved to volume. The solution is standardized and then diluted to the exact concentration required. For example, to prepare 0.020 N mercuric nitrate solution (see Section IV.10.) proceed as follows -

Dissolve about 7 g mercuric nitrate, $Hg(NO_3)_2.H_2O$, in 2000 ml of approximately 0.05 N nitric acid.

Remove 100 ml (using a dry cylinder) and transfer part to a 50 ml burette. Titrate against 10.0 ml of 0.050 N standard chloride solution (sodium or potassium chloride is suitable).

Let
T be the volume in ml of mercuric nitrate solution used in the titration (T should be slightly less than 25)

Then, its concentration is

$$\frac{10 \times 0.05}{T} = \frac{0.5}{T} \text{ N}$$

(which should be slightly greater than 0.02 N)

Now, 1900 ml of this solution remains. And this volume is equal to

$$\frac{1900 \times 0.5}{0.02 \times T} \text{ ml of 0.020 N solution}$$

$$= \frac{1900 \times 25}{T} \text{ ml}$$

Thus, the volume of water needed to dilute the mercuric nitrate solution to exactly 0.020 N is

$$1900 \left(\frac{25}{T} - 1\right) \text{ ml}$$

Add this volume of water, mix well and titrate the prepared mercuric nitrate solution with 10.0 ml of 0.050 N standard chloride solution to check that its concentration is 0.020 N.

Similar procedures are used to prepare standard solutions of sulphuric and hydrochloric acids. Calculated (approximate) volumes of the concentrated acids (see Appendix 1.) are diluted to the required volumes and the solutions are standardized and then diluted to the exact normalities required, as above. Standardization may be against a weighed amount of sodium carbonate, previously heated to 270°C to convert any bicarbonate to carbonate, or against a weighed amount of sodium borate decahydrate, preferably freshly recrystallized. Weighing bottles can be used since the amount of salt taken can vary although its exact weight must be known (usually to 0.1 mg). The end-point in the titration of sodium borate with acid may be detected accurately with methyl red - bromocresol green mixed indicator (see Section III.4.); but this indicator can only be used in the titration of sodium carbonate with acid if most of the acid is added and the carbon dioxide boiled out before com-

pleting the titration. A reasonably good end-point can be obtained in the sodium carbonate standardization by using methyl orange screened with indigo carmine or xylene cyanol FF (see Section IV.9.), without removal of carbon dioxide.

Very dilute standard solutions of acids are best prepared by the accurate dilution of more concentrated solutions, e.g. 0.010 N acid from 0.100 N or 0.200 N acid.

The commonest standard alkaline solution is sodium hydroxide. This cannot be prepared accurately from the solid because this absorbs water and carbon dioxide from air quite rapidly. A saturated solution is made (500 g sodium hydroxide added to 500 ml water) and allowed to stand; the sodium carbonate impurity is not soluble in the saturated sodium hydroxide solution and settles out, leaving a clear solution above, which is about 16 N. This is diluted to near the required normality with carbon dioxide free water, standardized and adjusted to exact concentration.

Occasionally, a standard solution needed in a titration is not stable (e.g. ferrous ammonium sulphate) and in this case a solution of approximately the correct concentration is made and standardized afresh with each batch of titrations. A limited volume is made, just enough to last about one or two weeks - or enough for a particular batch of analyses.

3-3.B. STANDARD SOLUTIONS FOR COLORIMETRY AND FLAME PHOTOMETRY.

In order to calibrate a colorimeter (or spectrophotometer or absorptiometer) or a flame photometer, a series of standard solutions is required containing exact and increasing amounts of a cation or anion over a selected range. Concentrations are usually in milliequivalents per litre (a 0.001 N solution contains 1 milliequivalent of either cation or anion per litre) or in parts per million (i.e. milligram per litre or microgram per ml).

These series of "working standards" are always prepared by dilution from more concentrated solutions, which, in the methods in this Guide, are usually made by dissolving exact weights of pure salts to a definite volume with a care and accuracy equal to that advocated for volumetric solutions for titrimetry. It is advisable to take an initial weight of at least 1-2 g of salt when using a balance accurate to 0.1 - 0.2 mg; amounts near 0.1 - 0.2 g (which are sometimes advocated in colorimetric methods) should be weighed on a more accurate balance.

Dilution to the series of working standards can be directly from this initial solution or through an intermediate stage, depending on the relative concentrations involved. It is convenient to take volumes of 5 to 25 ml of concentrated solution for dilution to 500 ml or 1000 ml in the preparation of the final series of standards for calibration. The volumes may be measured by bulb pipettes or by a burette, using high quality glassware.

Of course, in the preparation of these standard solutions, wide changes of temperature should be avoided and the water used should have reached equilibrium with the room temperature. Although volumetric glassware is calibrated in manufacture at a definite temperature (usually 20°C), no appreciable errors will arise from its use at other temperatures near this; but errors will be introduced if the room temperature changes much between measurement of a small volume of a concentrated solution and measurement of the large volume of the corresponding diluted solution. Thus all dilutions should be performed together.

3-3,C. OTHER STANDARD SOLUTIONS.

Solutions for the calibration of pH meters and conductivity meters must be prepared carefully from high grade chemicals and water but the weights of salts taken need not be quite so accurate (say, 0.1 per cent). Air-equilibrium water with a conductivity of about 1 micromho is suitable for these solutions, except for preparing 0.01 M sodium borate when carbon dioxide free water must be used.

Buffer solutions for pH work can be bought ready prepared; also, buffer tablets and buffer "concentrates" can be bought for dissolving in water and dilution with water to a definite volume. The composition of these tablets and solutions is not usually stated. The buffer solutions advocated for analyses III.1 and IV.2 are among those recommended by the United States National Bureau of Standards.

3-4. STORAGE

3-4A. SOLUTIONS.

Once prepared - usually in volumetric flasks - reagents and standard solutions should normally be transferred to storage bottles. (Solutions needed immediately for tests, then to be discarded, may be excluded from this "rule")

Bottles of plastic material (mostly polythene) are recommended for nearly all solutions - the one exception (in this Guide) being the standard solutions of sodium borate for the colorimetric determination of boron. Borosilicate glass bottles are suitable for acids but should not be used for alkalies. Soda glass bottles should only be used for cleaning solutions and perhaps some general qualitative reagents (and the boron standard solutions). When polythene storage bottles are used, there is no difficulty over stoppers sticking in the necks, as there is sometimes with glass stoppers and bottles. Alkaline solutions should, of course, never be stored in glass bottles with glass stoppers.

All storage bottles should be labelled clearly and permanently. A plastic adhesive strip which may be embossed with the necessary wording is recommended. In addition, the date of preparation should be recorded in grease pencil or on a paper label which can be changed when the solution is made afresh.

Most acid solutions keep in good condition during storage but alkaline solutions tend to absorb carbon dioxide unless a suitable trap is used. Even then, carbon dioxide is absorbed slightly when the solution is removed from the bottle. This is not usually serious but standard solutions of sodium hydroxide intended to be used for titrations over a long period should be stored in such a way that solution can be transferred to a burette without exposing it to carbon dioxide. Salt solutions often encourage mould growth and preservation with a crystal of thymol is then worth trying, although it is not always efficaceous; pH buffer solutions and solutions of alkali metal salts for flame photometry can certainly be preserved with thymol. Chloroform is another preservative but it is not suitable for solutions to be used in flame photometry. Some solutions are their own mould killers (e.g. mercuric nitrate). Solutions which tend to deteriorate chemically at room temperatures (e.g. stannous chloride) should be kept in a refrigerator at 3-5 ^{o}C.

3-4.B. WATER.

Having removed salts and impurities from water by distillation or by filtration and deionization, the pure product should be stored under clean and satisfactory conditions which prevent the re-entry of even small quantities of similar salts and impurities. Containers made of polythene are recommended throughout; this material cannot impart any salts to water and, since it is said to absorb borate ion, it thereby contributes an extra degree of purification by removing the traces of borates which may be present in glass-distilled water.

The prepared water should not be allowed to drip or run through the open neck of the main storage bottle or aspirator. This neck should be fitted with a 2-hole stopper containing borosilicate glass or rigid plastic tubes, one connected to the still or deionizing plant and one to a trap containing cotton or glass wool to prevent possible contamination from the air, the wool being supported on filter paper to stop small fibrous particles entering the air space above the water. If a series of bottles or aspirators is used, connected by siphons, the siphon tubes should be of polythene and each bottle should have a trap to keep out dirt. This applies particularly in large laboratories where the distilled or deionized water is prepared in a separate room. The main storage capacity at the preparation plant will vary according to individual requirements but bottles or aspirators of 100 litres or more are available.

For bulk storage in laboratories away from the main source, polythene aspirators of 20 - 50 litres are suitable, if fitted with polythene taps which do not leak. The mouths of the aspirators should be closed with traps against dirt, as in the case of the main storage containers. Bottles and siphon tubes of polythene may be used in place of aspirators, if preferred. Water needed for analytical purposes should not normally be stored in laboratories where ammonia or volatile acids are used; a second grade quality for rinsing glassware may be permitted.

Although it may seem superfluous, all containers of water should be permanently labelled, particularly if two or more grades are prepared. It is not usually necessary to store carbon dioxide free water; for the purposes needed in this Guide, it can be made as wanted.

I. 4. SOIL AND WATER SAMPLES

4-I. PACKING AND TRANSPORT.

As soon as a quantity of soil is removed from a field or profile pit and as soon as a volume of water is removed from a river or well, it becomes a sample for analysis and, as such, its immediate treatment is the responsibility of the soil and water laboratory. Thus, the laboratory staff should cooperate with samplers and decide, together, the most efficient methods of packing and labelling samples and transporting them to the laboratory in a condition which makes the subsequent expenditure of money and skill on analysis a worthwhile operation. (In general, a laboratory should not accept samples of soil or water submitted by unqualified persons or private individuals; apart from administrative considerations, these "samples" are often improperly packed - soils in newspaper or old tins, waters in roughly washed bottles bottles - and are almost certainly unrepresentative.).

The most suitable containers for soil samples are polythene bags made

of film about 0.13 mm thick, which may be sealed by twisting and tying the neck or by means of rubber bands or adhesive tape. They may be enclosed in strong paper bags or cloth bags (or in a second polythene bag) for extra protection and should be packed for transport in small cardboard cartons or wooden boxes (free of inward-projecting nails). Water samples should be transferred to polythene bottles with screw caps (unless boron is to be determined - see I.3-4.) and packed for transport in strong cardboard cartons or wooden boxes having divisions separating each bottle from its neighbours, of a type used universally for transport of bottles of liquid refreshment. Spaces in the boxes should be stuffed with packing material so that the soil bags or water bottles cannot move, because in many countries these boxes must be transported over rough roads and samples "jumping about" in the boxes can throw an undue strain on the sample containers.

Samplers should be aware of the analyses required on the soil samples taken so that these can be treated correctly and without detriment to the accuracy of subsequent work. In this Guide, only the determination of bulk density requires a soil sample in the undisturbed state, usually taken with a special sampling tool. In all other cases, a soil sample consists of a number of small borings taken over a selected area or of a number of portions from an horizon of a soil profile. The amount of soil sample should be adequate for the analyses required but not excessive; usually one kilogram is about right and if the sample taken exceeds this weight to any great degree, it should be well mixed and sub-sampled correctly (see I.4-3.) down to the average size. In the majority of cases, large stones and pieces of gravel can be discarded, especially if they have sharp edges. However, it is sometimes useful to know the percentage of gravel (diameter 7.6 to 2.0 mm) and in this case the whole sample, preferably of 2-3 kilogram, is kept. It is an advantage to dry out very wet samples, unless moisture studies are involved; the method of drying may vary according to the conditions under which sampling is being done but, in all cases, high temperatures must be avoided and great care must be taken to ensure that there is no contamination of one sample with another or with extraneous soil or dust. In tropical countries, air-drying is often convenient. The soil is broken up and spread out in a thin layer on strong paper or polythene film, preferably on a rack of wire mesh to allow air to circulate underneath, and mixed occasionally to expose fresh surfaces; samples should be well separated and the drying area protected from direct sun and wind. Drying should not be prolonged, particularly for clay soils, which are more easily ground at the laboratory if a small amount of moisture is present.

Since polythene is impervious to water vapour, a soil sample placed in a sealed polythene bag retains its natural moisture content, which is useful in soil-water studies. The sealed sample may, however, undergo chemical changes due to bacterial action and other causes during its transport to the laboratory and this must be borne in mind when certain analyses (mostly dealing with nitrogen compounds) are wanted (see I.4-3).

In general, treatment of soil samples immediately after they have been taken should aim at providing the soil laboratory with a series of samples of approximately the same size, free from large or sharp stones and large soil aggregates, and at a consistent moisture condition, which is usually air-dry but may be at a reasonable field moisture equilibrium for some analyses. Packing and transport is thereby made easier and a good deal is done to eliminate erratic effects on subsequent analytical results due to varying treatment of samples before they reach the laboratory.

Water samples normally need no treatment after they have been taken (for the analyses described in this Guide); if ammonia and nitrate are to be determined and the samples cannot be delivered at the laboratory for some time, it may be necessary to add toluene to kill organisms. The main care in taking water samples is to ensure that there is enough for the analyses required. Samples in which boron is to be determined must be taken and transported in soda glass bottles and, if this analysis is required, it is probably best to take two samples, one main one (one litre) in polythene bottles and one smaller (250 ml) in soda glass bottles.

4-2. LABELLING AND REGISTRATION.

Soil and water samples should be labelled by field staff so that they can be easily and clearly indentified subsequently by laboratory staff. Perhaps the simplest way of doing this is to use soil bags and water bottles which are already clearly numbered with waterproof ink or paint, these "bag numbers" or "bottle numbers" being entered in the sampler's record book, as each sample is taken, together with the other information he needs to identify and describe the samples. If soil samples are placed in polythene bags within bags of other material, both bags should be numbered (same number) so that a sample is quickly identified without unfastening the outer bag; and water bottles should be numbered in duplicate. Reliance should not be placed on a single number, as this may become defaced in transit.

This method of numbering only needs preliminary planning and organization before setting out on a sampling trip. It does not involve writing out labels in the field and tying them on bags or bottles from which they can be torn; and it does not involve laboratory staff in attempts to decipher labels placed inside soil bags and damaged in transit or in attempts to understand words written on bags and bottles in pencil or ink which has smeared.

However, labels may have to be used in some cases. If so, they should either have printed numbers on them already or waterproof ink should be used to write information on them (this excludes pencil, washable ink pens and ball-point pens). For soil samples, duplicate labels should be placed between the two bags, never in the bag with the soil; for water samples, duplicate labels should be fixed to the bottle with adhesive tape. The amount of information on a label should be kept to a minimum - preferably a number, which may be either a "bag (bottle) number" or a "sample number" (see below). Depths may be given usefully for soil profile samples in some cases. When labels are handwritten, special care should be taken to prevent ambiguity. For arabic numbers, "6" and "9" and combinations like "69" and "96" should be underlined; and "1" and "7" should be clearly distinguished. Where letters and numbers are used, "5" may easily be confused with "S"; and so on. This is why printed labels are always better.

Field samplers will normally have a numbering system of their own and may have a record book containing printed forms for the entry of information, serially numbered. These "sample numbers" are the main identification of soil and water samples for most purposes but the relevant form should also have a record of the "bag" or "bottle" number and the subsequent "laboratory number" (see below). When a box of samples is despatched to the laboratory, it should contain a packing note giving the total number of samples, the "sample number" of each sample and its corresponding "bag number" or "bottle number", the depth of soil samples from profile pits and other information needed by the laboratory staff for registration purposes (as agreed), particularly on the analyses required. A duplicate packing note should be sent

separately so that missing boxes can be investigated.

On arrival at the laboratory, the contents of a box should be checked against the packing note and any discrepancies reported to the samplers. Having established what analyses are required, the samples are registered, giving each sample a "laboratory number" according to a system suited to individual laboratory organizations. For small laboratories, soil and water samples may simply be numbered serially as they arrive. Larger laboratories may need to have two or more numbering systems, using a prefixed letter (or group of letters) to distinguish them, this procedure helping to channel samples into various analytical streams. Two-way cross-references to "sample numbers" are essential so that a sample can be rapidly traced either through its "laboratory number" or its "sample number". Either registration books or index cards can be used, as desired, these usually containing most of the information collected on a sample. Large laboratories may need to use a "punched card" system or some other means of storing complete information on all samples so that data can be recovered quickly.

It is essential to keep a record of the date of arrival and the source of all samples. Where samples come in regularly from a series of field centres, a table can be drawn up each month with a column for each centre and a row for each day. Row totals give the daily input and column totals give the monthly arrivals from each centre; a grand total shows the monthly arrivals from all centres. Such tables present a clear and immediate picture of the sample situation at any moment.

4-3. PREPARATION AND SAMPLING FOR ANALYSIS.

4-3.A. SOILS.

(i) Preparation.

As indicated in I.4-1, the first steps in the preparation of a soil sample for analysis may often be taken in the field by ensuring that samples are of a uniform size, are free of stones (unless the percentage of gravel is required), contain no soil aggregates bigger than about 1 cm across and (except in special cases) are at a consistent moisture content, which is normally air-dry. If samples arrive at the laboratory in this condition, they only need grinding and sieving.

When no preliminary field treatment has been given and a soil sample arrives at the laboratory more or less as it has been taken from the sampling tool, it is spread out on a tray of metal (aluminium, usually, unless exchangeable aluminium is to be determined) or plastic or even stout brown paper, stones are removed and large soil aggregates broken up. Usually, obvious pieces of undecomposed organic matter are also discarded at this stage, unless there is particular interest in the total organic content and special procedures are laid down. If the sample is unduly large, it is well mixed, spread out on a large sheet of paper in a thin layer and divided into four parts with a large spatula. Then either one or two (opposite) quarters are discarded completely, brushing off fine material as well as larger aggregates. (A sample splitter may be used if available). The remainder of the sample is returned to its tray.

After this preliminary preparation, the sample is labelled with its "laboratory number", which should preferably be printed on a piece of plastic material, since this label has to remain permanently with the sample until it is no longer required. Use of different coloured plastic

labels may help to distinguish quickly between samples in different numbering systems. Thick card may be used if plastic is not available It is usually inconvenient to label the trays containing the samples, since they must be used in rotation for many different samples; it is only necessary to ensure that the plastic or card labels are not accidentally transferred from one sample to another, or lost - and this is a matter of laboratory organization and discipline.

Samples are then normally left to attain equilibrium with the moisture of the air. Where samples are often received in a wet state, a slightly elevated temperature may be used to hasten "air-drying" but this should not exceed about 40°C. During air-drying, samples should be kept in well ventilated conditions so that water vapour can escape easily; shelves of open wire mesh are convenient and, if air conditioning is not installed, fans should circulate the air gently. Samples may be mixed during drying to expose fresh surfaces. For certain analyses or experimental work, field-moist samples may be required; after rapid preliminary treatment to remove stones, etc, these samples are rubbed through a wire mesh sieve with openings about 4-5 mm across and weighed immediately for analysis and dry matter; clearly, these samples must have been transported quickly to the laboratory in plastic bags and they must receive priority attention.

After air-drying, soil samples are crushed gently in a pestle and mortar and sieved through a 2 mm sieve, the process being continued until the material retained on the sieve contains no soil aggregates; the material larger than 2 mm is discarded unless the percentage of gravel is wanted. The pestle and mortar may be of porcelain or stoneware or iron for most analyses but, naturally, iron equipment cannot be used if analyses for iron are to be performed on the soil. Samples for minor metal analysis (copper, zinc, manganese, molybdenum) should be crushed in a mortar of porcelain or stoneware (or agate, if available) and sieved through a stainless steel or nylon sieve. Crushing should always be gentle to avoid breaking up gravel; care must be taken with samples containing soft chalk or limestone, where the degree of grinding can greatly affect the analytical result for calcium carbonate.

Crushing with rollers on flat hardwood or plastic boards may be employed. Special soil grinding machines have been developed which allow crushed material to pass through a 2 mm sieve during operation; machines which grind the whole sample (including gravel) must not be used.

The air-dry soil sample, passing the 2 mm sieve, should be returned to its tray and left on a shelf in a temporary storage space until needed for analysis (see I.4-3.A.(ii). Certain analyses require a sample passing a 0.5 mm sieve; the 2 mm sample is spread out in a thin layer and small portions, taken at random with a spatula, are transferred to a mortar until a sub-sample of the required size is obtained (usually, 25-50 g is ample). Alternatively, the sample may be halved and quartered or poured repeatedly through a sample splitter. The sub-sample is then ground until <u>all</u> of it passes through a 0.5 mm sieve and transferred to a suitable small tray or dish to await analysis.

(ii) <u>Sampling for Analysis.</u>

When the weight of air-dry soil required for analysis is 5 g or more, a 2 mm sample is suitable; for weights less than 5 g, it is advisable to use a 0.5 mm sample, thereby reducing the sampling error.

Because a 2 mm sample of soil contains particles of different sizes, the removal of small portions for analysis must be done in such a way that each portion contains, as far as possible, the same proportion of different sized particles as in the main sample. The safest way to ensure this is to spread out the well-mixed sample on a flat tray and take small portions at random with a spatual (as in the sub-sampling procedure above) until the required weight is obtained. The random spatula portions should be taken at the full depth of the soil layer and not just from the surface. It is inaccurate to take a 2 mm sample for analysis straight from a bottle or carton, the contents of which may not be uniformly mixed.

These considerations govern the recommendation (above) to leave a 2 mm soil sample, after grinding, in its tray until the requisite samples have been weighed for analysis; in this way, the soil can be well mixed easily and sampled accurately. Trays should not be stacked, one in another, for transport from the soil preparation room to the soil weighing room but should be wheeled in on a trolley having shelves so that each tray is accommodated separately. Only one tray at a time is placed by the balance during weighing, thus avoiding contamination of samples by accidental spillage.

For routine analyses involving large numbers of samples, sampling by volume may be used in place of sampling by weight; a spoon or scoop of the requisite volume is drawn through the soil sample (usually 2 mm), tapped down gently and the surface levelled with a spatula. Such a method of sampling is suitable for some pH and conductivity determinations. And in analyses for fertility levels, in which final results may be expressed in units such as "kilogram per hectare, 10 cm depth", it may be claimed that analysis of a volume of soil is more realistic than analysis of a weight; for the analytical figure on a weight basis has to be converted to a volume basis by taking an arbitrary figure for the weight of a "hectare 10 cm" volume of soil. If volume measures are used, the fact should be stated clearly in the records of analytical results, with a note of the volume of soil or its ratio to the volume of water or soil extractant used in the analysis (see I.6-2.).

A soil sample is usually weighed out on a scoop of glass, plastic material or metal (according to the analysis involved) and transferred to the bottle or flask or other suitable vessel for analysis, brushing off the scoop into the vessel with a clean camel hair or sable hair brush. In some cases, the sample may be weighed directly into the container used for analysis - e.g. for the determination of dry matter, into special aluminium soil moisture tins (with lids), the weights of which must also be known.

A soil sample taken by volume is tipped from the measuring spoon into the required vessel for analysis and any soil remaining in the spoon is dislodged by gentle tapping; the spoon may then be brushed out or wiped clean before proceeding to the next sample.

All measurements of soil samples for analysis should be done in a separate room because it is impossible to avoid contamination of the air with fine particles of soil during sampling. The measured samples may be treated with extracting solutions or water, etc. in the same room or transferred to other rooms for analysis after the vessels have been covered; indeed, it is a good practice to close a vessel immediately after a weighed or measured sample has been put into it, to avoid the accidental addition of a second sample or inadvertent contamination with foreign material.

"Air-dry" soils contain adsorbed water in amounts depending on their texture and on the humidity and temperature of the air. Sandy soils adsorb small quantities which vary only slightly with air conditions; but soils containing clay or organic matter or both adsorb large and variable quantities of water. As air-dry soils are heated, they usually lose water gradually over quite a wide range of temperature; and this loss of water may be accompanied by oxidation of organic matter, even at low temperatures. In addition to loss of adsorbed water from soil particle surfaces, structural water is gradually removed from clay minerals and water of crystallization from salts or minerals such as gypsum and limonite; and hydroxides may be converted to oxides. Furthermore, a soil heated at any particular temperature may continue to lose small amounts of water slowly for some days.

Thus, oven-drying (normally at 105°C) does not cause the loss of a precise category of soil water. However, when carried out under standard conditions it does produce a consistent "oven-dry" basis for calculating results of soil analyses and the advantage of this is that analytical figures from a number of countries with wide differences in climate can be compared more reliably than figures on an "air-dry" basis. With certain exceptions, it is recommended in this Guide that results be calculated on "oven-dry" soil. The procedure adopted for moisture determination is as follows:

(a) Air-dry samples

Transfer 10.0 g air-dry soil (2 mm or 0.5 mm or both) to a metal dry matter tin (moisture tin) having a closely fitting lid. Then transfer a convenient weight of the same air-dry soil, depending on the number of analyses required, to an air-tight container (a screw-capped bottle with a rubber or plastic ring for sealing is effective). Place the dry matter tin (lid removed) in an oven at 105°C during the closing period of a working day and leave until the next morning - a period of 16-18 hours, normally. Remove the tin from the oven, close with the lid and cool in a desiccator to room temperature. Weigh and so find the weight of "oven-dry" soil, which may be recorded to 0.1 or 0.05 g for most purposes.

(Note - do not alter the standard procedure in any way, for instance by leaving soils in the oven for the two or three day period over the normal weekly rest days).

Let the weight of oven-dry soil be D gram.

Then, 10 g of air-dry soil contains D g oven-dry material and thus, 1 g of oven-dry material is contained in

$$\frac{10}{D} \text{ g air-dry soil}$$

Obtain this value from a table of reciprocals and so calculate the weight of air-dry soil containing the weight of oven-dry soil needed for analysis (1.0, 2.0, 2.5, 5.0 etc.).

(b) Field moist samples

Proceed essentially as for air-dry soils, using material which has been rubbed through a 4-5 mm sieve and taking a larger weight (say, 25 or 50 g) on a rapid balance.

When weighing the required amount of air-dry or field-moist soil, the sample

is, preferably, tipped out of its air-tight container and mixed and sampled quickly, using a rapid balance; then it is returned at once to its container. No serious changes in moisture content can take place during this operation. For 0.5 mm air-dry soil, it is probably accurate enough to sample with care from the container.

An alternative method which can be adopted in some cases is to weigh out separate soil samples for analysis and moisture determination at the same time. In this case, the weight of oven-dry soil is not known and thus the method cannot be used if an exact ratio of oven-dry soil to extractant solution is required. However, it may be undesirable to keep field-moist soils for a day (until moisture contents are known) before sampling for analysis because of changes in composition through oxidation or microbial action; then sampling for analysis and moisture is done at the same time and subsequent analysical procedures are modified appropriately.

After the necessary samples have been taken for analysis, soils may be stored in the air-dry state in glass or polythene bottles or in polythene bags inside cardboard cartons, clearly labelled. Experimental samples on which further analyses may be required should be kept in conditions of reasonably constant temperature and humidity. Storage can affect some analyses and the effect may be influenced by the conditions of storage, which should therefore be kept constant and, if possible, recorded. Storage in isolated buildings exposed to heat or cold or dampness is not advisable.

4-3.B. WATERS.

Water samples naturally need no preparation for the analysis of insoluble matter. For most other analyses in this Guide, the sample should be free from insoluble material and thus should be filtered. Usually, the concentration of salts is sufficient to clarify the samples by flocculating clay and simple decantation through fine filter papers is effective; but ceramic filters may be necessary in difficult cases.

Complete clarification is not needed for the determination of pH and conductivity; and the determination of sulphate (colorimetric) and ammonia (by distillation or using zinc hydroxide) may also be done on turbid samples. (see Section IV.11-2 and IV.13.).

I. 5. ANALYTICAL ACCURACY

5-1. TYPES OF ERRORS AND THEIR CONTROL.

The procedures advocated in the methods of analysis in this Guide, if followed with care, should be capable of giving consistent results near to the true answers. Where they are used on a small scale for research purposes, adequate replication and calculation of a mean figure for an individual analysis should produce a fully reliable result.

However, in many of the laboratories for which this Guide is intended, some soil and water analyses are carried out on a large routine scale, with limited opportunities for replication and therefore with reliance on single values for the great majority of samples. Under the conditions imposed by the need for numerable and rapid analyses, a certain percentage of error is inevitable; but careful organization and sound training of staff can reduce this error to a minimum.

If it is assumed that the technique used in a particular determination is based on sound scientific principles, then the analytical result may deviate from the true answer through two main types of error -

(a) Errors due to faults in instruments, glassware or other apparatus employed in the determination; or to the use of samples or chemicals or solutions which have been improperly prepared or have deteriorated or become contaminated.

(b) Errors (more properly called mistakes) due to careless work in the actual analyses.

Clearly, errors under the heading (a) can be reduced to a safe minimum by working in well-designed laboratories, by proper selection of apparatus and its maintenance in good condition and by the careful preparation and storage of chemicals and reagents and samples for analysis. The guidance in these matters given in Parts 1 to 4 of this Section should increase the accuracy of soil and water analysis by the methods described in Sections II, III and IV.

Errors under the heading (b) can be reduced by patient and efficient training of staff and selection of suitable work for each individual. Particular attention should be given to -

1. Cleanliness and methodical organization of work.

2. Care of instruments and accurate reading of scales.

3. Manipulation of apparatus and correct use of volumetric glassware.

4. Judgment of titrimetric end-points - making allowances for partial colour-blindness, which should be investigated if judgment of end-points is uncertain or erratic.

5. Accurate recording of results and correct calculations.

It is particularly important that training should ensure reliability in preparation of samples and of reagents and standard solutions, where the two main types of errors overlap. Sometimes these duties are treated somewhat haphazardly so that soil samples become unrepresentative

or even incorrectly labelled and solutions are made from impure chemicals or inaccurate weights are taken.

Even when correct principles are efficiently applied to an analytical determination by well trained staff, certain inherent errors remain, which may lead to deviations from the true result. An example is the fact that scales on instruments or burettes must usually be assessed, since a true reading is difficult - perhaps because a galvanometer needle "hovers" over a range of values, as often happens in flame photometry. These errors are, however, mostly small and of no significance compared with the errors due to unsatisfactory laboratory conditions, faulty apparatus, poorly prepared samples, inaccurate solutions and careless work.

5-2. REPLICATION AND STANDARD SAMPLES. SCRUTINY.

In routine soil and water analysis, replication of all analyses is usually impossible and is probably undesirable on economic grounds. A system of duplication of a percentage of samples is often adopted to keep a check on the accuracy of analyses. For this system to be fully effective, certain rules should be followed -

1. Duplicate analyses should not be done on the same day.

2. They should preferably be done by different analysts, using different solutions and different instruments.

3. They should be done without the operator being aware that the sample has been analysed before - and certainly without a knowledge of the previous result.

In practice, a duplicate system can be easily organized to accommodate rule 1 but it is difficult to organize one incorporating rules 2 and 3 unless the laboratory work is on so large a scale that each method is carried out by two operators independently. In the more common case, when one assistant carries through a routine procedure for one determination each day, a compromise has to be reached. A suitable procedure for checking 10 per cent of analyses done at the rate of 50 per day by one operator would be -

> Each day, select five samples from the previous day's work, either at random or to cover a range of values. Include these in the present day's work, if possible without revealing to the operator which are duplicate analyses (although he should, in general, be aware of the laboratory practice of running 10 per cent duplication of his work). This is difficult if samples are numbered serially but it may be possible to conceal the duplicate samples in some cases by applying temporary fictitious numbers. Spread out the five duplicate samples over the day's quota and conceal the previous day's results by the use of laboratory work-sheets (see I.6-1.) rather than notebooks, in which operators can "turn back" to previous results.

Such a procedure should provide honest duplicate values if the operator is conscientious and well-trained. Variations can be adopted, of course; an interval of a few days can be allowed to elapse before including duplicate samples, or the operator can be told to take a different weight of sample (as in organic carbon analyses).

For some soil analyses, a large quantity of well-mixed, air-dry soil can be prepared and used as a "standard soil sample", being analysed

with the routine samples at selected intervals. Similarly, a large quantity of water containing known amounts of salts can be preserved with thymol and used as a "standard water sample", at any rate for a few weeks. A number of standard soil and water samples can, in fact, be chosen to cover different ranges of values in the routine analyses, it being necessary only to ensure that the concentrations of the elements or radicles being measured do not change with storage.

The series of values for analyses on standard samples provides a useful check on the reliability of routine results - although it is a drawback that, through constant repetition, the average analytical result for each analysis is bound to be known in advance.

It is fortunate that, in soil and water analysis, helpful checks on the accuracy of results are provided by inter-relationships of figures. A scrutiny of relative values quickly reveals discrepancies and hence the need for repetition of work. Examples of relationships which are useful in this way are -

1. In analyses of waters and water extracts of soils, the sum of the major cations (calcium, magnesium, sodium and potassium) should be nearly equal to the sum of the major anions (sulphate, chloride and bicarbonate - sometimes with carbonate) in milliequivalent per litre; also, there are fairly definite relationships between total salt concentrations and conductivity values (see Sections III.6 and IV.3).

2. In soil analyses, pH values correlate with various other analyses such as calcium carbonate content, amount of water soluble and exchangeable sodium, exchangeable hydrogen and lime requirement and so on. This applies not only to single pH values but to the ratios of pH values determined with different amounts of water.

3. Soil conductivity values are not only related to water soluble salts but also to the behaviour of soil-water suspensions, which clarify quickly by settling when the conductivity values are high, with calcium salts predominating. Also, high sodium can provide dark coloured extracts from organic soils due to solubility of humus.

4. Organic carbon figures are about 10-12 times total nitrogen figures for many agricultural soils but may rise to 15-20 times for highly organic peat and muck soils.

5. Particle size distribution figures can be judged approximately correct from soil texture assessments and saturation percentage values.

Furthermore, the reliability of a soil analysis can often be judged approximately from its known history or crop performance. Samples from the horizons of a profile also often show a gradation of properties. Such scrutiny, admittedly, only serves to reveal gross inaccuracies; but this is worthwhile and examination of soil analyses in this way should not be neglected. Sometimes an apparent "inaccuracy" turns out to be an abnormal result and then replication is necessary to confirm the figure so that the result can be reported confidently.

When replication or the analysis of "standard" samples or scrutiny reveals analytical errors, a programme of searching for the source of these errors must be set in motion, the routine work being halted temporarily. Such a programme should have three main objectives -

(a) Examination of all instruments used in the analysis for mechanical and electronic accuracy (most manufacturers give definite instructions on fault-finding in their literature).

(b) A check of all reagent and standard solutions for correct concentrations.

(c) Establishment of the reliability of the operator's technique, including entry of results and calculations.

Once the reason for discrepancies has been discovered, it is advisable to go back a little over the routine programme to ascertain the exact point at which faults arose and, of course, remove incaccurate results from the laboratory records.

5-3. DEGREES OF ACCURACY AND CALCULATIONS.

An analyst must assume that the sample he is handling is fully representative and therefore justifies careful work. He must then carry out his analysis and record the instrument scale reading or titration volume or precipitate weight, etc. with an accuracy appropriate to the operation involved. Thus, as examples -

(a) A soil sample of "5 g" for a pH determination is not weighed on an analytical balance with a sensitivity of 0.1 mg but rather on a rapid balance so that the weight lies between 4.9 and 5.1 g; while a similar weight for the determination of cation exchange capacity should be measured with a balance accurate to about 5 mg.

(b) A volume of 50 ml of an extraction solution may be added to a weighed soil sample with a measuring cylinder - but an aliquot volume of 50 ml from a water sample should preferably be taken by pipette.

(c) A titration volume should be recorded to the nearest 0.05 ml if the end-point can be judged correctly by the addition of one drop (0.05 ml) of the titrant solution; if, however, it is claimed that half a drop is sufficient to produce a clearly detectable colour change, then the burette reading may be recorded to 0.02 ml.

In general, an analyst should work intelligently so that he is neither straining for an unattainable degree of accuracy nor introducing unnecessary experimental errors. He must at all times use the appropriate instrument or piece of apparatus for each analytical operation and avoid both a haphazard attitude and too much attention to meticulous detail.

The final analytical result is calculated carefully (as set out in the methods in this Guide) and then recorded with an accuracy which is suited to the type of analysis and the technique used. The following examples show the principles involved and serve as a guide to the recording of other analyses.

1. Routine soil pH values should normally be recorded to the nearest 0.1 unit. Figures recorded to the nearest 0.05 or 0.01 unit may sometimes by justified in research work, after replication and calculation of means, but they rarely have practical significance.

2. Results for saturation percentage need only be recorded to the nearest whole number because the techniques involved do not justify greater accuracy.

3. Analyses for organic carbon can be recorded to two decimal places with fair confidence (unless the value is above about 5 per cent) if replicate analyses are done by a reliable technique and no recovery factors are involved. A method (such as the common Walkley-Black procedure) involving an average recovery factor cannot yield figures reliable to more than one decimal place, even with replication, when used for a variety of soil types. Conversion of organic carbon figures to "organic matter" is only a rough approximation but often the factor 1.724 (itself a falsely accurate figure based on the average carbon content of organic matter as 58 per cent) is used and the answer recorded to two or three decimal places. A better factor is 1.7 - and even a simple doubling of the organic carbon figure is accurate enough in most cases.

4. When values cover a wide range, itis often best to record results to an approximate percentage accuracy. Thus, in the determination of available potassium, it may only be possible to work with an overall accuracy of about one per cent; so values for "ppm K in soil" might be recorded as follows -

Up to 99	- nearest	1 ppm
100 - 248	- nearest	2 ppm
250 - 750	- nearest	5 ppm
Above 750	- nearest	10 ppm

When recording a result, an analyst should in general look particularly at the last digit he has written and ask himself if he is satisfied that this digit is correct and could not perhaps be one more or one less. Thus, a recorded figure of 31.76 implies that the analyst is sure that the true answer lies between 31.75 and 31.77 (or, strictly, between 31.755 and 31.765). If he feels this implication is not justified, then he should consider other ways of recording his result. To put 31.8 means that the true answer probably lies between 31.75 and 31.85 and in most cases this would be a more honest result; on the other hand, the analyst might feel he should return a result of 31.75, with a note that his work is recorded to the nearest 0.05, implying that the true answer lies between 31.73 and 31.77. It is impossible to lay down rules on this matter as each determination must be considered individually. But an analyst should never given spurious air of accuracy to his results by writing down too many significant figures. Shorter figures are nearly always better and easier to interpret in terms of soil composition and properties.

Calculations have been kept as simple as possible in this Guide, because it is often easy to arrange techniques so that a final titration value (say) is equal to - or a simple multiple or fraction of - the required answer. Where calculations are unavoidable (as in the case of the application of temperature factors), it is often worth while preparing tables for use in routine work (see Section IV.3).

Simple nomograms are also suited to sometypes of analysis. The determination of saturation percentage involves a division sum for each soil. This cannot be avoided or simplified because the weight of oven-dry soil (the denominator of the division sum) in a saturated soil paste cannot be fixed. But, by taking a weight of saturated soil paste within specified limits, the weights of water and oven-dry soil fall between known values and it is possible to prepare a nomogram from which the saturation percentage can be quickly read to the nearest whole number. (see Appendix 2.)

I. 6. LABORATORY RECORDS

6-1. WORK-SHEETS.

The data associated with a method of analysis - sample number, vessel numbers, aliquot taken, titration value, weight of precipitate, instrument scale reading, etc. - can be recorded either in notebooks or on laboratory work-sheets. Notebooks are suitable for research and development but as soon as a method is accepted for routine work, the data for it are best entered on a standard work-sheet, carefully designed to be as convenient as possible for the operator. For simple analyses like the determination of pH, a work-sheet need only consist of sets of three columns for laboratory sample number, beaker number and pH meter reading, with sufficient horizontal lines to permit the entry of an average day's work or a fraction of it (for large laboratories). In the case of more complicated analyses such as particle size distribution, a number of work-sheets are required, each designed very carefully according to individual laboratory conditions and procedures.

In Appendix 3, two examples are given of work-sheets which would be suitable for the recording of laboratory data in the determination of the sand fractions (USDA system) and the clay fraction (pipette method) in particle size distribution analysis (Section II.3). Typical analysis figures are included in these examples. The following points in design of work-sheets may be noted -

1. When subtractions are involved (weight of container plus material less weight of container - or the difference of two burette readings) it is best to arrange the work-sheet so that the sum is performed vertically. Subtraction of two numbers when they are entered side by side (horizontally) often leads to errors.

2. An individual soil sample can be defined throughout its analysis either by writing its laboratory number temporarily on all vessels used in the analysis for this sample - or by employing vessels which are permanently numbered or lettered. Work-sheet II.3.D. is designed for vessels with permanent numbers.

3. Only essential data should be included in the work-sheet. Thus, it is not necessary to record the temperature for the clay determination, although it has to be read to establish the settling time. If required later, it can be obtained from the recorded settling time by means of the tables in Appendix 4.

4. A brief record should be included of the essential fixed data required for calculations. For example, in the clay determination, a 20 ml aliquot is taken from 1 litre of suspension (and hence residue per litre = 50 R) and S is 1.00 in this partilular modification (see Section II.3-1. Note (5).

5. It is convenient to introduce a code system to serve as a constant reminder of the calculations involved.

Work-sheets are best printed on foolscap paper (34.5 x 21.5 cm) and the space filled as fully as possible. Thus, four lots of the data in work-sheet II.3.C. (example in Appendix 3) can be included comfortably. Two or more analyses should not be combined in one sheet, even where this is possible (e.g. pH determinations). The advantage of keeping one sheet to one analysis (or part of an analysis) is that replication is made more reliable by concealment of previous results (see I.5-2).

When completed, work-sheets are immediately filed according to analyses in order of laboratory numbers; thus there is quick and easy access to all present and past analytical results. It is useful, for some determinations, to have summary sheets on which groups of analyses can be recorded for rapid scrutiny (see I.5-2). Examples of such groups are

1. pH values at different soil-water ratios or using salt solutions.

2. Particle size distribution figures.

3. Exchangeable cations and cation exchange capacity.

4. Organic carbon, total nitrogen and the C/N ratio.

These summary sheets serve as half-way stages between individual analyses and full compilations of results (see below).

6-2. PRESENTATION OF RESULTS. OUTPUT RECORDS.

Analytical figures are preferably presented in small tables, grouped for convenience in interpretation. These tables may take various forms but for the methods in this Guide, suitable groupings of soil analyses might be -

1. The physical determinations of Section II, excluding method 5, which often needs a separate table.

2. pH values, calcium carbonate and soil acidity determinations (i.e. methods 1, 2 and 14 of Section III).

3. Conductivity and water soluble ions (methods 5 and 6 of Section III, method 6 normally consisting of the results of methods 4-11 of Section IV), with totals of cations and anions - and gypsum requirement (method 15) where appropriate.

4. Exchangeable cations and cation exchange capacity, coupled with organic carbon and total nitrogen (methods 3, 4, 7 and 8 of Section III).

5. Molecular ratios in the clay fraction and free iron oxides (methods 9 and 10 of Section III).

6. Available nitrogen, phosphorus and potassium (methods 11, 12 and 13 of Section III).

7. Minor elements. (method 16).

Results of water analyses are usually presented together but, if all the determinations of Section IV are done, the major cations and anions (methods 4-11), with their respective totals, are probably better in a table by themselves. Individual laboratories will naturally design their own groupings and small scale work can usually be presented in one table s ould not exceed 10-12.

The column headings should describe exactly the units in which results are presented and contain other essential data for unambiguous interpretation of the figures by a soil scientist who is completely unfamiliar with the laboratory procedures. If this involves too many words, descriptive footnotes should be added to the table. For example:

"pH" alone is not clear; the ratio of soil to water should be stated (see Section III.1); and "available" nitrogen, phosphorus or potassium results should be accompanied by a clear statement of the method of assessment. Also, if results are calculated to special units such as "pounds per acre", the basis of the calculation should be given (e.g. one acre of soil to a depth of 6 inches taken to weigh two million pounds).

All soil and water laboratories should keep records of analyses done and this is rendered simple by serial numbering of samples and use of dated work-sheets. Tables can be prepared of daily or weekly output for each method by noting the laboratory numbers of samples on completed work-sheets at appropriate times.

The analytical work involved in some determinations is far greater than in others and there is a wide difference in the skill and training needed for (say) a pH determination and a minor element analysis. A report that a laboratory carries out 10,000 soil analyses per year is meaningless unless this figure is broken down into details of the work done.

It is suggested that laboratory output would be better reported in terms of numbers of "determinations", using this word to mean a process resulting in a single analytical figure. Thus, the analysis of a soil for particle size distribution according to the USDA system involves 6 "determinations" (5 sand fractions and 1 clay fraction - the silt not counting as a "determination" since it is obtained by difference only) and thus the USDA mechanical analysis of 10 soils counts as 60 "determinations". "Weighting" analyses in this way helps to give a more realistic picture of the effort needed to obtain results, although variations in time and skill cannot be fully equalized. Perhaps analyses should be divided into "short", "medium" and "long" methods and the totals of "determinations" for each kept strictly separate in reviews of laboratory work.

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SECTION II

PHYSICAL ANALYSIS OF SOILS

INTRODUCTORY NOTE

These selected analyses provide basic information on density, particle size distribution and water retention.

A sample of soil in the undisturbed state is required for analysis II.I and, in some cases, for analysis II.5. The other analyses (including II.5) are carried out on air-dry soil samples which have been ground to pass a 2 mm sieve.

All results are recorded on an oven-dry soil basis (16-18 hours drying at 105°C.).

II. I. BULK DENSITY

I.A. PRINCIPLE.

Bulk density - or apparent density of soil - is the mass of oven-dry material per unit volume of soil in its natural undisturbed state. Its value is expressed in gram per cm^3 and may lie between 1.0 and 1.8 for mineral soils.

It is important that the soil sample be submitted to the laboratory with its natural structure undisturbed. If a core sampler of known volume (such as the Uhland type) is used, the determination of bulk density is simply a matter of drying the contents of the sampler and weighing. If, however, only a clod of soil of irregular shape is submitted, the volume must be found and this is normally done by finding the loss in weight in water after coating the clod with paraffin wax to prevent absorption of water.

I.B. APPARATUS

Balance, accurate to 10 mg
Moisture tins
Drying oven
Desiccator
Can for melting paraffin wax
Brush (optional)
Thread

I.C. REAGENT.

Paraffin wax, sp. gr. 0.90 ± 0.01

I.D. PROCEDURES.

(a) Sample of known volume submitted in core sampler.

Transfer the contents of the sampler completely to a tared moisture tin and dry in an oven at 105°C for 16-18 hours. Cool in a desiccator and weigh.

(b) Sample (clod of unknown volume submitted.

Break the clod into two pieces.

Take one piece and break it into smaller pieces to facilitate drying. Transfer immediately to a tared moisture tin and weigh the tin and soil. Dry in an oven at 105°C for 16-18 hours. Cool in a desiccator and weigh.

Tie a length of strong thread to the other piece of clod and weigh the sample. Coat the clod with paraffin wax by immersing it in melted wax or by brushing the melted wax carefully on to the surface. Allow the wax to solidify, then apply a second coat as quickly as possible. Weigh the coated clod in air and then immersed in water. Finally dry it with absorbent paper and check that the weight in air is unaltered. If the weight has changed (probably due to absorption of water through a small hole in the wax), apply another coat of wax and repeat the weighings in air and water.

I.B. CALCULATIONS.

(a) Sample of known volume submitted.

Let

V be the volume in cm^3 of the sampler

M be the weight in gram of oven-dry material contained in it

Then, the Bulk Density is $\frac{M}{V}$ gram per cm^3

(b) Sample of unknown volume submitted.

(i) Moisture determination.

Let

X be the weight in gram of the soil sample in its natural state, broken into small pieces

Y be the weight in gram of the same sample after oven drying

Then, the moisture percentage on an oven-dry basis is

$$\frac{100(X - Y)}{Y}$$

Let this be called M.

(ii) Bulk density determination.

Let

A be the weight in gram of the soil clod in its natural state

B be the weight in gram of the soil clod plus wax in air

C be the weight in gram of the soil clod plus wax in water

The weight of wax is (B - A) g and its volume is $\frac{B - A}{0.9}$ cm^3

The volume of the soil clod plus wax is (B - C) cm^3.

Thus the volume of the soil clod is $(B - C) - \frac{B - A}{0.9}$ cm^3

Let this be called B.

Since, from the moisture determination, (100 + M) g soil in its natural state contains 100 g oven-dry material,

Then, A g soil contains

$$\frac{100\ A}{100 + M}\ \text{g oven-dry material}$$

Thus the Bulk Density is

$$\frac{100\ A}{V(100 + M)}\ \text{gram per } cm^3$$

I.F. NOTES.

(1) The temperature of the melted paraffin wax should be only a few degrees above the melting point and treatment of the soil should not be prolonged.

(2) The volume of the wax-coated clod may be found approximately by displacement of water in a measuring cylinder.

(3) If only a small clod is submitted, measure A, B and C (see calculation (b) (ii) first, then remove the wax coating, break up the clod and measure X and M (calculation (b) (i)).

(4) With loose-textured soils of no stable structure, the wax coating method cannot be used. A sample of known volume is usually submitted to the laboratory in these cases. If this is not done, obtain the volume of the sample by transferring it to a dry measuring cylinder and tapping down gently.

(5) The accuracy of weighing depends on the size of clod under examination; often the nearest 0.1 g is sufficient. The bulk density value may be calculated to the nearest 0.01 gram per cm^3

I.G. REFERENCES.

AKROYD. pp. 43 to 46.

ASTAPOV. Chapter III.

BAVER. Chapter V, pp. 180 to 182.

BLACK. Chapter 30. (G.R. BLAKE)

Bibliographies 751 and 860

II. 2. PARTICLE DENSITY AND POROSITY

2.A. PRINCIPLE.

Particle density - or real density of soil - is the mass of oven-dry material per unit volume of air-free soil, averaged over the different sized particles below 2 mm diameter. Its value is expressed in gram per cm^3 and is near 2.65 for mineral soils. If the organic matter content is high, the value is usually lower.

The determination is based on finding the volume of the particles contained in a known weight of oven-dry soil by measuring the weight of a liquid of known specific gravity displaced by these particles. The liquid chosen is organic so that no salts are dissolved and no absorption takes place which might lead to swelling of the particles.

Porosity of soil in its natural state is defined as the percentage of the total volume which is occupied by air spaces between the soil particles. It is found by calculation from the real and apparant density values.

2.B. APPARATUS.

Analytical balance, accurate to I mg
Moisture tins
Drying oven
Desiccator
Pycnometers (density or specific gravity bottles) wide-mouth, 50 ml
Vacuum desiccator
Vacuum pump
Beaker, 250 or 400 ml
Thermometer, covering room temperatures

2.C. REAGENT

Kerosene, benzene, toluene or xylen, as convenient

2.D. PROCEDURE.

Dry a little more than 10 g of 2 mm soil in an oven at 105°C for 16-18 hours. Cool in a desiccator.

Dry the pycnometer and weigh (with stopper). Transfer the oven-dry soil to the pycnometer and weigh again. Cover the soil with the organic liquid chosen and place the pycnometer in a vacuum desiccator, together with a beaker containing more of the liquid. Reduce the pressure gradually to a vacuum of near 76 cm mercury so that air is removed from between the soil particles in the pycnometer and also from the liquid in the beaker. Leave overnight.

Realese the vacuum slowly and then reapply to ensure that all air has been removed; repeat if necessary. Fill the pycnometer with the air-free organic liquid, insert the stopper, clean the outside surface and weigh. Finally measure the temperature of the liquid.

2.E. CALCULATIONS.

(a) Particle density.

Let

A be the weight in gram of the pycnometer

B be the weight in gram of the pycnometer and oven-dry soil

C be the weight in gram of the pycnometer filled with soil and liquid

If the specific gravity of the liquid at the temperature of operation is G (from tables), the weight of liquid needed to fill the pycnometer (volume 50 ml) in the absence of soil is 50 G gram

The weight of liquid needed to fill the pycnometer in the presence of soil is (C - B) gram

Thus, the weight of liquid displaced by the soil particles is

50 G - (C - B) or 50 G + B - C gram

Thus, the volume of the soil particles is

$$\frac{50\,G + B - C}{G} \text{ cm}^3$$

The weight of the soil particles is (B - A) gram

Thus, the Particle Density is

$$\frac{G(B - A)}{50\,G + B - C} \text{ gram per cm}^3$$

(b) Porosity.

Let

B be the bulk density (or apparent density)

P be the particle density (or real density)

Then, a volume V cm^3 of soil in its natural state contains BV gram of oven-dry soil particles which occupy

$$\frac{BV}{P} \text{ cm}^3$$

Thus, the pore space is $V - \frac{BV}{P}$ or $V\frac{(P - B)}{P}$ cm^3

Expressing this as a percentage of V, the porosity is

$$\frac{100(P - B)}{P} \text{ per cent}$$

2.F. NOTES.

(1) The method given is a simplification of the accurate procedure using a constant temperature bath. It should give results correct to the second decimal place if weighings are made with an accuracy of about 2 mg and the determination is carried out at a reasonably constant temperature near the temperature of calibration of the pycnometer.

(2) The main source of error is failure to remove all air entrapped between the soil particles.

(3) The volume of the pycnometer may be checked by weighing it full of air-free distilled or deionized water of known specific gravity (from tables).

(4) The weight of liquid needed to fill the pycnometer may be determined directly by filling with the liquid (at the same temperature as used in the determination of particle density) and weighing. This also serves to check the specific gravity of the liquid.

2.G. REFERENCES.

AKROYD. pp. 46 to 54.

ASTAPOV. Chapter III.

BLACK. Chapter 29. (G.R. BLAKE)

RICHARDS. Chapter 6. Methods 39 and 40.

II. 3. PARTICLE SIZE DISTRIBUTION (MECHANICAL ANALYSIS)

GENERAL PRINCIPLES.

Mechanical analysis separates the inorganic mineral portion of soil into classified grades according to particle size and determines their relative proportions by weight. In a full analysis, the whole sample of soil and gravel would be examined; but in the procedures below only material less than 2 millimeters diameter is considered.

For agricultural purposes, two main systems of classification of the particle size grades below 2 millimeters diameter are recognised -

1. International System (also known as the Atterburg System)

	Particle Size Grades	
	millimeters	microns
Coarse Sand	2.0 - 0.2	2000 - 200
Fine Sand	0.2 - 0.02	200 - 20
Silt	0.02 - 0.002	20 - 2
Clay	less than 0.002	less than 2

2. United States Department of Agriculture (USDA) System

	Particle Size Grades	
	millimeters	microns
Very Coarse Sand	2.0 - 1.0	2000 - 1000
Coarse Sand	1.0 - 0.5	1000 - 500
Medium Sand	0.5 - 0.25	500 - 250
Fine Sand	0.25 - 0.10	250 - 100
Very Fine Sand	0.10 - 0.05	100 - 50
Silt	0.05 - 0.002	50 - 2
Clay	less than 0.002	less than 2

Since both these classifications are used to designate soil textures and study degree of weathering, clay movement and lithological discontinuities throughout soil profiles, procedures for determining both sets of particle size grades are described below. Sometimes shortened versions of the procedures may be sufficient, e.g. omitting the division of the sand fractions (particularly in the USDA system) in samples containing only small amounts of sand.

In general, the determinations involve three distinct stages -

(a) Removal or inactivation of cementing agents (mainly organic matter and calcium ion but including colloidal iron or aluminium oxides in some soils) and complete dispersion of the soil sample in an alkaline medium. (Pretreatment)

(b) Separation of the coarse sand fraction (International System) or the total sand fraction (USDA System) by wet sieving; followed by division of the total sand fraction (USDA System) by dry sieving.

(c) Determination of the clay fraction (both systems) and the silt fraction (International System) in the dispersed sample by

either (i) taking samples by pipette
or (ii) measuring specific gravity with a special hydrometer

each after calculated times which ensure that the required fraction is being determined.

These stages are described separately.

It is an agreed convention that the percentage of each particle size grade is reported on the basis of oven-dry soil free of organic matter. According to early recommendations, calcium carbonate is also removed from calcareous soils by acid treatment, so that, in these cases, the particle size grade percentages refer to oven-dry soil free of organic matter and calcium carbonate. This removal of calcium carbonate is now regarded as optional.

NOTE.

The International System was recommended in 1926 by the First Commission of the International Society of Soil Science, which also advocated the removal of both organic matter and calcium carbonate.

The United States Department of Agriculture adopted the system given above in 1938, although very similar systems had been in use in the United States from the beginning of the century.

II. 3-1. PRETREATMENT OF SOIL

3-1.A. PRINCIPLE.

Organic matter is oxidized by heating with hydrogen peroxide and the excess peroxide is destroyed by boiling. Calcareous soils may subsequently be treated (if desired) with sufficient dilute hydrochloric acid to dissolve the carbonate and provide an acid solution of about 0.2 N concentration. If the hydrogen peroxide treatment only is used and the soil is non-saline, the treated soil is heated to remove the bulk of the water and then oven-dried; if the acid treatment is used, the soil suspension is filtered and washed nearly free of acid before oven-drying. The oven-dry residue is weighed as inorganic soil free of organic matter and adsorbed water; and, if acid has been used, free of calcium carbonate. See Note 3.)

The prepared mineral portion of soil is treated with sodium hexametaphosphate solution and stirred mechanically at high speed to disperse the particles. The chemical used is effective with most soils mainly because it forms an undissociated complex with calcium ions, so inactivating their power of binding clay particles together. This is so even if the soil is calcareous and high in exchangeable calcium; but the treatment may not be effective with soils high in gypsum or colloidal iron and aluminium oxides. (see Notes)

3-1.B. APPARATUS.

Balance, accurate to 0.5 g
Beakers, tall form, 400 or 600 ml
Watch glasses, to fit beakers
Hot plate or sand bath
Measuring cylinders, 10 and 50 ml
Filtering media -

either (i) ceramic filters, e.g. Pasteur-Chamberland candles, fineness "F"
or (ii) hardened, fine-textured filter paper, Buchner funnels and filter flasks

Suction pump
Wash bottle, plastic
Glass rods, fitted with rubber 'policemen' or stoppers
Beakers, 250 ml
Drying oven
Desiccator
Balance, accurate to 10 mg
Pipette, 20 ml
High-speed stirrer, specially made for mechanical analysis
Interval timer

3-1.C. REAGENTS.

Hydrogen peroxide, 30 per cent, 100 volume
Hydrochloric acid, 2 N
Sodium hexametaphosphate dispersing solution -
Dissolve 35.7 g dry, powdered sodium hexametaphosphate and 7.94 g anhydrous sodium carbonate to 1 litre.
Dissolve the hexametaphosphate first by adding the dry powder slowly to about 750 ml water which is well stirred during the addition. Then add the sodium carbonate and make to 1 litre. (see note 5)

3-1.D. PROCEDURE.

Transfer 20 g (± 0.5 g) air-dry soil, passing 2 mm (but see Note 7) to a 400 or 600 ml tall-form beaker (using the larger beaker for soils containing much organic matter) and add 50 ml water. Add 5-10 ml 30 per cent hydrogen peroxide and cover with a watch glass. If effervescence is brisk, keep cool; otherwise warm gently on a hot plate or sand bath. Repeat the treatment with successive small portions of hydrogen peroxide until warming produces no further reaction. Then boil gently to remove excess peroxide. (see Note 1)

If the soil contains X per cent calcium carbonate and it is wished to destroy this, add a volume of (2X + 25) ml of 2 N hydrochloric acid together with sufficient water to make the total volume about 250 ml. Proceed carefully if the soil is very calcareous. Leave until effervescence ceases. If the soil is not calcareous or it is wished to include calcium carbonate in the analytical results, omit this acid treatment.

When acid has not been used, transfer the peroxide treated soil to a tared 250 ml beaker, evaporate the bulk of the water by gentle heating (see note 3) and finally dry the beaker and contents in an oven at 105°C for 16-18 hours. When acid has been used, filter the soil suspension by suction, using whichever filtering medium is convenient or effective, and wash the soil with water four or five times. Transfer the washed soil to a tared 250 ml beaker with the minimum quantity of water, using a rubber 'policeman' or stopper to remove the last traces of fine material from the surface of the filtering medium. Evaporate gently to dryness and then dry in an oven at 105°C for 16-18 hours. After cooling in a desiccator, weigh the beaker and contents to the nearest 10 mg and record the weight of soil for subsequent calculations.

Add 20 ml sodium hexametaphosphate dispersing solution by pipette to the dry soil and leave overnight. Then transfer the mixture with water to the cup of a high-speed stirrer and make the volume to about 500 ml.

Stir for 2-10 minutes depending on the soil and then wash down the stirrer blades as they are removed from the suspension.

3-1.E. NOTES.

(1) Remoral of small amounts of organic matter (organic carbon less than 0.5 per cent) is unnecessary.

(2) Soils which are non-calcareous and contain less than 0.5 percent organic carbon normally need no pretreatment prior to dispersion. Approximately 20 g soil is oven-dried and weighed before the final stage of stirring with dispersing solution. (but see Note 3)

(3) Saline soils may need special treatment, according to the amount and kind of salts present. This special treatment only arisee when acid is not used since, when acid is used, the subsequent filtration and washing with water will remove soluble salts or reduce them to small amounts unlikely to affect the analysis.

When acid is not used, the kind of salts present must be known and it is preferable to have the results of a soluble salt analysis (Section III.6.) Naturally, the quantities will affect the weight of oven-dry material and corrections may have to be applied (see II.3-3.5.(3)). Sodium salts do not normally affect practical procedures but calcium (and possibly magnesium) sulphate flocculates clay and, when present in large amounts, may counteract the dispersing power of sodium hexametaphosphate. When much gypsum is present and acid treatment is not used, the concentration of gypsum should be reduced by washing the soil four or five times with large quantities of water (gypsum being sparingly soluble) before oven-drying.

Washing soils entirely free of salts may lead to deflocculation of clay and passage of the clay particles through the filter. Therefore, washing should not be prolonged, except to reduce gypsum to amounts which will not interfere with proper dispersion of the silt and clay particles.

(4) Clay soils may be difficult to filter, particularly when associated with sodium ions. Pretreatment of alkaline sodium clays with acid to (remove carbonates) is not recommended, as subsequent filtration may be difficult.

(5) The dispersing solution is the one usually advocated. It is 0.35 N as sodium hexametaphosphate and 0.15 N as sodium carbonate; thus the solution is 0.5 N as sodium carbonate; thus the solution is 0.5 N in sodium ion. In order to ensure that these normalities are correct, the chemicals have to be dried and weighed exactly.

A mixture of sodium hexametaphosphate and sodium carbonate is obtainable under the trade name "Calgon". This may be dried and 50 g dissolved to 1 litre.

The solution is said to lose its effectiveness after a time but authorities seem uncertain how long it will last. Probably the solution should not be more than one month old.

However, care should be taken to avoid commercial washing powder preparations under the same "Calgon", which may contain different proportions of sodium hexametaphosphate and sodium carbonate or other chemicals; where the composition of "Calgon" is not stated, the separate chemicals should be used.

In the pipette method for determining fine particles, the concentration of salts in the dispersing solution has to be known exactly in order to apply a correction to the oven-dry weight of clay or silt+clay. 20 ml of the above dispersing solution contains 0.8728 g dry salts. However, since other concentrations of sodium hexametaphosphate have been advocated and the amount of sodium carbonate (to prevent reversion to orthophosphate) is uncritical, alternative and more convenient concentrations may be made. For example, using 40 g sodium hexametaphosphate and 10 g sodium carbonate (accurately weighed after drying) per litre, the solution contains 1.000 g dry salts per 20 ml and use of it leads to easier calculation of the silt and clay fractions in the pipette method, with a 20 ml aliquot of the dispersed soil.

(6) It is claimed that sodium hexametaphosphate is not effective in dispersing soils containing laterite (plinthite), much colloidal iron or aluminium oxides, or soils derived from volcanic ashes. Better dispersion may be obtained with sodium hydroxide, with ammonium carbonate and sodium hydroxide mixtures, with trisodium orthophosphate, with tetrasodium pyrophosphate, with sodium carbonate or even with ammonia. Very good dispersions are also obtained with Ultrasonics (see references).

(7) If the hydrometer method is to be used for determining silt and clay in medium or heavy textured soils, and pretreatment is to be carried out, rather more than 50 g of air-dry soil is taken so that, after oxidation with hydrogen peroxide and acid treatment (if employed), exactly 50 g of oven-dry soil can be weighed for analysis. For sands 100 g oven-dry soil is required but in this case pretreatment is rarely necessary. (refer to method II.3-4).

II. 3-2. SAND FRACTIONS

3-2.A PRINCIPLE.

In mechanical analysis according to the International System it is only possible to separate the coarse sand fraction by sieving, since no sieve having apertures as small as 0.02 mm diameter is available to separate "fine sand" from silt. But, for the USDA System, the whole of the sand fractions can be separated in this way, since the limit of "very fine sand" is set at 0.05 mm.

The pretreated soil suspension prepared in II.3-1 is passed through the appropriate sized sieve and the sand fraction is washed and oven-dried and weighed. In analyses for the USDA System, the dried total sand fraction is then sieved through four appropriate sized sieves by mechanical shaking and the separated fractions are weighed.

3-2.B. APPARATUS.

Funnel, 10-12 cm diameter, supported on stand
Measuring cylinders, 1 litre
Wash bottle, plastic
Glass rods, fitted with rubber 'policemen' or stoppers
Drying oven
Watch glasses, 10-12 cm diameter
Brush Small porcelain basins
Desiccator
Balance, accurate to 10 mg

PLUS either, for the International System

ASTM standard sieves No. 80, 3-inch or 5-inch diameter

or, for the USDA System -

ASTM standard sieves No. 325, 3-inch or 5-inch diameter
Set of ASTM standard sieves, 3-inch or 5 inch diameter, Nos. 20, 40, 70 and 170, with receiver
Mechanical sieve shaker
Interval timer

3-2.C. PROCEDURES.

(a) International System.

Arrange a No. 80 sieve on a stand over a funnel and 1 litre cylinder. Pour the dispersed soil suspension (from procedure 3-1.D.) through the sieve, which retains the coarse sand fraction. Wash this fraction, rubbing it VERY GENTLY with a rubber 'policeman' or stopper to assist finer particles through the sieve

Drain the sieve, place it on a watch glass and dry in an oven for 30-60 minutes. Shake the sieve well by hand (or use a sieve shaker if preferred) to remove particles less than 200 microns and then transfer the coarse sand fraction to a small tared basin, brushing off the sieve surfaces carefully, and dry at 105°C for two hours. Cool in a desiccator and weigh to the nearest 10 mg.

(b) USDA System.

Proceed as in (a) above, using a No. 325 sieve in place of a No. 80, so determining the total sand fraction.

Transfer the dry total sand fraction to a set of sieves (Nos. 20, 40, 70 and 170 - No. 20 at the top) and receiver. Place on a mechanical shaker and shake for five to fifteen minutes, according to the performance of the shaker. Transfer the finest fraction (very fine sand) to the original small tared basin and weigh to the nearest 10 mg. Add the fine sand fraction and weigh again. Obtain the successive weighings after adding the medium sand, coarse sand and very coarse sand fractions; and check that the final weight is the same as the weight of the total sand retained on the No. 325 sieve.

3-2.D. CALCULATIONS.

Let

M be the weight in gram of the oven-dry, organic free soil sample (see procedure 3-1.D.).

This figure is used in all calculations.

(a) International System.

Let

X be the weight in gram of coarse sand

Then, the coarse sand percentage is

$$\frac{100\ X}{M}$$

(b) USDA System.

Let

Y be the weight in gram of the total sand

Then, the total sand percentage is

$$\frac{100\ Y}{M}$$

Let

A be the weight in gram of the fraction 50 - 100 micron

B be the weight in gram of the fraction 50 - 250 micron

C be the weight in gram of the fraction 50 - 500 micron

D be the weight in gram of the fraction 50 - 1000 micron

Then, the percentages of the various sand fractions are

Very fine sand	$\frac{100\ A}{M}$
Fine sand	$\frac{100(B - A)}{M}$
Medium sand	$\frac{100(C - B)}{M}$
Coarse sand	$\frac{100(D - C)}{M}$
Very coarse sand	$\frac{100(Y - D)}{M}$

3-2.B. NOTES.

(1) The ASTM (American Society of Testing Materials) series of sieves has wire mesh screens forming square holes which differ in side length by the fourth root of 2 - and thus differ in area by the square root of 2. Sieves having side lengths of 1000, 500 and 250 microns are made but there are no sieves of 200, 100 or 50 microns side length.

Since the diagonal across a square aperture is longer than the side, the use of sieves consisting of square holes whose side length is exactly equal to the fraction diameter to be retained would tend to lead to low results in the retained sample, having to regard the irregular shape of the sand particles. Therefore, a slightly lower side length is used.

The sieves chosen to separate the sand fractions are -

Sieve No. (ASTM)	Side Length microns	Grade Division microns
20	840	1000
40	420	500
70	210	250
170	88	100
325	44	50
80	177	200 (Int. System)

(2) The wire mesh of the finer sieves is very delicate and must be treated with great care, particularly in the wet sieving processes. The N. 325 sieve tends to have a short life and a number of spares must be available.

(3) If the sand fractions are weighed to the nearest 10 mg, the sand percentages can be recorded to the nearest 0.1

II. 3-3. PIPETTE METHOD FOR SILT AND CLAY

3-3.A. PRINCIPLE.

The material passing through the No. 80 sieve (International System) contains the fine sand, silt and clay fractions; both silt and clay fractions are determined in this, giving the fine sand by difference. But the material passing through the No. 325 sieve (USDA System) only contains the silt and clay fractions; so that it is sufficient to determine just the clay fraction in this case, the silt being obtained by difference.

The volume of the suspension is made to 1 litre in a cylinder and it is well mixed and allowed to stand at a reasonably constant temperature. (see Note 1) The soil particles fall through the liquid at varying rates, depending on their size, according to Stokes' Law. After a calculated time an aliquot is removed by pipette from a definite depth below the surface and this is evaporated to dryness and the residue is oven-dried and weighed. Two different times of settling are necessary for the International System, one (short) to provide a measure of the silt+clay and the other (long) to provide a measure of the clay only. One time of settling is sufficient for the USDA System, in which clay is measured.

3-3.B. APPARATUS.

Measuring cylinders, 1 litre, as used in method 3-2
Special plunger for mixing, consisting of a circular brass disc, about 55 mm diameter, fastened to a 600 mm length of brass rod. The disc is pierced with 8 to 10 holes of 4-5 mm diameter.
Pipette, 20 or 25 ml, fitted to a rack by means of which it can be raised or lowered measured distances. (supplied specially for mechanical analysis)
Suction device for use with the pipette (see Note 2)
Interval timers, one for minutes and seconds, one for hours and minutes - or stop-watch - or accurate clock with seconds hand
Thermometer, covering room temperatures
Evaporating basins, capacity 35-50 ml.
Wash bottle, plastic
Water bath
Drying oven
Desiccator
Analytical balance, accurate to 0.2 mg

3-3.C. PROCEDURE.

Make the dispersed sample, collected in a cylinder, (from procedure 3-2.C.) to 1 litre and measure its temperature. Mix thoroughly with the special plunger, remove it and wait until the swirling motion of the particles has just given way to a steady settling under gravity. Start the timer or stop-watch; or record the time.

About 30 seconds before the appropriate sampling time (see Calculations and Appendix 4), lower the pipette (previously fixed above the centre of the cylinder) until the tip just touches the surface of the suspension. Note the vertical scale reading and then lower the pipette to the required depth. Fill the pipette by gentle and steady suction (see Note 2) and remove from the suspension. Transfer the aliquot to an evaporating

basin and wash the pipette twice with water, adding the washings to the basin. Evaporate to dryness on a water bath, dry the residue in an oven at 105°C for 16-18 hours, cool in a desiccator and weigh to the nearest 0.2 mg.

Wash the pipette with ethanol or acetone and dry by passing air through it. Then repeat the sampling it a second time (for the International System) after remixing the suspension with the plunger.

Dilute 20 ml sodium hexametaphosphate dispersing solution to 1 litre and fill the pipette with this diluted solution. Transfer to an evaporating basin and obtain the oven-dry weight of residue in the aliquot.

3-3.D. CALCULATIONS.

(a) Settling times and depths.

Stokes' Law, as normally quoted in the literature, states that the velocity of fall of a spherical particle through a liquid medium is

$$\frac{2\ (D_1 - D_2)\ G\ R^2}{9\ P} \text{ cm per second}$$

where -

D_1 is the density of the particle in gram per cm^3

D_2 is the density of the liquid in gram per cm^3

G is the acceleration due to gravity in cm per $(sec)^2$

R is the radius of the particle in cm

P is the viscosity of the liquid in poises (gram per cm per second)

In applying this Law to mechanical analysis, it is assumed that soil particles behave as spheres and that D_1 is 2.65 and D_2 is 1.00.

Also, G, at sea level, is 981.

Substituting these values, the velocity of fall becomes

$$\frac{359.7\ R^2}{P} \text{ cm per second}$$

or, the time taken to fall 1 cm is

$$\frac{P}{359.7\ R^2} \text{ seconds}$$

For the largest clay particles, R is 10^{-4} so that the time for these particles to fall 1 cm is

$$\frac{P \times 10^8}{359.7} \text{ seconds}$$

For the largest silt particles (International System), R is 10^{-3} and the time to fall 1 cm is

$$\frac{P \times 10^6}{359.7} \text{ seconds}$$

Viscosity varies markedly with temperature so that times of fall have to be calculated for the room temperatures of each laboratory.

Using these relationships, the tables of Appendix 4 are constructed. Laboratories situated well above sea level should use the appropriate (lower) value of G.

(b) Clay percentages (both systems)

Let

C be the weight in gram of the residue from the aliquot taken for clay determination

This weight consists of clay particles, plus sodium hexametaphosphate carbonate from the dispersing solution, plus any soluble salts not removed by pretreatment.

The weight of residue is corrected for these salts (see Note 3) by subtracting a weight F gram, so that the weight of clay only is

$$(C - F) \text{ gram}$$

Let the aliquot taken be A ml

Then, the weight of clay in the total volume (1000 ml) of suspension is

$$\frac{1000\ (C - F)}{A} \text{ gram}$$

As M is the weight in gram of the oven-dry, organic free soil sample from which the suspension was made (see 3-2.D.), the percentage of clay is

$$\frac{1000\ (C - F)}{A} \times \frac{100}{M}$$

$$\frac{(C - F) \times 10^5}{AM}$$

(c) Silt percentage (International System)

Let

SC be the weight in gram of the residue from the aliquot taken for silt+clay determination

By similar calculations to (b) above, the silt+clay percentage is

$$\frac{(SC - F) \times 10^5}{AM}$$

from which the silt percentage is obtained by subtracting the clay percentage.

(d) Final calculations.

Obtain the fine sand percentage (International System) by adding the coarse sand, silt and clay percentages and subtracting from 100.

Obtain the silt percentage (USDA System) by adding the total sand and clay percentages and subtracting from 100.

3-3.B. NOTES.

(1) Ideally, this determination should be carried out in a constant temperature room; or the cylinders may be placed in a large temperature controlled water bath. Where these facilities are not available, a room of only slightly fluctuating temperature should be chosen.

(2) The pipette should fill at a steady rate in about 20 seconds. It It may be attached to a suction pump having a controlled leak, previously adjusted. Or it may be connected to the air space (closed) above water in an aspirator bottle and water allowed to run out of the bottle at the rate of 20-25 ml per 20 seconds. This rate can be controlled by a length of capillary tubing in the outlet tube. Never fill the pipette by mouth.

All mechanical analysis pipettes have a 2-way tap at the 20 or 25 ml mark which is closed when the suspension rises above it. The small amount of suspension above the tap is discarded before allowing the aliquot to run out into the evaporating basin.

(3) The correction for the salts from the dispersing solution is obtained by experiment (see 3-3.C.), which is done as a check even if the original chemicals are carefully dried and weighed.

Soluble salts mostly need not be taken into account in calculations, either because they are low in the original soil or have been removed during pretreatment. If, in special cases, a soil containing high amounts of soluble salts in being analysed without removing salts (e.g. a non-calcareous subsoil clay), a correction can be made by one of two methods -

(i) Shake 10 g air-dry soil with 500 ml water and allow to stand in a cylinder. When sufficient liquid is clear, take out 25 ml and determine the salt content by evaporation and drying. A residue of Y g salts indicates that the soil contains 200 Y per cent of soluble salts. If the soil does not settle, then either the amount of salts is not enough to affect the results or the soil is very alkaline (i.e. contains sodium carbonate) and the quantity of soluble salts cannot be determined in this way. (see below)

Calculate the approximate percentage of soluble salt in the soil by multiplying the conductivity of a 1:5 suspension (see method III.5.) in millimhos by 0.3.

As a rough guide, soils having conductivities (1:5 suspension) above 1.5 millimhos should have a correction for soluble salts, if these are not removed during pretreatment and accurate mechanical analysis results are wanted.

(4) If the weighings of residues are made to 0.2 mg, it is possible to calculate the clay and silt percentages to the nearest 0.05 or 0.04 (depending on the aliquot taken). Results may be recorded to the nearest 0.1, as in the case of the sand fractions.

II. 3-4. HYDROMETER METHOD FOR SILT AND CLAY

3-4.A. PRINCIPLE.

The density of a soil suspension at a given depth becomes less as the particles settle. Its value at different times is related empirically to particle size, so that, by selection of times, a density reading can be a measure of either silt+clay or clay.

The density is measured with a special hydrometer of stream-lined design whose stem is calibrated directly in percentages (usually 0-60). These figures refer to the percentage of particles less than a definite size in a suspension containing 100 g of oven-dry soil per litre. Because the method was introduced by Bouyoucos in 1927 and advocated by him for many years, the hydrometer became known as the Bouyoucos hydrometer; it is calibrated at 20°C (68°F) but may be used (with suitable corrections) over the range 15-25°C (59-77°F). Another hydrometer - ASTM No.152 H - is now available; this has similar scale markings in gram per litre but is associated particularly with an alternative procedure developed by P.R. Day.

The technique recommended by Bouyoucos involves no pretreatments to remove organic matter or calcium carbonate, soils being simply dispersed with sodium hexametaphosphate. The results are then unavoidably approximate if the soils contain much organic or calcareous material. More reliable results are obtained by putting soils through the normal pre-treatment procedures (see II.3-1) before dispersion in sodium hexametaphosphate.

Bouyoucos advocates settling times for silt+clay and clay based on comparisons of his method (without removal of organic matter or calcium carbonate) with the standard pipette method (see II.3-3). These times are not derived strictly from Stokes' Law but seem to give reasonable results in many cases. (see Notes (1) and (2) More recently, Day has suggested different settling times based on a more rigid adherence to Stokes' Law and careful calibration of the ASTM 152 H hydrometer in soil suspensions. No definite ruling can be given on procedures which will suit all soils and each laboratory must choose its own technique based on the suggestions below:

3-4.B. APPARATUS.

Apparatus as given in 3-1 and 3-2 for pretreatment and separation of coarse sand (International System) or total sand (USDA System)
Special plunger for mixing, as in 3-3.B.
Thermometer, covering the temperature range 15-25°C
Interval timers, one for minutes and seconds, one for hours and minutes - or stop-watch - or accurate clock with seconds hand

Bouyoucos hydrometers or ASTM hydrometers No.152 H
Hydrometer jars, marked at 1000 ml.

3-4.C. REAGENTS.

Reagents as given in 3-1 for pretreatment and dispersion, using 5 per cent Calgon solution or 40 g sodium hexametaphospate plus 10 g sodium carbonate per litre.

3-4.D. PROCEDURES.

(a) Based on the traditional Bouyoucos' method.

Estimate the texture of the soil to be tested and classify it as either "sandy (sil+clay less than about 15 per cent) or "not sandy". Transfer 50 g oven-dry "not sandy" soil or 100 g oven-dry "sandy" soil (or an amount of air-dry soil containing such weights of oven-dry material) to a 250 ml beaker and add 100 ml 5 per cent solution of sodium hexametaphospate - sodium carbonate. Soak overnight and then transfer soil and solution to the cup of a mechanical stirrer, washing out the beaker and making the volume in the cup to about 500 ml with water. Stir for 2-5 minutes.

If the soil contains an appreciable amount of organic matter or calcium sulphate, reduce the amounts by treatment with hydrogen peroxide or water, as described in section 3-1; then dry and weigh as above (see Note 1).

Transfer the dispersed soil suspension to a hydrometer jar, washing out the stirrer cup and adjusting the volume in the jar to one litre with water. (see Note 3) Mix with a long glass rod and read the temperature, which should be between 15° and 25°C. Then mix with the special plunger (see 3-3.C.) and start timing. At the appropriate selected times, lower the Bouyoucos hydrometer carefully into the centre of the suspension and release it gently so that it does not rotate nor move up or down too violently. Take the reading on the scale to the nearest 0.5 unit.

The times advocated by Bouyoucos are -

Particles less than 50 microns - 40 seconds
Particles less than 20 microns - 4 minutes
Particles less than 5 microns - 1 hour
Particles less than 2 microns - 2 hours

However, these times (particularly that for 2 micron clay) may have to be changed in some cases (see Note 2).

Finally, prepare one litre of a 0.5 per cent solution of sodium hexametaphosphate - sodium carbonate (dilute the stock solution ten times), transfer it to a hydrometer jar and adjust the temperature to 20°C. Insert a Bouyoucos hydrometer and obtain the reading (to be used as a blank). Discard the solution.

(b) Based on Day's modifications.

Carry through the dispersion procedure given above, starting with either 40 or 50 g oven-dry material (or its equivalent), irrespective of texture and removing or reducing appreciable amounts of organic matter or calcium. Take readings with the ASTM hydrometer at 30 seconds and 1 minute (without removing the hydrometer) and subsequently at 3, 10, 30, 90, 270 and 720 minutes, where practicable. Alternatively take readings at specified times based on Stokes' Law and the temperature reading. (see 3-4.E.(ii) (c) and Note 5)

Obtain a blank reading when the hydrometer is immersed in a 0.5 per cent solution of sodium hexametaphosphate - sodium carbonate within ± 2°C of the temperature of the soil suspensions being analysed.

3-4.E. CALCULATIONS.

(i) Bouyoucos Method.

Correct the scale reading (if made at a temperature other than 20°C) by adding or subtracting the appropriate figure from the table below -

Temperature °C	Correction g per litre
15	- 2.0
16	- 1.5
17, 18	- 1.0
19	- 0.5
20	Nil
21	+ 0.5
22, 23	+ 1.0
24	+ 1.5
25	+ 2.0

Then subtract the blank reading obtained with the 0.5 per cent dispersing solution at 20°C, thus allowing for the apparent density of the solution without soil particles.

The figures so obtained are direct percentages of clay (less than 5 micron or 2 micron, according to time) or silt+clay (less than 50 micron or 20 micron, according to time) if 100 g oven-dry soil (or its equivalent) was taken for analysis; if 50 g oven-dry soil was taken, multiply the figures by 2 to give percentages.

Day Method.

(a) Theory

In section 3-3.D. it was seen that, from Stokes' Law, the velocity of fall of a particle of soil of radius R cm in a liquid of viscosity P poises is approximately

$$\frac{360\ R^2}{P} \text{ cm per second,}$$

assuming that the density of soil particles is 2.65 g per cm^3, the density of the liquid is 1.00 g per cm^3 and the acceleration due to gravity is 981 cm per sec per sec.

If the particle falls H cm in t seconds, then we have

$$\frac{H}{t} = \frac{360\ R^2}{P}$$

and so

$$R^2 = \frac{PH}{360\ t} \qquad (1)$$

It is more convenient to work in microns and to refer to diameters of soil particles rather than their radii; and it is also more convenient to work in minutes. Therefore, putting

$$R = \frac{X}{20{,}000}$$

and $t = 60\ T$

Where X = diameter of particle in microns

and T = time of fall in minutes.

equation (1) becomes

$$X^2 = 10^6 \cdot \frac{PH}{54} \cdot \frac{1}{T}$$

or $$X = 10^3 \sqrt{\frac{PH}{54}} \cdot \frac{1}{\sqrt{T}} \qquad (2)$$

The expression $10^3 \cdot \sqrt{\frac{PH}{54}}$ is called the "sedimentation parameter" (Θ) and so we have the simple relationship.

$$X = \frac{\Theta}{\sqrt{T}} \qquad (3)$$

Θ is not a constant when a hydrometer is used to measure the concentration of a soil suspension, since H (taken as the distance between the top of the liquid and the centre of the hydrometer bulb) varies with this concentration.

However, if the scale reading is called R, H is dependent on R and so the sedimentation parameter Θ is related to R and in fact may be calculated for various values of R by substituting for H the measured distances (in cm) from the scale readings R to the centre of the hydrometer bulb.

(b) Practice - (Accurate procedure)

Construct a 2-way table giving calculated values of Θ, the sedimentation parameter, for a range of values of R (put to 50) at normal room temperatures (which affect the viscosity, P.). If a constant temperature room or bath is used, simply draw up a list of values of Θ corresponding to the normal range of values of R.

The expression given above is accurate enough for calculation of Θ if the laboratory is situated near sea level and no information is available on the correct soil particle density. The full expression in terms of the density of the soil particles (D_1), the density of the liquid (D_2) and the acceleration due to gravity (G) is

$$\Theta = 10^3 \cdot \sqrt{\frac{30\ PH}{G\ (D_1 - D_2)}}$$

and more accurate values for G, D_1 and D_2 may be used where these are known.

For an individual analysis, let R be the actual scale reading at any chosen time.

Let R_L be the scale reading when the hydrometer is inserted in a 0.5 per cent solution of sodium hexametaphosphate - sodium carbonate at the same temperature.

Then the concentration of the suspension is given by

$$C = (R - R_L) \text{ g per litre}$$

If Y is the percentage of particles (less than the size corresponding to the time of reading) in oven-dry soil - i.e, the summation percentage, then

$$Y = 2C \quad \text{if 50 g oven-dry soil is used.}$$

or $$Y = 2.5C \quad \text{if 50 g oven-dry soil is used.}$$

Calculate Y for each time of reading (T minutes) and then calculate the largest particle diameter (X microns) at the same times from equation (3) above, using a value of Q for each calculation related to the observed value of R.

Plot values of Y (linear scale) against values of X (logarithm scale) and so construct the summation curve, from which the summation percentage at any selected particle diameter may be recorded.

(c) Practice - (Approximate procedure)

Equation (3) may be rearranged -

$$T = \left(\frac{Q}{X}\right)^2 \qquad (4)$$

and thus the time to take readings for a particular value of X (particle diameter) may be calculated for a given range of values of Q, these being dependent on R, the scale readings.

Therefore, prepare a 2-way table, giving values of T for various values of R, at appropriate temperatures (as already noted, if a constant temperature room or bath is used, this becomes a list of values of T for various values of R.) Prepare one tables for each particle size diameter needed i.e. usually, three tables are required for

X = 2 microns (clay)
X = 20 microns (silt+clay, ISSS)
X = 50 microns (silt+clay, USDA)

Having obtained a reading R at the appropriate time, correct it for the blank reading (R_L) and calculate the summation percentage as noted above.

3-4.F. NOTES.

(I) The hydrometer method was introduced by Bouyoucos primarily as a rapid technique which would give results fairly near the standard pipette method within a reasonable time, without tedious pretreatment and long periods of standing and avoiding accurate weighing of small amounts of colloidal material. It is still best suited to analytical programmes in which a large number of clay and silt determination are needed with only moderate accuracy on soils which are free of gypsum

and relatively low in organic matter. Then, after a series of comparisons with the pipette method, the simple Bouyoucos procedure, without pretreatment, may be used with some confidence.

2) The first three times of reading advocated by Bouyoucos (40 seconds, 4 minutes and 1 hour) correlate well with the particle size diameters (logarithmic basis) and agree approximately with Stokes' Law; but the time needed for 2 micron clay on the same basis is approximately 6.5 hours. However, this time was shortened to 2 hours by Bouyoucos as the result of numerous comparisons with the pipette method and the shorter time probably acts in some cases as an empirical correction to the errors introduced by the relatively poorer dispersing on soils which have not been pretreated to remove flocculating agents. Individual laboratories must choose their own times based on their experience with the soil types they are asked to analyse. In general it should be assumed that shorter times are needed when no pretreatment is used; when organic matter is removed (and in the absence of gypsum), more accurate results are probably obtained by taking hydrometer readings at approximately 6.5 hours.

3) The Bouyoucos procedure and apparatus has been modified from time to time. In earlier techniques, the volume of the suspension was made up to 1130 ml (50 g soil taken) or 1205 ml (100 g soil taken) after the hydrometer had been inserted, thus applying corrections for the volume of soil and the hydrometer bulb. Special hydrometer jars with appropriate marks at these volumes are still obtainable but are only needed with old-style hydrometers.

(4) Day's modifications improve the determination of the concentration of a soil suspension by means of a hydrometer and make it more scientifically correct and accurate. However, this is hardly worth while if the presence of flocculating agents introduces an uncertainty into the efficiency of dispersion. Thus the Day technique should really only be used on soil material which has been freed from organic matter and large amounts of calcium (whether present as sulphate or carbonate).

However, improvement of the procedure in this way destroys its usefulness as a rapid technique. 40 or 50 g of soil is needed (100 g in some cases) and pretreatment must take longer than with the 20 g considered suitable for the standard pipette method. Times of standing to cover 2-micron clay become impracticably long and do not fit into normal working-day routines (Day's suggested final reading is after 12 hours and periods of the order of 8–11 hours are needed for 2-micron clay determination at 20°C). There is no way of shortening these times (as with the pipette method, where the depth of sampling can be reduced).

Thus the Day method becomes an alternative to the standard pipette method, taking about the same time. Each laboratory must make its own decision on which method to adopt. In any case, comparison of hydrometer methods with the pipette method is always advisable.

(5) In taking hydrometer readings by the approximate Day procedure (see 3-4.E.(ii) (c) a difficulty arises in that the time T is dependent on the scale reading R. Observation on the soil under test will give a rough idea of the approximate scale reading to be expected and a time should be selected which corresponds to a value of R above this (T varies inversely with R). A reading is taken at this selected time and this gives a better idea of the right settling time to use so that it will correspond to the observed value of R; this time is of course later than the time selected for the first reading, provided the estimate of the probable value of R is reasonably good.

In determinations of silt+clay, when settling times are short, the hydrometer may be left in the suspension until the time corresponding to the observed scale reading R. For clay, it is best to remove the hydrometer carefully after the first reading.

GENERAL REFERENCES

AKROYD. pp 56 to 79

ASTAPOV. Chapter I.

BAVER Chapter III

BLACK Chapter 43. (P.R.DAY)

RICHARDS. Chapter 6. Method 41

Bibliographies 508 and 963.

II. 4. SATURATION PERCENTAGE

4.A. PRINCIPLE.

Saturation percentage is the weight of water in gram associated with 100 gram of oven-dry soil in a saturated soil paste. For mineral soils its value ranges from about 20 in sands to about 80 in silty clays. The presence of organic matter increases the value, however, and peat and muck soils may give high values over 200.

Soil is brought to the saturated condition with water either by mixing to a characteristic 'saturated soil paste' or by allowing it to absorb water under free capillary attraction. The amount of water retained is then determined by oven drying.

4.B. APPARATUS.

Beakers, plastic, with covers, 250 ml
Spatula
Crucibles, glass, with fritted glass discs, porosity 1 (coarse), 30-40 ml
Large flat tray, glass or plastic
Filter paper cups, made from 11.0 cm diameter hardened filter paper
Large flat tray containing washed fine sand, particle size between 100 and 500 microns
Moisture tins
Drying oven
Desiccator
Rapid balance, accurate to 0.1 g

4.C. PROCEDURES.

(a) Mixing method.

Place about 100-150 g soil (unweighed) in a 250 ml plastic beaker, add sufficient water to moisten the soil and stir with a spatula. Continue to add water and stir until the soil is just saturated. The saturated soil paste so formed glistens on the surface and slides smoothly off the spatula; and, for most normal soils, if a depression is made in the surface, no water collects in it and the depression only slowly fills by flow of the paste under gravity. (see Note 1)

Cover the beaker and leave for one or two hours to reach equilibrium. If liquid has collected on the surface after this time, add more soil to absorb it; on the other hand, if the paste has dried out, add more water to restore the saturated condition. Transfer about 25-30 g of the saturated soil to a tared moisture tin and weigh immediately. Dry in an oven at 105°C for 16-18 hours, cool in a desiccator and weigh.

(b) Capillary attraction methods.

(i) Using fritted glass crucibles.

Dry a fritted glass crucible at 105°C, cool in a desiccator and weigh. Place the crucible in water to saturate the glass disc, remove excess water with filter paper and weigh. Transfer about 25-30 g soil to the crucible, tap it down gently and level the surface. Immerse the crucible in water in a flat tray so that the water level is just above the upper surface of the fritted glass disc and leave under a cover

for a few hours. Then take the crucible out of the water, dry the outer glass surfaces and weigh immediately. Dry in an oven at 105° C for 16-18 hours, cool in a desiccator and weigh.

(ii) Using filter paper cups.

Transfer about 25-30 g soil to a filter paper cup and place this on a bed of washed fine sand which is well saturated with water. Leave under a cover for a few hours, making sure that the sand does not dry out. Then remove the cup from the sand bed, transfer most of the saturated soil to a moisture iin and weigh immediately. Dry in an oven at 105° C for 16-18 hours, cool in a desiccator and weigh.

4.D. CALCULATIONS.

(a) Mixing method and capillary attraction method (filter paper cup)

Let

A be the weight in gram of the dry moisture tin

B be the weight in gram of the moisture tin and saturated soil

C be the weight in gram of the moisture tin and oven-dry soil

Then, by definition, the saturation percentage is

$$\frac{100(B - C)}{C - A}$$

(b) Capillary attraction method (fritted glass crucibles)

Let

A be the weight in gram of the dry crucible

B be the weight in gram of the crucible with wetted disc

C be the weight in gram of the wetted crucible and saturated soil

D be the weight in gram of the dry crucible and oven-dry soil

Then, the weight of the saturated soil is (C - B) gram

And the weight of the oven-dry soil is (D - A) gram

Thus, the weight of water is (C - B) - (D - A) gram

Then, by definition, the saturation percentage is

$$\frac{100(A - B + C - D)}{D - A}$$

4.E. NOTES.

(1) In method (a) the assessment of the correct saturated paste condition is difficult with sands and with silts or clays which contain much sodium and with peat or muck soils. With sands, which have small powers of absorption, a little water nearly always collects on the surface when the 'paste' is left to stand; this criterion of saturation should therefore be ignored. With sodium clays or silts, there is a tendency for the saturated paste to pass gradually to a slurry

which does not show over-saturation by liquid collecting on its surface after standing; thus the addition of water should be stopped when the paste first glistens and slides smoothly off the spatula. Peat or muck soils, which have large powers of absorption, require a long period of wetting; they should be left overnight in a saturated atmosphere and then the criteria of saturation should be carefully checked.

It is best to use a capillary attraction method for all soils where there is uncertainty in judging the saturated paste condition by the mixing method.

(2) A formula has been published for calculating the saturation percentage from the weight of a known volume of saturated soil paste. This may be unreliable, particularly if the soil particle density is very much lower than 2.65. If it is necessary to measure saturation percentage fairly accurately without access to a drying oven, make a preliminary comparison of saturation percentage values (determined as above) with weights of a known volume of the saturated soil; and prepare a graph from which the saturation percentage values can be assessed.

Alternatively, if the soil particle density (see II.2.) for each sample is known, the published formula can be used, after substituting the known density for 2.65.

(3) Make all weighings to the nearest 0.1 g and record the saturation percentage values to the nearest whole number. The division sums may be avoided by using a nomogram. (see Appendix 2)

4.F. REFERENCES.

DEWIS. Appendix III. (Report paper)

JACKSON. Chapter 10, Sections 10-27 and 10-44.

LONGENECKER and LYERLY. (Journal paper)

RICHARDS. Chapter 6. Methods 27(a), 27(b) and 27(c).

II.5. WATER RETENTION UNDER CONTROLLED CONDITIONS

5.A. PRINCIPLE.

A saturated soil contains an amount of water which is dependent on the soil's physical and chemical composition and, to a certain extent, on its structure in the natural state. When this saturated soil is subjected to gradually increasing air pressures, the percentage moisture falls in a characteristic manner which is also dependent on the soil's natural properties. A study of the changing moisture percentages of a soil at different air pressures is essential in establishing soil:water relationships.

Three ways of expressing pressure values are normally used in connection with soil:water studies. They are -

(a) Atmospheres.

The average air pressure at sea level and normal temperature (20°C) is taken as "1 atmosphere". This is the unit of measurement. 1 atmosphere can support a column of mercury about 76 cm high.

(b) Pounds per Square Inch.

The average air pressure equivalent to 1 atmosphere is 14.7 pounds per square inch, written as 14.7 psi. 10 atmospheres is equivalent to 147 psi, 15 atmospheres to 220 psi and so on.

(c) pF Values.

A column of mercury 76 cm high is roughly equivalent to a column of water 1000 cm high. The logarithm (to base 10) of this height is taken as the "pF value". Thus 1 atmosphere is equivalent to pF 3.0 and 10 atmospheres to pF 4.0 and so on.

Pressures commonly selected for measuring recognised moisture characteristics of soils are -

(a) One-tenth atmosphere, 1.5 psi, pF 2.0

Measures the field capacity in light, sandy soils.

(b) One-third atmpsphere, 4.5 psi, pF 2.50-2.55

Measures the field capacity in medium and fine textured soils.

(c) Fifteen atmospheres, 220 psi, pF 4.2

Measures the wilting point in all soils.

In the method below, saturated soil is placed in a closed chamber, subjected to a known air pressure and allowed to stand while water is forced out of it through a porous plate or membrane to a graduated tube outside the chamber. After equilibrium has been reached, the moisture content of the sample is determined in the normal way by oven-drying. A second sample of the same soil is then subjected to a different pressure and the corresponding moisture content determined. This is repeated at as many different pressures as required and the moisture percentages (oven-dry basis) plotted against pF values.

It is necessary to use two different chambers in the measurements, one operating up to 1 atmosphere and one operating at higher pressures.

5.B. APPARATUS.

Beakers, plastic, with covers, 250 or 400 ml
Spatula
Moisture tins
Drying oven
Desiccator
Balance, accurate to 10 mg

Special soil moisture apparatus, as follows - (see Note 2)

Compressor, giving air pressures up to about 250 psi.
Two manifold assemblies, with valves and gauges, for control and measurement of air pressures; one operating up to 15 psi and one operating in the range 15 to 250 psi; both connected to the same compressor but controlled individually.
Pressure plate extractor, connecting hose and accessories, to hold soil samples at pressures up to 15 psi
Pressure membrane extractor or 15 bar ceramic plate extractor (see Notes 1 and 2) with connecting hose and accessories, to hold soil samples at pressures in the range 15 to 250 psi.

5.C. PROCEDURE.

If a study of water retention is required on a soil in its natural state, obtain a special sample of undisturbed soil in a ring fitted to a core sampler such as is used for analysis II.1; alternatively, slice off a portion of the soil core sample which will fit into the "retainer rings" or ceramic cups supplied with the extractors to be used. Allow this disc of soil to absorb water to the saturated state by placing it on filter paper on wet sand (see II.4.C(b) (ii)). Prepare a number of saturated discs for use as different pressures.

To study water retention of soil which has been air-dried and ground to pass a 2 mm sieve, prepare a saturated sample of the required size (depending on the number of different pressures to be used) as described in II.4.

Keep all these saturated soil samples in air-tight containers (or in a large desiccator containing water) until required. Then transfer them to the appropriate extractor, previously tested for leaks and having its plate or membrane wetted. Samples are normally held in these retainer rings or ceramic cups; press the soil down gently in these to achieve good contact with the porous surface and level with a spatula. Close the extractor and apply the required pressure. Leave until water ceased to flow out of the samples and then for some hours more to ensure equilibrium (overnight may be convenient).

Close the outflow tube (or tubes) with a clamp and gently release the pressure. Open the extractor, transfer most of each soil sample to moisture tins and weigh immediately. Dry in an oven at 105°C for 24 hours.

Repeat at other air pressures as required.

5.D. CALCULATIONS.

Calculate the moisture percentages on an oven-dry basis as given for the saturation percentage (II.4.D.(a)).

If the pressure gauges are marked in atmospheres, multiply the readings by 1000 and take the logarithms to base 10. If the gauges are marked in psi, multiply the readings by 70 and take the logarithms to base 10. These logarithms are the pF values.

5.E. NOTES.

(1) The "atmosphere" unit of pressure is also known as a "bar". Fractions of atmospheres may then be expressed in "millibars". e.g. 0.1 atmosphere is 100 millibars.

(2) This apparatus is supplied specially for soil moisture work and can be a permanent installation in the laboratory. The 15 bar ceramic plate extractor is an alternative to the pressure membrane extractor but both may be used. With a third manifold assembly (15)to 250 psi), all three extractors can be installed.

(3) Usually, a number of different soil samples are placed in one extractor and other samples in a second extractor at a different pressure. After opening an extractor, transfer the soils quickly to numbered moisture tins and close them. Then weigh.

(4) Weighings may be made to the nearest 10 mg and percentage moisture figures calculated to the nearest 0.1, since the moisture is determined at a precise pressure. (unlike the determination of saturation percentage, which is more uncertain)

pF values need only be recorded to the nearest 0.1 above 3.0 but more accurate values may be necessary in the range 3.0 to 2.0 (or lower), where small changes in pressure may produce large changes in moisture percentage.

Moisture percentages may be plotted against atmospheres or psi if preferred, using a logarithmic scale for the pressure values.

(5) The water held between pF 4.2 and pF 2.5 (or 2.0) is said to be "available water".

5.F. REFERENCES.

ASTAPOV. Chapter VII.

BLACK Chapter 8, Sections 8-1 and 8-2. (L.A. RICHARDS)

RICHARDS. Chapter 6. Methods 29 to 32.

SECTION III

CHEMICAL ANALYSIS OF SOILS

INTRODUCTORY NOTE

The analyses included in this section provide the chemical information normally required for soil classification and assessment of soil fertility. One soil sample will never need all the analyses and a selection is made according to the type of soil under test and the chemical data desired.

Soil samples which have been allowed to come into equilibrium with clean air without the application of heat and have then been ground to pass a 2 mm sieve are preferable as basic ("air-dry") samples for all analyses; when less than 5 g of soil is to be weighed, a sub-sample should be ground to pass 0.5 mm sieve.

Procedures 1 (pH values), 5 (conductivity) 14-2 (lime requirement) and 15 (gypsum requirement) may be carried out on air-dry 2 mm soil; procedures 2-1 and 2-2 (calcium carbonate) may be carried out on air-dry 2 mm or 0.5 mm soil, as appropriate. In all other cases it is recommended that air-dry moisture is determined by drying a known weight of 2 mm or 0.5 mm soil at 105°C for 16-18 hours (see I.4-3.A. (ii)) before carrying out analyses on the original air-dry samples; results should be reported on the basis of oven-dry soil.

When it is possible, the determination of available nutrients (phosphorus, potassium and the minor elements) may be usefully done on fresh soil samples; the moisture must also be determined by the standard oven-drying procedure and the results reported on the basis of oven-dry soil.

III. 1. pH VALUES

1.A. PRINCIPLE.

The pH value of the solution surrounding soil particles in the natural state fluctuates because of changing soil:solution relationships brought about by climate, cultivation, crop growth and other factors. A sample of soil may have a particular pH value at the time it is taken in the field but this changes in the sample as it is dried and prepared for analyses. In the laboratory, the soil is subjected to re-wetting processes with water and with certain salt solutions to establish the probable range of pH values it would have in its natural state.

A measured quantity of soil is shaken with a convenient volume of water or salt solution under consistent conditions and the pH of the suspension is determined electronically on a direct-reading pH meter, using a glass electrode with a saturated potassium chloride - calomel reference electrode. Almost any ratios and conditions can be employed but some have been found suitable for this work and the pH values so obtained are capable of useful interpretation. In the procedures below, three different ratios of soil to liquid are suggested and three salt solutions are included.

1.B. APPARATUS.

Balance, accurate to 0.5 g - or volume measures (see Note 1.)
Measuring cylinder, 50 ml - or dispensing burette, 250 or 500 ml
Wide-mouth screw-capped jars, 80-100 ml (4 ounces), preferably having a mouth wide enough to admit the pH electrode assembly
Reciprocating shaker
Interval timer
pH meter
Glass electrode
Reference electrode, saturated potassium chloride - calomel
Beakers, 100 ml
Wash bottle, plastic

1.C. REAGENTS.

Potassium hydrogen phthalate, 0.05 M -
Dissolve 10.21 g potassium hydrogen phthalate to 1 litre in air- equilibrium water. (see Section I.3. - 1.B.)

Potassium dihydrogen phosphate + Disodium hydrogen phosphate, each 0.025 M
Dissolve 3.40 g potassium dihydrogen orthophosphate and 4.45 g disodium hydrogen orthophosphate dihydrate (Sorensen's salt - $Na_2HPO_4.2H_2O$) to 1 litre in air-equilibrium water.

Sodium borate, 0.01 M -
Dissolve 3.81 g sodium borate ($Na_2B_4O_7.10H_2O$) to 1 litre in carbondioxide-free water. (see Section I.3.-1.B.)

Potassium chloride, 1 N -
Dissolve 372 g potassium chloride to 5 litres.

Potassium chloride, 0.1 N
Dissolve 37 g potassium chloride to 5 litres or dilute 1 N solution ten times.

Calcium chloride, 0.01 M -
Dissolve 7.5 - 8.0 g 'dried' calcium chloride (70-75 per cent $CaCl_2$) to 5 litres. Check that the concentration is near 0.01 M by titration of the chloride ion with mercuric nitrate or the calcium ion with EDTA. (see IV.10 and IV.5) Adjust if necessary.

I.D. PROCEDURE

Transfer 10 or 20 g - or a suitable volume measure - of air-dry soil to a 80-100 ml wide-mouth jar and add 50 ml water or 1 N potassium chloride or 0.1 N potassium chloride or 0.01 M calcium chloride, as required. Screw on the lid and shake on a reciprocating shaker for 15 minutes then allow to stand for 30-60 minutes so that the soil settles reasonably well.

Calibrate the pH meter with phthalate and phosphate buffer solutions according to the maker's instructions and wash the electrodes well; then arrange them in their holder so that the glass electrode is about 2 cm below the tip of the reference electrode (or, if the meter is used solely for pH measurements on soils, keep the electrodes arranged in this way). Insert the electrodes into the partly settled soil suspension, with the glass electrode in the soil at the bottom of the jar and the tip of the reference electrode just immersed in the top 1 cm of the suspension. Switch the meter to pH reading, wait 30 seconds and record the pH value to the nearest 0.1 unit.

Make pH readings also on a saturated soil paste (see II.4), inserting the electrodes very carefully to avoid abrasion of the glass electrode by sand.

If pH values above 8.5 are obtained, check the performance of the meter in this range with borate buffer solution.

I.E. NOTES

(1) The soil need only be weighed roughly, say to about $\pm$ 5 per cent. Routine work may be speeded up by using volume measures. These may conveniently be made from brass tubing, sheet and rod which is cut and soldered together to make a small cup with a handle attached. Suitable internal demensions for the cups are -

10 g soil (5.4 cm^3) Diameter of tube 19 mm, length 30 mm

20 g soil (16.8 cm^3) Diameter of tube 25.4 mm, length 33 mm

These dimensions assume an apparent specific gravity of about 1.2 for air-dry loam passing 2 mm. This figure can be checked or an alternative one found by measuring the average volume occupied in a dry cylinder by a constant weight (say, 50 g), of a number of the soils under test.

Fifteen minutes mechanical shaking is usually sufficient to bring most soil:water mixtures to equilibrium; if no shaker is available, shake or stir intermittently by hand for 30-60 minutes. Steady and accurate readings are usually obtained if the glass electrode is immersed in the settled soil and the calomel electrode only in the supernatant suspension (which will normally be clear if calcium chloride or potassium chloride is used). However, if the meter needle tends to drift when measuring the pH values of soil:water mixtures, allow it to reach a steady value. Soil:salt solution mixtures nearly always give steady readings.

The electrode stands should be fitted with a stop to allow the glass electrode to be lowered to the correct point without touching the bottom of the jar.

(3) As more water is used per unit weight of soil, pH values normally tend to rise, figures for a saturation paste often being 0.5 to 1.5 units less than those for a 1:5 suspension. Similar differences are also found when the ratio of 1 N potassium chloride is often independent of the soil:solution ratio. The presence of potassium chloride or calcium chloride generally lowers the pH.

(see III.14 for the use of 1 N potassium chloride in measurement of exchange acidity)

(4) pH values should always be reported precisely, according to the ratio and liquid used. For example, a pH value obtained by shaking 20 g soil (weighed), with 50 ml 1 N potassium chloride solution should be reported as "pH in 1 N KCl - 2:5 w/v". If volume measures are used, pH values may be recorded on w/v basis, although it is more correct to record as (for example), "pH in water - 1:6 v/v", using a 10 g measure of the above dimensions (Note 1), and 50 ml water. If pH values in 0.01 M calcium chloride are found to be independent of soil: solution ratio, the result can be reported simply as "pH in 0.01 M $CaCl_2$".

(5) Difficulties of procedure and interpretation sometimes arise with highly organic soils. These may absorb relatively large amounts of liquid so that a 2:5 w/v ratio is not even saturated. In these cases, it is best to use wider w/v ratios or keep to v/v ratios; and report the apparent specific gravity of the 2 mm soil as an additional help to interpretation.

(6) The "pH value" of a soil, if reported without any qualifying details, is usually understood to mean the pH of a soil:water suspension at a w/v ratio of 2:5. But it is always best to avoid uncertainty by reporting precisely.

(7) In the preparation of the phosphate buffer solution, 3.55 g anhydrous disodium hydrogen orthophosphate (dried at 105-130°C) may be used in place of Sorensen's salt.

(8) Keep the glass electrode in water when not in use and ensure that the reference electrode always contains saturated potassium chloride solution in contact with solid potassium chloride crystals.

(9) The correct pH values of the buffer solutions at normal room temperatures are given in Appendix 5.

1.F. REFERENCES.

BATES. Chapters 5, 9, 10, 11.

BEAR. Chapter 7. (L.F. SEATZ and H.B. PETERSON)

BLACK. Chapter 60. (M. PEECH)

JACKSON. Chapter 3, Sections 3-1 to 3-35

RUSSELL. Chapter VIII.

STROUTS. Vol. II, Chapter 17.

VOGEL. Chapter XVI, Sections XVI.1 and XVI.2

III. 2-1. CALCIUM CARBONATE - CALCIMETER

2-1.A. PRINCIPLE.

Soil is treated with dilute hydrochloric acid and the volume of carbon dioxide evolved from carbonates is measured at atmospheric temperature and pressure. The determination is conveniently and quickly done in a Collins' calcimeter, specially made for this analysis in soils and minerals.

The method does not distinguish between different forms of carbonate but for the purposes of calculation it is assumed that calcium carbonate is the most common in soils.

2-1.B. APPARATUS.

Balance, accurate to 5 mg (see Note 1)
Collins' calcimeter and special slide rule
Erlenmeyer flasks, 150 ml
Vials, plastic, marked at 15 ml
(both flasks and vials supplied with calcimeter)

2-1.C. REAGENT.

Dilute hydrochloric acid
Add 100 ml concentrated acid to 300 ml water

2-1.D. PROCEDURE.

(A simplified diagram of Collins' calcimeter is given in Appendix 6 and the letters quoted below refer to this diagram)

Transfer an appropriate weight of air-dry soil (see Note 1) to a 150 ml Erlenmeyer flask (F). Pour 15 ml dilute hydrochloric acid into a plastic vial (T), invert the vial into the flask and attach the flask to the calcimeter. Immerse the flask in the water jacket of the calcimeter and leave for a minute or two for temperature adjustment.

With taps A and B open, blow air gently by a rubber hand bellows (at Y) into the flask E until water has risen in tubes M and N as far as the zero mark on M. Close tap B, then close tap A. Expel the air from the reservoir of the hand bellows and open tap B, allowing the level of water in tubes M and N to drop, that in N dropping further because it is subject to atmospheric pressure.

Tip the flask F so that the acid acts on the soil and shake well. Put the flask in the water jacket and leave for a minute or two for temperature adjustment. Gently blow air into flask E until the levels of water in tubes M and N are equal and note the volume on the graduated tubes M. Repeat this process until a steady reading is obtained.

E. CALCULATION.

A slide rule is supplied with Collins' calcimeter. Set this to the atmospheric pressure and temperature of the water jacket and read off a factor K against 15 ml acid

Then, K is the weight in milligram of calcium carbonate which produces 100 ml carbon dioxide under the conditions of the determination

Let

W be the weight in gram of soil

V be the volume in ml of carbon dioxide produced

Thus, V ml carbon dioxide is produced from $\frac{KK\ V}{100}$ mg calcium carbonate and this is the amount in W g of soil.

Thus, 100 g soil contains $\frac{K\ V}{W}$ mg calcium carbonate, equivalent to

$$\frac{KV}{1000\ W} \text{ per cent } CaCO_3$$

F. NOTES.

(1) Carry out preliminary tests on the soil to establish a rough idea of the amount of carbonate present from the degree of effervescence with dilute acid. The following table shows how the appropriate weight of soil may be judged and includes the range of calcium carbonate percentage figures for values of V from 10 to 40 ml. (K taken as 425)

Degree of effervescence	Weight of air-dry soil gram	Range of $CaCO_3$ figures per cent
Moderate	5.0	0.8 to 3.4
Fairly vigorous	2.0	2.1 to 8.5
Vigorous	1.0	4.2 to 17
Very vigorous	0.5	8.5 to 34
Extremely vigorous	0.2	21 to 85

In order to reduce sampling error, the soil should be ground to pass a 0.5 mm sieve when weighings from 0.5 to 5.0 g are taken. Below 0.5 g it is advisable to grind more finely. Weighings may be made to within about 2 per cent of the weight required.

(2) If Collins' calcimeter is not available, other gas measuring apparatus may be used or a copy of the calcimeter made in the laboratory from the diagram in Appendix 6. The calcimeter, as purchased, is water-jacketed but this is not necessary if a room of reasonably constant temperature is used and time is allowed for the reaction flask to attain this temperature. Any apparatus used can be calibrated with a series of accurate weights of calcium carbonate and the same method can be employed to check the Collins' slide rule.

(3) Estimate K to the nearest 5 (mg) and V to the nearest 0.1 ml. Record percentage calcium carbonate results to about 2 per cent of the values found.

(4) Soils containing reactive manganese dioxide together with organic matter can release carbon dioxide in hydrochloric acid solution through oxidation of the organic matter by the manganese dioxide. This oxidation may be circumvented by adding a few crystals of a reducing agent (e.g. stannous chloride, ferrous sulphate or hydroxylamine hydrochloride) to the weighed soil sample before allowing it to react with the hydrochloric acid. This precaution is only likely to be necessary for soils rich in reactive manganese dioxide.

(5) See Note (4) of method III.2-2 for a possible correction to be applied to very alkaline soils containing sodium carbonate.

2-1.G REFERENCES.

BLACK. Chapter 91, Section 91-6. (L.E. ALLISON and C.D. MOODIE)

JACKSON. Chapter 4, Section 4-77.

III. 2-2. CALCIUM CARBONATE - ACID NEUTRALIZATION

2-2.A. PRINCIPLE.

Soil is treated with an excess of standard hydrochloric acid, destroying carbonates. The amount of excess acid is determined by titration with standard sodium hydroxide, after separation from the soil by filtration or centrifugation.

The acid dissolves a certain amount of iron and aluminium from oxides and soil material; and these metals are precipitates as hydroxides when the pH rises towards the end of the titration with alkali. The amount of acid destroyed in dissolving the metals is equivalent to the amount of alkali used to precipitate their hydroxides, so no error arises from this source. However, acid is lost by reaction with calcium and magnesium in clay and possibly by reaction with primary minerals. Alkaline soils of high pH also destroy some acid through neutralization by sodium carbonate. Results for calcium carbonate by this method are therefore high, particularly on heavy or very alkaline soils, although approximate corrections can sometimes be made (see Note 3).

2-2.B. APPARATUS

Balance, accurate to 10 mg
Beakers, 250 ml
Watch glasses, 90 mm diameter
Pipettes, 20 and 25 ml
Volumetric flasks, 100 ml
Funnels, 75 mm diameter
Wash bottle, plastic
Filter papers, 12.5 cm diameter (e.g. Whatman No 30)
  or Centrifuge, with 50 ml tubes
Erlenmeyer flasks, 150 ml
Hot plate
Burette, 25 ml with 0.1 ml divisions

2-2.C. REAGENTS.

Hydrochloric acid, 1.00 N
Sodium hydroxide, 0.20 N

Phenol phthalein
  1 per cent in 50 per cent ethanol

2-2.D. PROCEDURE.

Transfer a suitable weight of air-dry soil (see Note 1), passing 0.5 mm, to a 250 ml beaker and carefully add 25 ml of 1.00 N hydrochloric acid down the side of the beaker. Cover with a watch glass and stand for a about one hour, swirling occasionally to mix the contents. Then transfer the mixture quantitatively to a 100 ml volumetric flask, make to 100 ml and mix.

Filter through a dry filter paper into a dry flask - or centrifuge part of the mixture - and transfer 20 ml of the clear liquid to a 150 ml Erlenmeyer flask. Add a little water and bring just to the boil. Cool for a minute, add about 0.2 ml phenol phthalein and titrate hot with 0.20 N sodium hydroxide until the pink indicator colour persists for 30 seconds.

2-2.B. CALCULATION.

Let

W be the weight in gram of soil

T be the volume in ml of the titration with sodium hydroxide

Since 20 ml of liquid, after reaction with the soil, contains excess acid equivalent to T ml of 0.20 N sodium hydroxide, .100 ml contains T ml of 1.00 N excess acid.

Thus, the acid destroyed in reaction with the soil is (25 - T) ml of 1.00 N

Thus, W g soil contains 0.05(25 - T) g calcium carbonate

$$\Rightarrow \frac{5(25 - T)}{W} \text{ per cent}$$

which may be reported as an apparent calcium carbonate percentage or as a "neutralizing value".

2-2.F. NOTES.

(1) From the calculation, 5 g soil is suitable for apparent calcium carbonate values up to about 20 per cent; 2 g soil for up to about 50 per cent; and 1 g soil for higher values.

An idea of the weight to take is given by a preliminary test (see 2-1.F.(1)).

(2) The titration end-point is not sharp, being affected by the metal hydroxides, but it is improved a little by heating. Titration in the cold may be used if preferred.

(3) If a soil contains C milliequivalents per 100 g of exchangeable Ca+Mg (see III.8-2) then this is equivalent to 50C mg per 100 g of calcium carbonate, i.e. 0.05C per cent. Thus, an approximate correction can be made to the calcium carbonate percentage value found by acid neutralization - i.e.

$$\text{Corrected value} = \text{Determined value} - \frac{C}{20}$$

The correction assumes that all the Ca+Mg is replaced by H during the acid treatment, which is unlikely; but a corrected value for calcium carbonate is usually nearer that found by the calcimeter (see 2-1.). The correction does not apply if the experimental result is reported as a "neutralizing value".

(4) An alkaline soil containing soluble sodium carbonate amounting to S milliequivalents per 100 g will also give rise to a positive error of 0.05S on the calcium carbonate percentage value, this affecting the calcimeter method as well. The "error" is not usually large but may be applied to very alkaline soils.

2-2.G. REFERENCES.

BLACK. Chapter 91, Section 91-4. (L.E. ALLISON and C.D. MOODIE)
JACKSON. Chapter 10, Sections 10-121 to 10-126.
RICHARDS. Chapter 6. Method 23(c).

III. 3. ORGANIC CARBON

3.A. PRINCIPLE

Soil organic matter is oxidized under standardized conditions with potassium dichromate in sulphuric acid solution. A measured amount of potassium dichromate is used in excess of that needed to destroy the organic matter; and this excess is determined by titration with ferrous ammonium sulphate solution, using ferroin to detect the first appearance of unoxidized ferrous iron.

The most critical part of the determination is the oxidation process, which must be carried out in hot solution. The amount of heating is carefully controlled to give a high degree of oxidation of the soil organic matter without undue loss of dichromate by thermal decomposition. Simple air condensers reduce evaporation of water during the heating process, dichromate tending to be decomposed more easily in more concentrated solutions of sulphuric acid.

The calculation of the amount of organic carbon in the soil is based on the oxidation, under the same experimental conditions, of the disodium salt of ethylenediaminetetracetic acid, a convenient organic standard.

3.B. APPARATUS.

Analytical balance, accurate to 0.1 mg
Analytical balance, accurate to 1 mg
Erlenmeyer flasks, 500 ml, preferably having necks fitted with standard ground glass sockets
Air condensers, 400-500 mm long, with ground glass cones to fit the flasks or made from 8-10 mm internal diameter tubing inserted into rubber stoppers, for ordinary Erlenmeyer flasks
Electric hot plate, 30 x 45 cm, with variable heating control
Pipettes, 20 and 50 ml
Dispensing burette, 100 or 250 ml, with coarse jet
Measuring cylinders, 50 and 100 ml
Volumetric flask, 250 ml
Funnels, 75 mm diameter
Wash bottle, plastic
Erlenmeyer flasks, 250 ml
Pipette, 2 ml, with coarse jet
Burette, 25 or 50 ml, with 0.05 ml divisions

3.C. REAGENTS.

Potassium dichromate, 1.000 N
Dissolve 49.04 g dry potassium dichromate to 1 litre

Sulphuric acid, concentrated, sp.gr. 1.84, 98 per cent w/w

Sulphuric acid, 5 N (approximately)

Orthophosphoric acid, syrupy, sp.gr. 1.75

Ferrous ammonium sulphate, 0.2 N (approximately)
Dissolve 160 g ferrous ammonium sulphate, $(FeSO_4.(NH_4)_2SO_4.6H_2O)$ in 2 litres of 0.5 N sulphuric acid.
(use 28 ml concentrated sulphuric acid per 2 litres)

Ferroin indicator

Dissolve 0.695 g ferrous sulphate ($FeSO_4.7H_2O$) and 1.485 g orthophenanthroline monohydrate ($C_{12}H_8N_2.H_2O$) to 100 ml

3.D. PROCEDURE.

Transfer a suitable weight of air-dry soil (see Note 1), passing 0.5 mm, to a dry 500 ml Erlenmeyer flask. Add 20 ml 1.000 N potassium dichromate solution, mix with the soil and then add 20 ml concentrated sulphuric acid from a dispensing burette with constant shaking. Insert an air condenser and heat on an electric hot plate for one hour, adjusting the heat control so that the acid mixture just simmers quietly and a gentle reflux occurs in the base of the air condenser (the top being cool).

Remove the flask from the hot plate, allow it to cool a little and add about 100 ml water. Cool again, transfer quantitatively to a 250 ml volumetric flask and finally, after adjustment to room temperature, make the volume to 250 ml and mix. Leave overnight to allow the soil to settle; alternatively, centrifuge about 75 ml of the mixture.

Transfer 50 ml of the clear, supernatant liquid to a 250 ml Erlenmeyer flask, add 50 ml water and about 2 ml orthophosphoric acid. Mix, add two drops of ferroin indicator and titrate with approximately 0.2 N ferrous ammonium sulphate. As the dichromate ion is reduced the solution becomes greener and just before the end-point is a clear bluish-green; then, as soon as there is a slight excess of ferrous ion, the colour changes to a greyish-red, this being the red ferrous-orthophenanthroline complex masked by the green chromium ion. Record the volume of ferrous ammonium sulphate solution used to the nearest 0.05 ml.

Immediately before or after a batch of titrations, dilute 20 ml 1.000 N potassium dichromate to 250 ml, transfer 50 ml to a 250 ml Erlenmeyer flask, add 30 ml 5 N sulphuric acid, 20 ml water, about 2 ml orthophosphoric acid and two drops of ferroin indicator and titrate with the ferrous ammonium sulphate to determine its exact normality.

To find the quantitative relation between the volume of potassium dichromate solution reduced and the weight of carbon oxidized, dry a little EDTA (disodium salt of ethylenediaminetetracetic acid) at 80°C for two hours and cool in a desiccator. Weigh (to 0.1 mg) amounts varying from 25 to 125 mg and transfer them to dry 500 ml Erlenmeyer flasks. Oxidize and determine the volume of potassium dichromate decomposed by the above procedure. 1 gram of a clean form of powdered inert (non-organic) material such as pumice or fine sand may be included to simulate the physical effect of soil material on the heating process.

3.F. CALCULATIONS.

(a) Volume of potassium dichromate used in oxidation.

Let 50 ml diluted potassium dichromate solution (0.080 N) need A ml of ferrous solution in the standardizing titration

Then, the ferrous solution is

$$\frac{20}{A} \times 0.2 \text{ N}$$

Let this be F x 0.2 N i.e. the normality factor F is $\frac{20}{A}$

Let

T be the volume in ml of ferrous solution needed (in a determination) to reduce the excess dichromate in 50 ml of diluted solution, after oxidation.

This is equivalent to TF ml of 0.2 N ferrous solution

Thus, the 250 ml of diluted solution would need 5 TF ml of 0.2 N ferrous solution - or TF ml of 1.000 N solution.

The oxidizing solution, originally containing 20 ml of 1.000 N potassium dichromate, therefore contains after oxidation the equivalent of TF ml.

Thus, the soil organic matter is oxidized by

(20 - TF) ml 1.000 N potassium dichromate

(b) Relation between potassium dichromate and carbon.

From the results of oxidation of varying weights of EDTA, plot volumes of 1.000 N potassium dichromate decomposed (X ml) against weights of carbon present (Y mg), assuming EDTA contains 32.27 per cent carbon.

Calculate the regression equation between X and Y ($Y = aX + b$) and prepare a table listing weights of carbon (mg) corresponding to volumes of potassium dichromate from 3.0 ml to 14.0 ml (x 0.1 ml). It is useful to provide in the table the percentage carbon figures in soil corresponding to initial weights of 1, 2, 3 and 4 g of sample.

If there is Y mg carbon in W g soil, the percentage carbon is

$$\frac{100\ Y}{1000\ W} \quad \text{or} \quad \frac{Y}{10\ W}$$

3.F. NOTES.

(1) For many surface soils it is convenient to take 1.0 g air-dry soil, this covering a range of 0.9 to 4.8 per cent carbon if the 1.000 N potassium dichromate used lies between 3 and 14 ml. For subsoils and surface soils low in organic matter, it is better to take 2, 3 or 4 g soil so that the volume of potassium dichromate used it at least 3 ml. For highly organic soils, 0.5 g may be taken but, if the organic carbon is greater than 10 per cent, the volume of 1.000 N potassium dichromate added initially must be increased above 20 ml and corresponding adjustments made to the volume of concentrated sulphuric acid and to subsequent calculations. It is unsafe to have less than 6 ml potassium dichromate in excess after oxidation of the soil.

Because of the approximate nature of this determination, analyses on air-dry soil samples are usually satisfactory. But, if percentage carbon figures are required on oven-dry soil, determine the adsorbed moisture in air-dry samples by drying 5.00 g in an oven at 105°C for 16-18 hours, cooling in a desiccator and weighing. Calculate the weight of water (M g) associated with 100 g oven-dry soil; then either use this to correct the percentage carbon determined on the air-dry sample

(this becomes $\frac{10\ Y}{W(100 - M)}$)

or weigh out an amount of air-dry sample (stored in an air-tight container during moisture determination) containing W g oven-dry soil. (see 1.4-3.A.(ii))

(2) In oxidizing a batch of soils (10 or 12 is convenient for the hot plate specified), add the concentrated sulphuric acid as quickly as possible and place the flasks on asbestos in a sheltered position while this is being done. Then insert the air condensers and place all the flasks on the hot plate within one to two minutes. The hot plate should be switched on about 30 minutes before adding the acid.

(3) In the oxidation of soil organic matter it is generally assumed that 1.0 ml of 1.000 N potassium dichromate is equivalent to 3.00 mg carbon. The oxidation is also reckoned to be incomplete and recovery figures of 85 to 95 per cent have been reported for techniques similar to that given above, leading to figures from 3. 3 to 3.16 mg for the carbon equivalent to 1.0 ml of 1.000 N potassium dichromate.

In tests of the oxidation of EDTA, the figure of mg carbon equivalent to 1.0 ml of 1.000 N potassium dichromate varied from 3.0 when X (see above) was 3.0 ml to 3.4 when X was 14.0 ml, as compared with a theoretical value of 3.16.

(4) It is unwise to carry out a "blank" determination in an attempt to measure the amount of potassium dichromate destroyed by thermal decomposition and to subtract this "blank" value from an actual determination. Although up to about 0.5 ml 1.000 N potassium dichromate can be "used" in such blank determinations, the same amount is not necessarily destroyed during oxidation of organic matter.

(5) Chloride destroys dichromate and saline soils may therefore give rise to errors. For non-toxic levels of chloride, however, these errors are low and usually negligible in relation to the variations between replicates found in the determination of organic carbon by a wet oxidation process of the above type.

Other materials which may reduce potassium dichromate (elemental carbon, freshly formed manganese oxides and ferrous iron) are normally absent or very low in soil samples which have been properly prepared for analysis.

(6) Ideally, the procedure above should be compared with a standard procedure for organic matter, which is usually dry combustion of a soil (carbonate-free) in a stream of oxygen and measurement of the carbon dioxide evolved by absorption in a suitable alkaline medium. If this is possible, the values of carbon found in a series of soils of varying organic content should be related to volumes of 1.000 N potassium dichromate used in the above method either by use of a factor (if the relationship is constant) or by a regression equation, as described.

However, such a comparison with a standard procedure is often impossible or inconvenient and the method described must be judged approximate only (like all similar methods). Useful information on the validity of the methods of calculation suggested above may be obtained by taking varying weights of a single soil so that the volume of 1.000 N potassium dichromate used covers the range 3.0 to 14.0 ml.

It is recommended that organic carbon determinations should be done in duplicate, taking two different weights of soil.

3.G. REFERENCES

BLACK. Chapter 90. (L.E. ALLISON)

CHAPMAN and PRATT. Chapter 1, Section 1-26.

DEWIS. Unpublished data (1966).

JACKSON. Chapter 9.

KOLTHOFF and BELCHER. Chapter V.

RICHARDS. Chapter 6. Method 24.

VOGEL. Chapter III, Sections III.63 to III.65.

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III. 4. TOTAL NITROGEN

4.A. PRINCIPLE

Organic matter is oxidized by treating soil with boiling concentrated sulphuric acid, nitrogen in the organic compounds being converted into ammonium sulphate during the oxidation; ammonium ions in the soil are also trapped in the acid but nitrate and nitrite ions are lost. (see Note 7) Sodium or potassium sulphate is added to raise the boiling temperature of the acid and so provide more effective oxidation; and the reaction is catalysed by the addition of a copper sulpahte-selenium mixture. (see Note 3)

It has been found that a preliminary treatment of the soil with boiling dilute sulphuric acid often produces higher results, especially on clay soils. Ammonium ions can be present within the lattice structures of clay minerals and these ions may not be removed by direct treatment of the soil with concentrated sulphuric acid; use of dilute acid seems to break up the clay mineral more effectively and releases the ammonium ions.

After digestion, the mixture is made alkaline and the released ammonia is distilled quantitatively into dilute boric acid and titrated with standard acid to pH 5, the boric acid not affecting the end-point.

The determination may be carried out on either the macro or the semi-micro scale, according to preference; or the digestion can be done on the macro scale, the digest made to a definite volume and the distillation carried out on the semi-micro scale, using an aliquot of the diluted digest.

4.B. APPARATUS.

Macro-Method.

(a) Digestion

Balance, accurate to 10 mg
Kjeldahl flasks, long neck, 500 ml or 800 ml
Dispensing burette, 250 ml, with coarse jet.
Measuring cylinders, 50, 100 and 500 ml
Volume measure, to hold 10 g salt-catalyst mixture.
Kjeldahl digestion apparatus, for 500 ml or 800 ml flasks, with means of fume disposal (see Note 5)
Asbestos gloves

(b) Distillation

Erlenmeyer flasks, 350 ml
Kjeldahl distillation apparatus, to take 800 ml kjeldahl flasks or 1000 ml round bottom flasks.
Burette, 50 ml, with 0.1 ml divisions.

Semi-micro Method.

(a) Digestion

Balance, accurate to 1 mg
Kjeldahl flasks, long neck, 100 ml
Dispensing burette, 50 ml, with coarse jet.
Measuring cylinders 10, 25 and 50 ml.
Volume measure, to hold 2 g of salt-catalyst mixture.

Kjeldahl digestion apparatus, for 100 ml flasks, with means of fume disposal. (see Note 5)
Asbestos gloves
Volumetric flasks, 50 ml
Funnels, 45 mm diameter
Wash bottle, plastic

(b) Distillation

Erlenmeyer flasks, 150 ml
Pipette, 10 ml
Pipette, 5 ml, with coarse jet
Micro-distillation apparatus (e.g. 'Markham')
Steam generator
Interval timer
Burette, 10 ml, with 0.02 ml divisions.

Macro Digestion plus Semi-micro Distillation.

Apparatus given under "Macro-Method (a)" above, plus -

Volumetric flasks, 200 or 250 ml
Funnels, 75 mm diameter
Wash bottle, plastic

and apparatus given under "Semi-micro Method (b)" above.

4.C. REAGENTS

Sulphuric acid, concentrated, sp.gr. 1.84, low in nitrogen

Mixed salt-catalyst
Grind 100 parts of anhydrous sodium or potassium sulphate with 10 parts of copper sulphate ($CuSO_4.5H_2O$) and 1 part of selenium (red, precipitated).

Capryl alcohol (octan-2-ol)

Sodium hydroxide, 45 per cent
Dissolve 4.5 Kg sodium hydroxide in 10 litres water. Stand for a few days to allow insoluble sodium carbonate and impurities to settle, then syphon off the clear liquid into a 10-litre aspirator fitted with a carbon dioxide trap. This solution must not contain carbonate.

Mixed indicator
0.2 g bromocresol green and 0.1 g methyl red in 100 ml ethanol (see Note 8)

Plus, either, for macro-distillation -

Pumice, granulated, 5-10 mm
Boric acid, 2 per cent
Sulphuric acid or hydrochloric acid, 0.100 N

Or, for semi-micro-distillation

Boric acid, 0.25 per cent
Sulphuric acid or hydrochloric acid, 0.010 N

4.D. PROCEDURES.

(a) Macro Digestion.

Transfer a weight of air-dry soil (passing 0.5 mm) containing 5.00 g oven-dry material (see Note 1) to a 500 ml or 800 ml Kjeldahl flask and add 50 ml water, washing down any soil adhering to the neck of the flask. Wait 30 minutes, then add about 10 g salt-catalyst mixture (see Note 3) and 35 ml concentrated sulphuric acid and mix carefully, particularly if the soil contains calcium carbonate. Place on the Kjeldahl digestion apparatus and heat gently, controlling any frothing by adjustment of heating and addition of a drop of capryl alcohol, if necessary. When water has evaporated and frothing has stopped, bring the mixture to the boil. Swirl the contents of the flask from time to time and digest until the dark colour has turned to green-blue and then continue for another one to two hours. (see Note 4) Allow the mixture to cool until crystals begin to form and then add 50 ml water with continuous mixing. See aside to cool well.

(b) Semi-micro Digestion.

Transfer a weight of air-dry soil (passing a 0.5 mm sieve or finer) containing 1.00 g oven-cry material (see Note 1) to a 100 ml Kjeldahl flask and add 5-10 ml water. Wait 30 minutes, then add about 2 g salt-catalyst mixture and 6-7 ml concentrated sulphuric acid and mix carefully. Proceed with the digestion as described in (a) above finally adding 10 ml water.

(c) Macro Distillation.

Transfer the acid digest quantitatively to a 800 ml Kjeldahl flask or 1000 ml round bottom flask, using about 300 ml water and decanting from the sand fraction as much as possible. Add a few pieces of granulated pumice and cool (see Note 6). Transfer 25 ml of 2 per cent boric acid and 0.5 ml of mixed indicator to a 350 ml Erlenmeyer flask and place this in position under the condenser of the distillation apparatus with the tip of the delivery tube below the level of the liquid (adding a little water if necessary). Pour 100 ml of 45 per cent sodium hydroxide carefully down the neck of the distillation flask to form a layer under the acid mixture. Attach the flask to the distillation apparatus and mix by swirling gently. Apply moderate heat at first, then increase the heat and distil about 150 ml liquid into the receiving flask (30 to 40 minutes). Wash down the delivery tube and titrate the ammonium ion with 0.100 N acid to the neutral point of the mixed indicator (see Note 8).

(d) Semi-micro Distillation

(Based on the 'Markham' apparatus)

(i) Transfer the acid digest quantitatively to a 200 ml or 250 ml volumetric flask, decanting from the sand fraction as much as possible. Make to volume and mix well. Transfer 20 ml of 0.25 per cent boric acid and 0.2 ml of mixed indicator to a 150 ml Erlenmeyer flask and place this in position under the condenser of the distillation apparatus with the tip of the delivery tube just above or just touching the liquid. (Insertion of the tube into the boric acid is not necessary but may be done if desired). Transfer 10 ml of the diluted digest to the apparatus, add 5 ml

of 45 per cent sodium hydroxide and heat with steam until about 25-30 ml liquid has been distilled over (4-5 minutes). Wash down the delivery tube and titrate the ammonium ion with 0.010 N acid to the mixed indicator (see Note 8).

(ii) After Semi-micro Digestion.

Transfer the acid digest quantitatively to a 50 ml volumetric flask, decanting from the sand. Make to volume and mix well. Use 10 ml of this diluted digest for determination of ammonium nitrogen in the 'Markham' apparatus, as outlined above under (d) (i)

(e) Blanks.

Whichever method is used, carry out a full analyses without soil, this measuring the volume of standard acid consumed by traces of nitrogen in the reagents and by slight alkali spray during distillation.

4.E. CALCULATIONS.

Let

V be the volume in ml of standard sulphuric or hydrochloric acid (either 0.100 N or 0.010 N) used for titrating the ammonia nitrogen, after correction for the blank.

(a) Macro-Distillation.

The acid is 0.100 N and thus V ml corresponds to (0.1 x V) milli-equivalents of nitrogen.

This is present in 5 g oven-dry soil

Thus the soil contains 2V me per 100 g nitrogen
or (0.028 x V) per cent nitrogen

(b) Semi-micro Distillation.

The acid is 0.010 N and thus V ml corresponds to (0.01 x V) milli-equivalents of nitrogen.

(i) After Macro Digestion

(a) Digest diluted to 200 ml

The 10 ml aliquot of the diluted digest corresponds to 0.25 g oven-dry soil

Thus the soil contains 4V me per 100 g nitrogen
or (0.056 x V) per cent nitrogen.

(b) Digest diluted to 250 ml

The 10 ml aliquot corresponds to 0.20 g oven-dry soil

Thus the soil contains 5V me per 100 g nitrogen
or (0.070 x V) per cent nitrogen

(ii) After Semi-micro Digestion.

The 10 ml aliquot of the diluted digest corresponds to 0.20 g oven-dry soil.

Thus the soil contains 5V me per 100 g nitrogen
or (0.070 x V) per cent nitrogen.

4.F. NOTES.

There are many variations of the Kjeldahl method for total nitrogen in plant and animal organic material. The procedures given above may be modified to suit individual laboratory conditions and apparatus. Some of the reasons for choosing the details of the methods advocated are noted below, together with comments on possible alternatives.

(1) In the full macro method, 5.00 g oven-dry soil conveniently covers nitrogen values up to about 0.5 per cent, giving titrations up to 18 ml of 0.100 N acid. If the macro digestion is followed by semi-micro distillation, titration values are about 7 ml or 9 ml of 0.010 N acid (depending on the degree of dilution of the digest) for 0.5 per cent nitrogen in the soil.

Similarly, for the full semi-micro method, nitrogen values up to 0.5 per cent in the soil are conveniently covered, giving titrations up to 7 ml of 0.010 N acid.

Less soil should be taken if the nitrogen content is more than 0.5 per cent and in this case the sample should be very finely ground, if possible to pass a 100-mesh sieve (particles smaller than 0.15 mm). Peat and muck soils, which may contain up to 3 or 4 per cent of nitrogen, are probably best analysed by macro digestion, as the weight of soil for semi-micro digestion would be too small (about 0.10-0.15 g) for accurate sampling.

(2) Frothing is a danger with some soils, developing when the water has nearly evaporated and carrying particles of soil up into the neck of the Kjeldahl flask. It can be controlled by careful heating and use of capryl alcohol. If it is serious with certain types of soil, 800 ml Kjeldahl flasks should be used for macro digestion.

(3) The salt-catalyst mixture prescribed is one of the most effective; potassium sulphate is probably slightly better than sodium sulphate. Mercuric oxide or mercuric salts are sometimes used in place of selenium but are inconvenient as the mercuric ion must be precipitated before distillation to prevent ammonia being trapped as the mercury-ammonium complex; this precipitation is usually effected as the sulphide and leads to objectionable odours in the distillate and sometimes black deposits in the condenser.

Tablets containing specified amounts of the normal catalysts and sulphates, either singly or in combination, are obtainable and are most convenient to use.

(4) During digestion, if gas burners are used, the flame should not come into direct contact with the flask above the level of the acid mixture.

Bumping is often a serious hazard with sandy soils and finer grinding of such samples is advisable. The Kjeldahl flasks may be prevented

from bumping right off the digestion apparatus by having an asbestos covered rod resting on the neck, just at the shoulder.

After digestion, the mixture should not be allowed to cool completely or it may solidify and then be difficult to dissolve in water.

(5) The disposal of the sulphur dioxide and trioxide fumes given off copiously during digestion is best accomplished through absorption in water or alkali. If there is an adequate water supply and good acid-proof drainage facilities, the fumes can be extracted through a glass or lead water filter pump. An all-glass digestion unit containing an alkali trap is also available.

When fume disposal is carried out in special apparatus, it is best to evaporate off most of the water by boiling the mixture of soil and dilute acid until fumes just begin to appear; then the Kjeldahl flask can be attached to the fume disposal apparatus and digestion continued. Frothing must be more rigidly controlled when jointed all-glass units are used and it is wise to add a few drops of capryl alcohol before attaching the Kjeldahl flask; bumping is also more serious with these units and soil samples must be very finely ground.

Fumes from the digestion should not be released into the air, particularly in towns, because of the danger to health.

(6) Borosilicate glass deteriorates much more rapidly if subjected to the action of hot concentrated sulphuric acid and boiling alkaline solutions alternately. For this reason, it is unwise and, indeed, dangerous to use the same Kjeldahl flasks for digestion and distillation. Thus, if apparatus is used which employs Kjeldahl flasks for distillation, they should be marked and reserved for this operation only and not used for digestion also.

Transference of digest from one flask to another also effects separation of sand, which can be a cause of serious bumping during macro-distillation if direct heating with gas burners is used.

In macro-distillation, the acid liquid should not be warm or too concentrated when the alkali is added; on mixing, the heat produced may be sufficient to cause sudden boiling and loss of the analysis.

(7) Nitrogen present as nitrate or nitrite is lost during the digestion by conversion to volatile oxides of nitrogen. The amount of nitrate and nitrite in soil are usually very small in relation to the total nitrogen and they are normally neglected in this determination.

However, if there is reason to believe nitrate plus nitrite is high and it is wished to include it in the analysis, then the digestion procedure may be modified. Salicylic acid is added to the sulphuric acid and the mixture heated with the soil (without addition of water). The salicylic acid is nitrated and subsequent treatment with sodium thiosulphate reduces this to amino-salicylic acid which is oxidized quantitatively in the digestion.

For the macro digestion, the procedure is -

Transfer a weight of air-dry soil (passing 0.5 mm) containing 5.00 g oven-dry material to a 500 ml or 800 ml Kjeldahl flask and add 35 ml concentrated sulphuric acid containing 2.5 per cent salicylic acid. Mix and leave overnight. Add 5 g powdered sodium thiosulphate ($Na_2S_2O_3.5H_2O$) through a dry long-stemmed funnel and heat carefully

until frothing has ceased. Cool, add water and salt-catalyst and proceed in the normal way (4.D.(a) above)

For micro digestion adjust the quantities of sulphuric-salicylic acid and sodium thiosulphate appropriately.

(8) The relative amounts of methyl red and bromocresol green in the mixed indicator may be altered to suit individual reaction to colour. To the analyst's eye the colour should change from green through a neutral grey to pink, the end-point being taken at the first appearance of the pink colour.

(9) The carbon-nitrogen ratio is obtained by dividing the percentage of organic carbon (determination III.3) by the percentage of total nitrogen and expressing the result to one decimal place.

4.G. REFERENCES.

BLACK. Chapter 83. (J.M. BREMNER)

CHAPMAN and PRATT. Chapter 17, Section 17-1.

JACKSON. Chapter 8, Sections 8-1 to 8-28.

KOLTHOFF and STENGER. Chapter V, Section V.6. (pp. 168 to 176)

VOGEL. Chapter III, Section III.20.

WILSON. Vol. I.B, Chapter VIII. (3.c - A.A. JONES)

Vol. I.C, Chapter IX. (5.a.(a) - A.F. WILLIAMS)

Bibliographies 854, 860 and 1006.

III. 5. CONDUCTIVITY

5.A. PRINCIPLE.

The conductivity of a soil is the specific conductivity at 25°C of a water extract obtained from a soil and water mixture of a definite ratio. It is measured on a conductivity meter (see IV.3.) and is normally reported in millimhos, the value giving information on the total amount of water soluble salts present in soil, i.e. on the degree of salinity.

The most easily interpretable conductivity values are those on a saturation extract, prepared from a saturated soil paste (see II.4.). It is also useful to obtain routine conductivity readings on soil:water mixtures at other ratios, usually 2:5 or 1:5, separating soil as much as possible by settling.

5.B. APPARATUS.

Items for preparation of saturated soil paste (see II.4.)

Soil paste filtration apparatus, consisting of specially designed Buchner-type funnels and receiving bottles, mounted in a rack with suction control (see Note 1)
Vacuum pump
Filter papers, to fit funnels, 5.5 cm diameter (e.g. Whatman No 6)

Balance, accurate to 0.5 g
Measuring cylinder, 50 ml - or dispensing burette, 250 or 500 ml
Wide-mouth screw-capped jars, 80-100 ml (4 ounces),
Reciprocating shaker
Conductivity meter
Conductivity cell, pipette type, for small volumes
Thermometer, covering room temperatures

Centrifuge, with 50 ml tubes (optional)

5.C. PROCEDURE.

(a) Conductivity of saturation extract.

Prepare a saturated soil paste by one of the methods described in Section II.4, using 100-150 g soil. Transfer this to the funnel of a soil paste filtration apparatus, previously fitted with filter paper. Apply suction and collect the saturation extract in dry bottles (see Note 2)

Allow the extract to attain room temperature (it is cooled during suction) and fill the pipette type conductivity cell. Measure the conductivity value on a meter and record the temperature of the extract.

(b) Conductivity of soil:water mixtures.

Transfer an appropriate weight of air-dry soil, usually 10 or 20 g, to a 80-100 ml wide-mouth jar and add 50 ml water. Screw on the lid and shake on a reciprocating shaker for 30 to 60 minutes. Leave for a few hours or overnight in order to allow the bulk of the soil to settle - or centrifuge after about two hours, if preferred.

Fill the pipette type conductivity cell with the clearest portion of the

soil:water suspension from the surface layer (the tip of the cell need only be inserted a few millimeters - unless the liquid is clear) and measure the conductivity. Record the temperature of the mixture.

5.D. CALCULATIONS.

Check the conductivity cell constant with standard solutions of potassium chloride and calculate the soil conductivity at 25°C in micromhos as given in Section IV.3. Divide the result by 1000 to give the soil conductivity in millimhos.

5.E. NOTES.

(1) For the routine preparation of saturation extracts it is essential to use the soil paste filtration apparatus (see FAO Soils Bulletin No 3, Section 3E, item 1140), enabling the maximum amount of extract to be obtained from a paste. On a small scale, test-tubes (capacity about 25 ml) may be fixed to the stem of a small Buchner funnel with pressure tubing (containing a hole in the side) before fitting the funnel in a filter flask, so that the small amount of extract is collected in the test-tube.

(2) It is advisable to fit a vessel containing silica gel (self-indicating) between the filtration apparatus and the suction pump to prevent moisture condensing in the pump and causing corrosion.

(3) Saturation extracts are usually clear; if turbid at first, pour the extract back on to the paste in the funnel and substitute a clean dry bottle. Occasionally the filter paper breaks; if so, repeat the filtration with double papers.

The volume of saturation extract should be sufficient to enable the conductivity cell to be washed through once with the extract before filling. If this can be done, do not wash out the cell with water between determinations. When there is only sufficient saturation extract to fill the cell once, wash the cell with water and then with either ethanol or acetone and dry it with air.

(4) The presence of soil particles in the conductivity cell causes a slight increase in conductivity but this cannot be avoided when soluble salts are low. It does not detract from the usefulness of procedure (b) as a guide to soluble salt content. As the salt concentration rises, the soil settles more effectively and the conductivity reading becomes more accurate.

(5) As noted in IV.3, the accuracy with which it is possible to read the logarithmic scale of a conductivity meter varies with the magnitude of the reading. In general, soil conductivity figures need only be recorded with an accuracy of about 2 to 5 per cent of the value.

(6) Relationships between conductivity values and soluble salts are noted in Sections III.6 and IV.3.

(7) The direct conductivity of the saturated soil paste, as measured in a special cup (U.S. Bureau of Soils) can be used as a rough guide to soluble salt percentage in the soil (see III.6.).

5.F. REFERENCES.

BLACK. Chapter 62, Section 62-2. (C.A. BOWER and L.V. WILCOX)

DEWIS. Appendix IV. (Report paper)

JACKSON. Chapter 10, Sections 10-6 to 10-43.

RICHARDS. Chapter 2.

Chapter 6. Methods 4 and 5.

STROUTS. Vol. II, Chapter 19.

VOGEL. Chapter XVII, Sections XVII.1 and XVII.2.

III. 6. WATER-SOLUBLE CATIONS AND ANIONS

6.A. PRINCIPLE.

Soluble salts which may be present in soils consist mainly of the chlorides and sulphates of calcium, magnesium and sodium; there are usually small amounts of bicarbonate and potassium; and carbonate is present in very alkaline soils. This analysis is concerned with the extraction of these cations and anions and with interpretation of the results in terms of salts in the soil. Chemical analysis of the water extracts is dealt with in Section IV, methods 4 to 11.

Soil and water are mixed together in definite ratios and a clear extract is obtained by filtration or centrifugation or a combination of the two. Ratios of water to oven-dry soil of 2:1 and 5:1 by weight are commonly used; and the saturation extract (see III.5.) can also be prepared for analysis. However, because of variability in the kinds and amounts of salts in soil, no definite procedure can be laid down for extraction. In general, if only chlorides are present, a narrow ratio and a short time of contact are sufficient to bring them into solution; while, if sulphates are present, wider ratios and longer times of contact are necessary to ensure complete solution, particularly of calcium sulphate in the form of gypsum crystals. When times of contact longer than about six hours have to be used (overnight standing or shaking is often convenient) bacterial action may affect the ionic composition and a sterilizing agent is added.

During water extraction of soils high in soluble salts, cation exchange (and perhaps anion exchange) may take place between the ions dissolved and those attached to the soil colloidal complex. The ionic composition of the extract may not then be truly representative of the soluble salts present in the soil. However, in spite of this, the analysis is often useful in giving an approximate idea of the water-soluble cations (and anions) so that, in analyses for exchangeable cations, corrections can be applied for the quantity of extracted cations derived from salts rather than soil (see III.8.).

The preparation of a clear extract is usually easy if the concentration of soluble salts is moderate to high (conductivity of extract greater than 1 or 2 millimhos). When the concentration of salts is low, finer filtration media or faster centrifugation must be used. Purified barium sulphate is sometimes helpful in clarifying sodium soil extracts and pure activated carbon should be used to take out the colour of soluble organic matter

6.B. APPARATUS.

Balance, accurate to 10 mg
Bottles or Erlenmeyer flasks, with rubber stoppers, 500 ml
Measuring cylinder, 500 ml
Reciprocating or end-over-end shaker
Filter funnels or Buchner funnels, about 90 mm diameter
Filter papers, various grades and sizes
Ceramic filters, fine porosity (e.g. Pasteur-Chamberland, fineness "F")
Vacuum pump
Centrifuge, with 50 ml tubes, plastic

Plus apparatus for moisture determination and preparation of saturated soil paste and saturation extract, if required

6.C. REAGENTS.

Barium sulphate, specially purified for soil work
Activated carbon, pure, inert to cations and anions

6.D. PROCEDURES.

If the chemical analysis of a saturation extract is needed, prepare this as described in Section III.5, using sufficient soil to provide 25-30 ml of extract (see Note 1).

For water extracts at other ratios, first determine the moisture content of air-dry soil, if this is not known. Then transfer an appropriate weight of air-dry soil to a 500 ml bottle or flask and add the volume of water needed to give the required soil:water ratio (see Calculations). Shake mechanically for one to two hours. If gypsum is thought to be present (rapid settling during analyses for pH or conductivity is good evidence), allow to stand for up to six hours, with occasional additional shaking, or allow to stand overnight after addition of a crystal of thymol. Otherwise, allow to stand for about one hour.

Observe the degree of clarification of the supernatant liquid after standing. If a deep, clear layer appears, filter the extract through Whatman No 30 or 40 papers (or similar). If only a shallow, clear layer appears, centrifuge the extract at 2000-3000 rpm for 10-15 minutes and filter the supernatant liquid to remove any fragments of organic matter. If no clarification ensues, try filtering the extract under suction through the finest toughened filter papers (e.g. Whatman No 50 or 52) or through ceramic filters of fine porosity; or use very high speed centrifugation, if this is available.

When it is impossible to obtain a clear water extract with available apparatus, try shaking the turbid extract with barium sulphate, followed by filtration or centrifugation. If this does not produce a clear extract, add thymol to the turbid liquid, stopper the flask and allow it to stand in a cool place. Often, slow flocculation causes the clay particles to settle after a few days; then decant the supernatant liquid carefully through a fine filter paper.

If the extract is coloured, shake it with activated carbon and filter into a dry flask. Activated carbon is also sometimes useful in clearing turbid extracts.

Determine the conductivity of the water extract and then analyse it for calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride and sulphate (as appropriate) by the methods described in Section IV, 4 to 11. Preserve the extract with a little thymol while these determinations are being done.

For extracts of alkaline soils it is also advisable to add, for every 25 ml of extract, one drop of sodium hexametaphosphate solution (1000 ppm) to prevent precipitation of calcium carbonate; this does not introduce a significant error into the sodium analysis.

6.E. CALCULATION.

(a) Water-soil ratios.

Let

M be the weight in gram of water associated with 100 gram of oven-dry soil in an air-dry sample

Then, suitable weights of air-dry soil and volumes of water for extractions at various ratios in a 500 ml container are –

Ratio Water to oven-dry soil.	Weight of air-dry soil. gram	Volume of water. ml
2:1	150 + 1.5 M	300 – 1.5 M
5:1	60 + 0.6 M	300 – 0.6 M
10:1	30 + 0.3 M	300 – 0.3 M

(see Note 2)

(b) Concentrations of cations and anions in soil.

Results of analysis of water extracts are calculated in milliequivalents per litre. These figures are converted to milliequivalents per 100 g of oven-dry soil by multiplying by a suitable factor, as follows –

Ratio Water to oven-dry soil	Multiplication Factor
2:1	0.2
5:1	0.5
10:1	1.0

Saturation percentage : 100 (in saturated soil paste)

Saturation Percentage / 1000

(c) Concentration of gypsum in soil.

Soils containing gypsum must receive special treatment, by virtue of the sparing solubility of this salt. The presence of gypsum is shown not only by rapid flocculation of clay but also by conductivity values of about 2.3 millimhos at 25°C and calcium and sulphate concentrations of 30-32 milliequivalents per litre in water extracts, when other salts are low in amount.

In the saturation extract of a gypsiferous soil, it is likely that all the gypsum has not dissolved from the soil. The concentration of gypsum in solution may be taken as equal to either the calcium or the sulphate concentration, whichever is lower. In more dilute extracts, more gypsum dissolves and it is necessary to prepare extracts at ratios of 2:1, 5:1 and 10:1 and so on, increasing the ratio until the concentration of either calcium or sulphate falls below 30-32 me per litre. It may then be assumed that the sulphate brought into solution in addition to that in the saturation extract comes entirely from the gypsum in the soil. (The additional calcium may possibly be affected by cation exchange).

Thus, let

A be the concentration of calcium by saturation extraction

B be the concentration of sulphate by saturation extraction

C be the concentration of sulphate by dilute extraction
(all in milliequivalents per 100 g oven-dry soil)

Then, if A is less than B,

Gypsum in soil = (C-B) + A me per 100 g

or, if B is less than A,

Gypsum in soil = (C - B) + B = C me per 100 g

6.F. NOTES.

(1) The amount of soil needed to provide 25-30 ml of saturation extract depends on its texture. Appropriate weights of air-dry soil are -

Loamy sands	400-600 gram
Sandy loams	250-400 gram
Loams	150-250 gram
Silt loams and clay loams	100-150 gram
Clays	50-100 gram

(2) Air-dry soil should be used for water extraction because drying at 105°C may affect the salts present; e.g. gypsum, $CaSO_4.2H_2O$ may be changed partially to $CaSO_4.0.5H_2O$, which has a different solubility; and this may affect an analysis at a given ration. But the analytical results should be reported on an oven-dry basis and this involves a separate determination of air-dry moisture. Errors of calculation caused by changes in water of crystallization of salts during drying are normally small; but they may have to be taken into account in accurate work if gypsum is present in high amounts.

For light soils in dry atmospheric conditions, the air-dry moisture is low and no appreciable error is caused if it is neglected. For most soils in humid conditions, however, the given procedure should be followed.

(3) When the ionic concentrations in a water extract are expressed in milliequivalents per litre, the sum of the cation concentrations should be equal to the sum of the anion concentrations and this sum is also equal to the concentration of total salts in milliequivalents per litre. In practice there is usually a slight difference between the sum of cations and the sum of anions, partly due to neglect of other ions present in small amounts and partly due to analytical errors.

The ionic concentrations in milliequivalents per litre can be converted to concentrations in milligrams per litre (parts per million by multiplying by the appropriate ionic equivalent weight. The sum of all such ionic concentrations (cations plus anions) is the concentration of total salts in milligrams per litre.

By similar calculations, ionic concentrations in milliequivalents per 100 g oven-dry soil can be converted into concentrations in

milligrams per 100 g and hence, by summation, to milligrams of total salts per 100 g oven-dry soil; this can be expressed as a percentage.

(4) Studies have been made of the relationships in soil:water extracts between conductivity figures in millimhos at 25°C and total salt concentration in the extract or in the soil. These relationships can be used to calculate approximate salt concentrations from a measurement of conductivity only, aided by simple qualitative tests for calcium, sodium, chloride and sulphate to show the relative amounts of these ions. The following table gives a summary of useful data for this purpose –

Ionic nature of extract	Conductivity of 1 millimho at 25°C in the extract is equivalent to a total salt concentration of		Mean equivalent weight for total salts taken as
	milliequivalent per litre	gram per litre	
Mainly calcium and sulphate	12.5	0.85	68
Calcium, sulphate, sodium & chloride all present	10	0.64	64
Mainly sodium and chloride	8	0.48	60

The derived concentrations in the water extract can be converted to concentrations in oven-dry soil by means of the usual factors.

It must be remembered that such relationships are only approximate and may fail with soils containing much magnesium or carbonate (from sodium carbonate) or with soils which have been heavily fertilized. The relationships work best with naturally saline soils which are not alkaline.

(5) It is also possible to relate conductivity (or resistance) values on saturated soil pastes to percentages of soluble salts in soils, thus removing the need for preparation and analysis of water extracts. The measurements are made in a standard "resistance cup" (U.S. Bureau of Soils) and converted to percentages of salts in the soil by means of tables, taking into account the texture of the soil. The method is useful in the field and also in the laboratory as a very rough guide to the need for preparation of a water extract.

6.G. REFERENCES.

ASTAPOV.	Chapter IX.
BLACK	Chapter 62, Sections 62-1 and 62-3. (C.A. BOWER and L.V. WILCOX)
DEB.	(Report paper.)
JACKSON.	Chapter 10, Sections 10-27 to 10-31 and 10-48 to 10-54.
RICHARDS.	Chapter 6. Methods 3(a), 3(b) and 3(c)

III. 7. CATION EXCHANGE CAPACITY

7.A. GENERAL PRINCIPLE.

The cation exchange capacity of soil is traditionally determined by a basic two-stage process. The colloidal complex of the soil is first saturated with a selected cation (the saturating cation), all exchangeable cations originally associated with the complex being removed in this treatment (see 7.C.). Secondly, the saturating cation is displaced quantitatively by another selected cation (the replacing cation) and the amount displaced is measured and expressed in terms of milliequivalents per 100 g of oven-dry soil.

The first stage - saturation - is effected with a solution of a salt containing the saturating cation buffered at a definite pH (neutral to alkaline) to avoid secondary effects due to a change of hydrogen ion concentration during saturation. Acetates are often employed in concentrations of either 1.0 N or 0.5 N, these salts providing adequate exchanging power at buffered pH values and having very little solvent action on soil organic matter or iron compounds. Soil is subjected to a series of attacks with these solutions; each attack consists of treating 1 part of soil with 4 to 6 parts of solution, with shaking or standing, followed by filtration or centrifugation to separate the phases as much as possible. The residual soil is then treated again with a fresh portion of saturating solution. After four or five of such treatments in succession, making a final ratio of soil to solution of about 1:25 or more, the soil colloidal complex is considered to be fully saturated with the selected cation.

At this point in the determination, the soil is wet with saturating solution and therefore contains saturating cation in excess of that associated with the colloids. This excess must be removed or measured. Removal is effected by washing the soil with water or a water-ethanol mixture (in which the saturating salt is soluble) about three times, taking care to avoid hydrolysis and deflocculation of the colloids as the salt solution is washed away. Measurement is possible if the saturating solution contains an indicator ion (chloride is suitable) which is not absorbed by soil; then the washing process is omitted and the displacement of the saturating cation is carried out as given below, the concentration of indicator ion in the final solution being a measure of the excess saturating cation (see method 7-4).

The second stage - displacement of the saturating cation - is effected by salt solutions containing the replacing cation which are usually of similar concentration to the saturating solution but may have different pH values and need not always be buffered. Again, the cation-saturated soil is subjected to a series of attacks with the replacing solution, as in the saturation process. The successive portions of extract are combined and made to a volume which is 25-50 times the original weight of soil; and this final solution is analysed for the saturating cation (and for the indicator ion, if this is present).

7.B. GENERAL PROCEDURES FOR SATURATION, WASHING AND REPLACEMENT.

Procedures for treating soil with saturating, washing and replacing solutions can be varied but two basic methods are usually followed, depending on laboratory facilities.

Air-dry soil is used because oven-drying before treatment may alter

the exchange capacity of some samples. The air-dry moisture is determined separately.

(1) LEACHING.

(a) APPARATUS

Balance, accurate to 10 mg
Beakers, 250 ml
Stirring rods, with rubber tips
Watch glasses, 90 mm diameter
Measuring cylinder, 50 ml
Wash bottles, plastic
Buchner funnels, for 5.5 cm diameter filter papers
Filter papers, 5.5 cm diameter, hardened (e.g. Whatman No 542 or 544)
Filter flasks, 500 ml
Vacuum pump
Volumetric flasks, 250 ml
Funnels, 75 mm diameter

(b) PROCEDURE.

Transfer a weight of air-dry soil containing either 5 or 10 g of oven-dry material (see Note 1 and Section 1.4-3) to a 250 ml beaker and add 50 ml saturating solution. Stir, cover with a watch glass and leave overnight. Fix a filter paper into the Buchner funnel by wetting and applying gentle suction; then decant the supernatant solution from the beaker on to it, collecting the filtrate in a filter flask without suction. After the liquid has passed through, transfer the soil to the funnel with saturating solution and allow to drain. Leach the soil with 25-30 ml portions of saturating solution, allowing each portion to drain through before adding the next, until 200-220 ml of solution has been collected. If filtration under gravity is too slow, apply gentle suction; but the leaching process should take at least one hour and preferably longer. Save the liquid if exchangeable cations are to be determined.

Wash the soil by adding 25-30 ml portions of the wash liquid, draining between each addition, until a total of 75-100 ml of liquid has passed through (see Note 2).

Transfer the well-drained soil to a 250 ml beaker with replacing solution, make the volume to about 50 ml, stir, cover with a watch glass and leave overnight. Decant the supernatant solution on to a filter paper in the Buchner funnel (using a clean filter flask) and then proceed as in the initial saturating process until about 200 ml of liquid has been collected. Transfer this quantitatively to a 250 ml volumetric flask and make to 250 ml with replacing solution.

(2) SHAKING AND CENTRIFUGING.

(a) APPARATUS.

Balance, accurate to 10 mg
Reciprocating shaker
Centrifuge, with head to take 8 or 12 tubes
Centrifuge tubes, rigid plastic, 50 ml, with rubber stoppers (see Note 4)
Racks for centrifuge tubes
Stirring rods, tough plastic or metal
Balance for equalizing weights of centrifuge tubes

Measuring cylinder, 50 ml
Interval timer
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No 40 or 42)
Volumetric flasks, 200 ml.

(b) PROCEDURE.

Transfer a weight of air-dry soil containing 5 g of oven-dry material (see Note 1 and Section I.4-3) to a 50 ml centrifuge tube and add 35 ml saturating solution. Prepare a batch of 8 or 12 tubes to fill the centrifuge. Stopper the tubes, place them in a horizontal position in a reciprocating shaker and shake for 15 minutes. Remove the stoppers and wash the adhering soil into the tubes with saturating solution, balance the tubes in pairs (or bring them all to the same weight) and centrifuge at 2000-2500 rpm for 15 minutes. Pour off the supernatant liquid (through a filter into a 200 ml volumetric flask if needed for determination of exchangeable cations) and add another 30 ml saturating solution to the residual soil. Mix with a rod, breaking up the packed soil at the bottom of the tube, and wash down the rod with solution. Stopper, shake and centrifuge as before. Repeat until the soil has been treated five or six times (see Note 1).

Wash the soil in the same way, using three or four portions of 25-30 ml of washing liquid.

Finally treat the washed, saturated soil with replacing solution in the same way, using five or six portions of about 30 ml each and pouring off the supernatant liquid after each centrifugation through a filter paper into a 200 ml volumetric flask. Make the volume of collected extract to 200 ml with replacing solution.

7.C. CHOICE OF METHOD.

A wide range of cations has been suggested for saturation but the most commonly used are members of the alkali and alkaline earth groups and ammonium. The primary factor to be taken into consideration in selecting a cation from these is the type of soil undergoing analysis; with a range of soil types, more than one saturating solution is usually advisable for accurate work. Secondary considerations can be taken into account when more than one saturating solution is suitable for a particular soil type. These are mainly -

(a) The method to be used for determining the saturating cation in the presence of a large concentration of replacing salt; including availability of suitable apparatus.

(b) The need for determination of exchangeable cations in the liquid from the saturating process, which can only be done if the saturating cation is not one normally present in soil as an exchangeable cation (except in trace amounts).

Four different saturating cations and five solutions are suggested in the following methods 7-1 to 7-4, this being done to cover most normal soil types. As a guide to choice of method, the suitability of each solution for different soil types is indicated in the table below, together with the advocated method for chemical analysis of the final extract for the saturating cation and the possibility of estimating exchangeable cations in the extract after saturation. The kind of predominant clay

mineral in the soil can also affect choice of analysis and can be taken into account if known. (see Notes on each method).

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Saturating Cation pH of Solution	Ammonium 7.0	Sodium 8.2	Barium 8.0	Lithium 7.0	Lithium 8.2
Soil Type					
Acid pH (1:5 w/v in H_2O) less than 6.0			X	X	
Slightly acid to neutral. pH 6.0 to 7.5	X		X	X	
Calcareous.		X	X		X
Saline and/or gypsiferous.	X	X		X	X
Organic. more than 3 per cent carbon			X	X	X
Method for Determination of Saturating Cation	Distil-lation	Flame photometry	Grav. ppt. of barium sulphate.	Flame photometry.	
Suitability for Exchangeable Cations Analysis.	X		Exch. Acidity	X	X

The suggested pH values and carbon percentage are approximate.

7.D. NOTES.

(1) To ensure that the saturating cation displaces all the exchangeable cations, it is advisable to use, on average, 25 parts of solution to 1 part of soil. Sandy soils low in exchange capacity may be extracted satisfactorily at a ratio less than this; but, on the other hand, clay soils, particularly organic ones, may need to be treated at a ratio of 40:1 or 50:1 for accurate results.

Similar considerations apply to the replacement process, with the added factor in some cases that the final concentration of the saturating cation in the replacing solution should be convenient for chemical analysis. Thus a wide ratio may not only ensure complete replacement of the saturating cation but also dilute its concentration to a level more suitable for determination.

Peat and muck soils are more difficult to analyse, as the cation exchange capacity of humus is high and saturation and replacement

are often lengthy operations. It is advisable to use a wide ratio of 50:1 and carry out a duplicate determination at a wider ratio (say 75:1) to check the effectiveness of the exchanges.

(2) The removal of excess saturating solution may be accompanied in the final stages by hydrolysis and deflocculation of clay. It is impossible to lay down a precise procedure for all soil types and all saturating cations; but, in general, three treatments with the wash liquid should be sufficient to remove most of the saturating solution (see individual methods).

(3) In the second stage of the leaching procedure, the washed soil may be treated wholly on the Buchner funnel without transferring it to a beaker for an initial mixing with replacing solution. If this modification is adopted, plug the stem of the Buchner funnel, add 50 ml replacing solution and stir it carefully with the soil without tearing the filter paper. Then cover the funnel and allow the mixture to soak overnight before starting the leaching process.

(4) An ordinary type centrifuge tube allows solution to be mixed with the compacted soil mass (produced by centrifugation) more easily than a narrow-necked tube. However, the large rubber stoppers needed tend to slide out of the tubes, especially if wet. Special racks should be made to hold the tubes and stoppers tightly together during mechanical shaking.

(5) The processes of saturation, washing and replacement can be carried out wholly by allowing the appropriate solutions to percolate at a steady rate through a soil sample contained in a leaching column or a fritted glass crucible. Clay soils may have to be mixed with sand and "channeling" may lead to incomplete cation exchange but the method is worth consideration for large scale routine work.

(6) Analytical errors are unavoidable in the determination of cation exchange capacity, due mainly to incomplete exchange processes, too little or too much washing of the saturated soil and fixation of cations by clay minerals. Results should be recorded, therefore, only with an accuracy of about 1 per cent of the value obtained.

(7) The method of determination of cation exchange capacity should be reported with the result since the use of different saturating cations may lead to different figures, due to variation in cationic size, hydration and electric charge affecting the mechanism of exchange. Cation exchange capacity is not necessarily an absolute constant for a particular soil but may have a range of values according to the cation involved in its determination.

7.8. GENERAL REFERENCE.

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III. 7-1. CATION EXCHANGE CAPACITY - AMMONIUM SATURATION

7.1.A. PRINCIPLE.

Soil is treated with 1 N ammonium acetate at pH 7.0 to saturate the colloidal complex and the excess salt is removed with ethanol containing 5 per cent water. Then the ammonium ion is displaced with potassium by treatment with 10 per cent potassium chloride at pH 2.5 and finally the ammonia is measured by distillation from alkaline solution, absorption in boric acid and titration with standard acid. An alternative procedure is to omit the displacement of ammonium ion and measure it by direct distillation from the soil in alkaline solution.

7-1.B. APPARATUS.

Items for treatment of soil as in 7.B. (1) or (2)

Plus, either, for macro-distillation of solution -

- Pipette, 50 ml
- Measuring cylinders, 25 and 500 ml
- Distillation apparatus, consisting of 500 or 750 ml flasks, spray traps and condensers
- Erlenmeyer flasks, 350 ml
- Burette, 25 ml with 0.1 ml divisions

or, for micro-distillation of solution -

- Pipettes, 5 and 10 ml
- Pipette, 2 ml, with coarse jet
- Micro-distillation apparatus (e.g. 'Markham' design)
- Steam generator
- Interval timer
- Erlenmeyer flasks, 150 ml
- Burette, 10 ml, with 0.02 ml divisions

or, for macro-distillation of soil -

- Wash bottle, plastic
- Measuring cylinders, 25 and 500 ml
- Distillation apparatus, consisting of 750 ml flasks (or 800 ml Kjeldahl flasks), spray traps and condensers
- Erlenmeyer flasks, 350 ml
- Burette, 50 ml, with 0.1 ml divisions

7-1.C. REAGENTS.

Ammonium acetate, 1 N, pH 7.0 ± 0.1
Dilute 600 ml glacial acetic acid and 750 ml concentrated ammonia solution (sp.gr.0.91, 25 per cent NH_3) to 10 litres. If the pH is less than 6.9 or more than 7.1 adjust with ammonia or acetic acid.

Ethanol, 95 per cent (see Note 3)

Potassium chloride, 10 per cent, pH 2.5 ±0.1
Dissolve 1000 g potassium chloride in about 9 litres water, add 32 ml 1 N hydrochloric acid and make to 10 litres

Plus, for distillation -

Sodium hydroxide, 45 per cent
Mixed indicator

and, either, for macro-distillation -

Pumice, granulated, 5-10 mm
Boric acid, 2 per cent
Sulphuric acid or hydrochloric acid, 0.100 N

or, for micro-distillation -

Boric acid, 0.25 per cent
Sulphuric acid or hydrochloric acid, 0.010 N

(as given in Section III.4.C.)

7-1.D. PROCEDURES

Saturate 5 or 10 g oven-dry soil with ammonium ion and wash out the excess ammonium acetate, as in 7.B. (see Note 3). Then determine the absorbed ammonium ion by one of the two following methods.

(a) Leaching and distillation

Treat the washed soil with portions of acid potassium chloride as in 7.B., collecting the extract finally in a 200 or 250 ml volumetric flask and adjusting to volume with replacing solution. Determine the ammonia in this solution by either macro-distillation or micro-distillation -

(i) Macro-distillation.

Transfer 100 ml of solution to a 500 or 750 ml distilling flask and add 250 ml water and granulated pumice. Pour 20 ml of 45 per cent sodium hydroxide down the side of the flask to form a layer underneath the solution, connect to the distillation apparatus and mix. Distil into 25 ml of 2 per cent boric acid containing 0.5 ml of mixed indicator, previously placed under the condenser. Collect 150 ml of distillate and titrate with 0.100 N acid to the neutral point of the indicator. (see III.4.D.(b))

(ii) Micro-distillation.

Transfer 10 ml of solution (or 5 ml of solution plus 5 ml water for high cation exchange capacities) to a micro-distillation apparatus, add 2 ml of 45 per cent sodium hydroxide and distil with steam into 20 ml of 0.25 per cent boric acid containing 0.2 ml mixed indicator, previously placed under the condenser. Collect 25-30 ml of distillate and titrate with 0.010 N acid to the neutral point of the indicator. (see III.4.D.(c))

(b) Direct distillation.

Transfer the washed, ammonium-saturated soil and filter paper (if used) quantitatively to a 750 ml distillation flask or 800 ml Kjeldahl flask and make the liquid volume to about 350 ml. Add a little granulated pumice, pour 25 ml of 45 per cent sodium hydroxide down the side of theflask to form a layer underneath the solution, connect to the distillation apparatus and mix. Distil into 25 ml of 2 per cent boric acid containing 0.5 ml of mixed indicator, previously placed under the condenser. Collect 200 ml of distillate and titrate with 0.100 N acid to the neutral point of the indicator. (see Note 2)

Whichever distillation method is used, carry out a blank distillation on a similar volume of liquid and meaaure the amount of acid consumed.

7-1.E. CALCULATIONS.

Let

D be the weight in gram of oven-dry soil in the weight of air-dry soil taken for analysis (see Section I.4-3.)

V be the total volume in ml of the final solution containing the ammonium ion (from D g oven-dry soil)

T be the volume in ml of standard acid (either 0.100 N or 0.010 N) used for titrating the ammonia nitrogen, after correction for the blank

(a)(i) Macro-distillation of solution containing ammonium ion.

100 ml is distilled and the ammonia nitrogen is titrated with 0.100 N acid

Then, 100 ml ammonium solution containe (0.1 x T) milliequivalents cation

Thus, V ml contains $\frac{0.1\ TV}{100}$ milliequivalents (= $\frac{TV}{1000}$)
and this is the cation exchange capacity of D g oven-dry soil

Thus, cation exchange capacity = $\frac{TV}{10\ D}$ milliequivalents per 100 g

(a) (ii) Micro-distillation of solution containing ammonium ion.

The ammonia nitrogen is titrated with 0.010 N acid

If 10 ml ammonium solution is distilled,

V ml contains $\frac{0.01\ TV}{10}$ milliequivalents $(= \frac{TV}{1000})$

Thus, cation exchange capacity = $\frac{TV}{10\ D}$ milliequivalents per 100 g (as above)

If 5 ml ammonium solution is distilled,

cation exchange capacity = $\frac{TV}{5\ D}$ milliequivalents per 100 g

(b) Direct distillation of soil

The ammonia nitrogen is titrated with 0.100 N acid

Thus, D g oven-dry soil contains (0.1 x T) milliequivalents cation

i.e. cation exchange capacity = $\frac{10\ T}{D}$ milliequivalents per 100 g

7-1.F. NOTES

(1) The ammonium acetate method has been used a great deal for cation exchange capacity determinations but it is really only suited to neutral and non-calcareous soils, since displacement of hydrogen ions from acid soils may be incomplete and calcium and magnesium carbonates dissolve to a large extent in ammonium acetate at pH 7, the presence of calcium and magnesium ions in the saturating solution tending to interfere with the colloids-ammonium exchange. The method may also give low results if the soil contains predominantly 1:1 type clay minerals (kaolinitic or much organic matter. For nearly neutral, non-calcareous soils containing mainly 2:1 type clay minerals (montmorillonitic) and moderate amounts of organic matter, the method has the advantage of providing in the first saturation stage an extract in which exchangeable cations can be easily determined. (see III.8-1). Extraction with ammonium acetate is also a reliable method for determination of cation exchange capacity in acid soils if it is combined with another method for measurement of exchange acidity. The exchangeable calcium, magnesium sodium and potassium (and perhaps manganese) are determined in the ammonium acetate extract and exchange acidity (exchangeable hydrogen plus exchangeable aluminium) is determined with 1 N potassium chloride or barium chloride-triethanolamine (see III.14.). The sum of all the exchangeable cations then gives a good estimate of cation exchange capacity.

(2) The direct distillation of soil with sodium hydroxide may lead to partial breakdown of organic matter, thus introducing a possible error with most surface soils. Also, if the cation exchange capacity is large, the final titration will be large if 10 g soil is present (capacity value same as titration). Thus, for direct distillation of heavy clay soils, mainly montmorillonitic, it is better to take 5 g soil for analysis.

(3) The ethanol-water should be neutral in reaction and it may be purified from organic acids by distillation after adding calcium hydroxide. pH tests with a meter or indicator are unreliable.

In the washing process, the third portion of extract may be tested for ammonium ion with Nessler's reagent as a guide to the efficacy of the washing. After washing, do not allow the soil to dry out as this may cause loss of absorbed ammonia.

(4) Preparation of ammonium acetate from the salt is about twice as expensive and the reagent may be less pure. It is convenient to use reagents in the distillation as prepared for determination of total nitrogen.

7-1.G. REFERENCES.

BLACK. Chapter 57, Section 57-2. (H.D. CHAPMAN)

CHAPMAN and PRATT. Chapter 1, Sections 1-17 and 1-22.

JACKSON. Chapter 4, Sections 4-25 to 4-28.

III. 7-2. CATION EXCHANGE CAPACITY - SODIUM SATURATION

7-2.A. PRINCIPLE.

Saturation of the soil colloidal complex is effected with 1 N sodium acetate at pH 8.2 and the excess salt is removed with ethanol contair 5 per cent water, as in method 7-1. Then the sodium is replaced by ammonium, using 1 N ammonium acetate at pH 7.0 and the sodium is det mined in the final solution, after dilution, by flame photometry.

7-2.B. APPARATUS.

Items for treatment of soil as in 7.B. (2) (see Note 1)

Plus, for the determination of sodium -

Pipettes, 5 and 10 ml
Volumetric flasks, 250 ml
Flame photometer, with sodium filter

7-2.C. REAGENTS.

Sodium acetate, 1 N, pH 8.2 $\pm$ 0.1
Dissolve 1360 g sodium acetate, ($CH_3.COONa.3H_2O$) to 10 litres.
Adjust to pH 8.2 with 1 N sodium hydroxide - about 4-5 ml.

Ethanol, 95 per cent

Ammonium acetate, 1 N, pH 7.0
Prepare as given in 7-1.C

Sodium standard solutions for flame photometry -

(a) Stock solution containing 50 milliequivalents per litre in wa
Dissolve 1.4612 g dry sodium chloride to 500 ml

(b) Working standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre in 0.04 N ammonium acetate
Dilute 2, 4, 6, 8 and 10 ml of stock solution to 1 litre ea after incorporating in each solution 40 ml 1 N ammonium ace

7-2.D. PROCEDURE.

Use procedure 7.B.(2) to saturate 5 g oven-dry soil with sodium, was out the excess sodium acetate with 95 per cent ethanol and finally p pare 200 ml of 1 N ammonium acetate containing the absorbed sodium. (see Notes 1, 2 and 3). Prepare a batch of such solutions.

Dilute 10 ml of each of these ammonium acetate solutions to 250 ml w water. Calibrate the flame photometer with the sodium working stands over the range 0 to 0.5 milliequivalents per litre. (see Note 4) T determine the scale readings for the diluted extracts. If any readi are higher than 0.5, dilute 5 ml of the appropriate soil extracts ar 5 ml ammonium acetate replacing solution to 250 ml with water.

7-2.E. CALCULATIONS.

Let

A be the concentration in milliequivalents per litre of sodium in the diluted extract, from the calibration graph

Then, for the normal dilution of 1 to 25, the concentration of sodium in the 1 N ammonium acetate extract is 25 A milliequivalents per litre.

Since 200 ml of this extract is prepared from 5 g soil, 25 A me of sodium is present in 25 g soil.

Thus, the cation exchange capacity is

100 A milliequivalents per 100 g oven-dry soil

For a dilution of 1 to 50, the cation exchange capacity is

200 A milliequivalents per 100 g oven-dry soil

For the general case, when D g oven-dry material is present in 5 g of air-dry soil (or near this) taken for analysis, the above expressions become, respectively -

$$\frac{500\ A}{D} \quad \text{and} \quad \frac{1000\ A}{D}$$

7-2.F. NOTES.

(1) This method has been developed particularly for saline and saline-alkaline soils and those containing calcium and magnesium carbonates, which are not dissolved to any great extent by the saturating solution. Shaking and centrifuging is advocated for the soil treatment because sodium soils may leach rather slowly.

(2) The original method recommends leaching to 100 ml only, using 4 or 6 g soil initially, depending on texture. This may be sufficient for sandy soils but in general and especially for clay soils, leaching to 200 ml is safer.

(3) Only three washings with ethanol are advocated in the original method, which also states that the specific conductivity of the ethanol from the third washing should be less than 40 micromhos.

(4) Most flame photometers operate satisfactorily with sodium solutions containing up to 0.5 milliequivalents per litre (11.5 ppm). Other ranges may be used if more convenient, with appropriate adjustments to the degree of dilution of the final extract.

With the method advocated and 25 times dilution, cation exchange capacity values up to 50 milliequivalents per 100 g are covered.

7-2.G. REFERENCES.

BLACK. Chapter 57, Section 57-3. (H.D.CHAPMAN)

CHAPMAN and PRATT. Chapter 1, Section 1-23.

JACKSON. Chapter 4, Sections 4-23 and 4-24.

RICHARDS. Chapter 6, Method 19.

III. 7-3. CATION EXCHANGE CAPACITY - BARIUM SATURATION

7-3.A. PRINCIPLE.

The saturating solution is 0.5 N barium chloride buffered at pH 8.0 with triethanolamine instead of using the acetate. Barium chloride alone is used at the end of the saturating stage and the excess barium salt is washed out with water, hydrolysis and deflocculation of clay being less troublesome with a barium-saturated soil.

Barium is finally displaced by treatment with 1 N ammonium chloride at pH 8.0 and determined gravimetrically as sulphate. The precipitation of barium sulphate is carried out in homogeneous solution, the sulphate ion being generated by hydrolysis of sulphamic acid in hot solution -

$$NH_2HSO_3 + H_2O = NH_4^+ + H^+ + SO_4^{2-}$$

This method, particularly in the presence of ammonium chloride, produces a coarsely crystalline precipitate which filters easily.

7-3.B. APPARATUS.

Items for treatment of soil as in 7.B. (1) or (2)

Plus, for the determination of barium -

Pipette, 50 ml and graduated pipette, 5 ml, with 0.05 ml divisions
Measuring cylinder, 100 ml
Beakers, 250 ml
Water bath
Glass rods, fitted with rubber 'policemen'
Wash bottle, glass, for hot water
Drying oven
Muffle furnace
Desiccator
Analytical balance, accurate to 0.1 mg

And, either -

Funnels, 75 mm diameter
Filter papers, 11.0 cm diameter, (e.g. Whatman No 42)
Crucibles, porcelain or silica, 32 mm diameter

or -

Filter crucibles, porcelain or silica, fine porosity (see Note 4)
Filter flasks, with adapters for crucibles
Vacuum pump

7-3.C. REAGENTS.

Barium chloride, 0.5 N, buffered at pH 8.0 $\pm$ 0.1 with approximately 0.05 N triethanolamine

Dissolve 610 g barium chloride ($BaCl_2.2H_2O$) to about 5 litres.
In a separate vessel, dilute 70 ml triethanolamine (7.5 - 8.0 N) to about 300 ml and add 240 ml I N hydrochloric acid.
Mix the two solutions and make to 10 litres. Check the pH and adjust if necessary with triethanolamine (diluted) or hydrochloric acid.
Protect the solution from carbon dioxide.

Barium chloride, 0.1 N
Dissolve 61 g barium chloride ($BaCl_2.2H_2O$) to 5 litres

Ammonium chloride, 1N, pH 8.0 ± 0.1
Dissolve 535 g ammonium chloride to nearly 10 litres, add 100 ml 5 N ammonia solution and make to 10 litres. Check the pH value.

Hydrochloric acid, 5 N
Sulphamic acid

7-3.D. PROCEDURE.

Saturate 5 or 10 g oven-dry soil with barium chloride - triethanolamine solution as in 7.B. (see Note 2). Then treat the soil with three or four lots of 25-30 ml 0.1 N barium chloride, followed by three or four lots of 25-30 ml water. Finally displace the barium with ammonium chloride, preparing 200 or 250 ml solution.

Transfer 50 ml of final solution to a 250 ml beaker, make the volume to 100-125 ml with water and add 1.5 ml 5N hydrochloric acid. Add 1 g sulphamic acid and heat on a water bath, continuing the heating for 30 minutes after the precipitate begins to appear. Filter the barium sulphate immediately through a fine filter paper or a filtering crucible (see Note 4), wash with hot water and treat the precipitate finally as discribed in Section IV.11-1.

7-3.E. CALCULATION

Let

D be the weight in gram of oven-dry soil in the weight of air-dry soil taken for analysis (see Section I.4-3.)

V be the total volume in ml of the final solution containing the barium ion (from D g oven-dry soil)

W be the weight in gram of barium sulphate from 50 ml of the final solution

1 gram barium sulphate = 8.567 milliequivalents

Thus, 50 ml final solution contains (8.567 X W) milliequivalents barium

Therefore V ml contains

$$\frac{8.567\ WV}{50} \text{ milliequivalents}$$

and the cation exchange capacity is $\frac{8.567\ WV}{50} \times \frac{100}{D}$

$$= \frac{17.134\ WV}{D} \text{ milliequivalents per 100 g oven-dry soil}$$

7-3.F. NOTES

(1) This method is suited to all types of soils except those containing soluble sulphates in moderate to high amounts (particularly as gypsum) because of removal of barium from solution as barium sulphate during treatment. It is superior to ammonium acetate saturation for organic soils and those containing 1:1 type clay minerals; and since calcium and magnesium carbonates become coated with insoluble barium

carbonate and so do not dissolve, the method is particularly suitable for calcareous soils.

(2) The first extract with buffered barium chloride may be analysed for exchangeable cations if desired, although the presence of a high concentration of barium is a disadvantage. For acid soils, the first extract may be used in the determination of exchange acidity (see III.14.) but in this case it is preferable to use procedure 7.B.(1) with 10 g soil for the saturation of the soil with barium.

(3) In the original method, 5 per cent calicum chloride at pH 8.0 is used to displace barium after saturation. The precipitation of barium sulphate in the presence of high amounts of calcium (even in homogeneous solution) is liable to be affected by co-precipitation of calcium sulphate. Thus ammonium chloride at pH 8.0 is preferred.

(4) Porcelain or silica crucibles with porous bases are preferable to filter papers, as there is no danger from reduction of sulphate by carbon from the paper during ignition. (see IV.11-1.)

(5) For the normal range of cation exchange capacity values, a 50 ml aliquot of the final solution provides an amount of barium within the optimum range for accurate gravimetric determination. (see IV. II-I.) For sandy soils extracted at a ratio of 1:50, an aliquot of 75 or 100 ml might be better, increasing the amount of 5 N hydrochloric acid to 1.75 or 2.0 ml respectively. The calculation also needs adjustment.

7-3.G. REFERENCES.

BLACK. Chapter 59, Section 59-3. (M. PEECH)

CHAPMAN and PRATT. Chapter 1, Sections 1-19 and 1-20.

WILSON. Vol. I.A, Chapter VI. (5.e. - L. Gordon)

Vol. I.C, Chapter IX. (2.c. Barium. (a) - H. THOMAS)

III. 7-4. CATION EXCHANGE CAPACITY - LITHIUM SATURATION

7-4.A. PRINCIPLE

The saturating solution contains lithium at 0.5 N concentration, partly as the acetate at 0.1 N for buffering and partly as the chloride at 0.4 N to act as an indicator ion, so that the intermediate washing stage for removal of excess saturating salt can be omitted. The solution is buffered either at pH 8.2 for extraction of alkaline and calcareous soils or at pH 7.0 for the extraction of acid, neutral and non-calcareous soils. (see Note 1)

After saturation, the lithium attached to the colloidal complex is displaced by 0.2 N calcium acetate solution, buffered at the same pH value as the saturating solution, this process also removing the excess lithium salts. The final solution is analysed for lithium by flame photometry and for chloride by titration with mercurinc nitrate.

7-4.B. APPARATUS.

Items for treatment of soil as in 7.B (2)

Plus, for the determination of lithium -

Pipette, 10 ml
Volumetric flasks, 50 ml
Flame photometer, with lithium filter

and, for the determination of chloride -

Pipettes, 10 and 20 ml
Erlenmeyer flasks, 250 ml
Measuring cylinder, 50 ml
Graduated pipette, 1 ml
Burette, 25 ml, with 0.05 ml divisions

and in addition, for checking saturating solutions -

Volumetric flasks, 100 and 200 ml

7-4.C. REAGENTS.

Lithium saturating solutions -
Add 170 g anhydrous lithium chloride slowly to about 2 litres water. Cool and dilute to about 8 litres. Dissolve in this 102 g lithium acetate ($CH_3COOLi.2H_2O$) and finally make to 10 litres.

Adjust 10 pH 8.2 with 0.1 N lithium hydroxide or to pH 7.0 with 1 N acetic acid. Lithium salts tend to vary in purity but only a few ml of each of these adjusting solutions should be needed.

Determine the exact concentration of lithium and chloride. (see procedure)

Calcium acetate replacing solutions -
Dissolve 176 g calcium acetate ($(CH_3COO)_2Ca.H_2O$) to 10 litres

The pH is usually near 8.2: adjust to pH 8.2 (if necessary) with 1 N acetic acid or freshly made saturated calcium hydroxide - or to pH 7.0 with 1 N acetic acid.

Lithium standard solutions for frame photometry -

(a) Stock solution containing 100 milliequivalents per litre in water
Dissolve about 4.3 g anhydrous lithium chloride to 1 litre. Titrate 5 ml with 0.020 N mercuric nitrate to determine the concentration of chloride (see Section IV.10) and dilute to 0.100 N exactly.

(b) Working standards containing 1, 2, 3, 4, 6 and 8 milliequivalents per litre in 0.04 N calcium acetate.
Dilute 5, 10, 15, 20, 30 and 40 ml of stock solution to 500 ml each, after incorporating in each solution 100 ml 0.2 N calcium acetate.

Solutions for determination of chloride -

Nitric acid, 0.5 N
Mercuric nitrate, 0.020 N
Prepare as described in IV.10.
Diphenylcarbazone
0.5 per cent in ethanol

7-4.D. PROCEDURES.

Use procedure 7.B.(2) - (see Note 2) - to saturate 5 g oven-dry soil with lithium, collecting the extract in a 200 ml volumetric flask if exchangeable cations analysis is required. After saturation, remove the excess saturating solution and replace the absorbed lithium by treatment with calcium acetate, also as in 7.B.(2), collecting 200 ml of extract.

(a) Determination of total lithium.

Dilute 10 ml calcium acetate extract to 50 ml with water. Calibrate the flame photometer with the lithium working standards containing 2, 4, 6 and 8 milliequivalents per litre, using 0.04 N calcium acetate as a blank solution; then obtain readings for the diluted extracts. If readings are obtained indicating less than 4 milliequivalents per litre, recalibrate the flame photometer with lithium working standards containing 1, 2, 3 and 4 milliequivalents per litre and obtain new readings for the diluted extracts. (see Note 3)

(b) Determination of chloride, to measure excess lithium.

Transfer 20 ml calcium acetate extract to a 250 ml Erlenmeyer flask and dilute to 50 ml. Add 10 ml 0.5 N nitric acid and 0.5 ml diphenylcarbazone indicator. Titrate with 0.020 N mercuric nitrate to the first permanent pink-violet tinge. (see Note 4)

(c) Determination of the lithium:chloride ratio in the saturating solution.

Dilute 10 ml of saturating solution to 100 ml with water; then dilute 10 ml of the resulting solution to 100 ml after adding 20 ml 0.2 N calcium acetate. Calibrate the flame photometer over the range 0-8 milliequivalents lithium per litre (see above) and obtain a reading for the diluted saturating solution.

Dilute 10 ml of saturating solution to 200 ml with water. Transfer 20 ml to a 250 ml Erlenmeyer flask, add 20 ml 0.2 N calcium acetate and 10 ml water. Add 10 ml 0.5 N nitric acid and 0.5 ml diphenylcarbazone and titrate with 0.020 N mercuric nitrate to the first permanent pink-violet tinge. (see Note 4)

7-4.E. CALCULATIONS.

(a) Total lithium.

Let

A be the concentration in milliequivalents per litre of lithium in the diluted calcium acetate extract, from the calibration graph.

Then, the concentration in the 0.2 N calcium acetate extract is

5 A milliequivalents per litre

(b) Chloride.

Let

T be the volume in ml of 0.020 N mercuric nitrate used for titrating 20 ml calcium acetate extract, after correction for the blank

Then, 20 ml extract contains (T x 0.02) milliequivalents chloride

Therefore the concentration is

T milliequivalents per litre

(c) Lithium:chloride ratio.

Let

B be the conentration in milliequivalents per litre of lithium in the diluted saturating solution, from the calibration graph.

Then, the concentration of lithium in the saturating solution is

100 B milliequivalents per litre

Let

V be the volume in ml of 0.020 N mercuric nitrate used for titrating 20 ml diluted saturating solution

Then, the concentration of chloride in the saturating solution is

20 V milliequivalents per litre

Thus, the ratio of lithium to chloride is $\frac{100\ B}{20\ V}$

where B is near 5 and V is near 20

Let this ratio be R (near 1.25)

(d) Cation exchange capacity.

The concentration of excess lithium in the calcium acetate extract is

RT milliequivalents per litre

Thus, the concentration of lithium associated with the colloidal complex of the soil is

(5 A - RT) milliequivalents per litre

Since 5 g soil is extracted to 200 ml, the cation exchange capacity is

$$4(5\ A - RT) \text{ milliequivalents per 100 g oven-dry soil}$$

When D g oven-dry soil (near 5 g) is taken, the cation exchange capacity is

$$\frac{20(5\ A - RT)}{D} \text{ milliequivalents per 100 g}$$

7-4.F. NOTES.

(1) This method, with extraction at pH 8.2, has been developed for saline and calcareous soils but can be employed on all types of soils by adjustment of pH of the saturating and replacing solutions. The use of pH 8.2 solutions could be restricted to soils having pH values (1:5 w/v in water) of 7.6 and above; while pH 7.0 solutions could be used for all soils up to pH 7.5.

(2) Shaking and centrifuging is preferred as lithium-saturated soils may leach rather slowly. Also, since lithium is a weak exchanging ion, a series of mechanical shakings is more effective.

The first extract can be used for determination of exchangeable cations (see III.8-2.).

(3) Recommended ranges for the flame photometric determination of lithium are usually less than that given above but the range suggested is satisfactory, although there is not a linear relation between scale readings and concentration of lithium. Calibration over two ranges is advised so that the most accurate readings can be taken.

In the preparation of standard lithium solutions, the calcium acetate incorporated should really be of the same pH value as is used in the soil treatment, necessitating two sets of standards. However, in practice, one set of standards, made with either calcium acetate solution, is sufficient.

(4) It is advisable to prepare a colour standard for the chloride titration and at the same time estimate a blank value by titrating 10 ml 0.020 N magnesium chloride with 0.020 N mercuric nitrate, with and without the addition of 20 ml 0.2 N calcium acetate. (see IV.10.) The titration value in the presence of calcium acetate less the titration value without it is a blank to be subtracted from each determination. It may be necessary to carry out other blank determinations with different quantities of 0.020 N magnesium chloride (near those found for chloride in determinations).

The amount of 0.5 N nitric acid added to the calcium acetate solutions adjusts the acidity to a level providing a sharp end-point to the titration.

7-4.G. REFERENCE.

YAALON, (Journal paper)

III. 8. EXCHANGEABLE CATIONS.

8.A. GENERAL PRINCIPLES.

As noted in Section III.7, the extracts prepared during the saturation process in cation exchange capacity analyses contain the exchangeable cations of the soils, consisting mainly of calcium, magnesium, sodium and potassium, with sodium in larger amounts from saline soils and hydrogen and aluminium in addition from acid soils. When the ammonium ion or lithium is used to saturate soils, the extracts are suitable (with some exceptions, noted below) for the determination of calcium, magnesium, sodium and potassium by methods based on Sections IV.4 to IV.7 and analyses are normally restricted to these four cations. However, exchangeable manganese may be determined in the neutral ammonium acetate extract. (see III.16.) Special alternative methods are usually used to measure exchangeable hydrogen and aluminium in acid soils (see III.14.).

The determination of exchangeable cations is straight forward when the soil contains only very small amounts of water soluble salts of the cations concerned. But extracts of saline soils contain calcium, magnesium, sodium and potassium from the salts deposited in the soils and allowance has to be made for the amounts of these dissolved in the extraction process. It is virtually impossible to wash out the soluble salts without disturbing the relative proportions of the exchangeable cations; thus, extractions with ammonium acetate or lithium chloride - acetate are carried out in the normal way and separate determinations of water soluble cations are done (see III.6.). However, it is uncertain what is the most suitable soil: water ratio to use in determining the water soluble salts; some advocate the saturation extract and some one part of soil to two parts of water. When saline soils are neutral or alkaline, it is possible to check analyses partially from the fact that the sum of the exchangeable cations should be nearly equal to the cation exchange capacity. But analyses for exchangeable cations in saline soils are never very accurate and can only be an approximate guide to the cation situation in the soil which is complex and ever-changing.

Ammonium acetate at pH 7.0 dissolves considerable amounts of calcium and magnesium carbonates under the prolonged treatment in the extraction procedure and this solution cannot therefore be used for calcareous soils. The lithium extracting solution at pH 8.2 is, however, suitable. It is probable that the full analysis of calcareous soils for exchangeable calcium, magnesium, sodium and potassium is unnecessary in most cases, since it may be assumed that the exchange complex is predominantly associated with calcium - or with calcium and magnesium in dolomitic areas - and an analysis for sodium and potassium (plus cation exchange capacity) may be sufficient.

When a soil is both calcareous and saline, the lithium extracting solution can be used for determining exchangeable plus water soluble cations. Water extracts must also be made and analysed and it is useful to determine the cation exchange capacity so that the appropriate soil:water ratio can be found, as indicated above.

8.B. PROCEDURES FOR PREPARATION OF EXTRACTS.

Follow the procedures given in III.7.B.(1) or (2) to make 250 ml of ammonium acetate extract from a weight of 2 mm air-dry soil equivalent to 5.0 g oven-dry soil. Follow the procedure given in III.7.B.(2) to make 200 ml of lithium chloride - acetate extract, also from the equivalent of 5.0 g oven-dry soil. These ratios are suitable for most cultivated

soils but they may need to be widened for soils containing high amounts of organic matter, which often have a correspondingly high concentration of exchangeable cations. When these are analysed, reduce the weight of oven-dry soil (equivalent) to 2.5 g, using soil material ground to pass a 0.5 mm sieve. Very sandy soils with cation exchange capacity values less than 10 milliequivalents per 100 g oven-dry soil may be extracted with ammonium acetate using the equivalent of 10 g oven-dry soil; but this is inadvisable for the lithium extraction method.

8.C. GENERAL NOTES.

(1) The uncertainties and variabilities associated with exchangeable cation analysis make it unwise to record results with greater accuracy than 0.1-0.2 milliequivalents per 100 g oven-dry soil. Since end-points in titrations with 0.020 N EDTA can only be judged to about one drop (0.05 ml), this fits the advocated degree of accuracy; because, if one-tenth of the prepared extract is taken for titration (as advised in the following procedures), one drop EDTA corresponds to 0.2 milliequivalents of exchangeable cation (calcium or magnesium) per 100 g soil when 5 g soil is extracted (or to 0.1 me when 10 g soil is taken - or to 0.4 me when 2.5 g soil is taken)

Although, in the absence of major interferences, sodium and potassium can be determined by emission flame photometry over the range 0 - 2.5 milliequivalents per 100 g oven-dry soil to the nearest 0.01-0.02 me, it is usually unnecessary to aim at this accuracy when the figures are merely wanted for comparison (and summation) with calcium and magnesium figures which are normally much larger. In this case, interferences can often be neglected. If, however, these results are required for conversion to parts per million to assess availability (particularly of potassium), then interferences must be studied and an accuracy of 0.01 me per 100 g (4 ppm K in a soil) approached. (see III.13-1.)

(2) The need for "correction" of exchangeable cation values for water soluble cations may be judged conveniently from conductivity measurements on soil:water extracts or suspensions prepared for pH determinations. Thus, if a 1:5 suspension has a conductivity greater than 0.1 millimho, this means that the soil contains more than about 0.5 milliequivalents per 100 g soil of water soluble cations. Then, in accurate work, a water extract must be made and analysed; but this is often difficult if the concentration of water soluble cations does not exceed about 5 me per 100 g and sodium predominates. In these cases, it is often impossible (particularly with limited equipment) to produce reliable results for true exchangeable cations.

8.D. GENERAL REFERENCES.

BLACK. Chapter 54. (C.I. RICH)
Chapter 68. (W.R. HEALD)
Chapter 71, Section 71-3.) (P.F. PRATT)
Chapter 72, Section 72-3.)

CHAPMAN and PRATT. Chapter 23, Sections 23-1 and 23-2.

JACKSON. Chapter 5.
Chapter 18, Sections 18-24 and 18-25.

See also the references given for Sections IV.4, IV.5, IV.6 and IV.7.

III. 8-1. EXCHANGEABLE CATIONS - AMMONIUM ACETATE EXTRACTION

8-1.A. PRINCIPLES.

Calcium plus magnesium may normally be determined in ammonium acetate extracts of soils by direct titration with EDTA according to the principles outlined in Section IV.4.A. The presence of the ammonium acetate does not interfere with the titration if this is carried out by the procedure advocated below; and the amount of organic matter dissolved is usually too small to affect the colour change of the indicator.

Similarly, calcium alone may be determined by direct titration with EDTA according to the principles outlined in Section IV.5.A.

Sodium and potassium can also be determined by direct flame photometry in the soil extracts, using standards made up in neutral 1 N ammonium acetate. The main interference effects (calcium on sodium and sodium on potassium) may be studied as described in Section IV.6.D.(a) - in the presence of ammonium acetate - and appropriate measures taken to eliminate them or correct the results, if accurate analyses are required. (see III.8.C.(1)

The determination of exchangeable managanese in ammonium acetate extracts is described in Section III.16-2.

8-1.B. APPARATUS.

Apparatus for the determination of calcium plus magnesium, calcium, sodium and potassium, as given in Sections IV.4.B., IV.5.B., IV.6.B. and IV.7.B

8-1.C. REAGENTS.

Reagents for the determination of calcium plus magnesium and calcium only, as given in Sections IV.4.C. and IV.5.C.

Plus, for sodium -

Sodium chloride, 0.050 N
Dissolve 1.4612 g dry sodium chloride to 500 ml

Ammonium acetate, 2 N, pH 7.0 ± 0.1
Dilute 600 ml glacial acetic acid and 750 ml concentrated ammonia solution (sp.gr. 0.91, 25 per cent NH_3) to 5 litres. If the pH is less than 6.9 or more than 7.1, adjust with ammonia or acetic acid.

Sodium chloride, standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre, in 1 N ammonium acetate.

Dilute 2, 4, 6, 8 and 10 ml of 0.050 N sodium chloride solution each to 1 litre, after adding 500 ml 2 N ammonium acetate.

And, for potassium -

Potassium chloride, 0.050 N
Dissolve 1.8640 g dry potassium chloride to 500 ml

Ammonium acetate, 2 N, pH 7.0 ± 0.1 (see above)

Potassium chloride, standards containing 0.1, 0.2, 0.3, 0.4 and 0.5

milliequivalents per litre, in 1 N ammonium acetate.

Dilute 2, 4, 6, 8 and 10 ml of 0.050 N potassium chloride solution each to 1 litre, after adding 500 ml 2 N ammonium acetate.

8-1.D. PROCEDURES.

(a) Calcium plus magnesium.

Transfer 25 ml extract to a 250 ml Erlenmeyer flask and make the volume to about 50 ml with water. Add a few crystals of hydroxylamine hydrochloride (or ascorbic acid), 1 ml of 2 per cent potassium cyanide (from a burette), 1 ml of 2 per cent potassium ferrocyanide and 10 ml of ethanolamine buffer (see Note 1). Warm to about 60°C, add 0.2 ml eriochrome blue-black B and titrate with 0.020 N EDTA to a pure turquoise blue without any trace of red.

Before carrying out a batch of determinations, titrate 20 ml 0.02 N magnesium chloride solution with 0.020 N EDTA in the presence of 25 ml 1 N ammonium acetate solution. This provides a blue colour standard for the other titrations; the presence of ammonium acetate may effect the shade of blue but the end-point is still readily detectable. Record the "blank" value if traces of calcium plus magnesium are found in the ammonium acetate solution.

(b) Calcium only.

Transfer 25 ml extract to a 250 ml Erlenmeyer flask and make the volume to about 50 ml with water. Add hydroxylamine hydrochloride, potassium cyanide and potassium ferrocyanide as given above for calcium plus magnesium. Wait a few minutes, then add 4 ml 8 N potassium hydroxide and a spatula point of HHSNN indicator mixture. Titrate with 0.020 N EDTA to a pure blue without any trace of red.

Before carrying out a batch of determinations, titrate 20 ml 0.02 N calcium chloride solution with 0.020 N EDTA in the presence of 25 ml 1 N ammonium acetate solution. Record the "blank" value if traces of calcium are found in the ammonium acetate solution.

(c) Sodium.

1. Preliminary operations.

Study the calcium plus magnesium values in relation to the cation exchange capacity and exchange acidity of non-calcareous and acid soils. Assuming potassium to be comparatively low (say, less than 1 milliequivalent per 100 g) in most soils, assess the probable sodium level. If this is less than 2.5 milliequivalents per 100 g, (for 250 ml extract from 5 g soil), proceed with the sodium determinations on the undiluted extracts. If it is more than 2.5 me per 100 g, dilute the extracts appropriately as described below.

When cation exchange capacity and exchange acidity values are not available, assess the possible sodium levels in the extracts from other suitable data (e.g. conductivity, water soluble salts) or from known facts about the soils or from the appearance of the flame when the extracts are sprayed qualitatively. In general, extracts of cultivated soils can be sprayed directly but extracts of saline soils mostly need dilution.

2. Determinations.

If the sodium concentration of the extracts is assessed at less than 0.5 milliequivalents per litre, bring the flame photometer into use according to the maker's instructions. Spray a standard sodium solution and 1 N ammonium acetate alternately and operate the sensitivity controls until the standard reads a selected point on the photometer scale and the ammonium acetate reads zero (or a "blank" value). Spray the other standard sodium solutions and record the scale scale readings. Then spray the test solutions and record their values, checking the photometer performance at frequent intervals.

If the sodium concentration of the extracts is greater than 0.5 me per litre, make appropriate dilutions before calibrating the flame photometer. These dilutions may be made with 1 N ammonium acetate solution and the same standard solutions used for calibration; or they may be made with water and sodium standards prepared in the same dilution of ammonium acetate (see Note 2).

Use the preferred procedure to deal with any serious interference effects, which are mostly due to high calcium:sodium ratios. (see IV.6.D.(a))

(d) Potassium.

Bring the flame photometer into use as noted above, calibrating it with the potassium standards in 1 N ammonium acetate. Then spray the test solutions and record the photometer scale values.

Concentrations of potassium in ammonium acetate extracts (1:50) are rarely above 0.5 milliequivalent per litre and dilutions are not normally needed. It may be necessary to allow for the effect of high sodium:potassium ratios in the analysis of saline soils.

8-1.E. CALCULATIONS.

(a) Calcium plus magnesium; calcium.

Let

W be the weight in gram of oven-dry soil extracted to 250 ml

T be the volume in ml of 0.020 N EDTA used in the titration (for Ca+Mg or Ca, as appropriate) after correction for any traces of Ca+Mg or Ca in the extractant.

Then, as in IV.4.E. and IV.5.E., the EDTA used is equivalent to 0.02T me Ca+Mg or Ca.

This amount is derived from 0.1 W g oven-dry soil (for a 25 ml aliquot).

Thus, the concentration of Ca+Mg or Ca is

$$\frac{0.02\ T \times 100}{0.1\ W}$$

$$= \frac{20\ T}{W} \text{ milliequivalents per 100 g oven-dry soil}$$

Normally, when W = 5, this expression is 4 T me per 100 g

(b) Sodium: potassium.

Let

W have the meaning given in (a) above

G be the concentration in milliequivalents per litre (Na or K) of the prepared extract, obtained from the calibration graphs, corrected for any interferences and allowing for dilutions.

Then, the concentration of sodium or potassium in the soil is

$$\frac{100\ G}{4\ W} \text{ milliequivalents per 100 g oven-dry soil}$$

Normally, when W = 5, this expression is 5 G me per 100 g

(c) Exchangeable cations in saline soils.

Convert concentrations of calcium, magnesium, sodium and potassium in water extracts of saline soils (methods IV.4 to IV.7) to concentrations per 100 g oven-dry soil by multiplying by appropriate factors, as given in III.6.E.(b).

Subtract these values, respectively, from the concentrations of exchangeable plus water soluble cations (me per 100 g soil) obtained from ammonium acetate analyses to give an assessment of exchangeable calcium, magnesium, sodium and potassium.

8-1.F. NOTES.

(1) 10 ml of ethanolamine buffer should be adequate to give the required pH of 10.0 (± 0.1) but this should be checked. Ammonia - ammonium chloride buffer may be used if ethanolamine is not available.

(2) In the analysis of saline soils, large dilutions may be necessary for sodium analyses and then it is obviously better to dilute with water and so economize on ammonium acetate. Standards may be required in 0.2 N or 0.1 N ammonium acetate - or even less, Five times dilution covers sodium values up to 12.5 me per 100 g (W = 5) and ten times dilution up to 25 me per 100 g.

(3) If highly organic soils are analysed or difficulty is found with the advocated procedures for calcium and magnesium, a measured aliquot (say, 100 ml) of the ammonium acetate extract may be evaporated to dryness and treated with hydrogen peroxide and nitric acid to destroy organic matter and ammonium acetate. The residue is taken up in dilute hydrochloric acid, filtered and made to the original aliquot volume, giving a solution of calcium and magnesium of the same concentration as the original extract, as chlorides in very dilute hydrochloric acid.

If this is done, the amounts of ethanolamine buffer (Ca+Mg) or potassium hydroxide (Ca) may have to be adjusted to give the required pH values. In general, for most mineral soils, this extra treatment is unnecessary.

(4) All four exchangeable cations may be determined by atomic absorption spectrophotometry if the apparatus is available. Interference effects may be less but must be studied at the levels and ratios found in the soil extracts. (Appendix 11.)

8-1.G. REFERENCES.

CHAPMAN and PRATT. Chapter 1, Section 1-18.

RICHARDS. Chapter 6. Method 18.

III. 8-2. EXCHANGEABLE CATIONS - LITHIUM CHLORIDE-ACETATE EXTRACTION.

8-2.A. PRINCIPLES.

Calcium plus magnesium may be determined in lithium chloride-acetate extracts of soils by direct titration with EDTA according to the principles outlined in Section IV.4.A. As with ammonium acetate extracts, the presence of the extractant salts does not seem to interfere with the titration, apart from a possible slight alteration of the shade of blue at the end-point.

However, calcium alone cannot be determined by direct titration with EDTA according to the method given in Section IV.5.D. Therefore, calcium is precipitated and separated as calcium tungstate (the pH of the extracting solutions - either 7.0 or 8.2 - being suitable for this precipitation) and magnesium is determined in the remaining liquid by titration with EDTA.

Sodium and potassium can be determined by direct flame photometry in lithium chloride-acetate soil extracts, using standards made up in the extractant. The usual interference effects may be studied in accurate work.

8-2.B. APPARATUS.

Apparatus for the determination of calcium plus magnesium, sodium and potassium, as given in Sections IV.4.B., IV.6.B. and IV.7.B.

Plus, for calcium -

Centrifuge, with 50 ml tubes (glass)
Stirring rods
Bulb pipette, 1 ml
Water baths, for heating and cooling, with holder for centrifuge tubes (600 ml beakers may be used in small-scale work)

8-2.C. REAGENTS.

Reagents for the determination of calcium plus magnesium, as given in Section IV.4.C.

Plus, for calcium separation -

Sodium tungstate, 20 per cent
Dissolve 100 g sodium tungstate, $Na_2WO_4.2H_2O$, to 500 ml and filter

And, for sodium -

Sodium chloride, 0.050 N (see III.8-1.C.)

Sodium chloride, standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre, in lithium extracting solution

Dilute 2, 4, 6, 8 and 10 ml of 0.050 N sodium chloride solution each to 1 litre with lithium chloride-acetate extracting solution (see III.7-4.C. and Note 3)

And, for potassium -

Potassium chloride, 0.050 N (see III.8-1.C.)

Potassium chloride, standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre, in lithium extracting solution.

Dilute 2, 4, 6, 8 and 10 ml of 0.050 N potassium chloride solution each to 1 litre with lithium chloride-acetate extracting solution.

8-2.D. PROCEDURES.

(a) Calcium plus magnesium.

Transfer 20 ml extract to a 250 ml Erlenmeyer flask and make the volume to about 50 ml with water. Proceed as given in III.8-1.D.(a), carrying out a "blank" titration of 20 ml 0.02 N magnesium chloride solution in the presence of 20 ml of lithium extractant.

(b) Magnesium only.

Transfer 20 ml extract to a 50 ml centrifuge tube and warm in a water bath (or a beaker of water) to 80°C. Add 5 ml of 20 per cent sodium tungstate and stir. Leave for about five minutes, then wash down the stirring rod with 1 ml water. Cool the tubes in iced water and centrifuge at 2500 rpm for 5-10 minutes. Pour the supernatant liquid into a 250 ml Erlenmeyer flask, add 25 ml water to the calcium tungstate precipitate, centrifuge again and add the supernatant liquid to that already in the Erlenmeyer flask.

Determine magnesium in the calcium-free extract according to the procedure given in III.8-1.D.(a).

(c) Sodium and potassium.

Proceed as described in III.8-1.D.(c) and (d), using the appropriate standards and lithium extractant blanks. Note that in the procedure advocated for preparation of lithium chloride-acetate extracts (III.8.B.) 200 ml of extract is normally prepared from 5 g soil; thus, levels of sodium or potassium above 2.0 milliequivalents per 100 g oven-dry soil involve dilutions. (see Note 2)

8-2.E. CALCULATIONS.

(a) Calcium plus magnesium; magnesium.

Let

W be the weight in gram of oven-dry soil extracted to 200 ml

T be the volume in ml of 0.020 N EDTA used in the titration (for Ca+Mg or Mg, as appropriate) after correction for any traces of Ca+Mg or Mg in the extractant.

Then, as a 20 ml aliquot is taken from a total extract volume of 200 ml, the required concentration of Ca+Mg or Mg is

$$\frac{20\ T}{W}$$ milliequivalents per 100 g oven-dry soil

as noted in III.8-1.E.(a).

(b) Sodium; potassium.

Let

W have the meaning given in (a) above

G be the concentration in milliequivalents per litre (Na or K) of the prepared extract, obtained from the calibration graphs, corrected for any interferences and allowing for dilutions.

Then, the concentration of sodium or potassium in the soil is

$$\frac{100\ G}{5\ W} \text{ milliequivalents per 100 g oven-dry soil}$$

Normally, when W = 5, this expression is 4 G me per 100 g

(c) Exchangeable cations in saline soils.

Calculate these values as described in III.8-1.B.(c).

8-2.F. NOTES.

(1) The volume of extract is advised as 200 ml to conform to the published procedure (Yaalon et al) but, of course, 250 ml may be prepared and suitable adjustments made to the methods and calculations, where necessary (e.g. take 25 ml for the EDTA titrations). Since lithium is a weak replacing ion and its concentration is half that of the ammonium acetate extractant in III.8-1., it may be considered advisable to widen the ratio in all cases; certainly, as noted in III.8.B., the weight of soil taken should not be more than 5.0 g (oven-dry basis).

(2) Lithium salts are frequently contaminated with sodium and batches from different manufacturers must be tested before use. However, sources can be found with levels of sodium low enough to provide the required accuracy for most work, particularly in analyses of saline soils.

Lithium salts are expensive and dilutions in flame photometry are best done with water, calibrating with similarly diluted standards.

(3) The lithium extracting solution used in preparation of the standard sodium and potassium solutions may be either of pH 7.0 or 8.2; and the standards may be used in the analysis of extracts of either pH.

(4) All four exchangeable cations may be determined by atomic absorption spectrophotometry if the apparatus is available. Interference effects may be less but must be studied at the levels and ratios found in the soil extracts. (Appendix 11.)

8-2.G. REFERENCES.

BLACK. Chapter 68, Section 68-3.2.4. (W.R.HEALD)

VOGEL. Chapter V, Section V.43.B.

YAALON. (Journal paper).

III. 9. ELEMENTAL RATIOS IN THE CLAY FRACTION

9.A. GENERAL PRINCIPLES.

Characterization of soils is aided by a knowledge of the ratios involving silicon, aluminium, iron and titanium in the clay fractions, particularly in the horizons of a soil profile. Although titanium is usually present in small amounts, as compared with iron and aluminium, it is included in the analysis to give a more accurate total for the relevant metals. Other elements in the clay fractions, mainly calcium, magnesium, potassium and phosphorus (with small amounts of sodium and manganese) are not measured as they have no bearing on the ratios required.

In order to separate the clay minerals of a soil as much as possible from primary minerals, only particles smaller than 1 micron diameter are analysed. Separation is effected by repeated dispersion of the soil sample and removal of the 1 micron fraction after settling for a time calculated from Stokes' Law. After collection of the clay fraction (which also contains colloidal humus), it is washed to remove soluble materials and then dried and finely ground, using an agate mortar to prevent contamination with the elements to be determined.

A small sample of the 1 micron fraction is next ignited to destroy organic matter and remove combined water; and the ignited residue is accurately weighed. It is then fused with sodium carbonate and the fused material is dissolved in dilute hydrochloric acid, producing a solution containing silicic acid (which may partly precipitate) and the chlorides of the metals required. Silica is separated from the metallic salts by dehydration of the silicic acid with perchloric acid and, after filtration of the precipitated silica, iron, titanium and aluminium are determined in the filtrate by colorimetric methods. The procedures advocated should give results of sufficient accuracy for soil characterization through elemental ratios.

9.B. CALCULATION OF ELEMENTAL RATIOS.

The results of analysis in Sections III.9-3 to III.9-6 are recorded as percentages of silicon, iron, titanium and aluminium in the ignited clay fraction.

Let these results be, respectively, A, B, C and D per cent.

Dividing each result by the atomic weight of the element concerned (the nearest whole number being accurate enough), the respective gram-atom percentages are derived –

$$\text{Silicon} = \frac{A}{28}$$

$$\text{Iron} = \frac{B}{56}$$

$$\text{Titanium} = \frac{C}{48}$$

$$\text{Aluminium} = \frac{D}{27}$$

The required elemental ratios are then obtained by dividing the appropriate gram-atom percentages.

Thus, for example –

$$\frac{Si}{Fe} = \frac{A}{28} \times \frac{56}{B} = \frac{2\,A}{B}$$

$$\frac{Si}{Ti} = \frac{A}{28} \times \frac{48}{C} = \frac{1.7\,A}{C}$$

$$\frac{Si}{Al} = \frac{A}{28} \times \frac{27}{D} = \frac{0.96\,A}{D}$$

$$\frac{Al}{Fe} = \frac{D}{27} \times \frac{56}{B} = \frac{2.07\,D}{B}$$

Although an expression for the ratio of silicon to total metallic elements (Fe + Ti + Al) can be worked out in terms of A, B, C and D, it is easier to calculate the gram-atom percentages for each metal separately, add them and divide the total into the silicon gram-atom percentage.

9.C. NOTE.

It is perhaps more conventional to express the results of elemental analysis as percentages of the respective oxides (SiO_2, Fe_2O_3, TiO_2 and Al_2O_3) and to calculate from these figures the "molecular ratios" of the oxides. The calculations are straightforward and, if this convention is adopted, involve multiplying each percentage element figure by the ratio of oxide to element and then dividing by the molecular weight of the oxide to produce the "gram-molecule percentage". The latter is identical with the gram-atom percentage in the case of silicon and titanium; but, for iron and aluminium, the gram-molecule percentages are one half of the gram-atom percentages, since each oxide contains two atoms of the respective metal. Thus, the molecular ratios SiO_2/Fe_2O_3 and SiO_2/Al_2O_3 are each twice the respective elemental ratios Si/Fe and Si/Al; but the molecular ratios Al_2O_3/Fe_2O_3 and SiO_2/TiO_2 are the same as the respective elemental ratios Al/Fe and Si/Ti.

The conventional "silica/sesquioxide ratio" (commonly designated SiO_2/R_2O_3) can be calculated from the gram-molecule percentages of the oxides in a similar manner to the ratio of Si to (Fe + Ti + Al).

III. 9-1. SEPARATION OF CLAY FRACTION

9-1.A. PRINCIPLE.

Soil is dispersed in dilute ammonia solution and allowed to settle for a calculated time until particles larger than 1 micron diameter have fallen through a specified distance, according to Stokes' Law. The upper layer, containing clay particles and humus smaller than 1 micron diameter, is then removed; and the process is repeated until the majority of the dispersed material required has been separated.

The ammoniacal suspension is neutralized, the clay+humus is flocculated with magnesium chloride and then separated from the liquid by decantation and centrifugation. The flocculated material is next washed with ethanol and finally dried and ground.

9-1.B. APPARATUS.

Balance, general purpose
Reagent bottles, 1000 ml, tall type with rubber stoppers, marked at two levels, one near the shoulder and one 8 cm below.

Reagent bottles, 2000 ml
Shaker, end-over-end (see Note 2)
Apparatus for transfer of suspensions or supernatant liquid by suction or siphoning (see Note 4)

Measuring cylinders, 10, 25 and 500 ml
Centrifuge, with 50 ml polypropylene tubes
Wash bottle, plastic
Evaporating basins, 100-150 ml
Water bath, for evaporation
Agate mortar and pestle
Sieve, ASTM No. 100 (0.15 mm diameter holes)

9-1.C. REAGENTS.

Ammonia solution, 5 N) (see Appendix 1)
Acetic acid, 5 N)

Magnesium chloride, 1 N, pH 7.0
Add 102-105 g magnesium chloride, $MgCl_2.6H_2O$, to 800 ml water and read the pH value. Adjust to pH 7.0 with 5 N hydrochloric acid or magnesium hydroxide suspension, if necessary. Dilute to 1 litre.

Ethanol, 95 per cent, neutral (see III.7-1. Note 3)
Silver nitrate, 0.1 N (qualitative reagent)

9-1.D. PROCEDURE.

Transfer an appropriate weight of soil (see Note 1) to a 1000 ml reagent bottle, marked as described above. Add about 450 ml water and 10 ml 5 N ammonia solution, stopper and shake for two hours, preferably on an end-over-end shaker (see Note 2). Remove the stopper and fill the bottle with water to the marked level near the shoulder. Shake by hand, loosen the stopper and allow the soil to settle for a period of about 22 to 25 hours (see Note 3).

At the appropriate time remove the top layer of suspension to a depth of 8 cm, transferring it by gentle suction to a 2000 ml reagent bottle (see Note 4). Add 5 ml 5 N ammonia solution to the residual soil suspension, shake mechanically for one hour, refill to the upper level as before, shake by hand and allow to stand for a second period of 22 to 25 hours before removing the upper layer. Repeat two or three times for a total of four or five settling periods, depending on the amount of clay present. Stop when the upper 8 cm layer is only faintly turbid.

Add 5 N acetic acid to the combined suspensions until the liquid is neutral (test with pH paper). Then add 20 ml neutral 1 N magnesium chloride and shake well. Allow the flocculated clay+humus to settle and remove the clear supernatant liquid by suction. Transfer the solid to 50 ml centrifuge tubes, balance the tubes and centrifuge at 2500 rpm for about 15 minutes. Wash the clay+humus with neutral ethanol by mixing and centrifuging repeatedly until the supernatant liquid is free of chloride (test with silver nitrate).

Transfer the washed solid with ethanol to a 100-150 ml evaporating basin and evaporate to dryness on a water bath. Finally transfer the solid to an agate mortar and grind to pass a sieve having 0.15 mm holes.

9-1.E. NOTES.

(1) 5 to 10 gram of clay is needed for a reliable sample and the weight of soil taken depends on the 1 micron clay percentage. This is not normally known but it can be assessed roughly from texture or saturation percentage or the 2 micron clay percentage found in method II.3. The weight of humus can be neglected.

(2) Although an end-over-end shaker is advocated, a reciprocating type may be used if this only is available.

(3) The settling times for 1 micron clay to a depth of 8 cm at various room temperatures are obtained by multiplying the appropriate figures in Appendix 4.B by four. Over the room temperature range of 20-25°C the times are about 22 to 25 hours. There is no need to fix the settling period very accurately as the specific gravity of the clay particles may not be 2.65.

(4) A gentle suction device based on the running out of water from an aspirator (as used in Appendix 9) is convenient (see also Section II.3-3. Note 2). The end of the tube inserted in the suspension should be turned up to avoid removing too much material below 8 cm from the surface.

9-1.F. REFERENCE.

MACKENZIE, (Journal paper)

III. 9-2. PRELIMINARY TREATMENT

9-2.A. PRINCIPLE.

Adsorbed and combined water and humus are all removed by ignition and the residue is accurately weighed, the concentration of elements being calculated on an ignited soil basis. Ignition converts the clay minerals mostly into oxides of silicon, aluminium and iron; while other metallic elements (titanium, calcium, magnesium, etc.), present in smaller amounts, are also converted into oxides or are present in the ignited material as phosphates, carbonates, sulphates or other salts in trace amounts.

The mixed oxides and salts, together with any unchanged silicates, are fused with sodium carbonate to convert the silicon into soluble sodium silicate. This fused material is then dissolved in dilute hydrochloric acid to decompose carbonates and produce a solution containing silicon as soluble silicic acid (although part may precipitate at this stage) and the required metallic elements as chlorides.

9-2.B. APPARATUS.

Balance, general purpose
Platinum crucible, capacity 20-30 ml, with lid
Muffle furnace
Tongs, platinum tipped
Desiccator
Analytical balance, accurate to 0.1 mg
Stirring rod and brush
Burner, Meker type
Tripod and pipeclay triangle
Beakers, 250 ml, with watch glass covers
Measuring cylinder, 25 ml (or pipettes, as required)
Wash bottle, plastic

9-2.C. REAGENTS.

Sodium carbonate, anhydrous
Hydrochloric acid, 5 N

9-2.D. PROCEDURE.

Transfer approximately 0.5 g clay+humus fraction to a tared, ignited platinum crucible and place in a cold muffle furnace. Raise the temperature slowly to 700-800°C and maintain at this level for 30 minutes. Remove the crucible and allow it to cool to 100-150°C, then complete the cooling to room temperature in a desiccator. Weigh and record the weight of ignited residue (M g) to 0.1 mg.

Add 2 g sodium carbonate to the crucible and mix it well with the ignited residue, brushing off the stirring rod carefully; add another 1 g sodium carbonate on the top, without mixing. Place the lid on the crucible and support the crucible at a slight angle on a triangle. Heat gently with a low oxidizing flame for 10 minutes, keeping the crucible covered; then carefully raise the lid to let in a little air, making sure the mixture has passed any possible spattering stage (cautious heating should prevent any spattering at all). Then slowly raise the temperature until the crucible bottom is bright red (about 900°C.). Remove the lid and rotate the crucible to ensure that all the mixture is melted together, replace the lid so that air can enter through about a quarter of

the space and heat strongly for 10 minutes. Remove the lid, heat for 2 minutes longer, observing that the melt is quiet, and then turn out the flame. As the molten material cools, rotate the crucible so that the liquid solidifies partly over the sides and does not collect in a hard mass at the bottom.

When the crucible is cool, add sufficient water to cover the solid material and heat very gently. The bulk of the fused mass should dislodge; transfer this to a 250 ml beaker, add 5 ml 5 N hydrochloric acid to the crucible, dissolve remaining particles and transfer the liquid quantitatively to the beaker. Also clean and wash the crucible lid with water and a few drops of 5 N hydrochloric acid, adding the washings to the beaker. Finally add another 20 ml 5 N hydrochloric acid carefully to destroy all carbonate and make the solution acid. Keep the quantity of water used in these operations to a minimum.

Proceed as in III.9-3,D.

9-2.E. NOTES.

(1) Various temperatures from 600 to 900°C are advocated for the ignition of soil material. 700-800°C should be adequate for the removal of combined water from clay minerals and complete oxidation of organic matter.

(2) The fusion with sodium carbonate may be carried out in a muffle furnace if no suitable gas burners are available. But the fusion process cannot be controlled so well.

(3) Platinum crucibles are expensive and they should be treated with care. Instructions for their use are given in the references.

It is stated that material high in iron or manganese may lead to attack of platinum crucibles but in analyses of normal clay minerals the amounts of these two elements are not likely to be dangerous. But the point should be watched.

(4) If the procedure advocated does not loosen the fused residue in the crucible, put the crucible in the 250 ml beaker, cover the beaker with a watch glass and carefully add 25 ml 5 N hydrochloric acid. When effervescence ceases remove the crucible and wash it well into the contents of the beaker.

9-2.F. REFERENCES.

BLACK. Chapter 63. (Y. KANEHIRO and G.D. SHERMAN)

CHAPMAN and PRATT. Chapter 1, Section 1-3.

JACKSON. Chapter 11, Sections 11-1 to 11-18, 11-35, 11-36 and 11-102 to 11-109.

STROUTS. Vol. 1, Chapter 4, pp.81 to 83.

VOGEL. Chapter II, Section II.37.
Chapter V, Section V.70.

III. 9-3. SILICON

9-3.A. PRINCIPLE.

The liquid containing the soluble products from the fusion in III.9-2 is heated in the presence of perchloric acid and, when water has evaporated, boiled with the concentrated acid. This effectively and quickly converts silicic acid to insoluble silicon dioxide without coprecipitating more than trace amounts of the metals to be determined later in the analysis. The silica is filtered off, ignited and weighed.

The filtrate from this operation is collected and reserved for the determination of iron, titanium and aluminium.

9-3.B. APPARATUS.

Measuring cylinder, 10 ml

Water bath)
Hot plate or sand bath) under efficient fume hood

Funnels, 50 or 60 mm diameter
Filter papers, 9 cm diameter, ashless (e.g. Whatman No. 42)
Beakers, 250 ml
Wash bottles, plastic
Platinum crucible, 20-30 ml
Muffle furnace
Desiccator
Analytical balance, accurate to 0.1 mg

9-3.C. REAGENTS.

Perchloric acid, 60 per cent
Hydrochloric acid, approximately 0.5 N

9-3.D. PROCEDURE.

(continued from III.9-2.D.)

Add 10 ml 60 per cent perchloric acid to the acid solution and digest on a water bath until the volume is reduced to near 25 ml. Then heat more strongly on a hot plate or sand bath until fumes of perchloric acid appear. Cover the beaker and boil gently for 10 minutes. Allow to cool.

Add about 10 ml water, boil to dissolve salts and filter through an ashless 9 cm paper (e.g. Whatman No. 42), collecting the filtrate in another 250 ml beaker. Wash the precipitated silica 4 or 5 times with 0.5 N hydrochloric acid and then 4 or 5 times with water, collecting the washings in the same beaker. Reserve the filtrate for subsequent analyses (see III.9-4.D.).

Transfer the precipitate and paper to a tared, ignited platinum crucible and dry in an oven at 105°C. Then place the crucible in a muffle furnace, raise the temperature gradually to 900°C and ignite for 15 minutes. Remove from the furnace, allow to cool to 100-150°C, transfer to a desiccator, cool to room temperature and weigh the crucible and contents. Record the weight of silica to 0.1 mg.

9-3.E. CALCULATION.

Let

W be the weight in gram of silicon dioxide obtained

Then, since Si/SiO_2 = 28.086/60.085,

W gram of silicon dioxide contains 0.4674 W gram of silicon

This is produced from M gram of ignited clay (see III.9-2.D.)

Thus, the clay contains

$$\frac{46.74\ W}{M} \text{ per cent silicon}$$

If the result is required in terms of the oxide, the clay contains

$$\frac{100\ W}{M} \text{ per cent silicon dioxide}$$

9-3.F. NOTES.

(1) Silicic acid can be dehydrated by evaporation to dryness with concentrated hydrochloric acid; but the process is longer (two or three evaporations are necessary) and there is more danger of coprecipitation of metals, particularly iron.

(2) More accurate results may be obtained (if desired) by treating the weighed silica with sulphuric and hydrofluoric acids and evaporating to remove silicon as volatile silicon tetrafluoride. After a second ignition, any residue (metallic oxides carried down during the dehydration of silicic acid) is weighed and the difference in weight between this and the original ignited silica is taken as the accurate weight of silica.

If this procedure is adopted and a measurable amount of metallic oxides is left after volatilization of silica, the residue must be refused with sodium carbonate, dissolved in acid and the solution added to the main solution for determination of iron, titanium and aluminium. With perchloric acid dehydration of silicic acid, this extra work is rarely necessary.

(3) The ignition of the silica may be done with a gas burner (Meker type), if preferred, so that the destruction of the filter paper can be observed and controlled more carefully.

(4) As usual in gravimetric analysis, the crucible can be reheated after weighing and cooled and reweighed, to check that the weight is constant.

9-3.G. REFERENCES.

JACKSON. Chapter 11, Sections 11-110 to 11-121

VOGEL. Chapter V, Section V.70.

WILSON. Vol. I.C. Chapter IX. (4.b.(a) - H. THOMAS)

III. 9-4. IRON

9-4.A. PRINCIPLE.

The acid solution left after removal of silicon is treated with ammonia solution in the presence of ammonium chloride at pH 6.2 (not more alkaline than pH 6.4) to precipitate the hydroxides of iron, aluminium and titanium and so separate these metals from calcium, magnesium and manganese and from excess sodium and perchlorate ions. If phosphate is present, this will also precipitate as iron or aluminium phosphates but this does not affect the analysis. The precipitate is washed and then redissolved in hydrochloric acid to give a solution containing only iron, aluminium and titanium chlorides (with a little phosphate) from the clay fraction. This solution is made to a definite volume.

Iron is determined in a suitable aliquot of this solution by reduction to the ferrous state with hydroxylamine hydrochloride and formation of the orange-red ferrous-orthophenanthroline complex. The reaction proceeds best at pH 3-5 and the solution is therefore buffered near pH 4 with acetic acid - ammonium acetate. Although iron and aluminium phosphates can precipitate at this pH and so introduce turbidity as well as affecting the iron concentration, the amount of phosphate present in the aliquot is usually too small to cause serious error or trouble.

9-4.B. APPARATUS.

Measuring cylinders, 10 or 25 ml and 50 ml
Graduated pipettes, 1 ml and 10 ml, with 0.1 ml divisions
Hot plate (or gas burner, tripod and gauze)
Funnels, 75 mm diameter
Filter papers, 11.0 cm diameter, for gelatinous precipitates and hardened (e.g. Whatman No. 54)
Beakers, 250 ml
Stirring rods
Wash bottles, glass, for hot liquids
Volumetric flasks, 200, 100 and 50 ml
Bulb pipettes, 10 and 2 ml
Spectrophotometer, with cells or tubes of 1.0 - 1.5 cm cross-section

9-4.C. REAGENTS.

Hydrochloric acid, 5 N)
Ammonia solution, 5 N) (see Appendix 1)

Bromo-cresol purple indicator
0.05 per cent in ethanol

Ammonium chloride, 1 per cent, pH above 6.0
Dissolve 10 g ammonium chloride in 1 litre of water and check the pH. if this is below 6.0, bring it up to 6.0-6.5 by adding 5 N ammonia solution.

Hydroxylamine hydrochloride (hydroxyammonium chloride), 10 per cent

Orthophenanthroline, 0.25 per cent in water
Add 0.25 g orthophenanthroline to 80 ml water, warm to dissolve, cool and make to 100 ml

Acetic acid - ammonium acetate buffer solution, pH 4.1 - 4.2 (Acetic acid, 1.5 N plus ammonium acetate, 0.5 N)

Add 120 ml glacial acetic acid to 500 ml water, then add 37.5 ml concentrated ammonia solution (sp.gr. 0.91, 25 per cent NH_3), cool and make to 1000 ml. Check that the pH is near 4.1 - 4.2.

Standard ferric iron solution, 500 ppm Fe (see Note 1)
Mix 50 ml 5 N sulphuric acid (see Appendix 1) with about 200 ml water, add 3.511 g ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, and dissolve. Stir and slowly add 25 ml of 1 per cent potassium permanganate solution; then continue to add the same solution drop by drop (about another 3 ml is required) until the pink colour just stays. Transfer to a 1 litre volumetric flask and make to volume.

Standard ferric iron solution, 50 ppm Fe
Dilute 25 ml 500 ppm solution to 250 ml

9-4.D. PROCEDURE

(i) Separation of Iron, Titanium and Aluminium.

Add to the filtrate from the silica separation (see III.9-3,D.) 10 ml 5 N hydrochloric acid and about 0.3 ml bromo-cresol purple indicator. Bring the liquid just to boiling and add 10 ml 5 N ammonia solution; continue to heat and add 5 N ammonia solution drop by drop until the colour of the liquid becomes purple. Boil for one minute, allow the precipitate to settle and check the colour of the supernatant liquid; if this has become yellow again, add more ammonia solution to restore the purple colour, reheat for one minute and allow the precipitate to settle.

Decant most of the clear liquid through a hardened filter paper suited to gelatinous precipitates (e.g. Whatman No. 54), then add 50 ml hot 1 per cent ammonium chloride solution to the beaker, stir with the precipitate, allow to settle and decant the clear liquid through the filter paper, as before. Then transfer the precipitate to the paper and wash it with hot 1 per cent ammonium chloride solution two or three times, without allowing the precipitate to become dry. Discard the filtrate.

Unfold the filter paper inside a clean 250 ml beaker and wash off most of the precipitate with hot water. Then run 10 ml hot 5 N hydrochloric acid over the paper to dissolve any remaining precipitate and wash it again with hot water. Stir the precipitate in the hot acid until it is completely dissolved, allow to cool and then transfer the solution to a 200 ml volumetric flask and make to volume.

Designate this Solution X, to be used for the determination of iron (see below), titanium (see III.9-5.) and aluminium (see III.9-6.).

(ii) Determination of Iron

Dilute 10 ml solution X to 100 ml and designate this Solution Y (to be used also for the determination of aluminium).

Transfer 5 or 10 ml solution Y (see Note 3) to a 50 ml volumetric flask and, at the same time, transfer 1, 2, 3 and 4 ml of the standard iron solution (50 ppm Fe) to four other 50 ml volumetric flasks; include a flask for the blank. Add 2 ml 10 per cent hydroxylamine hydrochloride and 10 ammonium acetate - acetic acid buffer to each flask. Finally add 2 ml 0.25 per cent orthophenanthroline solution and make each volume to 50 ml. Leave for 30 minutes to ensure complete reduction of iron

(the temperature should be at least 20°C), then read the absorbance or transmittance of light of 508 millimicron wavelength (blue-green filter) against the blank, containing the same amounts of reagents.

9-4.E. CALCULATION

Plot the absorbance or transmittance values obtained with the standard iron solutions against the amounts of iron present. With the method specified, these amounts are 0 - 200 microgram Fe.

From this graph, record the number of micrograms of iron corresponding to the absorbance or transmittance values given by the test solutions.

Let

G microgram Fe be an individual value

A ml be the aliquot taken (usually 5 or 10)

Then, solution Y contains

$$\frac{100\ G}{A} \text{ microgram Fe}$$

And solution X contains

$$\frac{2000\ G}{A} \text{ microgram or } \frac{2\ G}{A} \text{ milligram Fe}$$

This is derived from M g of ignited clay (see III.9-2.D.)

Thus, the percentage of iron is

$$\frac{2\ G}{A} \times \frac{100}{1000\ M} = \frac{G}{5\ A\ M}$$

If the result is required in terms of the oxide, since 111.69 Fe is equivalent to 159.69 Fe_2O_3, the percentage is

$$\frac{1.43\ G}{5\ A\ M}$$

9-4.F. NOTES.

(1) The ferrous ammonium sulphate used for the standard solution (500 ppm Fe) must be from a recently-opened bottle of good quality material. Alternatively, pure iron wire may be used, dissolving 0.500 g in about 55 ml 5 N sulphuric acid (warming may be necessary), oxidizing with potassium permanganate and diluting to 1 litre.

These standard solutions need not necessarily be oxidized to the ferric condition but it is advisable to do so; the standard solution then contains iron in the same state as the test solutions. The introduction of manganous ion by the oxidation does not affect the analysis, by the procedure advocated.

(2) Hydroquinone, which is sometimes suggested as a reducing agent, is said to give a brown colour with titanium and so is less suitable than hydroxylamine hydrochloride, although the concentration of titanium may be too small, in most cases, to give serious trouble.

(3) With the quantities advocated, a 5 ml aliquot of solution Y covers values up to about 16 per cent Fe (23 per cent Fe_2O_3) in the ignited clay (M near 0.5 g). For values below 8 per cent Fe (11.5 per cent Fe_2O_3), a 10 ml aliquot should be taken.

9.4.G. REFERENCES.

BLACK. Chapter 65, Section 65-1.3.3. (R.V. OLSON)

CHAPMAN and PRATT. Chapter 12, Section 12-2.

JACKSON. Chapter 15, Sections 15-6 to 15-14.

SANDELL. Chapter XXII, (II.B).

VOGEL. Chapter X, Section X.12.

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III. 9-5. TITANIUM

9-5.A. PRINCIPLE.

Tetravalent titanium forms a yellow complex with hydrogen peroxide in and acid medium, preferably sulphuric acid of a concentration between 1.5 N and 3.5 N. Of the other elements present in solution X (see III. 9-4.F.), only iron may possibly interfere by contributing a slight yellow colour of its own, if the concentration is high. The effect of this is compensated by comparing the test solution against a blank containing the same concentration of iron but without hydrogen peroxide. Phosphate may reduce the colour of the titanium - hydrogen peroxide complex but the amounts of phosphate normally present in clay material (and the associated humus) are negligible in this respect.

9-5.B. APPARATUS.

Bulb pipettes, 10, 20, 25 and 50 ml
Graduated pipettes, 5 or 10 ml, with 0.1 ml divisions
Volumetric flasks, 100 ml
Spectrophotometer, with cells or tubes of 1.0 - 1.5 cm cross-section

Beakers, 25 or 50 ml (optional)

9-5.C. REAGENTS.

Sulphuric acid, 20 N (approximately)
Add 555 ml concentrated acid to 450 ml water, cool and adjust the volume to 1 litre.

Hydrogen peroxide, 3 per cent (10-volume)
Prepare fresh from more concentrated solution (preferably 30 per cent)

Standard titanium solution, 500 ppm Ti
Transfer 3.697 g pure potassium titanium oxalate to a 500 ml Kjeldahl flask and add 8 g ammonium sulphate and 100 ml concentrated sulphuric acid. Heat gradually until boiling and boil for 10 minutes. Cool and pour the liquid into about 700 ml water, washing out the flask well. Cool the diluted solution and make to 1 litre.

9-5.D. PROCEDURE.

Transfer 75 ml (50 ml + 25 ml by pipettes) of solution X (see III.9-4.D.) to a 100 ml volumetric flask, add 10 ml 20 N sulphuric acid and make to volume. Transfer two lots of a suitable aliquot (10 A ml, where A = 1 or 2, usually) to dry vessels (e.g. the tubes or cells fitting the spectrophotometer). To one aliquot - the blank - add A ml of water; to the other add A ml of 3 per cent hydrogen peroxide. Mix and obtain the absorbance or transmittance of light of 410 millimicron wavelength (deep blue or violet filter) by the peroxidized sample, as against the blank.

At the same time, transfer 1, 2, 3, 4 and 5 ml of standard titanium solution to five 100 ml volumetric flasks, add 10 ml 20 N sulphuric acid to each and make to volume. Transfer 10^{A} ml of each solution (where the value of A is the same as the value used in the test solution) to five dry vessels and add A ml of 3 per cent hydrogen peroxide to each. Mix and determine the absorbance or transmittance of light of 410 millimicron wavelength, against a water blank.

9-5.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard titanium solutions against the amounts of titanium present in the aliquots of standard solution taken. With the volumes specified, these amounts are 0.5 - 2.5 milligram Ti.

From this graph, record the number of milligrams of titanium corresponding to the absorbance or transmittance values given by the test solutions.

Let

G milligram Ti be an individual value

Then, 200 ml of solution X contains

$$\frac{200\ G}{75} \text{ or } \frac{8\ G}{3} \text{ milligram Ti}$$

This is derived from M g of ignited clay (see III.9-2.D.)

Thus, the percentage of titanium is

$$\frac{8\ G}{3} \times \frac{100}{1000\ M} = \frac{4\ G}{15\ M}$$

If the result is required in terms of the oxide, since 3.00 Ti is equivalent to 5.00 TiO_2, the percentage is

$$\frac{4\ G}{9\ M}$$

9-5.F. NOTES.

(1) Potassium titanium oxalate is obtainable as a pure analytical grade reagent and therefore is very suitable as a starting point for the preparation of standard titanium solutions. Preparation from other materials (e.g. titanium dioxide or potassium fluotitanate) seems to be less convenient.

(2) If the amount of iron in the sample is low and first tests show there is negligible absorbance by the blank solution (as compared with water), the procedure may be modified for subsequent analyses on similar materials, as follows -

> After adding the 20 N sulphuric acid to the aliquot of solution X to produce the required acidity, add 10 ml of 3 per cent hydrogen peroxide and make to 100 ml. Use a similar method for the standards and make all spectrophotometric readings against a water blank.

On the other hand, if the amount of iron is high and a considerable absorbance is recorded for the blank, it may be better to reduce the iron colour by adding 5 or 10 ml orthophosphoric acid (concentrated acid diluted with an equal volume of water) to the aliquot of solution X plus 20 N sulphuric acid before making to 100 ml. Then proceed as in 9-5.D. above, adding the phosphoric acid to the standards as well, because of the slight bleaching effect of phosphate on the oxidized titanium colour.

(3) Solution X is about 0.25 N as HCl and some procedures advocate heating this with the sulphuric acid to fuming, in order to expel the chloride ion. This ion may increase the iron colour but the procedures given above take care of this effect. Thus this extra evaporation to fuming may normally be avoided.

(4) With the method given, concentrations of titanium up to about 1.3 per cent (2.2 per cent TiO_2) in the ignited clay (M near 0.5 g) are covered. This is adequate for most samples.

9-5.G. REFERENCES.

BLACK. Chapter 66, (G.D. SHERMAN and Y. KANEHIRO)

JACKSON. Chapter 11, Sections 11-155 to 11-161

SANDELL. Chapter XLV, (II.A).

VOGEL. Chapter X, Section X.14.

III. 9-6. ALUMINIUM

9-6.A. PRINCIPLE.

Ammonium aurintricarboxylate ("Aluminon") forms a red lake with aluminium in a weakly acid solution of pH 4.0 – 4.9, with the optimun pH value at about 4.2. The reaction is very sensitive, 50 ml of coloured solution preferably containing 0 – 40 microgram aluminium; solution Y therefore has to be diluted further.

Ferric iron forms a red-purple complex with aluminon under the same pH conditions but, at the concentrations of iron normally present in diluted solution Y, the formation of this complex can be prevented by addition of thioglycollic acid, which reduces the iron and forms its own (colourless) complex. As a secondary effect, thioglycollic acid lowers the basic colour of the aluminon reagent (also red) and the colour of the aluminon-aluminium complex; but this effect is not a disadvantage.

For convenience, the acetic acid – ammonium acetate buffer solution made for the iron determination (see III.9-4.) can be used in this procedure.

9-6.B. APPARATUS.

Bulb pipettes, 5 and 10 ml
Graduated pipettes, 5 and 10 ml, with 0.1 ml divisions
Volumetric flasks, 50 and 100 ml
Spectrophotometer, with cells or tubes of 1.0 – 1.5 cm cross-section

9-6.C. REAGENTS.

Acetic acid – ammonium acetate buffer solution, pH 4.1 – 4.2
(see III.9-4.C.)

Thioglycollic (mercaptoacetic) acid
Dilute 2.5 ml of the acid as bought (about 90 per cent) to 50 ml.
A fresh solution is best.

Aluminon, 0.2 per cent in water (see Note 1)

Standard aluminium solution, 250 ppm Al (see Note 2)
Dissolve either 4.200 g ammonium alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$, or 4.396 g potassium alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, in about 500 ml water, add 10 ml 5 N hydrochloric acid and make to 1 litre.

Standard aluminium solution, 5 ppm Al
Dilute 10 ml 250 ppm solution to 500 ml

9-6.D. PROCEDURE.

Dilute 10 ml solution Y (see III.9-4.D.(ii).) to 100 ml. Transfer 10 ml (or 5 ml for high aluminium concentrations) of this diluted solution to a 50 ml volumetric flask. At the same time, transfer 2, 4, 6, 8 and 10 ml of standard aluminium solution (5 ppm Al) to five 50 ml volumetric flasks and include a sixth flask for the blank.

Add to each flask 10 ml acetic acid – ammonium acetate buffer solution, 1 ml diluted thioglycollic acid and 2 ml 0.2 per cent aluminon reagent. Dilute to 50 ml and allow to stand for 30 minutes. Then read the absorbance or transmittance of light of 520 millimicron wavelength (green

filter), setting the blank solution at zero absorbance (optical density) or maximum transmittance.

9-6.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard aluminium solutions against the amounts of aluminium present. With the method specified, these amounts are 0 - 50 microgram Al.

From this graph, record the number of micrograms of aluminium corresponding to the absorbance or transmittance values given by the test solutions.

Let

G microgram Al be an individual value

Then, for a 10 ml aliquot of diluted solution Y (1:10), solution Y itself contains

100 G microgram Al

and solution X contains

2000 G microgram or 2 G milligram Al

This is derived from M g of ignited clay (see III.9-2.D.)

Thus, the percentage of aluminium is

$$2\,G \times \frac{100}{1000\,M} = \frac{G}{5\,M}$$

If the result is required in terms of the oxide, since 53.963 Al is equivalent to 101.961 Al_2O_3, the percentage is

$$\frac{1.89\,G}{5\,M}$$

(If a 5 ml aliquot of diluted solution Y is taken, multiply each of the above percentage expressions by 2)

9-6.F. NOTES.

(1) Some batches of aluminon give rather deeply coloured solutions and these should be avoided if possible. The volume of reagent should be accurately measured and it may be preferable (if only deeply coloured aluminon is available) to make 0.04 per cent reagent solution and add 10 ml.

(2) The ammonium or potassium alum used for the standard solution must be from a recently-opened bottle of good quality material. Pure aluminium metal may be used instead, dissolving 0.250 g in 15 ml 5 N hydrochloric acid and diluting to 1 litre.

(3) With the method given, using a 10 ml aliquot of diluted (1:10) solution Y, values up to about 20 per cent Al (38 per cent Al_2O_3) in the ignited clay (M near 0.5 g) are covered. If the graph is unsatisfactory above 40 microgram aluminium, the limiting value is 16 per cent Al (30 per cent Al_2O_3). For higher values, a 5 ml

aliquot of diluted solution Y is taken.

9-6.G. REFERENCES.

BLACK. Chapter 67, Section 67-3.3. (E.O. MACLEAN

CHAPMAN and PRATT. Chapter 4, Section 4-1.

JACKSON. Chapter 11, Sections 11-86 to 11-99

SANDELL. Chapter V. (II.A).

GENERAL COMMENTS

(1) The "clay" fraction obtained by the procedure advocated contains humus particles which remain in suspension in the ammoniacal 8 cm layers. Because humus has a specific gravity lower than 2.65, some of these particles have diameters larger than 1 micron.

During subsequent oxidation by ignition, although the greater part of the humus is volatilized, small quantities of some elements may be added to the residue. It is considered that, for the mineral soils normally subjected to elemental analysis, the amounts of silicon, iron, titanium and aluminium added from humus are negligible in their effects on the elemental ratios required and the amounts of other elements added are too small to interfere with the analyses.

The humus in the clay fraction can be destroyed by heating it with hydrogen peroxide; but, if it is desired to prepare a true organic-free clay fraction (say, from a highly organic clay soil) uncontaminated with any possible mineral elements associated with the humus, it is safer to subject the whole soil sample to the preliminary treatment with hydrogen peroxide and acid described for the determination of particle size distribution (see II.3-1.) before the dispersion with ammonia in III.9-1. above.

(2) The methods described have been selected and simplified solely to give a fairly rapid means of determining elemental ratios of use in characterizing clays. They can, of course, be modified or extended to provide other analytical results. Thus -

(a) The air-dry clay sample (near 0.5 g) can be accurately weighed, dried in an oven at 105°C and weighed again to measure adsorbed water. After ignition and weighing, a "loss on ignition" figure can be calculated. These modifications would enable the results for silicon, iron, titanium and aluminium to be calculated on an air-dry or oven-dry basis.

(b) Phosphorus can be measured in the solution left after removal of silica or in solution X.

(c) Instead of discarding the filtrate after precipitation of iron, titanium and aluminium, it can be used for the determination of total calcium, magnesium and manganese in the clay fraction.

(d) The precipitate of iron, titanium and aluminium hydroxides can be dried and ignited to the oxides and weighed. Subsequently, the oxides are fused with potassium pyrosulphate and dissolved in dilute sulphuric acid for colorimetric analysis of the metals. The weight of combined oxides serves as a check on the metal analyses - and, of course, it is a direct measure of "sesquioxides" (R_2O_3). The presence of phosphorus in small amounts does not seriously affect this procedure.

(3) A gravimetric macro-procedure is selected for silicon, although a good colorimetric method is available, because silicon is normally present in high amounts in clay material and also it is best to remove it before proceeding with the other determinations.

(4) Because of the large dilution factors involved in the iron and aluminium determinations, results cannot be accurate to more than about 1 per cent. It is probably advisable to carry out analyses on the prepared clay fraction in duplicate or triplicate and calculate mean values.

III. 10. FREE IRON OXIDES

10.A. PRINCIPLE.

The "free" iron oxides haematite and limonite (but not magnetite and ilmenite, the double oxide with titanium) and amorphous ferric oxide coatings on soil particles are conveniently removed by reduction with sodium dithionite and dissolution as ferrous salts. A subsequent treatment with dilute acid dissolves any precipitated ferrous sulphides formed by the reduction process. The reduction and acid treatment processes are repeated once or twice to ensure complete removal of the iron oxides.

The acid solution, containing excess dithionite, is usually slightly turbid with colloidal sulphur and sometimes coloured with soluble organic matter. Both turbidity and colour are removed by treatment with pure activated carbon and filtering (see Note 1). The clear, colourless solution contains ferrous iron which is determined colorimetrically by means of the orange-red ferrous-orthophenanthroline complex, as used in III.9-4. The iron oxide extraction process normally removes no elements or radicles in sufficient quantities to interfere with this colorimetric procedure.

10.B. APPARATUS.

Balance, accurate to 5 mg
Centrifuge, with 50 ml tubes (glass)
Water bath, with holders for centrifuge tubes
Stirring rods
Volumetric flasks, 250 and 50 ml
Funnels, 75 and 55 mm diameter
Erlenmeyer flasks, 100 or 125 ml
Filter papers, 11.0 cm diameter (e.g. Whatman No. 40)
Bulb pipettes, 1, 2, 5 and 10 ml (as required)
Spectrophotometer, with cells or tubes of 1.0 - 1.5 cm cross-section

10.C. REAGENTS.

Sodium dithionite, powder, $Na_2S_2O_4$
Hydrochloric acid, 0.02 N
Activated carbon, Darco G.60

Hydroxylamine hydrochloride, 10 per cent)
Orthophenanthroline, 0.25 per cent in water) see III.9-4.C
Acetic acid - ammonium acetate buffer

Standard ferrous iron solution, 500 ppm Fe
Proceed as in III.9-4.C, omitting the oxidation with permanganate

Standard ferrous iron solution, 50 ppm Fe
Dilute 25 ml 500 ppm solution to 250 ml

10.D. PROCEDURE.

Transfer 1.00 g air-dry soil, passing 0.5 mm, to a 50 ml centrifuge tube and add 30 ml water. Warm in a water bath at 40-45°C for 15 minutes, then add 1 g sodium dithionite powder and stir rapidly to dissolve with a glass rodd. Digest for 15 minutes, stirring occasionally; wash down the rod with 1 ml water and remove it. Centrifuge at 2500 rpm for 10 minutes and pour off the clear supernatant liquid into a 250 ml volumetric flask.

Add 25 ml 0.02 N hydrochloric acid to the soil residue, stir with a glass rod and digest in the water bath at 40-50°C for 5 - 10 minutes. Wash and remove the rod as before and centrifuge, adding the supernatant liquid to the dithionite extract in the 250 ml volumetric flask. Repeat the dithionite and acid treatments once or twice (see Note 2), combining all supernatant liquids. Finally make the volume of extract to 250 ml with water and mix well.

If the extract is turbid or coloured, pour about 50 ml into a dry 100 or 125 ml Erlenmeyer flask and add a little (about 0.2 g) activated carbon. Mix, stand for a few minutes and filter into a dry flask.

Transfer a suitable aliquot of the clarified extract (see Note 3) to a 50 ml volumetric flask, add 10 ml acetic acid - ammonium acetate buffer and 2 ml 0.25 per cent orthophenanthroline solution and make the volume to 50 ml. At the same time prepare standard iron solutions and a blank as described in III.9-4.D.(ii), using hydroxylamine hydrochloride to ensure that the iron in the standards is reduced (see Note 4). Leave for about 30 minutes and then read the absorbance or transmittance of light of 508 millimicron wavelength against the blank (or against water).

10.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard iron solutions against the amounts of iron present. With the method specified (see III.9-4.E.), these are 0 - 200 microgram Fe.

From this graph, record the number of micrograms of iron corresponding to the absorbance or transmittance values given by the test solutions.

Let

G microgram Fe be an individual value

A ml be the aliquot taken (usually 1 to 5 ml)

Then, the extract contains

$$\frac{250\ G}{A} \text{ microgram Fe}$$

and this is derived from 1.00 g air-dry soil

Thus, the concentration of iron as free iron oxides is

$$\frac{250\ G}{A} \text{ ppm Fe in air-dry soil}$$

or $$\frac{G}{40\ A} \text{ per cent Fe in air-dry soil}$$

or $$\frac{1.43\ G}{40\ A} \text{ per cent } Fe_2O_3 \text{ in air-dry soil}$$

10.F. NOTES.

(1) The pure activated carbon should be tested for absorption of ferrous ions; this is negligible with the Darco G.60 product. In some cases the carbon treatment may be unnecessary because only small aliquots are taken and are diluted in the colorimetric procedure to 50 ml.

(2) For levels of free iron oxides below 3-4 per cent Fe, one repetition of the dithionite-acid procedure is sufficient. If the first analysis shows a level much above 3 per cent Fe, it is advisable to repeat with 0.50 g soil or to treat 1.00 g soil three times with dithionite and acid.

(3) Aliquots of 1 to 5 ml are usually suitable and 2 ml should be tried in the first instance; this covers the range 0 - 2.5 per cent Fe (0 - 3.6 per cent Fe_2O_3). If preferred, the extract can be diluted five times and aliquots of the diluted extract of 5 to 25 ml taken for colorimetry.

(4) The excess dithionite in the extract seems to keep the iron in the ferrous state satisfactorily and there is normally no need to add hydroxylamine hydrochloride to the test solutions, although this may be done as a precaution if there is some delay in analysing the extracts after their preparation.

(5) An alternative method of extraction involves chelation of the ferrous iron with citrate at a pH of 7-8, using sodium bicarbonate as buffer. This procedure gives a clear extract, usually containing more organic matter and iron in the ferric state by rapid oxidation in air. Clarification with activated carbon can still be used to remove the organic matter and iron can then be measured with orthophenanthroline if hydroxylamine hydrochloride is used for reduction, according to the procedure given in III.9-4.

The dithionite-citrate-bicarbonate method may be more suitable for soils containing much calcium carbonate, which will tend to neutralize the acid used in the procedure given above. Alternatively, the acid concentration may be increasecd quantitatively to allow for the calcium carbonate present.

(6) Analyses for free iron oxides are normally reported on air-dry soil but may, of course, be reported on oven-dry soil if required.

10.G. REFERENCES.

BLACK. Chapter 44, Section 44-4. (G.W.KUNZE)
Chapter 65, Section 65-4. (R.V.OLSON)

JACKSON. Chapter 7, Sections 7-105 to 7-111.

SANDELL. Chapter XXII. (II.B).

VOGEL. Chapter X, Section X.12.

Bibliography 876.

III. 11. AVAILABLE NITROGEN

11.A. PRINCIPLE

During growth, non-leguminous plants depend very largely for their nitrogen supply on nitrate ions absorbed from the soil solution. These ions are produced from the decomposition of organic material in the soil by micro-organisms, mainly bacterial in form. Thus, the "availability" of nitrogen in soils for non-leguminous plant growth is dependent on the activity of the various micro-organisms which eventually produce nitrate ions.

Attempts to measure "available" nitrogen by purely chemical means have mostly been unsuccessful because it is almost impossible to imitate the bacterial decomposition processes. Therefore, traditional methods have concentrated on speeding up the natural activity of the soil's micro-organisms by placing samples in an environment conducive to rapid production of nitrate; i.e. by keeping well aerated samples of soil of optimum moisture content at 30-35°C for a definite period of time (usually two to three weeks). The amount of nitrate produced under these standard conditions has been measured by extraction and distillation or colorimetric analysis (see IV.12)

More recently, better correlations with responses to nitrogenous fertilizers have been obtained by measuring the ammonium and nitrite nitrogen produced during incubation, as well as the nitrate nitrogen. In investigational studies, the inorganic forms of nitrogen may be determined separately but, for routine availability tests, the total inorganic nitrogen can be conveniently measured, after extraction, by a simple distillation with alkali, using Devarda's alloy to reduce nitrite and nitrate to ammonia.

The adjustment of the water content of soils to the optimum amount is simplified by mixing soils with sand to equalize the texture differences as much as possible. After incubation, the inorganic forms of nitrogen are extracted with a fairly concentrated solution of potassium chloride, which is used to ensure complete removal of exchangeable ammonium ions.

In practice, the amounts of (NH_4 + NO_2 + NO_3) produced during incubation are often affected greatly by differences in the period and conditions of storage, in the air-dry state, before incubation. Although no definite optimum periods and conditions can be laid down, it is recommended that standardized procedures should be followed in air-drying and storage of soil samples which are to be analysed for "available" nitrogen by incubation methods. (see also Note 3).

11.B. APPARATUS.

(Excluding that for preparation of soils and for moisture determination)

Balance, accurate to 0.02 g
Bottles, 250 ml, with special closure devices (see Note 1) and solid rubber stoppers.
Incubator.
Dispensing burette, 50 ml
Measuring cylinder or dispensing burette, 100 ml
Reciprocating shaker
Filtering apparatus (optional)
Bulb pipettes, 20 ml

All-glass distillation apparatus, for steam distillation (see Note 2)
Erlenmeyer flasks, 100-150 ml
Measuring spoons, 0.2 g each, for magnesium oxide and Devarda's alloy
Graduated pipette, 1 or 2 ml, with 0.02 ml divisions
Burette, 5 or 10 ml, with 0.01 ml divisions.

11.C. REAGENTS.

Sand, purified
Pass fine quartz sand through a sieve of between 30 and 60 mesh (particle size diameters 250-590 microns) and discard material retained on the sieve. Wash the sieved sand with dilute hydrochloric acid (about 5 N) and then with water. Dry and store in an air-tight container, away from ammonia fumes.

Potassium chloride, 2 N
Dissolve 744 g to 5 litres

Magnesium oxide, heavy, purified
Heat the oxide at 600-700°C for 2 hours to destroy any carbonate, cool in a desiccator and store in an air-tight container.

Devarda's alloy, (50 per cent copper, 45 per cent aluminium and 5 per cent zinc)
Use a product which is very finely ground, having particles smaller than 150 microns in diameter (100 mesh sieve)

Boric acid, 0.25 per cent)
Mixed indicator) see III.4.C.
Sulphuric acid, 0.010 N)

Standard nitrogen solution, containing 40 milliequivalents ammonium ion and 40 milliequivalents nitrate ion per litre.

Dissolve 1.3215 g dry ammonium sulphate and 2.0222 g dry potassium nitrate to 500 ml

Standard nitrogen solution, containing 1 milliequivalent ammonium ion and 1 milliequivalent nitrate ion per litre.

Dilute 25 ml above solution (40 me per litre each ion) to 1 litre

11.D. PROCEDURE.

Dry soil samples in air under standardized conditions of temperature and humidity as far as possible, then crush them to pass a 2 mm sieve. Take sub-samples of about 50 g and grind them to pass a 0.5 mm or 0.2 mm sieve, as convenient. Store these samples in air-tight containers at a constant temperature for several weeks before analysis (see Note 3).

One day before the start of incubation, remove 5.00 g of soil and determine the adsorbed moisture by drying overnight at 105°C, cooling in a desiccator and weighing. Calculate the weight of air-dry soil containing 10.0 g oven-dry soil (see I.4-3.A.(ii)). Weigh out two lots of this amount, mix each with 30 g sand and transfer to two 250 ml bottles containing 6 ml water.

Add the soil-sand mixture to one bottle so that it is spread evenly in the water and level the surface by tapping; then close the bottle with

the special closure device or with polythene film securely fastened with adhesive tape. Weigh it (nearest 0.1 - 0.2 g) and place it in an incubator at 30°C. (see Note 4)

Add to the second bottle a volume of 2 N potassium chloride equal to 94 ml less the volume of water in the soil sample, giving exactly 100 ml of liquid (see Note 5). Shake on a reciprocating shaker for one hour and either filter or allow to stand so that the soil settles. Transfer 20 ml of the filtrate or supernatant liquid to the flask of the steam distillation apparatus. Transfer 20 ml of 0.25 per cent boric acid and 0.2 ml of mixed indicator to a 100-150 ml Erlenmeyer flask and place this under the condenser of the distillation apparatus, with the tip of the condenser just in the liquid. Add to the distillation flask, through a dry funnel, 0.2 g magnesium oxide, followed by 0.2 g Devarda's alloy. Steam distil until about 25-30 ml of distillate has been collected and then titrate the ammonia with 0.010 N acid to the neutral point of the mixed indicator.

After 14 days of incubation (see Note 4), weigh the first bottle to check that the weight is unchanged and then extract the soil with 2 N potassium chloride as described above. Determine the (NH_4 + NO_2 + NO_3) nitrogen in 20 ml of the extract, as described above.

Check the distillation procedure periodically by distilling 20 ml of standard nitrogen solution (2 milliequivalent NH_4 + NO_3 ions per litre) for which the titration (after correction for any blank) should be 4.00 ml of 0.010 N acid.

11.E. CALCULATION.

Let

X be the volume in ml of 0.010 N sulphuric acid used for titrating the (NH_4 + NO_2 + NO_3) nitrogen after incubation

Y be the volume in ml of 0.010 N sulphuric acid used for titrating the (NH_4 + NO_2 + NO_3) nitrogen before incubation

Then,

(X - Y) ml 0.010 N acid is equivalent to the (NH_4 + NO_2 + NO_3) nitrogen produced during incubation, designated available nitrogen.

This is (X - Y) x 0.01 milliequivalents available nitrogen and it is produced by 2 g oven-dry soil.

Thus, the available nitrogen is

0.5(X - Y) milliequivalents per 100 g oven-dry soil

or 70(X - Y) parts per million (oven-dry basis)

(see Note 6)

11.F. NOTES.

(1) The closure device employs a permeable membrane to allow free passage for gases but not for water vapour. Thus oxygen and carbon dioxide can circulate through the bottle during incubation but no water is lost from the moist soil. Polythene film is also effective in the same manner.

(2) The Markham design of apparatus noted in method III.4 is not

suitable here. The distillation chamber should have a capacity of 80–100 ml and it is more convenient to have one with a special entry for the dry powders. (see below)

(3) The period of storage seems to have variable effects on the available nitrogen result with different soils. Individual laboratories should carry out their own tests on the optimum period suited to their soils. Probably at least three months is advisable in most cases.

It is claimed (Hesse-private communication) that, after any length of storage, useful information is obtained by incubation in two stages. Thus, duplicate soil samples are incubated for two weeks, then one is extracted and analysed while the other is incubated for a further two or three weeks before extraction and analysis. The first two-week incubation measures mainly the (variable) nitrification induced by storage; the second period of incubation then measures available nitrogen more accurately.

(4) Although various temperatures between 25 and 35°C have been advocated for incubation, 30°C seems best; 35°C should not be exceeded. The time of incubation may be varied but should not normally be less than 10 days.

(5) The volume of water in the air-dry soil will usually be only about 1 ml or less but it may rise to 2 ml for heavy organic soils in humid atmospheres. The volume of 2 N potassium chloride added need only be measured to the nearest 0.5 ml. There is a dilution of the potassium chloride by the 6–8 ml water but this is unimportant in this analysis.

(6) Since the available nitrogen is measured by a difference between two titrations, based on identical distillations with the same aliquot size, the blanks should be the same and can be ignored. However, because the two extractions and distillations are separated by 14 days (or some suitable period), it is important to measure these blanks to ensure that the reagents (2 N potassium chloride, magnesium oxide and Devarda's alloy) have not become contaminated during the incubation period. If a larger aliquot is taken for the distillation before incubation, because of the lower nitrogen content, a blank must certainly be carried out.

When recording results, report the period and conditions of storage as well as details of the incubation technique.

11.G. REFERENCES.

BLACK. Chapter 88. (J.M. BREMNER)

Bibliographies 766, 854, 966 and 1006

III. 12. AVAILABLE PHOSPHORUS

12.A. GENERAL PRINCIPLES.

In the determination of "available" phosphorus an attempt is made measure by chemical means that portion of the total soil phosphorus which can be utilized (or bears some consistent relation to that utilized) by plants. Many different solutions have been suggested for the extraction of this "available" phosphorus; some have had more general success than others and four of these have been selected for inclusion in this Guide.

The first is a slightly alkaline solution of sodium bicarbonate and this is most suited to the analysis of calcareous soils, although its use need not be restricted to them. The second is a dilute solution of sulphuric acid buffered at a pH of 3.0 and this has been found to give a good indication of phosphorus availability in acid soils. The third and fourth are weak solutions of ammonium fluoride, made acid to two different degrees with hydrochloric acid; these solutions are suited to most types of soils.

The extraction of available phosphorus from soils is affected, in general, by the following physical factors, apart from the chemical reactions involved -

1. The nature and moisture content of the soil sample - i.e. whether field-moist or air-dry.

2. The amount of grinding to which the soil is subjected in its preparation for analysis, reflected mainly (but not wholly) in the mesh size of the sieve through which it is finally passed.

3. The ratio of soil to extractant solution. (see Note 1.)

4. The time of contact between soil and extractant solution, including both the shaking period and the time taken to filter.

5. The kind and degree of mechanical shaking.

6. The temperature (usually room temperature) of extraction.

With all these factors liable to cause variation in the phosphorus content of the extracted solution, it is clear that the procedure of extraction must be rigorously standardized so that any differences in the phosphorus measured in extracts of different soils can be ascribed solely to chemical or physico-chemical reasons and thus, possibly, to availability of soil phosphorus.

Published methods usually say whether a soil sample should be fresh or air-dried and specify suitable soil:solution ratios and shaking times. These need not be strictly followed and, in fact, the extraction of available phosphorus (by the solution selected here) is nearly always done by individual laboratories with their own variations, which suit their working conditions or which have given good correlations with phosphorus responses on local soils.

As there is so much variation in the methods of extraction usually used, the procedures given below for each extractant solution (see 12-1.D, 12-2.D and 12-3.D) merely record the most common ratios of soil to solution and the shaking times normally suggested. However, because

the extraction of phosphorus can be affected by so many physical factors, a general procedure is described (see 12.B.) which lays emphasis on the precautions necessary to minimize these effects.

The concentration of phosphorus in a soil extract is almost universally determined by adding a soluble molybdate and a reducing agent under precise conditions of acidity and concentration of molybdate and reductant, when a blue colour ("molybdenum blue") develops which is directly related to the quantity of orthophosphate ion. Many variations of this colorimetric technique are available, selection depending mainly on the quantity of phosphorus to be measured and on the nature and amount of interfering ions.

In the method selected, the determination of phosphorus in each of the extracts has been standardized so that the same molybdate solution and the same reductant (stannous chloride) can be used, irrespective of the solution employed to extract the soil phosphorus. The procedure described (see 12.C.) is the most sensitive, the optimum working range being 0 - 25 microgram P in a total volume of 50 ml, enabling very low phosphorus levels to be measured accurately. The molybdenum blue colour is developed in a solution which is 0.40 N as sulphuric acid and which has a molybdate concentration of 0.1 per cent. Under these conditions, there is no interference from silicon (reduction to molybdenum blue of a silicate-molybdate-acid mixture can occur only at lower acidities) and ferric iron up to about 100 micrograms can be tolerated - this amount being greater than that in suitable aliquots of the extracts prepared below. Only arsenate can cause high results, because an arsenate-molybdate-acid mixture is also reduced to molybdenum blue under the conditions specified; so that the method given is unsuitable for soils which are contaminated with arsenate from arsenious plant sprays.

The molybdenum blue colour develops at a rate depending on the temperature and the stannous ion concentration; it is stable for a certain limited period and then begins to fade somewhat rapidly. Thus the analysis of the soil extract should be carried out under constant temperature conditions and the depth of colour must be read within the period of stability. As with the extraction of phosphorus from soil, rigorous standards must be established to give consistent and accurate results for the determination of phosphate ion in soil extracts.

12.B. GENERAL PROCEDURE FOR EXTRACTION OF AVAILABLE PHOSPHORUS.

(i) Preparation of soil and determination of moisture content

Proceed as outlined in Section I.4-3A. (ii). Use either field-moist soils which have been rubbed through a wire-mesh sieve with openings about 4-5 mm across or air-dry soils which have been dried under consistent conditions of temperature and humidity, as far as possible, certainly avoiding wide differences in temperature. Air-dry soils should be ground to pass a 0.5 mm sieve.

While the moisture is being determined, keep the bulk soil samples in air-tight containers. After the final weighings, calculate the weight of water (M g) associated with 100 g of oven-dry soil in the original field-moist or air-dry sample.

(ii) Calculation of soil weight and extractant volume.

Select the ratio of oven-dry soil to extractant solution (this may vary from 1:5 w/v to 1:200 w/v) and hence fix suitable values for the weight of oven-dry soil and volume of extractant. Usually, 1 to 5 gram of soil is extracted with 20 to 200 ml of solution.

Let

D be the weight in gram of oven-dry soil required for analysis

R be the ratio between the volume of solution (ml) and the weight of oven-dry soil (g)

Then, the volume of extractant solution required is RD ml

Let

M be the weight in gram of water associated with 100 g of oven-dry soil in an air-dry or field-moist sample.

Then, in general, the weight of air-dry or field-moist soil required is

$$(D + 0.01\ MD)\ \text{gram}$$

and the volume of liquid needed to extract it is

$$(RD - 0.01\ MD)\ \text{ml}$$

In most cases, 0.01 MD is small in relation to RD and the addition of RD ml of the extractant solution to (D + 0.01 MD) g soil is allowable without introducing significant errors. But, for moist soils extracted at narrow ratios (R = 10 or less) the water in the soil sample may have an appreciable dilution effect on the extractant solution. In these cases, prepare an extractant having twice the concentration of the normal one; then add to (D + 0.01 MD) gram of moist soil (0.5 RD - 0.01 MD) ml water and (0.5 RD) ml of the double concentration extract solution. (see Note 1)

(iii) Shaking and filtering.

Carry out all operations involved in the preparation of soil extracts for phosphorus determination at a constant temperature. If this is not practicable, study the effect of change of temperature on extraction and apply a correction factor or factors. (see Note 2.)

Use bottles or flasks of identical shape for all extractions; the capacity should vary according to the soil:solution ratio chosen and should have a constant relation to the volume of solution used (i.e. 250 ml capacity for 100 ml, 125 ml capacity for 50 ml and so on.) The aim should be to have a consistent type of swirling motion imparted to the soil during the shaking period. Always use the same kind of mechanical shaking machine (usually reciprocal), running at the same speed and with the same load.

For a selected "shaking time", make the actual contact time between each soil sample and its appropriate volume of extractant as constant as possible. With long shaking times and small batches of samples, individual addition of solution to soil before

shaking and individual filtering after shaking does not cause much variation in the total contact time; but with short shaking periods (one minute and less have been advocated - see 12-3.), it is impossible to do routine work consistently without a dispensing apparatus which adds solution to all soils (one load in the shaking machine) simultaneously nor without a device for the simultaneous pouring of all mixtures (after shaking) into the filtering funnels.

In filtration, use dry apparatus and filter papers large enough to hold a volume of soil-extractant mixture which will give a volume of filtrate adequate for the normal aliquots needed for molybdenum blue colour development. In the methods given below, the largest aliquot is 25 ml and it is really only necessary to collect about 35 ml of extract (unless duplicates are to be done). Filtering a large amount of soil-extractant mixture often introduces variation in the total contact time according to the speed of filtration, as influenced by soil texture.

Filtration usually produces a clear solution at once but, if not, wait until the filtrate is passing through clearly and then discard the turbid part. If the loss of solution cannot be tolerated or soil particles persist in passing the filter, allow the mixture to "filter" for the normal time (producing a little more than the required volume of liquid) and then clarify the extract by filtration through a finer paper or a ceramic filter, if possible. A turbid filtrate should not be poured back through the soil on the filter paper unless it is established that this action does not affect the extraction of phosphorus.

12.C. "MOLYBDENUM BLUE" COLOUR DEVELOPMENT AND MEASUREMENT.

(i) Apparatus.

Bulb pipettes, as required for aliquots
Measuring cylinder, 50 ml
Volumetric flasks, 50 ml
Bulb pipette, 5 ml; or dispensing burette, 50 ml (for molybdate)
Graduated pipette or burette, 5 or 10 ml, with 0.05 ml divisions (for reductant)

Wash bottle, plastic
Spectrophotometer (or colorimeter, with red filter), with cells or tubes of 1.0 - 1.5 cm cross-section

Reagents.

Ammonium molybdate, 1 per cent in 4.N sulphuric acid
Dissolve 10 g powdered ammonium molybdate in about 250 ml warm water and cool. In a separate vessel, add 112-113 ml sulphuric acid (sp.gr. 1.84) to 500 ml water and cool. Add the ammonium molybdate solution to the sulphuric acid with continual stirring, cool and dilute to 1 litre.

Stannous chloride, approximately 0.1 M
Heat 1.2 g pure tin foil in 10-12 ml concentrated hydrochloric acid containing a crystal of copper sulphate. As soon as the tin has dissolved (apart from a few black particles) cool and make to 100 ml. Filter into a bottle containing a small piece of tin foil and store in a refrigerator at 3-5°C. (see Note 3)

Standard phosphorus solution, 500 ppm P
Dissolve 2.197 g dry potassium dihydrogen phosphate or 2.873 g disodium hydrogen phosphate dihydrate (Sorensen's salt - $Na_2HPO_4.2H_2O$) to 1 litre.

Standard phosphorus solution, 100 ppm P
Dilute 50 ml 500 ppm solution to 250 ml

Standard phosphorus solutions, 1, 2, 3, 4 and 5 ppm P
Dilute 5, 10, 15, 20 and 25 ml 100 ppm solution respectively to 500 ml.

(iii) Procedure.

Transfer a suitable aliquot (A ml, where A is not more than 25) of the soil extract to a 50 ml volumetric flask and bring the volume up to a fixed quantity (X ml, normally equal to the largest aliquot taken) by adding (X - A) ml of extractant. In method 12-1, treat the extract with acid as described. Then, in all cases, make the volume to about 35 ml with water.

Add 5 ml ammonium molybdate reagent, wash down the neck of the flask with water and shake without stoppering and inverting the flask. Add 0.25 ml stannous chloride reagent, mix, make to 50 ml with water and then stopper the flask and shake well.

At the same time, transfer 5 ml of each of the standard phosphorus solutions (1, 2, 3, 4 and 5 ppm P) to five 50 ml volumetric flasks. Add to each flask (and to a sixth flask, for the blank) X ml (X as above) of the appropriate extractant and make the volume to about 35 ml with water. Treat with molybdate and stannous reagents as already described.

Leave all solutions for 10 minutes (assuming the room temperature to be in the range 20-25°C), then read the absorbance or transmittance of light of 660 millimicron wavelength (red filter) as compared with the blank solution (set at zero or 100). By adding the stannous chloride at suitable timed intervals (say every 30 seconds) ensure that readings of molybdenum blue colour are made at near 10 minutes after such additions - and, in any case, at not more than 20 minutes after such additions.

12.D. CALCULATION

For each method, plot the absorbance or transmittance values obtained with the standard phosphorus solutions against the amounts of phosphorus present (0 - 25 microgram P).

From the graphs, record the number of micrograms of phosphorus corresponding to the absorbance or transmittance values given by the test solutions.

Let
G microgram P be an individual value

Also, we have

A is the aliquot (in ml) of the soil extract taken

R is the ratio of extractant (ml) to oven-dry soil (g) (see 12.B above)

Thus, the concentration of phosphorus in the soil extract is

$$\frac{G}{A} \text{ parts per million}$$

and hence the concentration of phosphorus in the oven-dry soil is

$$\frac{G\,R}{A} \text{ parts per million.}$$

12.E. NOTES.

(1) The method given in 12.B.(ii) for fixing the weight of air-dry or field-moist soil in relation to the volume of extractant and for ensuring that the concentration of the extractant is constant, is a precise one for use in investigational work on the suitability of extractant solutions. It gives final results strictly as ppm P on an oven-dry basis (microgram P per gram of oven-dry soil) which are unaffected by differences or changes in the moisture content of air-dry or moist samples.

When RD ml of extractant solution is added in all cases to soil samples containing varying amounts (0.01 MD) of water, two errors are introduced -

a. The volume of liquid becomes (RD + 0.01 MD) ml and the ratio of this to the weight of oven-dry soil (D) becomes (R + 0.01 M) in place of R.

b. The extractant is diluted by the addition of M/R ml water per 100 ml extractant.

In the case of air-dry soils, M may vary from 1 or less for sandy soils in dry atmospheres to 20 or more for heavy organic soils in humid atmospheres (in the absence of air conditioning). Thus, the dilution effect is unlikely to be serious, M/R probably not exceeding 5 ml and being much less in most cases.

But the effect on the ratio R may be worth considering and this only means an adjustment of calculation. Thus, if M is 20 and a narrow ratio (R = 5) is being used, the corrected value for the ratio is 5.2; then, for example, a concentration of 2.0 ppm P in the soil extract should be recorded as 10.4 ppm P in oven-dry soil, instead of 10.0 ppm P.

In the case of field-moist soils, M is capable of a much wider range of values, rising to 100 or more for heavy organic soils sampled under wet conditions. It is therefore advisable to adopt the precise procedure of 12.B.(ii) in most cases, only excluding drier soils extracted at wide ratios.

For routine work on a large scale, designed to provide rapid and approximate estimates of soil phosphorus availability, the addition of a constant volume of extractant to a constant weight (or even volume) of air-dry soil is normal practice. In this case, results are bound to have inherent experimental errors from variations in R (apart from other effects) and the figures should not be recorded with any great accuracy. Over the range 0 - 25 ppm P in air-dry soil, which covers deficiency levels in most cases, the nearest 1 ppm P is probably sufficiently accurate.

(2) Rise of temperature usually increases the extraction of phosphorus, presumably due to more active solubility and ion exchange processes. The proportionate increase is not normally constant for all types of soil but it may be possible to relate correction factors to a few well-marked soil types. The effect of temperature change on any selected phosphorus extraction method must be studied if room temperatures fluctuate.

(3) The stannous chloride solution made by the method given is stable for a week at least if stored in a refrigerator. Solutions may also be made by dissolving 2.26 g stannous chloride crystals, $SnCl_2.2H_2O$, in 10 ml concentrated hydrochloric acid and diluting to 100 ml, provided the stannous chloride is fresh. Old stocks of stannous chloride must not be used without testing for the concentration of stannous ion.

In order to establish whether a solution of stannous chloride is suitable for molybdenum blue colour development, proceed as follows -

Transfer 10 ml of prepared solution to a 200 ml glass-stoppered flask and add 25 ml water, 25 concentrated hydrochloric acid and 5 ml carbon tetrachloride. Titrate with 0.1 N potassium iodate (5.35 g KIO_3 per litre). At first, the iodine liberated is rapidly converted to iodine monochloride but, after 10-12 ml potassium iodate has been added (assuming the stannous solution is near 0.1 M) the iodine persists for a longer time and dissolves in the carbon tetrachloride layer. Titrate more slowly, stoppering and shaking the flask frequently, until the violet colour of the carbon tetrachloride layer just disappears.

0.1 M solutions of stannous chloride give a titration of 20 ml of 0.1 N potassium iodate. Solutions giving titrations of 18 ml or more (i.e. at least 90 per cent stannous ion) are acceptable for molybdenum blue colour development.

(4) Calibration curves for phosphorus may vary slightly from day to day, according to fluctuations in temperature, slight deterioration of stannous chloride solutions and perhaps other causes. It is advisable to include a full set of standards for calibration with each batch of determinations.

If molybdenum blue colour development must be done below 20°C or above 25°C, investigate the period during which colours are stable at their maximum level.

(5) Alkaline washing powders (which often contain phosphates) should not be used to clean glassware needed for phosphorus determinations. Thorough cleaning with fairly concentrated hydrochloric acid is advisable, although chromic acid cleaning solution can be used.

Do not allow molybdenum blue solutions to stand in volumetric flasks. Wash the flasks (and spectrophotometric cells or tubes) immediately after use. If a deposit of tin does form inside glassware, dissolve it with hot hydrochloric acid.

12.F. GENERAL REFERENCES.

BLACK. Chapter 73, Sections 73-1 and 73-4. (S.R. OLSEN and L.A. DEAN)

BOLTZ. Chapter II. (D.F. BOLTZ and C.H. LUECK)

CHAPMAN and PRATT. Chapter 26, Sections 26-22 to 26-24.

DEWIS. Appendix I. (Report paper)

JACKSON. Chapter 7, Sections 7-1 to 7-25 and 7-65 to 7-104.

Bibliographies 661, 779, 983, 1004 and 1012.

(NOTE: References to the origianl papers by OLSEN, COLE, WATANABE and DEAN and by BRAY and KURTZ are given in BLACK, Section 73-5; reference to the original paper by TRUOG is given in JACKSON, p.155 - footnote.)

III. 12-1. 0.5 M SODIUM BICARBONATE EXTRACTION. (OLSEN ET AL).

12-I.A. PRINCIPLE.

All soils contain "insoluble" phosphates, maily the di- and tri-calcium phosphates in neutral and alkaline soils and aluminium and ferric phosphates in acid soils. Phosphate ions (HPO_4 and H_2PO_4) are however present in small concentrations in the soil solution, according to the relative amounts of calcium, aluminium and ferric ions. If the concentrations of the metallic ions are reduced, the concentration of the phosphate ions increases in order to maintain the various solubility products at their constant values.

An alkaline (pH 8.5) bicarbonate solution can repress the concentration of calcium ions by precipitation as calcium carbonate and of aluminium and ferric ions by precipitation as hydroxides. Thus phosphate ion concentrations are increased and "available" phosphate can be extracted from soil by shaking with alkaline sodium bicarbonate and filtering. The extraction is particularly dependent on time of contact and on temperature and these factors have to be taken into account.

The solution selected for this method has two minor disadvantages, It tends to dissolve organic matter, producing coloured extracts; and it must be acidified before molybdenum blue can be developed, producing carbon dioxide bubbles which interfere with colorimetry. Thus, activated carbon must be used with most soils to adsorb the soluble organic matter (this must be phosphate free and without effect on phosphate ions) and it is necessary to allow time for the carbon dioxide bubbles to escape.

12-1.B. APPARATUS.

Balance, accurate to 0.01 g
Shaking machine
Suitable glassware for soil and extractant mixtures and for filtering as already noted (12.B.(iii)).

Apparatus for molybdenum blue colour development and measurement, as given in 12.C.(i)

12-1.C. REAGENTS.

Extracting solution: 0.5 M sodium bicarbonate, pH 8.5
Dissolve 420 g sodium bicarbonate (sodium hydrogen carbonate, $NaHCO_3$) to 10 litres, incorporating about 45 ml 5 N sodium hydroxide to adjust the pH to 8.5 ± 0.1

Activated carbon, purified.
Test the carbon for phosphorus by shaking with extractant (at a ratio near that used in the actual determinations), filtering and developing molybdenum blue. If a measurable amount of phosphorus is obtained, shake the main stock of carbon with extracting solution, filter and wash the carbon well with water. Dry in an oven and pulverize to a powder. Retest to establish the absence of phosphorus.

Do not use stocks which are grossly contaminated with phosphate.

Sulphuric acid, slightly greater than 1 N.
Dilute 60 ml sulphuric acid (sp.gr. 1.84) to 2 litres.

PLUS

Reagents given in 12.C.(ii)

12-1.D. PROCEDURE.

Transfer a suitable quantity of the field-moist or air-dry soil, containing the selected weight (D is normally 2.5 or 5.0 g) of oven-dry soil, to the extraction vessel and add a small quantity of activated carbon, depending on the observed amount of organic matter. Add the required volume of extractant and shake for the selected time (see Note 1.) Filter

Transfer 10 ml of extract (this can normally be used in the first instance, whatever value of R is selected) to a 50 ml volumetric flask and add 5 ml of sulphuric acid slightly greater than 1 N. Prepare standards also containing 10 ml extractant and 5 ml sulphuric acid. Shake all flasks without stoppering at intervals for 1 hour (or leave overnight if convenient) to eliminate carbon dioxide bubbles. Then proceed with molybdenum blue colour development and measurement as described in 12.C.(iii).

If the colour from 10 ml of extract is greater than the top standard, take a 5 ml aliquot, add 5 ml extractant and 5 ml sulphuric acid, as above; or (for very deep colours) take a 2 ml aliquot, add 8 ml extractant and 5 ml sulphuric acid.

12-1.E. NOTES.

(1) The published method advocates a soil:extractant ratio of 1:20, uses air-dry soil and a shaking time of 30 minutes; but it is made clear that more phosphate will be extracted by a longer shaking time in some cases.

(2) Using R = 20 and A = 10, the method covers the range 0-50 ppm P in oven-dry soil, which is adequate for most cases. If the levels of phosphorus are consistently lower than 10 ppm P, it would be better to take 20 ml of extract (adding 10 ml of sulphuric acid) and thus work over the range 0-25 ppm P. In this case, the standard phosphorus solutions should be treated with 20 ml extractant and 10 ml sulphuric acid.

III. 12-2. 0.002 N SULPHURIC ACID EXTRACTION. (TRUOG).

12-2.A. PRINCIPLE.

The phosphate soluble in dilute acids can be a useful measure of the availability of phosphorus in acid and neutral soils. Sulphuric acid buffered at pH 3.0 is suitable and provides an extract in which phosphate can be determined directly without any pre-treatment.

Wide soil:extractant ratios are advocated (R = 100 or 200) to encourage maximum solubility. And it is claimed that better correlations with responses to phosphatic fertilizers may be obtained by analysing fresh field-moist samples. The method is unsuitable for calcareous soils, as the extractant is quickly neutralized or reduced in acidity.

12-2.B. APPARATUS.

As given for 12-1.B.

12-2.C. REAGENTS.

Extracting solution: 0.002 N sulphuric acid, pH 3.0
Prepare by diluting 0.20 N acid one hundred times, adding 3 g potassium sulphate or 3 g ammonium sulphate per litre of extractant made.

PLUS Reagents given in 12.C.(ii)

12-2.D. PROCEDURE.

Transfer a quantity of field-moist or air-dry soil containing 1.00 g of oven-dry soil to the extracting vessel and add either 100 ml or 200 ml extractant (see Note 1.). Shake for 30 minutes or any selected time and filter.

Transfer 25 ml of extract to a 50 ml volumetric flask and develop and measure molybdenum blue as already described, in association with standards containing 25 ml extractant. (see Note 2.)

12-2.E. NOTES.

(1) Small weights of soil must be taken in this method and duplicate analyses are advisable, especially for field-moist samples. Although R is traditionally 200, the lower value of 100 has been used and this is probably better for soils low in phosphorus.

(2) When R = 200 and A = 25, this method covers the range 0-200 ppm P in oven-dry soil. Use of a smaller aliquot of extract is rarely necessary for field samples.

III. 12-3. AMMONIUM FLUORIDE - HYDROCHLORIC ACID EXTRACTION. (BRAY & KURTZ)

12-3.A. PRINCIPLE.

Fluoride ions from ammonium fluoride complex aluminium and ferric ions in acid solution in the form of double fluorides, $AlF_3.3NH_4F$ and $FeF_3.3NH_4F$; thus, in contact with aluminium and ferric phosphates, the aluminium and ferric ion concentrations are reduced and so the phosphate ion concentration is increased to maintain the solubility products at their constant levels (compare 12-1.A.).

When ammonium fluoride in acid solution is used to extract acid or neutral soils, it will remove some phosphate ions from "insoluble" phosphates of iron and aluminium and also dissolve a little calcium phosphate. Increase of acidity tends to dissolve more calcium phosphate. When similar solutions are used on alkaline soils containing calcium carbonate, the acidity of the extractant is reduced or destroyed, depending on the amount of carbonate and the ratio of soil to solution. But, in neutral solution, ammonium fluoride still forms the aluminium complex (but not the iron complex) and some phosphate is extracted; the chemical reactions with alkaline soils are, however, more variable and the determination of available phosphorus may be less satisfactory.

Two solutions of different acidities were chosen by the authors of this method. With a common ammonium fluoride concentration of 0.03 N, the acidity of "BRAY I" is 0.025 N (as HCl) and this is said to remove "adsorbed" phosphorus; the acidity of "BRAY II" is 0.10 N (as HCl) and this is said to remove both "adsorbed" and "acid-soluble" phosphorus.

Very short shaking times (one minute or less) are advocated. In fact, for many soils, there is little change in the phosphate concentration of the extract with increase of time; but, for some soils, either more or less phosphate is extracted - and this may be useful information.

The fluoride ion has a slightly depressant effect on molybdenum blue colour development, so its concentration must be kept constant in tests and standards. The addition of boric acid to eliminate the fluoride ion interference is not fully effective and is omitted in the procedure below.

12-3.B. APPARATUS.

As given for 12-1.B.

12-3.C. REAGENTS.

Ammonium fluoride, 1 N
Dissolve 37 g ammonium fluoride to 1 litre. Store in polythene.

Hydrochloric acid, 5 N (see Appendix 1)

Extracting solutions;

(a) Ammonium fluoride, 0.03 N in hydrochloric acid, 0.025 N ("BRAY I")
Dilute 300 ml 1 N ammonium fluoride and 50 ml 5 N hydrochloric acid to 10 litres

(b) Ammonium fluoride, 0.03 N in hydrochloric acid, 0.10 N ("BRAY II")
Dilute 300 ml 1 N ammonium fluoride and 200 ml 5 N hydrochloric acid to 10 litres

(see Note 1)

12-3.D. PROCEDURE

Transfer a suitable quantity of the field-moist or air-dry soil, containing the selected weight of oven-dry soil, to the extraction vessel and add the required volume of extractant (see Note 2). Shake for the chosen time and filter (see Note 3).

Transfer 5 ml of extract (see Note 4) to a 50 ml volumetric flask; prepare standards also containing 5 ml of extractant. Develop and measure molybdenum blue as described in 12.C.(iii).

12-3.E. NOTES.

(1) The extracting solutions are very stable and thus large volumes may be made.

(2) The original ratio of soil to extractant, based on air-dry soil, was 1:7 but ratios of 1:10 and 1:50 have also been advocated. Using the narrower ratios, the volume of extractant may be 21 ml (R = 7; D = 3.0) and 20 or 25 ml (R = 10; D = 2.0 or 2.5), giving sufficient extract for the subsequent molybdenum blue development. When R = 50, D should be either 1.0 or 2.0.

(3) The advocated shaking times were 1 minute for "BRAY I" and 40 seconds for "BRAY II", both of which require carefully organized procedures and special apparatus in routine work. Periods up to 5 minutes have also been tried; and longer periods can, of course, be used. But it is probable that shorter shaking times are more suitable for these extractants.

(4) Owing to the effects of the fluoride ion on molybdenum blue colour development, not more than 5 ml of extract should be taken, even if soils are very low in available phosphorus. When R = 10, the range covered is 0-50 ppm P in oven-dry soil. For phosphate-rich soils, reduce A to 2 ml and add 3 ml of extractant to keep the fluoride ion concentration constant; the range is extended to 125 ppm P in oven-dry soil.

III. 13-1. AVAILABLE POTASSIUM - AMMONIUM ACETATE EXTRACTIONS

13-1.A. PRINCIPLE.

The total potassium in the extracts made with neutral 1 N ammonium acetate, as in procedures III.7.B., is traditionally considered to be available to plants. For most soils the potassium removed is largely that associated with the clay and humus complex as exchangeable ions but in some saline soil extracts there may be a fair amount of water-soluble potassium (see III.8.). In the assessment of availability, exchangeable and water-soluble potassium ions are not differentiated, the sum of the two simply being measured in the soil extract, usually by flame photometry.

In routine studies it is accurate enough to shake soil with ammonium acetate solution in a fairly wide ratio (1:20 or more), a procedure which normally removes 90-95 per cent of the exchangeable potassium and all the water-soluble potassium; or, alternatively, soil (or a soil:sand mixture) may be leached with ammonium acetate solution in a similar ratio to give 95-100 per cent extraction of the exchangeable potassium. Extraction of field-moist soil (which is often advocated) is best done by shaking.

Whereas exchangeable and water-soluble potassium values are usually reported in milliequivalents per 100 g oven-dry soil, available potassium values are always reported in parts per million potassium in the soil.

13-1.B. APPARATUS.

(a) For extraction by shaking.

Balance, accurate to 10 mg
Erlenmeyer flasks, with stoppers, 250 or 500 ml
Erlenmeyer flasks, 125 or 150 ml
Measuring cylinders, 100, 200 and 250 ml, as required
Funnels, 55 or 75 mm diameter
Filter papers, 11.0 or 12.5 cm diameter (e.g. Whatman No. 40)
Reciprocating shaker.

(b) For extraction by leaching.

Balance, accurate to 10 mg
Leaching columns, borosilicate glass tubes, about 2 cm diameter and 40-50 cm long, fitted with stoppers and capillary tubes or specially made with tapering ends, mounted in suitable stands

Filtering media (see below)
Beakers, 50 ml
Funnels, 40 mm diameter
Volumetric flasks, 100 ml

Plus

Flame photometer, with potassium filter
Small beakers or sample holders.

13-1.C. REAGENTS.

Extracting solution, ammonium acetate, 1.0 N, pH 7.0 ± 0.1
(see III.7-1.C.)

Ammonium acetate, 2.0 N, pH 7.0 ± 0.1
(see III.8-1.C.)

Potassium chloride, 1000 ppm K
Dissolve 1.907 g dry potassium chloride to 1 litre

Potassium chloride, standards containing 5, 10, 15, 20 and 25 ppm K in 1.0 N ammonium acetate
Dilute 5, 10, 15, 20 and 25 ml of 1000 ppm K standard solution each to 1 litre, after adding 500 ml 2.0 N ammonium acetate

Sand, washed (K-free), 0.5 - 2.0 mm (for extraction by leaching)

13-1.D. PROCEDURES.

(a) Extraction by shaking.

Transfer a weight of air-dry soil containing 5.00 g oven-dry soil to a 250 ml Erlenmeyer flask and add 100 ml 1.0 N ammonium acetate solution. Shake on a reciprocating shaker for 30 minutes and filter

If field-moist soil is analysed, use a weight containing 10.0 or 12.5 g oven-dry soil and shake with 200 or 250 ml of extractant in a 500 ml Erlenmeyer flask. If the soil is very wet, allow for the volume of water in it as described in III.12.B.(ii).

(b) Extraction by leaching.

Prepare the leaching column with its filtering medium, which may be a disc of filter paper or a pad of filter pulp or asbestos or a sintered glass disc, as preferred. Pour about 5 g dry washed sand on to the filter.

Mix the required weight of air-dry soil (containing 5.00 g oven-dry soil) with 15 to 25 g sand, according to texture. Pour this mixture into the leaching column and add 5 g sand on top. Place a 100 ml volumetric flask under the column and then soak the soil:sand mixture with 15 ml extractant. After one hour add another 15 ml extractant to the column and allow this to pass through. Continue to add five more lots of 15 ml of extractant, allowing each lot to pass through before adding the next. Remove the volumetric flask when the volume of extract has reached 100 ml and mix the contents.

(c) Determination of potassium in extracts.

Measure the potassium concentration of the extracts by flame photometry, as indicated in III.8-1.D., calibrating the photometer with the above standards containing 0-25 ppm K in 1.0 N ammonium acetate. Make allowances for any interference from sodium in the analysis of saline soils.

13-1.E. CALCULATION

From the calibration graph, let the concentration of an individual soil extract be

A ppm K

Then, the concentration in oven-dry soil is

$$20.A \text{ ppm K}$$

Thus, the range covered by the standard procedure is 0-500 ppm K in soil.

13-1.F. NOTES.

(1) The advocated procedures may be modified to suit different soils, although it is unwise to use less than 20 parts of extractant to 1 part of soil, even with sandy, potassium-deficient samples. If results are consistently less than 200 ppm K, the flame photometer should be calibrated with standards in the range 0-10 ppm K. On the other hand, if potassium-rich soils (above 500 ppm K) are analysed, it is safer to extract the equivalent of 2.50 g oven-dry soil with 100 ml extractant.

(2) If exchangeable potassium values are determined by method III.8-1., in milliequivalents per 100 g soil (nearest 0.01 me), multiply the potassium values (without correction for water-soluble potassium) by 391 to obtain available potassium values in ppm K.

(3) It is usually accurate enough to record available potassium values to the nearest 5 ppm K, up to 500 ppm K; above this, the nearest 10 ppm K is adequate.

III. 13-2. AVAILABLE POTASSIUM - SULPHURIC ACID EXTRACTION.

13.2.A. PRINCIPLE

It is claimed that some potassium temporarily fixed by clay minerals in a non-exchangeable form may be available to plants. This potassium can be removed by treatment of soil with hot dilute mineral acids; and a convenient method of doing this is to use the heat of dilution of concentrated sulphuric acid with water which is already in contact with soil. After this initial attack, the soil is washed and leached with 0.1 N sulphuric acid to a definite volume.

The resulting extract is in a fairly concentrated acid solution (about 3.6 N in the procedure below) and it is advisable to neutralize most of this acidity with ammonia before spraying into a flame photometer. Analysis of the extract measures the sum of water soluble, exchangeable and "fixed" potassium.

13-2.B. APPARATUS.

Balance, accurate to 10 mg
Beakers, 100 ml, with covers
Measuring cylinders, 10 and 25 ml
Stirring rods
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No. 40)
Volumetric flasks, 50 and 100 ml
Bulb pipettes, 25 ml (and as required)

Flame photometer, with potassium filter
Small beakers or sample holders

13-2.C. REAGENTS.

Concentrated sulphuric acid (sp.gr. 1.84)
Sulphuric acid, 0.1 N (approximately)
Prepare by dilution of 5 N stock solution (see Appendix 1)

Ammonium sulphate - sulphuric acid, approximately 3.6 N as sulphate, pH less than 3
Add 400 ml concentrated sulphuric acid to about 2 litres water and cool. Carefully add 1050 ml ammonia solution (sp.gr. 0.91, 25 per cent NH_3), cool and make to 4 litres.

Sulphuric acid, 3.6 N (approximately)
Dilute concentrated acid 10 times

Ammonia solution, 5 N (see Appendix 1)

Potassium chloride, 1000 ppm K
See III.13-1.C.

Potassium chloride, standards containing 5, 10, 15, 20 and 25 ppm K in ammonium sulphate - sulphuric acid, approximately 1.8 N as sulphate, pH less than 3

Dilute 5, 10, 15, 20 and 25 ml of 1000 ppm K standard solution each to 1 litre, after adding 500 ml ammonium sulphate - sulphuric acid mixture (approximately 3.6 N, as above)

13-2.D. PROCEDURE

Transfer a weight of air-dry soil containing 5.00 g oven-dry soil to a 100 ml beaker and add 25 ml water. Then carefully add 10 ml concentrated sulphuric acid, stir well, cover the beaker and leave on an asbestos sheet for 30 minutes. Pour off the supernatant liquid through a filter paper (e.g. Whatman No. 40) into a 100 ml volumetric flask and wash the soil by decantation with four 10 ml lots of 0.1 N sulphuric acid. Finally, transfer the soil to the filter paper and leach with 0.1 N sulphuric acid until the volume of extract is 100 ml.

Transfer 25 ml of extract to a 50 ml volumetric flask, add 15 ml 5 N ammonia solution and make to 50 ml with water. Determine the potassium concentration of this partially neutralized extract by flame photometry, calibrating the photometer with the standards containing 0-25 ppm K in ammonium sulphate - sulphuric acid of a concentration resembling that in the soil extracts. If the concentration is greater than 25 ppm K, repeat the analysis by taking 20 or 10 ml of the original extract, making the volume to 25 ml with 3.6 N sulphuric acid, adding 15 ml 5 N ammonia solution and diluting to 50 ml with water; then spray this solution.

13-2.E. CALCULATION.

Let

A ppm K be the concentration of an individual diluted soil extract

X be the volume in ml of original soil extract diluted to 50 ml

Then, the concentration of potassium in the original soil extract is

$$\frac{50\ A}{X} \text{ ppm K}$$

and the concentration in oven-dry soil is

$$\frac{1000\ A}{X} \text{ ppm K}$$

13-2.F. NOTES.

(1) As X (in the calculation) is normally 25, the range covered by the standard procedure is 0-1000 ppm K, which is adequate for many soils, in spite of the fact that the technique may extract much more potassium from some soils than the ammonium acetate procedure. If results are consistently less than 400 ppm K, modify the flame photometry by calibrating with standards in the range 0-400 ppm K.

The method is scarcely affected by the presence of carbonates in calcareous soils; possibly, for very calcareous soils, some adjustment may have to be made to the volume of 5 N ammonia used for neutralizing the bulk of the acidity.

GENERAL REFERENCES.

BLACK. Chapter 71, Section 71-4. (P.F. PRATT)

JACKSON. Chapter 6, Sections 6-67 to 6-74

Bibliography 720, 1004, 1086 and 1093.

III. 14. SOIL ACIDITY

GENERAL INTRODUCTION.

A material is normally judged to be acid when its pH value is below 7.0. But in the case of a soil, "pH" may have a range of values according to the procedure adopted for determination (see III.1.) Therefore it is difficult, when this pH range embraces the neutral point of 7.0, to say when a particular soil is "acid" and when its "acidity" should be studied for its effect on plant growth.

The lowest pH value for a soil can usually be produced by shaking with 1 N potassium chloride at a narrow ratio (say, 1:1 w/v); if this minimum value is 7.0 or above, then the soil is certainly not acid. Strictly, if this value falls below 7.0, then the soil has some small measure of "acidity" - but this may be considered negligible. It is suggested that if the pH of a soil in 1 N potassium chloride at a ratio of 1:1 w/v is below 6.0, then it may be useful to investigate its exchange acidity (see below), even though the traditional "pH" (at a ratio of soil:water of 1:5 or 2:5 w/v) may be above 7.0.

The hydrogen ions in acid soils are able to release aluminium ions from clay minerals and the sum of the concentrations of these two ions (in milliequivalents per 100 g oven-dry soil) is the "exchange acidity" of the soil. This is also the difference between the cation exchange capacity and the sum of the exchangeable "bases" (i.e. calcium, magnesium, potassium, sodium and, perhaps, manganese). Exchange acidity can be measured by extraction of exchangeable hydrogen and aluminium ions with a neutral salt solution (method III.14-1.) or by determination of the loss of alkalinity of a solution of barium chloridetriethanolamine (pH 8.0) after it has been used to extract an acid soil. (see III.14-1. F.(3)).

In a soil or a soil-water mixture, the acidic groups are only weakly dissociated (giving rise to the pH value) but, nevertheless, most of them become dissociated and release their hydrogen during extraction with a netural salt solution. However, a small amount of hydrogen is strongly held by the clay and organic matter and can only be removed by treatment with alkalies. Thus, although the amount of alkali needed to "neutralize" an acid soil can be fairly well assessed from its exchange acidity value in relation to its cation exchange capacity, a direct titration is the more reliable method. This leads to an estimation of "lime requirement", a term which is uncertain in its meaning in the same way that an "acid" soil is uncertain. Although lime requirement may be defined as the amount of pure lime (usually calculated as calcium carbonate) needed to bring the soil, to (say) a pH of 7.0, this definition involves the secondary definition of "pH of 7.0." Therefore, the result of a laboratory test should be reported in precise terms so that the expected effect of the advocated dressing of calcium carbonate is clear.

III. 14-1. EXCHANGE ACIDITY

14-1.A. PRINCIPLE

Soil is leached under consistent conditions with neutral 1 N potassium chloride solution, exchangeable hydrogen and aluminium passing into solution. The leachate is thus acid and can be titrated with a standard solution of an alkali, the amount of alkali used being equivalent to the sum of the hydrogen ions and aluminium ions -

$$H^+ + OH^- = H_2O$$

$$Al^{3+} + 3\ OH^- = Al(OH)_3$$

The titration is taken to the alkaline side (pH 9), using phenolphthalein as indicator; the aluminium hydroxide tends to make the end-point a little uncertain and to absorb indicator but a fairly good titration can usually be obtained.

The aluminium is then complexed with sodium fluoride, releasing an equivalent quantity of alkali

$$Al(OH)_3 + 6\ NaF = Na_3AlF_6 + 3\ NaOH$$

The released alkali is titrated with standard acid to measure the exchangeable aluminium. Alternatively, if preferred - or if there is difficulty with the second titration - the aluminium may be determined colorimetrically in the original leachate with aluminon (see III.9-6.)

14-1.B. APPARATUS.

Balance, accurate to 0.05 g
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No. 42)
Volumetric flasks, 100 ml
Measuring cylinders, 10 or 25 ml
Bulb pipette, 50 ml
Erlenmeyer flasks, 150 or 200 ml
Graduated pipette, 1 ml
Burettes, 25 ml, with 0.1 ml divisions

Plus, if needed, apparatus for determination of aluminium as given in III.9-6.B.

14-1.C. REAGENTS.

Potassium chloride, 1 N, pH 7.0
Dissolve 372 g potassium chloride to 5 litres. Check the pH.

Sodium hydroxide, 0.050 N
Hydrochloric acid, 0.050 N

Sodium fluoride, 1 N
Dissolve 42 g sodium fluoride to 1 litre.

Phenol phthalein, 1 per cent in 50 per cent ethanol

Plus, if needed, reagents for determination of aluminium as given in III.9-6.C.

14-1.D. PROCEDURE.

Transfer a weight of air-dry soil containing 10.0 g oven-dry soil (see Note 1.) to a dry filter paper in a funnel in a 100 ml volumetric flask. Add 10 ml of 1 N potassium chloride to the soil and allow the solution to percolate through. Add a further nine portions, each 10 ml, of 1 N potassium chloride at approximately 13-minute intervals so that the leaching process takes not less than 2 hours. If the filtration rate is too slow, repeat the analysis after mixing a second weighing of soil with 20-30 g fine sand or 5-10 g powdered cellulose.

Adjust the volume of the leachate to 100 ml with 1 N potassium chloride. Measure its pH value, especially if the pH of the soil in 1 N potassium chloride has not been determined.

(a) Determination of exchange acidity.

Transfer 50 ml of soil extract to a 150 or 200 ml Erlenmeyer flask, add 0.2 ml phenol phthalein and titrate with 0.050 N sodium hydroxide until the solution (containing a gelatinous precipitate of aluminium hydroxide) is just permanently pink. Add an extra drop of indicator if the colour is absorbed by the alumina gel.

(b) Determination of exchangeable aluminium by titration.

Just destroy the colour (after the above titration) with one or two drops of 0.050 N hydrochloric acid and add 10 ml of 1 N sodium fluoride. If exchangeable aluminium is present, the solution becomes pink again by release of hydroxide ions from the aluminium hydroxide. Titrate with 0.050 N hydrochloric acid until the solution is colourless for at least two minutes.

(c) Determination of exchangeable aluminium by colorimetry.

Transfer 5 ml (or less) of the potassium chloride extract (depending on its pH and the determined exchange acidity) to a 50 ml volumetric flask and determine aluminium as described in III.9-6.D. Prepare a blank and standards containing the same (constant) volume of 1 N potassium chloride as in the test solutions.

14-1.E. CALCULATIONS.

(a) Titration methods.

Let

X be the volume in ml of 0.050 N sodium hydroxide used in the first titration.

Y be the volume in ml of 0.050 N hydrochloric acid used in the second titration.

These volumes correspond to (0.05 x X) and (0.05 x Y) milliequivalents respectively; and these amounts are both derived from 5 g oven-dry soil.

Thus, the soil contains -

X me per 100 g oven-dry soil exchange acidity

Y me per 100 g oven-dry soil exchangeable aluminium

(X - Y) me per 100 g oven-dry soil exchangeable hydrogen

(b) Colorimetric method for aluminium.

Let

A be the volume in ml of the aliquot taken for analysis.

G be the number of microgram Al found in this aliquot.

Then, the concentration of aluminium in the extract is

$$\frac{G}{A} \text{ parts per million}$$

and the concentration of exchangeable aluminium in the soil is

$$\frac{100G}{A} \text{ ppm (oven-dry soil basis)}$$

This corresponds to

$$\frac{G}{9\ A} \text{ milliequivalents per 100 g oven-dry soil}$$

14-1.F. NOTES

(1) The accuracy of this method does not really justify the return of the results on an oven-dry soil basis but, if these results are to be compared with cation exchange capacity figures, they must be on the same basis. For routine examination of exchange acidity air-dry soil is satisfactory.

(2) If cation exchange capacity and exchangeable cations have been determined (methods III.7 and III.8), add the exchangeable calcium, magnesium, sodium and potassium figures (plus exchangeable manganese if much is present) and subtract the total from the cation exchange capacity figure (all in milliequivalents per 100 g oven-dry soil). This method may not give a very accurate result for exchange acidity because the errors of the individual cation determinations may be cumulative.

(3) If cation exchange capacity is to be determined by method III.7-3 with barium chloride - triethanolamine on acid soils, preserve the extracts made during the saturation with barium and make the volume to 250 ml with saturating solution (starting with 10 g oven-dry soil). Transfer this quantitatively to a 500 ml Erlenmeyer flask, washing out the volumetric flask with water, add 0.5 ml bromocresol green - methyl red mixed indicator (see III.4.C.) and titrate with 0.20 N hydrochloric acid to the end-point of the indicator (just pink). Similarly titrate 250 ml of barium chloride - triethanolamine saturating solution.

If the titrations are X ml for the saturating solution and Y ml for the soil extract, then (X - Y) ml of 0.20 N acid corresponds to the exchange acidity of 10 g oven-dry soil and thus the exchange

acidity is 2(X − Y) milliequivalents per 100 g oven-dry soil.

(4) Reports have been received by the authors that potassium chloride does not remove exchangeable hydrogen quantitatively from some tropical soils, although it is effective in removing exchangeable aluminium. In these cases, use of the barium chloride-triethanolamine technique (in Note 3) would be preferable for exchange acidity.

III. 14-2. LIME REQUIREMENT

14-2.A. PRINCIPLE

Samples of constant weight of the soil under test are treated with constant volumes of calcium hydroxide solution of increasing concentration. After equilibration, which normally takes about three days, the pH values are measured and the effect of the calcium hydroxide on the soil pH studied graphically.

14-2.B. APPARATUS.

Balance, accurate to 0.5 g
Wide-mouth screw-capped jars, 80-100 ml (see III.1.B.)
Dispensing burette, 100 ml, fitted with a carbon dioxide trap.
Reciprocating shaker,
pH meter
Glass electrode
Reference electrode, saturated potassium chloride - calomel
Wash bottle, plastic

14-2.C. REAGENT.

Calcium hydroxide solution, saturated (approximately 0.04 N)

Maintain about 10 g calcium hydroxide in contact with 4-5 litres of carbon dioxide free water for a day or two, shaking occasionally. Allow the excess solid to settle and siphon off the clear liquid into an aspirator fitted with a carbon dioxide trap (see Note 1). Determine the calcium hydroxide concentration by titration with standard 0.10 N hydrochloric acid.

14-2.D. PROCEDURE.

Transfer six 10 g portions of air-dry, 2 mm soil to wide-mouth screw-capped jars and add, respectively, 0, 10, 20, 30, 40 and 50 ml calcium hydroxide solution. Make each volume to 50 ml with water. Screw on the lids and shake on a reciprocating shaker for 15 minutes. Then leave to reach equilibrium for three days, shaking occasionally if convenient (leaving over a week-end break is suitable, without shaking). Finally shake on the reciprocating shaker for 15 minutes and allow to stand undisturbed for 30-60 minutes.

Read the pH values as described in III.1.D.

14.2.E. CALCULATION.

Let

C be the concentration in milliequivalents per litre of the calcium hydroxide (C is near 40 at 20-25°C)

Then, the solution contains soluble calcium equivalent to 50 C milligram per litre of calcium carbonate.

Thus, the amounts of calcium carbonate added to 10 g soil under test are, respectively, nil, 0.5 C, 1.0 C, 1.5 C, 2.0 C and 2.5 C milligram.

And so the amounts added to 100 g soil would be, respectively, nil, 5 C, 10 C, 15 C, 20 C and 25 C milligram.

Plot these values against the respective pH values found in the test.

From the graph, let

M be the number of milligram of calcium carbonate required to produce the chosen pH level (1:5 w/v water basis) in 100 g soil.

Then, 100 kilogram soil requires M gram calcium carbonate.

Let one hectare of soil to a depth of 15-17 cm be taken to weigh 2,500,000 kilogram.

Then, the lime requirement is 25,000 M gram per hectare

= 25 M kilogram calcium carbonate per hectare

14-2.F. NOTES.

(1) The calcium hydroxide solution may need filtering through a very fine paper or a ceramic filter candle.

(2) The method advocated is for soil of moderate to high acidity and it may only be necessary to use it in full for soils having a pH value (1:5 w/v in water) of 5.0 and under. If the lime requirement is needed for adjustment to pH 6.5 only (a normal figure for mineral soils), the analytical work may be reduced for sandy soils with pH values between 5.1 and 6.4 by using only 10, 20 and 30 ml portions of calcium hydroxide solution. Other modifications can be made in the light of texture differences, amount of organic matter and so on, with particular regard to the degree of neutralization needed for specific crops.

(3) Kilogram per hectare may be taken as roughly equal to pound per acre. Neutralization in the field is less effective than in the laboratory and a "field factor" (usually 2 or 3) is normally used on calculating the field dressing.

GENERAL REFERENCES.

BEAR. Chapter 7. (L.F. SEATZ and H.B. PETERSON)

BLACK. Chapter 59, Sections 59-1 and 59-3. (M. PEECH)
Chapter 61. (M. Peech)
Chapter 67, Section 67-3. (E.O. MACLEAN)

CHAPMAN and PRATT. Chapter 26, Section 26-11.

JACKSON. Chapter 4, Sections 4-50 to 4-65.

RUSSELL. Chapter XXVIII

Bibliographies 869, 870, 922 and 979.

III. 15. GYPSUM REQUIREMENT

15.A. PRINCIPLE

Soils containing high amounts of exchangeable sodium in relation to exchange capacity can sometimes be effectively reclaimed by the help of treatment with gypsum which, in conjuction with adequate rainfall (or irrigation) and drainage, accelerates the required replacement of sodium by calcium. An approximate assessment of the amount of gypsum required for reclamation of a particular soil may be obtained by a quantitative test with saturated calcium sulphate solution.

The soil is shaken at a fairly wide ratio with saturated calcium sulphate solution and filtered. During shaking, calcium is removed from the solution by cation exchange for sodium; and it is also possible that some magnesium may be removed from the soil by exchange processes. Although the sodium ion is the main cause of poor physical conditions in saline soils, magnesium ion can also contribute to loss of structure; thus the amount of calcium ion lost by exchange with both sodium and magnesium is considered to be a measure of the gypsum requirement of the soil. This loss in determined as the difference between the calcium concentration of the original calcium sulphate solution and the calcium concentration of the soil filtrate.

The required concentrations are conveniently determined by EDTA titration as described in Section IV.5.

15.B. APPARATUS.

Balance, accurate to 5-10 mg
Erlenmeyer flasks, 250 ml, with stoppers
Erlenmeyer flasks, 150 ml.
Cylinder, measuring, 100 ml
Reciprocating shaker
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No. 30)

Plus apparatus for EDTA titrations as listed in Section IV.4.B, using 50 ml burette instead of 25 ml burette.

15.C. REAGENTS.

Calcium sulphate solution, saturated
Shake 5 g calcium sulphate dihydrate, $CaSO_4.2H_2O$, with 1 litre of water for 1 hour (or more) and filter.

Plus reagents for determination of calcium as listed in Section IV.5.C. IV.5.C.

15.D. PROCEDURE.

Transfer 5 g air-dry soil to 250 ml Erlenmeyer flask and add 100 ml saturated calcium sulphate solution. Insert a stopper and shake on a reciprocating shaker for 30 minutes. Filter into a dry 150 ml flask.

Transfer 20 ml of the filtrate to a titration flask and determine the Ca+Mg concentration by titration with 0.020 N EDTA solution as

set out in Section IV.5.D. Similarly, titrate 20 ml of the original calcium sulphate solution to determine the calcium concentration.

15.E. CALCULATIONS.

(i) Using 20 ml aliquots, the titration values are numerically equal to the concentrations of Ca in the saturated calcium sulphate solution and the soil filtrate, respectively, measured in milliequivalents per litre.

Let

A be the concentration in me per litre of calcium in the saturated calcium sulphate solution

B be the concentration in me per litre of calcium-plus magnesium in the soil filtrate

Then, the "calcium ion" lost is (A - B) me per litre

But, 1 litre of soil filtrate corresponds to 50 g air-dry soil

Thus, the calcium ion difference is 2(A - B) me per 100 g soil

(ii) Let 1 hectare of soil to a depth of 16-17 cm be taken to weigh 2,500,000 kg.

Since, from the above calculation, 100 kg soil requires 2(A - B) equivalents of calcium ion, then 2,500,000 kg requires 50,000(A - B) equivalents

i.e. 1 hectare requires 50,000(A - B) equivalents gypsum

or, since the equivalent of gypsum is 86, 1 hectare requires

$$4{,}300(A - B) \text{ kg gypsum}$$

Suitable practical applications would be -

(a) 4.5(A - B) metric tons per hectare

(b) 2(A - B) tons per acre (6-7 inches deep)

15.F. NOTES.

(1) The concentration of calcium in saturated calcium sulphate is about 30 me per litre. The prepared solution should not have a concentration less than 28 me per litre.

(2) If the concentration of Ca in the soil filtrate is found to be greater than the concentration of calcium in the saturated calcium sulphate solution, then the soil contains sufficient calcium for reclamation.

15.G. REFERENCES.

BEAR. Chapter 7. (L.F. SBATZ and H.B. PETERSON)

JACKSON. Chapter 4, Sections 4-44 to 4-49.

RICHARDS. Chapter 6. Method 22(d).

RUSSELL. Chapter XXXIII (p.600)

III, 16, MINOR ELEMENTS FOR PLAN NUTRITION

INTRODUCTION.

Knowledge of the total concentrations of the minor elements in soils is rarely useful in correlation of soil analyses with deficiency or toxicity effects in crops. If required for research or academic purposes, the total amounts of minor elements may be determined more conveniently by spectrography or activation analysis than by chemical methods. Both of these are outside the scope of this Guide.

As in the case of the major elements, there have been many attempts to find suitable extractant solutions for the determination of "available" minor elements. Solubility in water is usually so low that analyses of the water extract are difficult; this method has only met with success (in terms of correlation with crop performance) in the case of boron - for which hot water extraction is used - and possibly manganese. Since four of the minor elements are metals (molybdenum is extracted and measured as molybdate), determination of exchangeable forms by treatment of soil with neutral salt solutions has been tried but has only been useful in interpretation of manganese results. Generally, for soils which are uncontaminated, the minor elements must be encouraged to pass into solution by increasing the hydrogen ion concentration of the extractant to dissolve "acid-soluble" forms or by including chemicals or ions which combine with the minor elements to form complexes or which break up complexes in the soil holding the elements in "Unavailable" forms. Use of a simple acid (0.1 N HCl) is sometimes effective in measuring available copper and zinc; and an acid buffer like ammonium acetate - acetic acid at pH 4.8 is a "general purpose" extractant which may give useful figures for available iron, manganese, copper and zinc - and aluminium in the case of acid soils. (It may be noted that sodium acetate - acetic acid at pH 4.8 - Morgan's solution - may often be used in place of the ammonium buffer). Techniques involving these two extractants are described below.

Other acids or acid salts or acid and salt mixtures have been advocated and may be highly correlated with crop performances in limited areas or on certain soil types; these must not be ignored by individual laboratories.

For molybdenum extraction, as molybdate, the acid salt is an oxalate and the extractant combines acid solubility and complex formation and possibly anion exchange to bring molybdate ions into solution. In one successful method for manganese, a reducing agent is used in a neutral salt solution to reduce manganese ions of high valency to the divalent form. (This technique is similar to that used to measure "free" iron oxides - see III.10). Copper and zinc are extracted in higher amounts from soils by including complex formers - EDTA to chelate copper and dithizone to form zinc dithizonate.

While single extraction solutions have been included for available iron, molybdenum and boron on the grounds that these have proved useful on a wide range of soils, it has been difficult to select any one "best" extractant for available manganese, copper and zinc; thus, three extraction methods are offered in each case.

The literature on extraction of minor elements contains not only many different extraction solutions but also a variety of soil:solution ratios and shaking times and extraction techniques. Prolonged treatment by a leaching procedure may be assumed to give the highest yield in most cases

but often, if the amount of the minor element is at a deficiency level, a simple shake at a convenient narrow ratio may not only give a similar high yield but also result in a solution more suitable for the chemical analysis of the element concerned, mainly because it is more concentrated. Except in the boron method, where the extraction procedure is fairly well established, it is suggested here that shaking at a ratio of one part of oven-dry soil to 5 or 10 parts of extractant should be used as a preliminary treatment to investigate levels of concentration. Other ratios can then be used if necessary to provide more efficient extraction; or leaching techniques can be adopted.

Chemical determination of the minor elements is by colorimetry. Methods have been made as simple as possible and should be successful on all normal soils. Although the major interferences have been dealt with, soils of unusual character may give rise to analytical troubles which must be overcome according to the nature of the interfering cation or anion or other material. The range of values found may be wide, covering deficient and toxic levels; adjustment of aliquot size or extraction technique usually deals with this aspect of minor element analysis, having due regard to the conditions (often precise) under which the final colorimetric analysis must be made. Thus, taking a larger aliquot to increase the amount of minor element also increases the amount of the salt or acid in the extractant, which may be undesirable; then a suitable modification must be introduced into the method.

The analysis of soils for minor elements can only be satisfactorily carried out if care is taken to exclude contamination from all sources. During sampling of the soil and preparation for analysis, no metal apparatus must be used which may introduce measurable amounts of the element to be determined or undesirable quantities of interfering elements. Thus, for example, passage of soil through a brass sieve would contaminate it with copper and zinc; and crushing in an iron mortar might introduce molybdenum as well as iron. In analyses, too, contact with metal apparatus is similarly bad; and there are other instances of possible contamination - zinc from rubber, boron from borosilicate glass, copper from metal stills, and so on. It is possible to reduce contamination from impurities in reagents by purchasing specially prepared "micro-analytical reagents" which are well worth their extra cost. Failing this, purification in the laboratory by distillation or solvent extraction of the unwanted element can be fairly easily done in most cases.

In the following directions (16-1 to 16-6) all the analyses are carried out on air-dry soil for convenience, although results are returned on an oven-dry basis. Analysis of field-moist soil is sometimes recommended in the literature (e.g. for manganese) and this can be done if circumstances are favourable. No attempt has been made to interpret possible results in terms of "low", "medium" and "high" availability because criteria are so variable; but the determination of available minor elements in soils is useless without some form of correlation with crop responses or symptoms.

Finally, it may be mentioned that the determination of iron, manganese, copper and zinc (and probably molybdenum) in soil extracts may be done by atomic absorption spectrophotometry if the laboratory is equipped with this apparatus. For large scale routine work, this method is certainly preferable; but for small scale investigations, colorimetric methods are likely to be useful for some time.

III. 16-1. AVAILABLE IRON

16-1.A. PRINCIPLE.

Iron is extracted by treatment of soil with 1 N ammonium acetate solution buffered near pH 4.8. Shaking at a ratio of 1:5 (w/v) is convenient and effective for a preliminary assessment of available iron level; then, if desired, modified ratios may be used or a leaching technique adopted. (see Notes 2 and 3).

The extract is analysed for iron by reduction with hydroxylamine hydrochloride and development of the ferrous-orhtophenanthroline colour as described in III.9-4. One advantage of the use of ammonium acetate buffer at pH 4.8 for extraction is that no adjustmnet of pH is normally needed before developing the iron colour. When calcareous soils are analysed, however, (and these are the most likely to show iron deficiency) the acid in the extractant may be partly or wholly neutralized and it is advisable to check the pH of the soil extract and adjust it if necessary before proceeding with the iron determination.

The extract may be coloured with small amounts of soluble organic matter. This may be removed with activated carbon; or a compensatory method may be used in the colorimetric procedure. (compare III.9-5.)

16-1.B. APPARATUS.

Balance, accurate to 10 mg
Erlenmeyer flasks, 100 ml, with stoppers
Measuring cylinder, 50 ml
Reciprocating shaker
Funnels, 55 cm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No 40)

(Note - alternative apparatus may be needed for other extraction or leaching procedures)

Volumetric flasks, 50 ml
Bulb pipettes, 2, 5 and 10 ml
Graduated pipette, 5 ml with 0.1 ml divisions
Spectrophotometer, with cells or tubes of 1.0-1.5 cm diameter (or larger, if available)

16-1.C. REAGENTS.

Ammonium acetate - acetic acid, 1 N each, pH 4.6 to 4.8
Add 120 ml glacial acetic acid to 500 ml water, then add 75 ml concentrated ammonia solution (sp.gr. 0.91, 25 per cent ammonia), cool and make to 1 litre. Check that the pH is between 4.6 and 4.8.

Activated carbon, Darco G.60 (optional)
Acetic acid, glacial and 5 N solutions. (optional in the case of some calcareous soils)

Hydroxylamine hydrochloride (hydroxyammonium chloride) 10 per cent
Orthophenanthroline, 0.25 per cent in water
(see III.9-4.C.)
Standard ferric iron solutions, 500 ppm and 50 ppm Fe.
(see III.9-4.C.)

16-1.D. PROCEDURES.

Transfer a weight of air-dry 2 mm soil containing 10 g oven-dry soil to a 100 ml Erlenmeyer flask, add 50 ml ammonium acetate - acetic acid extractant and shake mechanically for 30 minutes. Filter into dry flask through an acid-washed paper (e.g. Whatman No 40).

If the extract is appreciably coloured, add a little activated carbon, shake and filter, using dry apparatus. Alternatively, use the compensatory method for colour comparison described below. If the soil is calcareous, read the pH value of the extract.

(a) Direct method for determination of iron in colourless extracts.

Transfer 10 ml of extract to a 50 ml volumetric flask. If the pH is above 4.8, add 2 ml 5 N acetic acid. Add 2 ml of 10 per cent hydroxylamine hydrochloride solution and 2 ml of 0.25 per cent orthophenanthroline solution and make to volume with water. At the same time, transfer 1, 2, 3 and 4 ml of the standard iron solution (50 ppm Fe) to four 50 ml volumetric flasks; add to each (and to a fifth flask as blank) 10 ml extractant solution, 2 ml of 10 per cent hydroxylamine hydrochloride solution and 2 ml of 0.25 per cent orthophenanthroline solution and make each to 50 ml with water. Leave all flasks for 30 minutes to ensure complete reduction of the iron.

Determine the absorbance or transmittance of light of 508 millimicron wavelength (blue-green filter) against the blank.

(b) Compensatory method for determination of iron in coloured extracts.

Transfer two aliquots of the coloured extract (each 10 ml) to two 50 ml volumetric flasks. To one add hydroxylamine hydrochloride and orthophenanthroline as described above; to the other add hydroxylamine hydrochloride only. Make each to 50 ml with water, allow to stand for 30 minutes and then determine the absorbance or transmittance of light of 508 millimicron wavelength for both solutions against the normal blank. Prepare the standards and blank as described in (a) above.

If the colours of the ferrous-orthophenanthroline complex are very pale, corresponding to less than about 25 microgram iron, repeat the analysis with a larger aliquot of extract (up to 40 ml if possible - after making more extract), using the same volume of extractant in the standards and blank. Alternatively (or in addition for very low amounts of iron), use tubes or cells in the spectrophotometer having a light path of 2 or 4 cm, where these are available. (see Note 1)

16-1.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard iron solutions against the amounts of iron present. With the method specified, these amounts are 0 - 200 microgram Fe.

From this graph, record the number of micrograms of iron corresponding to the absorbance or transmittance values for the soil extracts.

Let

G microgram Fe be an individual value

A ml be the aliquot taken (initially 10 ml)

Then the soil extract contains $\frac{G}{A}$ ppm Fe

And the soil contains (for a 1:5 soil:extract ratio)

$\frac{5\ G}{A}$ ppm available Fe (on an oven-dry basis)

(see Note 1)

In the case of the compensatory method (b), allow for the apparent concentration of iron produced by the colour of the soil extract by taking the number of micrograms of iron as the difference between the two values, one for the extract treated with orthophenanthroline and one for the extract not treated with orthophenanthroline.

16-1.F. NOTES.

(1) With the normal procedure suggested, available iron values over the range 0 - 100 ppm in oven-dry soil are covered. This is probably too wide for many soils and the procedure should be modified if consistently low values are found. By taking an aliquot of 40 ml of extract, the range can be reduced to 0 - 25 ppm Fe in the soil; and by using cells of 2 or 4 cm light path (and reducing the iron in the standards appropriately to, say, 0 - 100 or 0 - 50 microgram), the range can be reduced to 0 - 10 ppm Fe or less, giving more accurate values for iron-deficient soils.

If the compensatory method is used for 40 ml aliquots, naturally a greater volume of extract must be made (i.e. shake 20 or 25 g soil with 100 or 125 ml extractant. Also, if 40 ml extract is used and the pH value is above 4.8, add 1 or 2 ml glacial acetic acid, depending on the actual pH figure.

(2) Iron-deficient soils can be extracted at a narrower ratio (1:4 or 1:2) in order to increase the iron concentration in the extract, if desired. But, if large aliquots are needed, more extractant must be used; thus, 40 or 50 g soil (oven-dry equivalent) may need to be shaken with 100 ml extractant - or an appropriate volume allowing for the volume of water in the soil (see III.12.B.(ii)).

Soils having moderate to high amounts of available iron may be leached, using a technique similar to that for cation exchange capacity (III.7.B.(1)) or for exchangeable aluminium (III.14.). In this case, ratios should not be wider than 1:10

(3) Ammonium acetate - acetic acid extraction at pH 4.8 is suitable for the assessment of "available" manganese, copper and zinc in some soils; and it is also advocated for the determination of "extractable" aluminium in acid soils. Thus, in a preliminary survey of minor element availabilities, four elements can be determined in this one extract (five if the soil is acid). Procedures for manganese, copper and zinc are noted in the appropriate following sections, III.16-2, III.16-3 and III.16-4. Although different ratios of soil to extractant may be advocated

for each element, an extraction at 1:5 or 1:10 (w/v) can serve for an approximate assessment of their relative amounts.

Leaching is most suited to the determination of "extractable" aluminium in acid soils, using a final ratio of 1:10 and a procedure similar to that given in III.14-1.D for removal of exchangeable aluminium. Determine aluminium in 5 or 10 ml of the leachate by adding thioglycollic acid and aluminon reagents, as described in III.9-6.D., there being no need to adjust the pH of the extract if the ammonium acetate - acetic acid extractant solution is added to the standards (volume equal to aliquot taken) in place of the buffer of pH 4.1-4.2 used in III.9-6.D

16-1.G. REFERENCES.

BLACK. Chapter 65, Section 65-3. (R.V. OLSON)

JACKSON. Chapter 15, Sections 15-6 to 15-26.

SANDELL. Chapter XXII, (II.B)

VOGEL. Chapter X, Section X.12.

Bibliography 876 and 877.

III. 16-2. AVAILABLE MANGANESE

16-2.A. PRINCIPLE.

A variety of extraction solutions have been used to assess the availability of manganese which, although classed as a minor element, is often present in soils in quite high total amounts. Most methods try to assess the actual or potential levels of divalent manganese, the form absorbed by plants. Water soluble manganese is sometimes sufficiently high to be conveniently measured; and exchangeable manganese may be extracted in addition with the traditional neutral 1 N ammonium acetate - or with calcium or magnesium nitrates - the amount removed by these neutral salts (water soluble plus exchangeable) being designated "available" manganese. (Compare "available" potassium, III. 13-1.A). Extraction with acids or acid salts removes "acid soluble" manganese in addition and solutions proposed for these methods include 0.2 N acetic acid, 0.1 N phosphoric acid, 3 N ammonium dihydrogen phosphate and ammonium acetate - acetic acid (or sodium acetate - acetic acid) buffered at pH 4.8. Also, in attempts to measure the potential available manganese level, neutral ammonium acetate containing quinol has been used to extract "easily reducible" manganese, the extract also containing water soluble and exchangeable manganese. Convenient extractions with the solutions based on ammonium acetate are described in this method, leading to assessments of "available", "acid soluble" and "easily reducible" manganese.

Determination of manganese in these extracts is based on its quantitative oxidation by periodate to the coloured permanganate ion in a sulphuric or nitric acid medium (or both). Organic compounds and anions and all reducing substances must be absent, so these are oxidized by a preliminary evaporation of part of the extracts to dryness with sulphuric or nitric acid and hydrogen peroxide, destroying acetate, quinol (where used), organic matter and any traces of reducing ions. Chloride ion reacts with permanganate and it is best to remove it from extracts of saline soils by evaporation and heating with sulphuric acid (which drives off hydrochloric acid gas) before adding nitric acid and hydrogen peroxide (see Note 1). A recommended acidity of 3.5 N as sulphuric or nitric is used during the periodate oxidation for the normal range of manganese levels (up to 250 microgram Mn in a 50 ml volume); and phosphoric acid is also added to suppress the colour of ferric iron and prevent precipitation of manganese as iodate or periodate. Excess periodate ion ensures that the permanganate colour is stable - and, in fact, standards (once prepared) may be kept for some weeks in the dark and used for checking the calibration of the spectrophotometer with each subsequent batch of analyses.

16-2.B. APPARATUS.

Balance, accurate to 10 mg
Erlenmeyer flasks, 250 ml
Measuring cylinders, 25 and 100 ml
Reciprocating shaker
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No 40)

OR - leaching apparatus (III.7.B.(1)), if preferred

Beakers, 100 ml
Bulb pipettes, 2, 5, 10 and 25 ml
Hot plate

Water bath
Volumetric flasks, 50 ml
Spectrophotometer, with cells or tubes of 1.0-1.5 cm cross-section

16-2.C. REAGENTS.

Extractants.

(1) Ammonium acetate, 1 N, pH 7.0
See III.7-1.C.

(2) Ammonium acetate - acetic acid, 1 N each, pH 4.8
See III.16-1.C.

(3) Ammonium acetate, 1 N, pH 7.0, containing 0.2 per cent quinol
Prepare as for (1) above and dissolve 2 g quinol in each litre of solution, immediately prior to use for extraction.

Sulphuric acid, concentrated, sp.gr. 1.84
Nitric acid, concentrated, sp.gr. 1.42
Hydrogen peroxide, 30 per cent (100 volume)
Orthophosphoric acid, sp.gr. 1.75
Potassium periodate, solid (see Note 2)

Standard manganese solution, 1000 ppm Mn
Dissolve 2.877 g potassium permanganate in about 250 ml water to which 10 ml concentrated sulphuric acid has been added. Boil for a few minutes, then carefully add 12 g sodium sulphite crystals, $Na_2SO_3.7H_2O$, to reduce the permangante ion to divalent manganese. Boil again to remove the sulphur dioxide, cool and make to 1 litre. (see Note 3)

Standard manganese solution, 25 ppm Mn
Dilute 25 ml of 1000 ppm solution to 1 litre. (see Note 3)

16-2.D. PROCEDURES.

(a) Extraction of manganese.

For the most accurate assessment of the various categories of soil manganese, make extracts with the different extracting solutions at the same time, under the same conditions, on three lots of air-dry soil, normally as follows -

Transfer three lots of air-dry, 2 mm soil, each equivalent to 10 g oven-dry soil, to three 250 ml Erlenmeyer flasks. Add, respectively, 100 ml 1 N neutral ammonium acetate, 100 ml ammonium acetate - acetic acid at pH 4.8 and 100 ml 1 N neutral ammonium acetate containing quinol. Shake on a reciprocating shaker for 30 minutes and then leave for at least six hours with intermittent shaking. Filter.

If neutral 1 N ammonium acetate extracts are being made for the determination of exchangeable cations by leaching (see III.7.B and III.13-1.D), similar processes may be used for extractions with acid ammonium acetate and neutral ammonium acetate containing quinol.

(b) Determination of manganese.

Transfer 25 ml extract (see Note 5) to a 100 ml beaker and evaporate to dryness on a hot plate, continuing to heat until fumes have ceased. If the soil contains chlorides above trace amounts, add 2 ml concentrated

sulphuric acid before evaporation and heat at the fuming stage of the acid for about five minutes (see Note 1). Cool, add 10 ml concentrated nitric acid (6 ml if sulphuric acid has been used) and 2 ml 30 per cent hydrogen peroxide; evaporate gently to dryness to oxidize organic matter, etc and drive off excess peroxide (see Note 4). Cool.

Add 25 ml water, 5 ml orthophosphoric acid and 0.2 g potassium periodate (see Note 2). Bring the solution to the boil and digest on a water bath for 1 hour. Cool, transfer quantitatively to a 50 ml volumetric flask and make to 50 ml with water.

Prepare three blanks by evaporating 25 ml of each of the extractant solutions and carrying these through the same processes: include a fourth blank (with one extractant) if sulphuric acid is used. Prepare standards by transferring 0,2, 4, 6, 8 and 10 ml of manganese solution (25 ppm Mn) to six beakers, adding water to make 15 ml, then 10 ml concentrated nitric acid, 5 ml orthophosphoric acid and 0.2 g potassium periodate and digesting these mixtures for 1 hour on the water bath.

Measure the absorbance or transmittance of light of 540 millimicron wavelength for all blanks, standards and test solutions, against the blank containing no manganese.

16-2.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard manganese solutions against microgram manganese (50, 100, 150 200 and 250).

From this graph, record the number of micrograms of manganese corresponding to the absorbance or transmittance values for the soil extracts.

Let

G microgram Mn be an individual value (corrected for any manganese) in the appropriate extractant solution)

Then, by the suggested procedure, this is derived from 2.5 g oven-dry soil

Thus, the concentration of manganese in the soil is

$$\frac{4G}{10} \text{ ppm (on an oven-dry basis)}$$

If

A is manganese extracted by neutral 1 N ammonium acetate

B is manganese extracted by acid ammonium acetate at pH 4.8

C is manganese extracted by neutral 1 N ammonium acetate with quinol

Then,

A may be called "available manganese" (exchangeable plus water soluble)

B may be called "extractable manganese" (compare aluminium - III.16-1.F.(3))

B - A may be called "acid soluble manganese"

C - A may be called "easily reducible manganese".

16-2.F. NOTES.

(1) It is claimed that the normal amounts of chloride in extracts of non-saline soils do not interfere with the manganese colour development, as the concentration of periodate is sufficiently great to counteract the reducing action of the chloride. No clear information is available on the actual concentration of chloride which could interfere under the experimental conditions advocated; accordingly, if conductivity values on saline soils show moderate levels of salts (specific conductivity for a 1:5 extract above 0.5 millimhos), it is considered safer to assume the presence of interfering amounts of chlorides and carry out the sulphuric acid treatment. As the concentration of soluble salts becomes greater, however, the use of sulphuric acid to remove chloride may lead to the formation of amounts of calcium sulphate which do not dissolve completely in 50 ml of final coloured solution. This arises in the standard procedure (using 25 ml extract) if 100 g soil contains more than about 60 milliequivalents calcium - as exchangeable calcium or gypsum or forms of calcium carbonate - dissolvable by the extracting solutions; i.e. the level of calcium must be greater than about 30 milligrams in the aliquot taken for analysis. If this level is exceeded and turbidity from calcium sulphate is unavoidable, filter or centrifuge the final solution after adjustment to 50 ml.

(2) Potassium periodate is the normal periodate chosen but the sodium salt may be used instead. These are metaperiodates. The use of trisodium paraperiodate, $Na_3H_2IO_6$, has also been advocated.

(3) The potassium permanganate used for the standards must be of very good analytical grade quality. The ordinary laboratory supply of distilled or deionized water is satisfactory for the preparation of the concentrated standard manganese solution, as boiling destroys any slight amounts of organic matter which may be present.

The dilute standard manganese solution should preferably be made with water of low conductivity which has been boiled to sterilize it.

(4) Control of the acidity near 3.5 N as sulphuric or nitric or a mixture ture of both depends on the acid treatments of the residues being carried out under consistent conditions. Prolonged or too vigorous heating during the nitric acid - hydrogen peroxide treatment may lead to loss of acid and this must be avoided. Slight losses are acceptable if they are reasonably constant.

(5) The procedure suggested covers the range 0-100 ppm Mn in oven-dry soil. For the analysis of manganese deficient soils, 50 or 75 ml of extract can be taken; and for the analysis of soils containing toxic levels of manganese, 10 or 5 ml may be suitable, covering concentrations up to 500 ppm Mn in the soil.

(6) Water soluble manganese may be determined in water extracts of soil (see III.6) if desired. Levels may be low, however, and there is then a danger of incomplete oxidation by the method given for the ammonium acetate extracts. More complete oxidation may be obtained by developing the permanganate colour in 2 N sulphuric acid containing about 10 mg silver nitrate.

Water extracts of saline soils may give undue amounts of salts if large volumes need to be evaporated for manganese analysis; use of sulphuric acid to remove chlorides is then prolonged and incon-

venient and it may also lead to formation of undesirable quantities of calcium sulphate (see Note 1). A better procedure is to precipitate manganese from the water extract with sodium or potassium hydroxide, adding about 10 mg ferric iron to provide ferric hydroxide, as a collector (although calcium and magnesium hydroxides may also act in the same manner). The precipitate is coagulated by boiling, filtered off and washed with 0.1 per cent alkali and finally dissolved in nitric acid for the colour development given in the normal procedure.

A rapid method for estimation of manganese in neutral or acid ammonium acetate extracts (or acid sodium acetate extracts) is based on oxidation with sodium bismuthate which does not need heating. If the extract is free of chlorides, decolourize it with activate carbon and then transfer 25 ml to a 50 ml centrifuge tube, add 2 ml concentrated sulphuric acid or 5 ml concentrated nitric acid and mix. Add 0.2-0.4 g sodium bismuthate powder, mix and leave for 30 minutes with occasional stirring. Centrifuge at 2500 rpm for 10 minutes, decant the clear liquid into a 50 ml volumetric flask, wash the tube and residue once with 10 ml water (mixing and centrifuging) and finally make to 50 ml with water.

If levels are low, the clear supernatant liquid after centrifuging can be transferred directly to the spectrophotometer tube or cell without dilution to 50 ml. Treat standards in the same way as the test solutions.

16-2.G. REFERENCES.

BLACK. Chapter 69. (F. ADAMS)

CHAPMAN and PRATT. Chapter 15, Sections 15-1 and 15-4
Chapter 26, Sections 26-18.

JACKSON. Chapter 5, Sections 5-65 to 5-78
Chapter 15, Sections 15-27 to 15-40

SANDELL. Chapter XXVI, (I and II.A)

VOGEL. Chapter III, Section III.60
Chapter X, Section X.13

III. 16-3. AVAILABLE COPPER

16-3.A. PRINCIPLE.

Levels of available copper are normally low in soils unless contamination has resulted from the use of fungicidal sprays containing copper. Very little of the soil copper is water soluble or exchangeable; thus, acids or salt-acid buffers are frequently used for extraction and some success has been achieved with solutions (alkaline, neutral or acid) containing ethylenediaminetetraacetate (EDTA) to complex the copper. As noted in section III.16-1, extraction of soils with 1 N ammonium acetate - acetic acid at pH 4.8 can be helpful in assessing the available levels of minor elements and it is included in the methods suggested here; extraction with 0.1 N hydrochloric acid is useful for measuring organically held copper and this extract can also be employed to measure available zinc (see III.16-4); and use of 0.05 M ammonium EDTA salt at pH 4.0 is an example of the extraction methods involving chelation of copper. (see Note 1)

A number of organic reagents are available for the colorimetric determination of small amounts of copper. The dithiocarbamates can remove copper from its EDTA complex and thus are suitable for the determination of copper in ammonium-EDTA soil extracts; accordingly, the same reagent is used, as a matter of convenience, for the prescribed method in analysing the other extracts with acid ammonium acetate and hydrochloric acid. (see Note 2) The traditional copper reagent is sodium diethyldithiocarbamate, although zinc dibenzyldithiocarbamate is also recommended (see Note 3).

Sodium diethyldithiocarbamate gives a brown colloidal complex with cupric ion which can be dissolved out by solvent extraction with carbon tetrachloride or chloroform to give a yellow solution. The reaction between copper and the diethyldithiocarbamate suffers some interferences from iron, manganese, cobalt, nickel and bismuth by the production of coloured compounds; however, iron, manganese, cobalt and nickel can be complexed by EDTA in ammoniacal solution and the amount of bismuth in soil extracts is negligible. Addition of citrate also helps to complex iron. Zinc does not interfere because its complex with diethyldithiocarbamate is colourless. For normal soils, the interfering metals are likely to be so low in amount that no EDTA need be added but it is usual to do so as a precaution.

Care must be taken to avoid or remove contamination with copper during the analyses. (see Notes 4 and 5)

16-3.B. APPARATUS.

Balance, accurate to 0.1 g
Erlenmeyer flasks, 150 ml
Measuring cylinder, 50 ml
Reciprocating shaker
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter, (e.g. Whatman No 40)
Separating funnels, 100 ml
Bulb pipettes, 1, 10 and 25 ml
Spectrophotometer, with tubes or cells having a cross- section of 1.0-1.5 cm

venient and it may also lead to formation of undesirable quantities of calcium sulphate (see Note 1). A better procedure is to precipitate manganese from the water extract with sodium or potassium hydroxide, adding about 10 mg ferric iron to provide ferric hydroxide, as a collector (although calcium and magnesium hydroxides may also act in the same manner). The precipitate is coagulated by boiling, filtered off and washed with 0.1 per cent alkali and finally dissolved in nitric acid for the colour development given in the normal procedure.

A rapid method for estimation of manganese in neutral or acid ammonium acetate extracts (or acid sodium acetate extracts) is based on oxidation with sodium bismuthate which does not need heating. If the extract is free of chlorides, decolourize it with activate carbon and then transfer 25 ml to a 50 ml centrifuge tube, add 2 ml concentrated sulphuric acid or 5 ml concentrated nitric acid and mix. Add 0.2-0.4 g sodium bismuthate powder, mix and leave for 30 minutes with occasional stirring. Centrifuge at 2500 rpm for 10 minutes, decant the clear liquid into a 50 ml volumetric flask, wash the tube and residue once with 10 ml water (mixing and centrifuging) and finally make to 50 ml with water.

If levels are low, the clear supernatant liquid after centrifuging can be transferred directly to the spectrophotometer tube or cell without dilution to 50 ml. Treat standards in the same way as the test solutions.

16-2.G. REFERENCES.

BLACK. Chapter 69. (F. ADAMS)

CHAPMAN and PRATT. Chapter 15, Sections 15-1 and 15-4
Chapter 26, Sections 26-18.

JACKSON. Chapter 5, Sections 5-65 to 5-78
Chapter 15, Sections 15-27 to 15-40

SANDELL. Chapter XXVI, (I and II.A)

VOGEL. Chapter III, Section III.60
Chapter X, Section X.13

phases to separate. Run off the lower (organic) layer through a small filter paper or plug of cotton wool into the spectrophotometer tube or cell; it is sometimes necessary to discard the first 1 or 2 ml which may be affected by drops of the aqueous phase.

Prepare blanks by transferring 25 ml of each of the extractant solutions to three separating funnels; prepare standards by transferring 0, 1, 2, 3, 4 and 5 ml of copper solution (5 ppm Cu) to six separating funnels. Add to all blanks and standards 10 ml ammonium EDTA and proceed as described above for soil extracts.

Read the absorbance or transmittance of light of 440 millimicron wavelength for all blanks, standards and test solutions, against the blank containing no copper.

16-3.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard copper solutions against microgram copper (5, 10, 15, 20 and 25).

From this graph, record the number of micrograms of copper corresponding to the absorbance or transmittance values for the soil extracts.

Let

G microgram Cu be an individual value (corrected for any copper in the appropriate extractant solution).

Then, by the suggested procedure, this is derived from 5 g oven-dry soil.

Thus, the concentration of copper in the soil is

$$\frac{G}{5} \text{ ppm (on an oven-dry basis)}$$

16-3.F. NOTES.

(1) When neutral or alkaline solutions containing EDTA are used, [illegible]due amounts of organic matter are dissolved from some soils, especially if the sodium salt is employed. When ammonium EDTA at pH 4 is used, almost no organic matter is dissolved.

Performance of the extracting solutions with calcareous soils is uncertain. Presumably the ammonium EDTA salt would be effective; and sufficient extra acid could be added to the 0.1 N hydrochloric acid extractant to neutralize the carbonate in any particular soil (see III.16-4.D.(a)).

(2) If the EDTA extraction is not included, other organic reagents may be used for estimation of copper in acid ammonium acetate and 0.1 N hydrochloric acid extracts. The most specific is 2,2'-biquinoline (2,2'-diquinolyl), which reacts with the cuprous ion to give a purple coloured complex, extractable by amyl alcohol (either n- or iso-) in which the reagent is normally dissolved. Unfortunately, 2,2'- biquinoline is very expensive - at present about 400 times the cost of purified sodium diethyldithiocarbamate.

(3) Zinc dibenzyldithiocarbamate gives a reaction with cupric ions similar to sodium diethyldithiocarbamate but the coloured solution in carbon tetrachloride is more stable to light. There is also less interference from iron, cobalt and nickel. The extraction of copper

from aqueous solution is carried out at an acidity of 1 N and it is presumed this would be satisfactory with the extracts made above.

(4) In the preparation of reagents, use the purest chemicals obtainable. Thus, it is possible to buy triammonium citrate which is guaranteed low in copper and specially pure copper sulphate for the standard solutions. Use water which has been deionized – or distilled in an all-glass apparatus; never use distilled water from a copper still.

If blanks are high, the extractants can be purified of copper (and some other metals) by shaking them with small portions (20 ml for up to 1 litre of solution) of 0.01 per cent dithizone in carbon tetrachloride (see III.16-4.A.) until the colour of the organic phase remains green; this method can be used with the ammonium citrate solution also. After this treatment, traces of dithizone are removed by shaking with carbon tetrachloride alone until all green colour has gone.

Carbon tetrachloride and ammonia solutions can be purified by distillation but this is rarely necessary; however, it is worth recovering carbon tetrachloride from the coloured solutions after analysis. To do this, add granula dried calcium chloride to about 2 litres of waste carbon tetrachloride and allow to stand to absorb water. Pour off into the flask of an all-glass distillation apparatus, add 10-20 g calcium oxide and distil, discarding the first 100 ml.

(5) The soil must not be sieved through a brass sieve; use nylon or stainless steel. The extraction flasks must be closed with plastic stoppers or rubber stoppers which have been covered with plastic film especially if the extracts are to be analysed for zinc (III.16-4.F.(2)).

(6) A ratio of 1:5 (soil:extract) is a useful general one if the analysis is being done without any idea of the available copper level. It can be changed according to the level found. Three hours shaking is recommended for removal of copper with EDTA but less time may be sufficient for the other extractants. The amount of soluble organic matter in the extracts is normally very low and does not interfere in the subsequent procedure.

(7) Using standards containing 0-25 microgram copper and the suggested procedure, available copper concentrations of 0-5 ppm in the soil are covered. This is suitable for most uncontaminated soils; for soils containing toxic levels of coppper, smaller aliquots can be taken or wider ratios used for extraction.

(8) The sodium diethyldithiocarbamate-copper complex is affected by sunlight and the final stages of the analysis should be performed in a darkened room or by artificial light. (see Note 3)

16-3.G. REFERENCES.

BLACK. Chapter 77. (J.G.A. FISKELL)

JACKSON. Chapter 15, Sections 15-41 to 15-68.

PIZER. Journal paper.

SANDELL. Chapter IV, (II.B)
Chapter XVI, (II.A and B)

Bibliographies 719 and 1090

III. 16-4. AVAILABLE ZINC

16-4.A. PRINCIPLE

As in the case of copper, available zinc is comparatively low in soils unless contamination arises; and this is caused only in unusual circumstances such as contact with galvanized iron materials in old glasshouses. The extractants used to measure copper may also be used to measure zinc and two of them (ammonium acetate - acetic acid at pH 4.8 and 0.1 N hydrochloric acid) are included here; the third extractant is replaced by neutral 1 N ammonium acetate used in conjunction with an immiscible carbon tetrachloride solution of dithizone which complexes zinc and thus acts in principle like the ammonium-EDTA salt for copper.

Dithizone is, in fact, the only common, reliable organic reagent for the colorimetric determination of zinc. It is diphenylthiocarbazone and dissolves in chloroform or carbon tetrachloride to give a green solution; it forms a red zinc dithizonate when the organic solutions are shaken with aqueous solutions of zinc under specified conditions. When working in the proper range, the production of increasing amounts of the red zinc dithizonate is accompanied by a gradual reduction of the green dithizone colour. While some procedures advocate removal or the excess dithizone, this is not really necessary (and may affect the zinc dithizonate) and it is quite possible to measure the red zinc colour in the presence of the remaining green dithizone colour - or to measure the gradual decrease in green colour.

Dithizone forms coloured dithizonates with other metals and those present in the relevent soil extracts in more than negligible amounts are probably iron, manganese, copper, cobalt, nickel and lead. Iron only forms an unstable dithizonate when in the ferrous form; ferric iron tends to oxidize dithizone in alkline solution; and manganese dithizonate is very unstable through oxidation of the manganous ion. Thus, although dithizone reacts with many metals, the only ones which may interfere in the analysis of the soil extracts suggested are copper, cobalt, nickel and lead. (see Note 1).

Control of pH of the aqueous solution can be partly used to separate the dithizonates of the interfering metals but addition of complex formers is also necessary. Zinc reacts with dithizone in carbon tetrachloride when present in slightly acid solutions (near pH 5); if sodium thiosulphate is added in sufficient excess, copper and lead do not react - and if potassium cyanide is also added, cobalt and nickel do not react. In practice - and for most normal soils - the addition of sodium thiosulphate alone is enough, as the dithizonates of cobalt and nickel will only interfere if their concentration is high. These considerations make it practicable to determine zinc in acid ammonium acetate extracts directly (because its pH is near the optimum desired) and also to use the same procedure for the 0.1 N hydrochloric acid extracts, after adjustment to near pH 4.8.

The third extraction procedure results in a carbon tetrachloride solution containing zinc and other dithizonates. This is shaken with dilute hydrochloric acid and only zinc and lead are quantitatively extracted into the aqueous phase. The adjustment of pH and treatment with sodium thiosulphate can follow as in the other procedures.

Care must be taken to avoid or remove contamination with zinc during the analyses. (see Note 2)

16-4.B. APPARATUS.

Balance, accurate to 10 mg
Erlenmeyer flasks, 150 ml
Measuring cylinder, 50 ml
Reciprocating shaker
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No 40)
Separating funnels, 50 and 100 ml
Centrifuge, with 50 ml tubes
Bulb pipettes, 1, 5 and 10 ml
Spectrophotometer, with tubes or cells of 1.0-1.5 cm cross-section

16-4.C. REAGENTS

Extractants. (see Note 2)

(1) Ammonium acetate - acetic acid, 1 N each, pH 4.8
See III.16-1.C.

(2) Hydrochloric acid, 0.1 N

(3) (a) Ammonium acetate, 1 N, pH 7.0
See III.7-1.C.

(b) Dithizone in carbon tetrachloride, 0.01 per cent
Dissolve 0.1 g dithizone in 1 litre carbon tetrachloride

Hydrochloric acid, 0.02 N
Dilute 4 ml of 5 N acid to 1 litre

Sodium thiosulphate, 25 per cent

Dithizone in carbon tetrachloride, 0.001 per cent
Dilute 100 ml of 0.01 per cent solution to 1 litre

Standard zinc solution, 500 ppm Zn
Dissolve 0.5000 g pure zinc powder or 0.6224 g zinc oxide, ZnO, in 5 ml 5 N hydrochloric acid and dilute to 1 litre.

Standard zinc solution, 1 ppm Zn
Dilute 10 ml of 500 ppm solution to 100 ml with water and then dilute 5 ml of this diluted solution (50 ppm Zn) to 250 ml

16-4.D. PROCEDURES.

(a) Extraction of zinc.

Prepare extracts at 1:5 ratio with ammonium acetate - acetic acid at pH 4.8 and with 0.1 N hydrochloric acid as described for copper (III 16-3.D.). If the soil is calcareous, add extra hydrochloric acid to neutralize the carbonates and leave 0.1 N solution in excess (see Note 3).

To extract soil with ammonium acetate - dithizone, transfer 25 ml neutral 1 N ammonium acetate solution and 25 ml 0.01 per cent dithizone solution in carbon tetrachloride to a 150 ml Erlenmeyer flask and add a weight of air-dry 0.5 mm soil containing 2.5 g oven-dry soil. Shake for one hour and then transfer the mixture to a 100 ml separating funnel. Allow the

organic phase and soil to settle, then run this into a 50 ml centrifuge tube. Centrifuge at 2500 rpm for 10 minutes and remove particles of soil and any remaining aqueous phase on the surface by suction. (See Note 4)

(b) Determination of zinc - preliminary treatments.

(i) Ammonium acetate - acetic acid extracts.

Transfer 5 ml to a 50 ml separating funnel and add 5 ml water. Proceed as in (c) below.

(ii) 0.1 N hydrochloric acid extracts.

Transfer 5 ml to a 50 ml separating funnel and add 5 ml ammonium acetate - acetic acid extractant (pH 4.8). Proceed as in (c) below.

(iii) Ammonium acetate - dithizone extracts.

Transfer 10 ml of dithizone extract to a 50 ml separating funnel and add 10 ml 0.02 N hydrochloric acid. Shake for 1-2 minutes, allow the phases to separate and run off the carbon tetrachloride layer into a second 50 ml separating funnel. Add 5 ml 0.02 N hydrochloric acid to the second funnel, shake for 1 minute and allow the phases to separate. Run off the carbon tetrachloride layer and discard it (its colour is a guide to the amount of copper present - in the absence of large amounts of cobalt and nickel). Combine the two hydrochloric acid solutions, containing zinc and lead, in one separating funnel and add 5 ml ammonium acetate - acetic acid extractant. Proceed as in (c).

(c) Determination of zinc - final operations.

Add to the aqueous phases containing zinc (at pH 4.5 - 4.8) 1 ml of 25 per cent sodium thiosulphate solution, mix and add exactly 10 ml 0.001 per cent dithizone in carbon tetrachloride. Shake for one minute and allow the phases to separate. Run off the carbon tetrachloride layer through a small filter paper or plug of cotton wool into the spectrophotometer tube or cell, discarding the first 1 or 2 ml if necessary (see III.16-3.D.).

Prepare blanks by taking 5 ml of acid ammonium acetate extractant and 5 ml 0.1 N hydrochloric acid through the same procedures used for the corresponding soil extracts. For the third blank, shake 25 ml neutral 1 N ammonium acetate with 25 ml 0.01 per cent dithizone in carbon tetrachloride for one hour, separate the phases and take 10 ml of the organic phase through the operations given in (b)(iii) and (c) above.

Prepare standards by transferring 0, 2, 4, 6 and 8 ml of standard zinc solution (1 ppm Zn) to five separating funnels, adding 5 ml ammonium acetate - acetic acid at pH 4.8 and making each to 15 ml with water. Add 1 ml 25 per cent sodium thiosulphate and extract the zinc with dithizone as given in (c) above.

Read the absorbance or transmittance of light of 535 millimicron wavelength for all blanks, standards and test solutions, either against the 0.001 per cent dithizone solution or carbon tetrachloride alone, as preferred.

16-4.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard zinc solutions against microgram zinc (2, 4, 6 and 8).

From this graph, record the number of micrograms of zinc corresponding to the absorbance or transmittance values for the soil extracts.

Let

G microgram Zn be an individual value (corrected for any zinc in the appropriate extractant solution - this blank must be very small)

Then, by the suggested procedure, this is derived from 1 g oven-dry soil.

Thus, the concentration of zinc in the soil is

G ppm (on an oven-dry basis)

16-4.F. NOTES.

(1) When the ammonium acetate - dithizone extractant is used, it is fairly certain that more of the interfering elements will be extracted (if present in the soil) through formation of their dithizonates. But treatment of the carbon tetrachloride solution with dilute acid effects useful separations, only zinc and lead passing completely into the aqueous phase. If cobalt and nickel are present, their concentrations in the aqueous phase will be much reduced and copper will be absent.

Stannous tin forms a red dithizonate under the conditions specified but it is unlikely to be present in more than trace amounts in normal soils. Care should be exercised, however, in analyses of soils from areas near deposits of tin ores.

(2) As with the reagents for copper, only the purest chemicals should be used. Dithizone, carbon tetrachloride and sodium thiosulphate are often obtainable in a grade which can be used without purification. The extractants (including the neutral ammonium acetate) can be purified if necessary by shaking with 0.01 per cent dithizone in carbon tetrachloride; and carbon tetrachloride can be recovered after the analyses by drying and distillation. (see III.16-3.F.(4))

Water must be zinc-free, easily produced by deionization in borosilicate glass or polythene apparatus. Contact with metal fittings containing zinc must be avoided at all stages of the analysis; similarly, contact with rubber is inadmissable. Soils must of course be sieved through nylon or stainless steel sieves. And it is wise to reserve specially cleaned borosilicate glass ware for use in zinc analyses only.

(3) Published methods recommend that extraction of calcareous soils with 0.1 N hydrochloric acid should be done by a number of treatments until the final extract is acid (pH less than 2). A similar effect can be obtained by shaking with acid of such a concentration that the carbonates are neutralized and 0.1 N acid is left in excess.

For a soil containing X per cent of calcium carbonate (by method III.2-2), dilute (2X + 5) ml of 1 N hydrochloric acid to 50 ml and add this to 10 g soil (oven-dry equivalent) in the extraction

procedure. In shaking, allow the carbon dioxide to escape.

(4) Some procedures advocate extracting the soil with ammonium acetate-dithizone in a separating funnel which is shaken vertically in a special device. If this apparatus is not available, the extraction can be done in a flask and the mixture transferred to a separating funnel afterwards. This is perhaps more convenient if only occasional zinc analyses are called for.

(5) The ratios of extraction can be changed in accordance with the zinc concentration found in the 1:5 extract; and different aliquots can be taken for analysis. The procedures suggested cover the range 0-8 ppm Zn in the soil and the amounts of zinc present in the final stage must be adjusted to cover a similar range in microgram Zn.

(6) If preferred, the final spectrophotometric readings may be done with light of 620 millimicron wavelength, which measures the concentration of dithizone left after reaction with zinc.

It is also quite possible to assess the level of zinc with a fair degree of accuracy by visual means. At the concentrations given, there are distinct colour changes from green through blue, grey, grey-violet, violet and red-violet to increasing depths of red and these can be detected for differences in amount of zinc of 1 microgram or less. If this method is adopted, there is no need to use separating funnels; carry out the final extraction of zinc with dithizone in glass-stoppered test tubes (selected for uniformity of diameter) and judge the colour of the carbon tetrachloride layer after settling. Standards varying by 1 microgram are essential.

16-4.G. REFERENCES.

BLACK. Chapter 78. (F.G.VIETS, JNR. and L.C. BOAWN)

CHAPMAN and PRATT. Chapter 26, Section 26-28.

JACKSON. Chapter 15, Sections 15-69 to 15-92.

SANDELL. Chapter IV, (II·A)
Chapter XLIX, (I.B and II.A)

Bibliographies 690, 719, 1077 and 1090

III. 16-5. AVAILABLE MOLYBDENUM

16-5.A. PRINCIPLE.

Molybdate ion is extracted from soil by shaking with 0.2 N oxalic acid buffered at pH 3.3 with ammonium oxalate. An aliquot of the extract is evaporated to dryness and ignited to destroy oxalate and the residue is taken up in dilute hydrochloric acid.

The molybdate ion in this solution is reduced (7-valent molybdenum becoming 5-valent) by stannous chloride in the presence of thiocyanate and an amber-orange coloured complex is formed between the thiocyanate ion and 5-valent molybdenum. Because amounts of molybdate are usually small in most soil extracts, the coloured complex is dissolved out of the aqueous phase into a small volume of immiscible organic solvent, a mixture of carbon tetrachloride and iso-amyl alcohol being most suitable. A preliminary treatment of the solution (prior to addition of thiocyanate and reducing agent) with the organic solvent ensures that the aqueous phase is saturated with it and therefore there is no subsequent volume change of the organic phase when the thiocyanate-molybdenum complex is finally and quantitatively extracted. The thiocyanate and stannous solutions are made up in a concentrated form so that only 1 ml of each is needed.

When the thiocyanate-molybdenum complex is formed, the acidity (as HCl) should be near 1 N and the thiocyanate concentration should be at least 0.5 per cent (1 per cent as the potassium salt). Considerable variation in the concentration of stannous chloride is, however, allowable; a final concentration of 1-2 per cent is usually used. The presence of at least 1 milligram of iron ensures full colour development of the thiocyanate-molybdenum complex and there is no adverse effect from larger amounts; thus about 1 milligram if iron (ferrous or ferric may be used) is added, although some may be present already in the soil extract. The stannous chloride reduces ferric iron and so prevents the formation of red ferric thiocyanate.

Interferences are possible from tungsten, titanium, vanadium and platinum but none of these is likely to be present in acid oxalate soil extracts in amounts sufficient to cause serious errors.

16-5.B. APPARATUS.

Balance, accurate to 0.1 g
Erlenmeyer flasks, 250 and 500 ml
Measuring cylinders, 10 and 250 ml
Reciprocating shaker
Funnels, 75 mm diameter
Filter papers, 15.0 cm diameter (e.g. Whatman No 40)
Evaporating basins, silica or porcelain, capacity 30-35 ml
Muffle furnace
Separating funnels, 50 ml, preferably with plastic stopcocks and having short exit tubes for easy drying (Squibb type)

Holders or stands for separating funnels
Bulb pipettes, 1, 2 and 5 ml
Spectrophotometer, having cells or tubes of 1.0-1.5 cm cross section and a capacity of 5 ml or less (see Note 3)

16-5.C. REAGENTS.

Extractant solution, 0.2 N oxalic acid with 2.5 per cent ammonium oxalate, pH 3.3
Dissolve 250 g ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$, and 126 g oxalic acid, $H_2C_2O_4.2H_2O$, to 10 litres.
Check that the pH value is near 3.3

Hydrochloric acid, 5 N (see Appendix 1)

Ferrous or ferric iron solution, 500 ppm Fe (see III.9-4.C or III.10.C.)
OR
Ferrous ammonium sulphate, approximately 0.01 N (as reductant)
Dilute 0.2 N solution (see III.3.C.) twenty times.

(Note - 2 ml of any of these iron solutions contains 1 milligram Fe)

Potassium thiocyanate, 30 per cent
(Sodium or ammonium thiocyanate of the same concentration may be used)

Stannous chloride, 30 per cent in 1 N hydrochloric acid
Add 30 g stannous chloride, $SnCl_2.2H_2O$, to 20 ml 5 N hydrochloric acid and dilute to 100 ml. Filter if turbid and store in the refrigerator.

Organic solvent.
Mix equal volumes of carbon tetrachloride and iso-amyl alcohol (3-methylbutan-1-ol)

Standard molybdenum solution, 1000 ppm Mo
Dissolve 1.500 g molybdenum trioxide, MoO_3, in 5 ml of 5 N sodium hydroxide, dilute to about 500 ml and just acidify with about 2 ml of 5 N hydrochloric acid. Finally dilute to 1 litre.

Standard molybdenum solution, 10 ppm Mo
Dilute 5 ml of 1000 ppm solution to 500 ml. Prepare only as required.

16-5.D. PROCEDURE.

Transfer a weight of air-dry soil containing 25 g oven-dry soil to a 500 ml Erlenmeyer flask, add 250 ml acid oxalate extractant and shake for a convenient time (see Note 1). Filter.

Evaporate a total of 200 ml of extract to dryness in a silica or porcelain basin (capacity 30-35 ml) which has been lightly greased round the top with vaseline to prevent the oxalate creeping over the edge. Include 200 ml of extractant solution in a separate basin as a blank. Ignite the residue at 450°C for 3-4 hours in a muffle furnace to destroy oxalate (and the grease on the edge of the basin).

When cool, add 5 ml 5 N hydrochloric acid, dissolve the salts and transfer the liquid to a 50 ml separating funnel, bringing the volume to 20-21 ml. (see Note 2) Then add 2 ml iron solution and mix. Prepare a blank (in addition to the blank on the extractant solution) and standards by transferring 0, 1, 2, 3, 4 and 5 ml of standard molybdenum solution (10 ppm Mo) to six separating funnels, adding 5 ml 5 N hydrochloric acid and 2 ml iron solution to each and making the volume to 22-23 ml.

Add 2-3 ml organic solvent and shake well for two minutes to saturate the aqueous phase. Allow the phases to separate, tapping the funnel or swirling the liquid to produce a clean boundary line; then run off the

lower (organic) phase. Add 1 ml 30 per cent potassium thiocyanate solution to the aqueous phase, mix, add 1 ml 30 per cent stannous chloride solution and mix again. Then add exactly 5 ml organic solvent and shake well for two minutes. Invert the funnel in a stand so that the stopcock is uppermost and dry the exit tube and stopcock bore with absorbent paper or suction, as convenient. After 15 minutes, shake the liquids again quickly and allow them to separate once more, with the funnel supported in the normal position. Make sure the exit tube is still dry and then run off the coloured organic phase into a suitable spectrophotometer tube or cell.

Read the absorbance or transmittance of light of 470 millimicron wavelength, as compared with the blank containing no molybdenum.

16-5.E. CALCULATION

Plot the absorbance or transmittance values obtained with the standard molybdenum solutions against microgram molybdenum (10, 20, 30, 40 and 50).

From this graph, record the number of micrograms molybdenum present in the extracts analysed.

Let

G microgram Mo be an individual value (corrected for any molybdenum in the acid oxalate extractant)

Then, by the suggested procedure, this is derived from 20 g oven-dry soil.

Thus, the concentration of available molybdenum in the soil is

$$\frac{G}{20} \text{ ppm (on an oven-dry basis)}$$

16-5.F. NOTES.

(1) The method given conforms basically to that published (see References) but the advocated shaking times for extraction of the soil vary from 8 to 16 hours (i.e. overnight). It would seem more convenient to use two short shaking periods (say, 1 hour each) with an overnight standing period. It is assumed that a long period of contact is essential to extract all the available molybdenum from all soils; but this may not be so.

(2) If the residue does not dissolve completely in the acid, the liquid may be filtered through a small paper into the separating funnel, washing the paper well. Slight turbidity is not harmful, however.

(3) The range of values covered by the normal procedure is 0–2.5 ppm Mo. This would be suitable for soils known to give crops having excess molybdenum, toxic to animals. Not very accurate results are possible, however, with molybdenum deficient soils. For these, larger amounts of soil can be taken and it seems possible to reduce the soil:extract ratio to 1:5, finally evaporating a volume of extract equivalent to 50 g oven-dry soil. Alternatively, 50 g soil can be leached with the extractant (see III.7.B,(1)) and the whole of the extract used for analysis. The range covered then becomes 0–1.0 ppm Mo.

The range may be reduced also by using less than 5 ml organic solvent, provided spectrophotometer micro-cells (or tubes) are available with a light path of at least 1 cm and a capacity of only 2-3 ml.

16-5.G. REFERENCES.

BLACK. Chapter 74. (H.M. REISENHAURR)

CHAPMAN and PRATT. Chapter 16. Chapter 26, Section 26-19.

SANDELL. Chapter XXVIII, (II.A)

VOGEL. Chapter XV, Section XV.13.

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III. 16-6. AVAILABLE BORON.

16-6.A. PRINCIPLE

The concentration of water-soluble borate ion in soil is a useful measure of boron availability. The amount of borate dissolved by treatment with water can vary in some soils according to the ratio of soil to water and the conditions of extraction; thus any method selected must be carefully standardized and correlated with boron deficiency and toxicity symptoms.

The most used procedure is to subject soil to the solvent action of boiling water for five minutes under a reflux which keeps the volume of liquid constant and the soil:water ratio at 1:2 (w/v). Use of water alone may cause subsequent difficulty in the preparation of a clear extract, unless the soil is saline; thus a dilute neutral solution of magnesium chloride us used instead to flocculate colloidal material (as in III.9-1.), the presence of the salt having no influence on the water solubility of borate.

The clear extract produced is suitable for the direct colorimetric determination of boron by the carmine method described in Section IV.14, unless the boron content of the soil is less than 1 ppm. Then it is better to concentrate the extract by evaporation of a larger aliquot to dryness in the presence of a mild alkali (to prevent loss of borate) and subsequent dissolution of the residue in a small volume of dilute acid; clarification of this solution may be necessary.

Precautions must be taken to prevent contamination by borate ion from borosilicate glassware.

16-6.B. APPARATUS.

Balance, accurate to 0.1 g
Erlenmeyer flasks, boron-free glass, 250 ml
Dispensing burette, 100 or 250 ml
Reflux condensers, boron-free glass, water-cooled or air-cooled, as available (see Note 3)
Electric hot plate
Centrifuge, with 50 ml tubes or filtering apparatus, in lieu (see Note 4)
Bulb pipettes, 2 ml
Dispensing burettes, (2), 100 ml, with coarse jets, fitted with moisture traps
Erlenmeyer flasks, 50 ml, stoppered, boron-free glass if possible
Spectrophotometer, with cells or tubes which can be stoppered or covered.

Plus, for concentration of extracts if needed -

Silica basins, capacity 30-35 ml
Bulb or graduated pipettes, 4, 5, 20 and 25 ml, as convenient
Centrifuge tubes, 15 ml

16-6.C. REAGENTS.

(see Note 1)

Magnesium chloride, 0.02 N (approximately)
Dissolve 2 g magnesium chloride, $MgCl_2.6H_2O$, to 1 litre. Or, if 1 N magnesium chloride (see III.9-1.C.) is available, dilute 20 ml to 1 litre.

Calcium hydroxide, saturated.
See III.14-2.C., however, the solution need not be separated from the solid for this method - and standardization is not necessary.

Hydrochloric acid, 0.5 N
Dilute 44 ml concentrated acid (sp.gr. 1.18) to 1 litre - or dilute stock 5 N acid ten times.

Plus - Reagents for the colorimetric determination of boron, given in Section IV.14.C.

16-6.D. PROCEDURE.

Transfer a weight of air-dry, 2 mm soil equivalent to 25 g oven-dry soil to a 250 ml Erlenmeyer flask and add a volume of 0.02 N magnesium chloride solution sufficient to make the total volume of liquid 50 ml (see Note 2). Insert an air condenser or a water-cooled reflux condenser, as preferred (see Note 3) and bring the mixture to the boil. Continue to boil for exactly five minutes, then allow to cool to room temperature with the condenser still in place.

Remove the condenser and decant the liquid into a 50 ml centrifuge tube or on to a dry filter paper. Centrifuge or filter to obtain a clear solution (see Note 4). Transfer 2 ml of the water extract to a 50 ml Erlenmeyer flask and add two drops of concentrated hydrochloric acid. Then proceed to develop the carmine-borate colour as described in IV.14. D in both the soil extracts and standards.

If the level of water-soluble boron is below 1 ppm in the soil, more reliable results may be obtained by concentration of the extract. Transfer 25 ml of the extract (if available - use 20 ml if not) to a silica basin and add 5 ml saturated calcium hydroxide. Evaporate to dryness and add 5 ml (4 ml if 20 ml of extract is taken originally) of 0.5 N hydrochloric acid. Mix well with a rubber 'policeman' and pour into a dry 15 ml centrifuge tube. Centrifuge to clarify the solution and use 2 ml of the clear liquid for colorimetric determination of boron. At the same time as soil extracts are being concentrated in this way, treat 20 ml water (boron-free) in each of six silica basins with 5 ml of standard boron solutions (0, 1, 2, 3, 4 and 5 ppm B respectively), add 5 ml saturated calcium hydroxide and take the solutions through the procedure given for soil extracts. (see Note 5)

When the carmine-borate colours have developed, determine the absorbance or transmittance of light of 585 millimicron wavelength, using the red liquid obtained with 2 ml pure water for the reference solution.

16-6.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard boron solutions against microgram boron (2, 4, 6, 8 and 10).

From this graph, record the microgram boron present in the 2 ml of extract taken for analysis. For the normal procedure (1:2 extraction without concentration), this is equal to the concentration of boron in the soil in ppm B on an oven-dry basis.

If the 1:2 extract has been concentrated five times (as above), divide the number of micrograms of boron by 5 to obtain ppm B in the soil.

16-6.F. NOTES.

(1) The extracting solution and reagents used for the concentration of the extract should be prepared with boron-free water. This is best made by deionization and stored in polythene bottles. Similarly, the reagents should be stored in polythene or soda glass bottles. (Note - the standard boron solutions should not be kept in polythene bottles: see IV.14.C.)

The dilutions of 1 N magnesium chloride and 5 N hydrochloric acid should only be done if the original solutions have been kept in boron-free bottles.

(2) With the narrow ratio of 1:2, moisture in the air-dry soil can affect the procedure markedly. (see III.12.B.(ii) and III.12.B.(1)) Thus, for an air-dry soil with 10 g water per 100 g oven-dry soil, 27.5 g of air-dry sample must be weighed and 47.5 ml of extractant must be added. There is no need to allow for the dilution effect of the water on the solution because the magnesium chloride is only present to act as a flocculant. If the soil is sufficiently saline, water alone may be used as extractant.

(3) Air condensers are satisfactory and more suitable for routine work; they may be made from ordinary soda glass tubing fitted into rubber stoppers. (compare III.3.) Water-cooled reflux condensers are usually made from borosilicate glass and these are unsuitable; special ones made from boron-free glass must be obtained.

(4) If the soil contains particles of undecomposed organic matter, filtering is advisable even after centrifugation; thus filtering is often easier.

(5) Alkali soils may give coloured extracts containing soluble organic matter. It is then necessary to evaporate an aliquot to dryness with calcium hydroxide and ignite gently (not above 450°C - to prevent volatilization of borate) to destroy organic matter. The residue is taken up in a volume of 0.5 N hydrochloric acid to give a five times concentration of the extract; and, if this is too concentrated, (alkali soils may contain more borate) the solution can be diluted.

(6) Soils from arid regions may contain more than 10 ppm B. Then a wider ratio (e.g. 1:5) may be used for extraction, although this may affect the relative amount of borate ion dissolved.

(7) Alternative methods of extraction are to add boiling water to the soil and shake; to subject soil to a continuous extraction process (similar to a Soxhlett procedure); and to repeat the boiling treatment a number of times, finally making the cooled extract to a definite volume. All these methods are longer and some may be less precise; but they may be adopted if preferred. Also, water alone may be used for extraction and the suspension flocculated after cooling by the addition of a few crystals of magnesium or calcium chloride.

Other colorimetric methods for the determination of borate ion may of course be employed; that using 1:1 dianthrimide is more sensitive and may be suitable for deficiency levels of boron without

concentration of extract.

16-6.G. REFERENCES.

BLACK. Chapter 75. (J.I. WEAR)

BOLTZ. Chapter XI. (II.B). (G. PORTER and R.C. SHUBERT)

CHAPMAN and PRATT. Sections 6-2 and 26-15.

JACKSON. Chapter 14. Sections 14-35 to 14-50.

RICHARDS. Chapter 8, Method 73(b).

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SECTION IV

ANALYSIS OF WATERS AND WATER EXTRACTS OF SOILS

INTRODUCTORY NOTE

These analyses are primarily selected for assessment of the suitability of river, well and ground waters for irrigation and storage in reservoirs. Analysis IV.1 must be done on the water sample in its natural state; and analyses IV.2, 3, 11-2 and 13 may all be done on turbid samples of water, if necessary. Other analyses require water samples completely clear of insoluble matter.

Analyses IV.3 to IV.11 provide information on the main water soluble salts in saline or alkali soils, when carried out on clear water extracts.

IV. 1. INSOLUBLE MATTER IN WATER

1.A. PRINCIPLE

This determination is only carried out on samples of natural water, in which "insoluble matter" usually consists of fine particles on clay and silt, less than 50 micron in diameter; but some water samples may contain sand particles, greater than 50 micron in diameter, which settle fairly rapidly. If the water contains only a small amount of total soluble salts or much sodium in relation to calcium, clay particles may be deflocculated and remain in suspension for long periods and pass through filters.

Thus, while simple filtration may effectively separate soluble and insoluble matter in many cases, some samples can only be analysed satisfactorily by sub-sampling and evaporation. If such samples also contain sand particles, these are separated on a 50-micron sieve before sub-sampling, as it is very difficult to take an accurate sub-sample from a water containing sand.

Two procedures are therefore presented, the choice of which to use depending on the nature of the insoluble matter; it is assumed in these procedures that a chemical analysis of the sample is also required.

1.B. APPARATUS.

Measuring cylinders, 250, 500 and 1000 ml
Crucibles, glass, with fritted glass discs, porosity 4 (fine), 30-40 ml
Filter flasks, 1000 ml, with adapters for crucibles
Vacuum pump
ASTM standard sieves No 325, 3-inch diameter (see Note 1)
Beakers, various sizes and watch glasses, various sizes
Glass rods fitted with rubber 'policemen' or small stoppers
Small brushes
Special sampling apparatus (see Appendix 9)
Evaporating basins, capacity 25 and 75 ml
Water bath
Drying oven
Desiccator
Analytical balance, accurate to 1 mg

1.C. PROCEDURES.

Shake the water sample, pour rapidly into a dry 1000 ml cylinder and record the volume to the nearest 5 ml. If the sample volume is greater than 1000 ml, use a second cylinder of appropriate size.

(a) Analysis of waters containing flocculated clay, with or without other material.

Filter the sample by suction through a tared crucible fitted with a fritted glass disc fine enough to retain the solid particles, collecting the filtrate in a dry filter flask. After separation, remove the flask and reserve the clear liquid for subsequent chemical analysis.

Reconnect the filter flask and crucible, transfer any remaining solid from the cylinder(s) to the crucible and wash the insoluble matter free of salts, taking care that clay particles are not dispersed as salts are removed. Dry the crucible at 105°C for a few hours, cool in a desiccator and weigh to the nearest 0.02 g.

(b) Analysis of waters containing dispersed clay, with or without other material.

Mix the sample thoroughly and pour it through an ASTM No 325 sieve, collecting the liquid in a large beaker. If any residue is left in the cylinder(s), transfer some of the liquid which has passed through the sieve back to the cylinder(s), shake to mix the residue and pour rapidly through the sieve again (see Note 2). Drain the sieve into the liquid but do not wash the material on it; then place it on a watch glass and dry at 105°C for about one hour. Transfer all the solid particles from the sieve and watch glass to a small tared basin, cleaning the sieve surfaces with a soft brush. Dry at 105°C for a few hours, cool in a desiccator and weigh to the nearest 0.02 g.

Stir the liquid which has passed through the sieve and transfer about 500 ml to 600 ml beaker as rapidly as possible. Using the special sampling apparatus (see Appendix 9), transfer 50 ml to a tared basin and evaporate to dryness on a water bath. Dry the residue at 105°C for a few hours, cool in a desiccator and weigh to the nearest 0.001 g.

1.D. CALCULATIONS.

Let

V be the volume in ml of the whole sample

(a) Analysis of waters containing flocculated clay.

Let

M be the weight in gram of insoluble matter

Then, the concentration of insoluble matter is

$$\frac{1000\ M}{V} \text{ gram per litre}$$

(b) Analysis of waters containing dispersed clay.

Let

M be the weight in gram of the material not passing the sieve

W be the weight in gram of the residue from 50 ml of liquid passing the sieve

S be the weight in gram of soluble salts per litre of water, either assessed from the conductivity value (see Appendix 10) or calculated from the full chemical analysis (see III.6 and IV.3)

Then, the concentration of material not passing the sieve is

$$\frac{1000\ M}{V} \text{ gram per litre}$$

and the concentration of material passing the sieve is

$$20\ W \text{ gram per litre}$$

but this concentration includes soluble salts

Thus, the concentration of total insoluble matter is

$$\left(\frac{1000\ M}{V} + 20\ W - S \right) \text{ gram per litre}$$

1.E. NOTES.

(1) It is not essential to use a standard sieve and any sieve near the aperture size of the ASTM No 225 (44 micron square) may be used. Whichever sieve is chosen, the relative amounts of insoluble matter in the "sand" and "silt+clay" classes may be of interest.

(2) The procedure given for separating "sand" is accurate enough for most purposes. If it is felt that too much material is left in the cylinder (usually because it consists of larger sand particles), this may be washed out into a tared basin, the water evaporated (it may be possible to decant some) and the residue weight added to the weight of the material from the sieve. Such samples may also tend to leave sand particles behind in the original sampling bottle when the volume is measured and these may also be treated in the same way.

The material not passing the sieve may contain fibrous organic matter. This is usually of negligible weight but if there is considerable bulk, the fraction may be gently ignited to destroy the organic matter before weighing.

(3) Water samples containing dispersed clay are difficult to clarify for chemical analysis (by methods numbered 4 onwards in this section) unless very fine filter candles or very high speed centrifugation is available. The water may be shaken with pure barium sulphate and perhaps activated carbon and then filtered by suction through a fine medium; or it may be left to stand for some days, with a little thymol in it to prevent chemical changes, when slow flocculation may occur (see III.6.). It may be mentioned that clarification is not necessary for methods 11-2 and 13.

(4) When full chemical analysis is not required, a water sample containing dispersed clay may (after determination of pH and conductivity) be treated with saturated calcium sulphate solution to flocculate the clay and then examined for insoluble matter by method 1.C.(a) above.

(5) The accuracy of weighing specified produces a final figure to the nearest 0.02 gram per litre, which is suitable for most purposes.

1.F. REFERENCE.

OLTMAN, (Report paper)

IV. 2. pH VALUE

2.A. PRINCIPLE.

The pH value is measured electronically on a direct-direct-reading pH meter, using a glass electrode with a saturated potassium chloride - calomel reference electrode.

2.B. APPARATUS.

Beakers, 100 ml
pH meter
Glass electrode
Reference electrode, saturated potassium chloride - calomel
Wash bottle, plastic

2.C. REAGENTS.

Potassium hydrogen phthalate, 0.05 M
Potassium dihydrogen phosphate + Disodium hydrogen phosphate, each 0.025 M
Sodium borate, 0.01 M

Prepare these three buffer solutions as described in Section III.1.

2.D. PROCEDURE.

Calibrate the pH meter with phthalate and phosphate buffer solutions according to the maker's instructions and wash the electrodes well. Transfer about 50 ml water or water extract of soil to a 100 ml beaker and insert the electrodes. Switch the meter to pH reading and record the pH value to the nearest 0.1 unit.

If values above 8.5 are obtained, check the performance of the meter in this range with borate buffer solution. (see IV.8.)

2.E. NOTES.

(1) If ample amount of water or water extract is available, discard the sample used for pH determination as it may be affected by slight leakage from some types of saturated potassium chloride - calomel reference electrodes. If there is a limited supply of liquid for analysis, determine conductivity first, then pH; the same sample may subsequently be used for cation-anion analyses except potassium and chloride.

(2) Keep the glass electrode in water when not in use and ensure that the reference electrode always contains saturated potassium chloride solution in contact with solid potassium chloride crystals.

(3) The correct pH values of the buffer solutions at normal room temperatures are given in Appendix 5.

2.F. REFERENCES.

BATES. Chapters 5, 9, 10 and 11.

STROUTS. Vol. II, chapter 17.

VOGEL. Chapter XVI, Sections XVI.1 and XVI.2

IV. 3. CONDUCTIVITY

3.A. PRINCIPLE.

If a liquid fills a cube of 1 cm sides, the conductivity between two opposite faces is the specific conductivity, which increases according to the concentration of ions in the liquid and varies also with the nature of these ions. In its measurement, a high-frequency alternating voltage is applied by a conductivity meter to two electrodes placed at a fixed distance apart and having a sample of the liquid between them. The electrodes may be of bright platinum, platinum coated with platinum black or graphite; they are usually sealed into an open glass or plastic tube which may be dipped into the liquid or used as a pipette. The re istance across the electrodes is recorded by the meter, which is normally calibrated in micromhos.

The conductivity value obtained is adjusted to a standard temperature of 25°C, it is usually reported in micromhos for natural water samples and in millimhos for water extracts of soil.

3.B. APPARATUS.

Beakers, 50 or 100 ml
Conductivity meter
Conductivity cell, pipette type or dip type
Thermometer, covering room temperatures

3.C. REAGENTS.

Potassium chloride, 0.050 N
Dissolve 3.728 g dry potassium chloride to 1 litre

Potassium chloride, 0.010 N
Dilute 50 ml 0.050 N solution to 250 ml

Potassium chloride, 0.005 N
Dilute 25 ml 0.050 N solution to 250 ml

Potassium chloride, 0.002 N
Dilute 50 ml 0.010 N solution to 250 ml

3.D. PROCEDURE.

Transfer a little water or water extract of soil to a suitable small beaker. If a pipette type conductivity cell is used, rinse this with some of the sample and then fill it; if a dip type cell is used, make sure this is dry and insert it in the sample so that the electrodes are fully covered. Obtain a scale reading on the conductivity meter, according to the maker's instructions; and record the temperature of the sample.

Check the cell constant and meter performance by obtaining scale readings for each of the standard potassium chloride solutions, which cover the values to be expected for waters and water extracts of soil.
(see Note 2)

3.E. CALCULATIONS.

(a) Cell constant and meter performance.

Most conductivity meters have a logarithmic scale marked in micromhos and also a range switch giving a number of multiplication factors which are powers of 10, so that the meter can measure specific conductivities from about 1 to 100,000 or 1,000,000 micromhos.

Let

S be the scale reading in micromhos obtained with a standard potassium chloride solution

R be the range or multiplication factor

C be the cell constant

M be the published conductivity value in micromhos of the standard potassium chloride solution, at the temperature of reading. (see Appendix 7)

Then, ... or $C = \frac{M}{SR}$ (see Note 2)

(b) C ...ctivity of water or water extract of soil

Let

S, R and C have the meanings given in (a)

t be the temperature of reading in degrees Centigrade

F be the temperature factor (see Appendix 8)

Then, the conductivity of the sample at $t^{o}C$ = SRC micromhos

Thus, the conductivity of the sample at $25^{o}C$ = SRCF micromhos

3.F. NOTES.

(1) As the scales of conductivity meters are divided logarithmically, the absolute accuracy with which readings can be taken becomes less as the values increase from 1 to 10. In general, results should be recorded only to about 2 to 5 per cent of the value obtained, depending on the scale reading.

(2) The cell constant is usually an integer (1, 2, 5 or 10) which is reported and claimed to be correct by the maker. Occasionally, a cell or a meter may have a slight error and the presence of such an error must be established and allowed for in calculations.

(3) If the cell constant (calculated as in 3.E.(a) above and so including any instrument error) is found to be other than an integral value, it is advisable to prepare a table relating scale readings (left-hand column) and range or multiplication factors (other column headings) to conductivity values in micromhos or millimhos at $t^{o}C$, recording these values with the possible degree of accuracy. A further table may relate conductivity values at $t^{o}C$ (left-hand column) and various values of t (other column headings) to the conductivity values at $25^{o}C$. again recording these values with the possible degree of accuracy.

These tables, once prepared, save a good deal of time in routine work and ensure that results are recorded with consistent accuracy. They are useful even if the cell constant has an integral value.

(4) Most natural waters contain mainly bicarbonates and sulphates of calcium and magnesium, with small amounts of sodium, potassium and chloride and traces of nitrates. In general, a conductivity value of 1000 micromhos corresponds to about 10 milliequivalents per litre total salts or about 0.70 g per litre (700 ppm), based on an average equivalent weight of 70 for the predominant salts. (see Section III.6.F.(5)) Using this relation, table A of Appendix 10 has been constructed, for use in determination IV.1. when no quantitative cation-anion analysis is available and simple qualitative tests have shown that sodium and chloride are low or absent.

(5) Saline waters contain moderate to high amounts of sodium and chloride but also usually contain the bicarbonates and sulphates of calcium and magnesium, with small amounts of potassium and traces of nitrates. For these, a conductivity value of 1000 micromhos corresponds to about 9.0 - 9.5 milliequivalents per litre total salts or about 0.60 g per litre (600 ppm), based on an average equivalent weight of 64 for the mixed salts. (see also Section III.6.F.(5)) Using this relation, table B of Appendix 10 has been constructed, for use in determination IV.1. when no quantitative cation-anion analysis is available and simple qualitative tests have shown that sodium and chloride are moderate to high.

(6) Relationships between conductivity and soluble salts for water extracts of soils are discussed in Section III.6.

(7) Conductivity values may be reported more precisely, if desired, as "specific conductivity in micromhos (millimhos) at 25°C" or as "conductivity in micromhos (millimhos) per cm at 25°C". Instead of conductivity, the word "conductance" or the abbreviation "EC" (i.e. electrical conductivity or conductance) may be used.

3.G. REFERENCES.

JACKSON. Chapter 10, Sections 10-18 to 10-24 and 10-33 to 10-41.

RICHARDS. Chapter 8. Method 72.

STROUTS. Vol. II, Chapter 19.

VOGEL. Chapter XVII, Sections XVII.1 and XVII.2.

IV. 4: CALCIUM PLUS MAGNESIUM

4.A. PRINCIPLE

At an optimum pH of 10.0 the ethylenediaminetetraacetate ion (EDTA) forms soluble complexes with calcium and magnesium ions, thus removing them from solution without precipitation. The reaction is stoichiometric and essentially instantaneous at temperatures near 60°C and the complexes formed are very stable. At the same pH the dye eriochrome blue-black B has a turquoise blue colour in the absence of calcium and magnesium ions but forms red compounds with them which are less stable than the EDTA-Ca and EDTA-Mg complexes.

Thus, if a buffer solution is added to a solution containing calcium and magnesium ions (or either separately) so that a pH of about 10 is produced and then eriochrome blue-black B is added, a red colour is formed. If EDTA is then slowly added, the calcium and magnesium ions are gradually transferred from the dye complexes to the more stable EDTA complexes until, when all have been transferred, the red colours of the dye complexes give way to the pure turquoise blue of the dye itself. This colour change is not very sharp if calcium only is present but it is much improved by the presence of magnesium, even if this is in the EDTA-Mg form; a small amount of EDTA-Mg complex is therefore added (by incorporation in the buffer solution) to promote a sharper colour change, in cases where magnesium is very low or absent in the solutions being analysed.

Many other metals interfere in this determination and those which may sometimes be present in natural waters and water extracts of soils in sufficient amount to cause trouble are zinc, manganese, copper and iron. Zinc and manganese (Mn^{2+}) are complexed by EDTA and do not affect the eriochrome blue-black B so that they are titrated if present, leading to erroneously high results for the calcium plus magnesium analyses. Manganese (Mn^{4+}) and iron (Fe^{3+}) oxidize eriochrome blue-black B, causing the colour to fade rapidly: iron (Fe^{2+}), however, forms a complex with EDTA which is very unstable and hence does not sensibly interfere. Copper forms a very stable complex (red) with eriochrome blue-black which is not affected by EDTA and this makes the titration of other metals impossible.

These metal interferences may be stopped by the addition of three reagents. First, a reducing agent (hydroxylamine or ascorbic acid) is added to reduce iron and manganese; second, potassium cyanide is used to form the unionized and very stable cyanides or copper and zinc (it also complexes iron (Fe^{2+}) as ferrocyanide); third, excess potassium ferrocyanide is added to precipitate manganese ferrocyanide. Addition of all these reagents may not always be necessary but it is advisable to include them as a precautionary measure; certainly, cyanide improves the titration end-point, making the colours brighter and the change to turquoise blue sharper.

4.B. APPARATUS.

Pipettes, 10, 20 and 50 ml, as required for aliquots
Dispensing burettes, 10, 25 or 50 ml, with 0.1 ml divisions
Measuring cylinder, 50 ml
Erlenmeyer flasks, 250 ml
Spatula

Electric hot plate; or gas burner, tripod and gauze
Thermometer, 0-100°C
Interval timer
Graduated pipette, 1 ml, with 0.1 ml divisions
Burette, 25 ml, with 0.05 ml divisions

4.C. REAGENTS.

Hydroxylamine hydrochloride (hydroxy-ammonium chloride) or ascorbic acid - both in solid form

Potassium cyanide, 2 per cent (see Note 1)

Potassium ferrocyanide, 2 per cent
Make enough for a few days only and keep cool

thanolamine buffer solution, incorporating EDTA-Mg complex
Dilute 250 ml concentrated hydrochloric acid to about 1 litre and carefully add 620 ml ethanolamine (2-hydroxyethylamine, sp.gr. 1.017) with constant stirring. Allow to cool.
Titrate 50 ml 0.02 N magnesium chloride with 0.02 N EDTA, recording the exact volume (V ml) needed. Prepare EDTA-Mg complex by adding 2V ml 0.02 N EDTA to 100 ml 0.02 N magnesium chloride.
Add the EDTA-Mg complex solution to the ethanolamine hydrochloride and dilute to 2 litres. (see Note 2)

Eriochrome blue-black B, 0.5 per cent in ethanol (see Note 2)

Ethylenediaminetetraacetic acid. disodium salt, 0.020 N
Dry the disodium salt of ethylenediaminetetraacetic acid (EDTA - $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$) at 80°C for about two hours and cool in a desiccator. Dissolve 7.4450 g to 2 litres, using water of very low conductivity.

Magnesium chloride, 0.02 N
Dissolve 4.1 - 4.2 g magnesium chloride, $MgCl_2.6H_2O$, to 2 litres. Standardize by titration with 0.020 N EDTA and dilute to 0.02 N exactly. (The initial solution may be used for preparation of the EDTA-Mg complex needed for the buffer solution)

4.D. PROCEDURE.

Transfer a suitable aliquot of the water sample or water extract of soil (see Note 3) to a 250 ml Erlenmeyer flask and make the volume to about 50 ml with water. Add a few crystals of hydroxylamine hydrochloride (or ascorbic acid), 1 ml of 2 per cent potassium cyanide (from a burette), 1 ml of 2 per cent potassium ferrocyanide and 5 ml of ethanolamine buffer (see Note 4). Warm to about 60°C (see Note 5), add 0.2 2 ml eriochrome blue-black B and titrate with 0.020 N EDTA to a pure turquoise blue without any trace of red.

Before carrying out a batch of determinations, titrate 20 ml 0.02 N magnesium chloride with 0.020 N EDTA in order to check the EDTA concentration and provide a pure blue standard for use in the subsequent titrations. It should be possible to titrate and record to the nearest 0.05 ml.

4.E. CALCULATIONS.

Let

V be the volume in ml of the aliquot taken for analysis

T be the volume in ml of 0.020 N EDTA used in the titration

Since 1 ml 0.020 N EDTA complexes 0.02 milliequivalent calcium plus magnesium, T ml complexes (0.02 x T) milliequivalent and this is the amount of calcium plus magnesium in V ml of sample.

Thus, the concentration of calcium plus magnesium in the water or water extract of soil is

$$\frac{0.02 \times T \times 1000}{V} = \frac{20\ T}{V}$$ milliequivalent per litre

4.F. NOTES.

(1) Extreme care should be taken in the handling of potassium cyanide. All solutions containing it must be discarded immediately after a batch of analyses is finished and all apparatus thoroughly washed. The drains must be well flushed and no acid allowed to come into contact with the cyanide solutions.

(2) The more common ammonia - ammonium chloride buffer and eriochrome black T (see references) may be used if preferred. The ethanolamine buffer advocated has no smell; and eriochrome blue-black B is stable in solution for some weeks, whereas eriochrome black T must be used in solid form to give good colours.

Eriochrome blue-black B is sodium 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulphonate; eriochrome black T contains a nitro group in addition and is sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate.

(3) Where there is plenty of sample, 50 ml of a natural water is a suitable aliquot for this determination. For water extracts of soils (other than the saturation extract), 20 ml is about right, though 10 ml is better for gypsiferous soils.

(4) Add 5 ml buffer to 50 ml water and read the pH, which should be 10.0 ± 0.1. Adjust the volume of buffer or its original preparation if necessary (samples of ethanolamine may vary and need more or less hydrochloric acid). It is unlikely that variations in the salt concentrations in waters or water extracts of soil will affect the functioning of the buffer.

The buffer may be added before the other reagents without any effect on their reactions with interfering metals.

(5) Preliminary tests with about 55 ml water and a thermometer will establish the length of time (say, about 2 minutes) needed to bring this volume of liquid to near 60°C. In routine work, timing is more convenient than temperature measurement for each solution.

(6) Atomic absorption spectrophotometry may be used to determine Ca and Mg separately, if the apparatus is available. (Appendix 11.)

4.G. REFERENCES.

BLACK. Chapter 62, Section 62-3.2. (C.A. BOWER and L.V. WILCOX
Chapter 68, Sections 68-2.3 and 68-3. (W.R. HEALD)

VOGEL. Chapter IV, Sections IV.13 and IV.19.

WILSON. Vol. I.B, Chapter VII. (9.e.(iv) and 9.e.(v) - H.A. FLASCHKA and A.J. BARNARD JR)
Vol. I.C, Chapter IX. (2.b.(b)(iii) - E. BOOTH)

IV. 5. CALCIUM

5.A. PRINCIPLE.

If a solution containing calcium and magnesium ions is made strongly alkaline (pH about 12), magnesium is selectively precipitated as magnesium hydroxide, although when the amount of magnesium is small no evidence of a precipitate is seen. At the same pH, the dye 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (referred to as HHSNN or Patton and Reeder's indicator) forms a red compound with calcium ions but is not affected by magnesium present as magnesium hydroxide. As with eriochrome dyes, the colour of HHSNN in alkaline solution in the absence of calcium ions is turquoise blue; also, the HHSNN-Ca complex is less stable than EDTA-Ca complex.

Thus, if a natural water or a water extract of a soil is made strongly alkaline and treated with HHSNN, a red colour develops by reaction of the dye with calcium ions. If EDTA is then slowly added, the calcium ions are gradually transferred from the dye complex to the more stable EDTA complex, until, when all have been transferred, the liquid acquires a pure turquoise blue colour. The reaction is virtually instantaneous at normal room temperatures.

Interferences from zinc, manganese, copper and iron are similar to those found for the calcium plus magnesium determination (IV.4,) and the same means of stopping the interferences are adopted.

5.B. APPARATUS.

Pipettes, 10, 20 and 50 ml, as required for aliquots
Dispensing burettes, 10, 25 or 50 ml, with 0.1 ml divisions
Measuring cylinder, 50 ml
Erlenmeyer flasks, 250 ml
Spatulas
Burette, 25 ml, with 0.05 ml divisions

5.C. REAGENTS.

Hydroxylamine hydrochloride (or ascorbic acid), potassium cyanide and potassium ferrocyanide, as used in determination IV.4.

Potassium hydroxide, 8 N

HHSNN indicator mixture
Mix 1 g HHSNN intimately with 100 g anhydrous sodium sulphate.
Store in a dark bottle away from light.

Ethylenediaminetetraacetic acid, disodium salt, 0.020 N
Prepare as described in determination IV.4.

Calcium chloride, 0.020 N
Dissolve 1.001 g calcium carbonate in 25 ml of 1 N hydrochloric acid and neutralize the excess acid with ammonia (bring the pH to near 5, using indicator paper). Dilute to 1 litre.

5.D. PROCEDURE

Transfer a suitable aliquot of the water sample or water extract of soil (see Note 1) to a 250 ml Erlenmeyer flask and make the volume to about 50 ml with water. Add a few crystals of hydroxylamine hydrochloride (or ascorbic acid), 1 ml of 2 per cent potassium cyanide (from a burette) and 1 ml of 2 per cent potassium ferrocyanide. Wait a few minutes (see Note 2), then add 4 ml 8 N potassium hydroxide and a spatula point of HHSNN indicator mixture. Titrate with 0.020 N EDTA to a pure turquoise blue without any trace of red.

Before carrying out a batch of determinations, titrate 20 ml 0.02 N calcium chloride (a little 0.02 N magnesium chloride may be added) with 0.020 N EDTA in order to check the EDTA concentration. It should be possible to titrate and record to the nearest 0.05 ml.

5.E. CALCULATIONS.

Let

V be the volume in ml of the aliquot taken for analysis

T be the volume in ml of 0.020 N EDTA used in the titration

Then, as in the determination of calcium plus magnesium, the concentration of calcium in the water or water extract of soil is

$$\frac{20\ T}{V} \text{ milliequivalent per litre}$$

5.F. NOTES.

(1) See Note 3 in determination IV.4.

(2) Manganese ferrocyanide forms a little slowly at normal room temperatures and it is advisable to wait after adding the potassium ferrocyanide. In analysis IV.4. the solution is warmed at this stage and the manganese ferrocyanide forms quickly at the higher temperature.

(3) The HHSNN colour sometimes tends to fade rather quickly and a permanent blue standard cannot normally be used for matching. If HHSNN is not available, murexide may be used, although the colour change is much less satisfactory. Mix 0.2 g murexide with 40 g dry potassium sulphate powder and store in a dark bottle away from light.

(4) To obtain the concentration of magnesium in the water or water extract of soil, subtract the calcium analysis from the Ca + Mg analysis result (IV.4.)

(5) Atomic absorption spectrophotometry may be used to determine calcium and magnesium (separately), if the apparatus is available (Append. 11)

5.G. REFERENCES.

BLACK. Chapter 62, Section 62-3.2. (C.A. BOWER and L.V. WILCOX)
Chapter 68, Sections 68-2.3 and 68-3. (W.R. HEALD)

VOGEL. Chapter IV, Section IV.19.

WILSON. Vol.I.C, Chapter IX. (2.c. Calcium.(d)) - H. THOMAS

IV. 6. SODIUM

6.A. PRINCIPLE.

Sodium is readily excited in a flame, producing an intense yellow light. This colour is mainly due to radiation of 589.6 millimicron wavelength, commonly known as the D-line of sodium. Although other radiations of different wavelengths are emitted, these are less powerful and they may be blocked by a suitable yellow glass (sodium filter) which effectively allows only the D-line emission to pass through.

If a solution containing sodium ions is fed, as a fine spray, into a flame under controlled and standard conditions and the emitted light is passed through a sodium filter, the intensity of the D-line emission may be measured photoelectrically and related to the concentration of sodium in the original solution. The flame photometer used for such measurements may be calibrated with a series of standard sodium chloride solutions and then used to find the sodium concentration of a solution under analysis, within the same range. For a particular instrument and type of flame, there may be interference effects from some of the other cations and anions present in the solution and these effects must be studied and either suppressed or measured.

In the analysis of natural waters and water extracts of soils, the only ion which may cause serious interference to sodium measurements is calcium; in some types of flames, this tends to enhance the sodium emission and the effect may be measured for a range of calcium concentrations or calcium:sodium ratios and appropriate corrections applied or the interference may be neutralized by the addition of aluminium ion, usually as aluminium nitrate.

Since sodium is easily excited, very small concentrations can be measured by flame photometry and a solution containing 5 ppm sodium (about 0.2 milliequivalent per litre) can give a full scale reading with many instruments when these are set at maximum sensitivity; and under these conditions a linear relation normally exists between concentration of sodium and intensity of the D-line emission. However, by decreasing the sensitivity, the photometer may usually be made to function satisfactorily and accurately over the range 0 - 0.5 or 0 - 1.0 milliequivalent per litre, although saturation of the flame at the higher levels may cause the concentration - emission graph to become non-linear.

6.B. APPARATUS.

Flame photometer, with sodium filter
Small beakers or sample holders
Pipettes and volumetric flasks, as required for dilutions, tests of interference effects and possible additions of aluminium solution

6.C REAGENTS.

Sodium chloride, 0.050 N
Dissolve 1.4612 g dry sodium chloride to 500 ml

Sodium chloride, working standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre
Dilute 2, 4, 6, 8 and 10 ml 0.050 N solution each to 1 litre (see Note 1)

Saturated calcium sulphate, approximately 0.030 N
Shake about 20 g calcium sulphate, $CaSO_4.2H_2O$, with 5 litres water at intervals for some hours and filter.

Aluminium nitrate, 0.5 N
Dissolve 62.5 g aluminium nitrate, $Al(NO_3)_3.9H_2O$, to 1 litre.

6.D. PROCEDURE.

(a) Interference effects.

Study the literature supplied with the flame photometer to be used and note if interference effects are possible from calcium, magnesium, potassium, sulphate, bicarbonate and carbonate at the highest levels to be expected in natural waters and water extracts of soils. Make a preliminary study of the actual effects, where these are likely, by preparing sodium standard solutions containing a possible interfering ion (see Note 2) and comparing the flame photometer scale readings obtained from these solutions with those obtained from the pure sodium standard solutions. When a measurable effect is produced, either test if this effect can be neutralized (see example below) or study the effect at various ratios of interfering ion to sodium, so that a correction can be applied to solutions under analysis.

Example - effect of calcium.

As already noted, this cation tends to enhance the sodium emission in many types of flame photometer and in water extracts of some soils it may be present, mainly as sulphate, in a much higher concentration than sodium. For instance, water extracts of gypsiferous soils can contain up to 30-32 milliequivalents per litre of calcium while the sodium level may be less than 1 milliequivalent per litre; and in studies of the effects of application of gypsum on saline soils, water extracts may contain calcium and sodium in a wide range of ratios.

Prepare a series of standard sodium chloride solutions containing 0.1 - 0.5 milliequivalents per litre by dilution from 0.050N solution (see 6.C.) but using saturated calcium sulphate solution in place of water. These solutions contain about 30 milliequivalents per litre calcium as sulphate. Calibrate the flame photometer with pure sodium chloride standards (see below), then spray the standards containing calcium sulphate and measure any interference effects. If the effects are serious, make up a pair of sodium standards, each of concentration 0.3 milliequivalents per litre sodium, one containing 500 ml saturated calcium sulphate per litre, the other 500 ml saturated calcium sulphate and 30 ml 0.5 N aluminium nitrate per litre. Also make up a blank solution containing 30 ml 0.5 N aluminium nitrate only per litre. Spray these three solutions to study the effect of addition of aluminium (at the same concentration as calcium, which is known to be correct in some cases) on the interfering effect of calcium on sodium, allowing for any sodium impurity in the aluminium nitrate.

If the aluminium neutralizes or partly neutralizes the calcium effect, make further studies to find the best aluminium:calcium ratio. Alternatively, make a detailed study of the calcium effect on sodium at various calcium:sodium ratios and prepare graphs relating scale readings to sodium concentration at various calcium levels. (see Note 3)

(b) Determination of sodium.

Make a preliminary assessment of the probable sodium concentration in the water sample or water extract of soil from the conductivity value and the calcium-plus-magnesium concentration (see Calculations). If this assessment indicates a sodium concentration outside the range of the sodium standards, make an appropriate dilution. When aluminium is used to neutralize any calcium effect, always make a dilution and incorporate a measured volume of aluminium nitrate solution to give the required aluminium:calcium ratio in the diluted solution.

Bring the flame photometer into use according to the maker's instructions and adjust the gases to the standard type of flame. Spray a standard sodium solution and water alternately and operate the sensitivity control until the standard reads a selected point on the photometer scale and the water reads zero. (see Note 4) Spray the other sodium standard solutions and record the scale readings.

Spray the samples for analysis and record the readings. Check the performance of the photometer at frequent intervals by spraying some of the standard solutions and adjust the sensitivity as necessary.

6.E. CALCULATIONS.

(a) Preliminary assessment of sodium concentration.

Let

C be the conductivity at 25°C in millimhos of the water sample or water extract of soil

X be the concentration in milliequivalents per litre of calcium-plus-magnesium in the same solution, from analysis IV.4.

Then, as a first approximation, the total salt concentration is 10 C milliequivalents per litre and the probable sodium concentration is (10 C - X) milliequivalents per litre.

If (10 C - X) is high in relation to X, a closer approximation for sodium is given by (8 C - X); while, if (10 C - X) is low in relation to X, a closer approximation for sodium is given by (12 C - X)

(the concentration of potassium may be neglected in these calculations)

(b) Determination of sodium concentration.

Prepare a graph relating sodium concentrations in milliequivalents per litre to the photometer scale readings obtained with the standard sodium solutions. From this graph obtain the sodium concentration of the sample under analysis in milliequivalents per litre. If this is a dilution of the original sample, multiply by the appropriate factor.

When calcium affects the sodium emission and it is not neutralized, read off the sodium concentration from a graph relating photometer scale readings to sodium concentrations in the presence of calcium near the level found in the sample under analysis. (see 6.D.(a) above)

6.F. NOTES.

(1) The range of sodium standards suggested may be altered (say, to 0.2, 0.4, 0.6, 0.8 and 1.0 milliequivalents per litre) if this is

more suited to the flame photometer in use and to the samples normally under analysis.

(2) In testing general interference effects, add the cations as chlorides and the anions as soluble salts of a non-interfering cation (e.g. potassium).

(3) The calcium effect on sodium emission produced by the procedure suggested includes any effect due to sulphate. In water extracts of soils, calcium is more likely to be associated with sulphate than with other anions and calcium sulphate solution is therefore used for the tests. In natural waters, calcium may be present more often as bicarbonate as well as sulphate. A saturated calcium bicarbonate solution may be prepared by passing carbon dioxide through a calcium carbonate suspension in water and then filtering; and this may be used (after standardization - see IV.9.) for testing calcium effects on sodium in water samples.

(4) In calibration, it is not obligatory to make the highest sodium standard read the highest point on the scale. It is often more convenient to adjust the sensitivity so that one of the intermediate standards gives a reading about halfway along the photometer scale.

(5) Sodium may be determined also by atomic absorption spectrophotometry, if the apparatus is available. Calcium does not normally interfere in this technique.

6.G. REFERENCES.

BLACK. Chapter 54. (C.I. RICH)

JACKSON. Chapter 18, Sections 18-1 to 18-34.

STROUTS. Vol. II, Chapter 26. (pp.397 to 403)

VOGEL. Chapter XIV

IV. 7. POTASSIUM

7.A. PRINCIPLE.

Potassium, like sodium, is also excited in a flame (though less readily) producing a lilac colour. However, the strongest radiation is in the near infra-red region at a wavelength of 767 millimicron and this is used to measure the potassium emission in a flame photometer by a method similar to that for sodium, using a potassium filter which blocks most radiations in the visible region up to near 750 millimicron wavelength. Interference effects from other cations and anions are usually less serious than with sodium but they must be studied.

The concentration of potassium in natural waters and water extracts of soils is normally very low (mostly less than 1.0 milliequivalent per litre) but calcium, magnesium, sodium, chloride, sulphate and bicarbonate may be much higher. Interference effects from these ions are small with most flame photometers and the only one liable to cause measurable effects is sodium, particularly at the high levels which may be present in water extracts or very saline soils. The sodium effect cannot be neutralized, neither can the sodium ion be removed without affecting the potassium; thus the effect must be measured and a correction applied.

As with sodium, most flame photometers are capable of detecting small concentrations of potassium at maximum sensitivity (about 10 ppm giving a full scale reading) but the sensitivity may be reduced and a satisfactory performance obtained over the range 0 - 0.5 or 0 - 1.0 milliequivalent per litre.

7.B. APPARATUS.

Flame photometer, with potassium filter
Small beakers or sample holders
Pipettes and volumetric flasks, as required for dilutions and tests of interference effects

7.C. REAGENTS

Potassium chloride, 0.50 N
Dissolve 1.864 g dry potassium chloride to 500 ml

Potassium chloride, working standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 milliequivalents per litre
Dilute 2, 4, 6, 8 and 10 ml 0.050 N solution each to 1 litre (see Note 1)

Sodium chloride, 1.0 N
Dissolve 29.2 g sodium chloride to 500 ml

7 D. PROCEDURE.

(a) Interference effects - particularly of sodium.

Prepare a series of standard potassium chloride solutions containing 0.1 - 0.5 milliequivalents per litre by dilution from 0.050 N solution (see 7.C.) but incorporating 50 ml 1.0 N sodium chloride in each. These solutions contain 50 milliequivalents per litre sodium, a concentration which may easily be found in water extracts of saline soils.

Calibrate the flame photometer with pure potassium chloride standards (see below), then spray the standards containing sodium chloride and

measure any interference effects. If these are serious, study the effects of other concentrations of sodium (less than 50 me per litre).

Study also the effects of calcium as sulphate and as bicarbonate by the use of saturated solutions (as given in IV.6.D.). Also, as a precaution, study the effects of magnesium (sulphate) and carbonate (sodium) at the highest levels encountered in analysis.

(b) Determination of potassium.

Bring the flame photometer into use according to the maker's instructions and adjust the gases to the standard type of flame. Spray a standard potassium solution and water alternately and operate the sensitivity controls until the standard reads a selected point on the photometer scale and the water reads zero. (see Note 3) Spray the other potassium standard solutions and record the scale readings.

Spray the samples for analysis and record the readings. Check the performance of the photometer at frequent intervals by spraying some of the standard solutions and adjust the sensitivity as necessary. If the potassium concentration is higher than the top standard, make an appropriate dilution.

7.E. CALCULATIONS.

Prepare a graph relating potassium concentrations in milliequivalents per litre to the photometer scale readings obtained with the standard potassium solutions. From this graph obtain the potassium concentration of the sample under analysis in milliequivalents per litre. If this is a dilution of the original sample, multiply by the appropriate factor.

When sodium affects the potassium emission, read off the potassium concentration from a graph relating photometer scale readings to potassium concentration in the presence of sodium near the level found in the sample under analysis. (see 7.D.(a) above)

7.F. NOTES

(1) The range of potassium standards suggested may be altered (say, to 0.2, 0.4, 0.6, 0.8 and 1.0 milliequivalents per litre) if this is more suited to the flame photometer in use and to the samples normally under analysis.

(2) The sodium effect on potassium emission produced by the procedure suggested includes any effect due to chloride. Sodium is likely to be present in waters and water extracts mainly in the form of sodium chloride but the sodium effect may be tested by using solutions of sodium sulphate if samples low in chloride are being analysed.

(3) In calibration, it is not obligatory to make the highest potassium standard read the highest point on the scale. ((See IV.6.F.(4))

(4) Potassium may be determined also by atomic absorption spectrophotometry if the apparatus is available.

7.G. REFERENCES

BLACK.	Chapter 54. (C.I. RICH)
JACKSON.	Chapter 18, Sections 18-1 to 18-34
STROUTS.	Vol. II, Chapter 26. (pp.397 to 403)
VOGEL.	Chapter XIV.

IV. 8. CARBONATE

8.A. PRINCIPLE

When the pH value of a sample of natural water or water extract of a soil is above 8.4, carbonate ion is present, normally as sodium carbonate. If the sample is titrated with a standard mineral acid to a pH of 8.4, the carbonate ion is converted to bicarbonate -

$$CO_3^{2-} + H^+ = HCO_3^-$$

and the amount of acid used is a measure of the carbonate present. (see IV.9.)

The titration is best carried out potentiometrically; but the end-point may also be assessed by use of the mixed indicator cresol red - thymol blue, which changes from violet at pH 8.8 to yellow at pH 8.0, with a distinctive rose-red hue at pH 8.4. The end-point is judged in the titration with indicator by matching the colour to that of the same volume of buffer solution at pH 8.4 containing the same amount of indicator.

Standard hydrochloric acid is used because sulphuric acid may give rise to turbidity from calcium sulphate with calcium-rich samples.

8.B. APPARATUS .

Pipettes, 10, 20 or 50 ml, as required for aliquots
Burette, 10 or 25 ml, with 0.05 ml divisions

Plus, either, for potentiometric titration -

Beakers, 50 or 100 ml
pH meter and electrodes (see III.1 or IV.2.)
Magnetic stirrer and followers

or, for indicator titration -

Erlenmeyer flasks, 100 or 200 ml
Graduated pipette, 1 ml, with 0.01 ml divisions

8.C. REAGENTS

Hydrochloric acid, 0.020 N
Boric acid - sodium borate buffer, pH 8.4
Dissolve 6.1845 g boric acid and 7.4555 g potassium chloride to 500 ml. Mix 25 ml of this solution with 4.3 ml of 0.2 N sodium hydroxide and dilute to 100 ml. Check the pH value and adjust if necessary.
Cresol red - thymol blue indicator
Dissolve 0.025 g cresol red and 0.075 g thymol blue in 100 ml of ethanol.

8.D. PROCEDURES.

(a) Potentiometric titration.

Transfer a suitable aliquot of natural water or water extract of soil

(see Note 1) to a small beaker, place on the platform of a magnetic stirrer and insert a "follower". Calibrate the pH meter with phosphate and borate buffers (see III.1.) and then insert the electrodes in the sample for analysis. With the pH meter switched on, start the stirrer and add 0.020 N hydrochloric acid drop by drop until the pH falls to 8.4. Stop the stirrer and check the pH, adding more acid and stirring again if necessary (see Note 2). Record the volume of acid needed.

(b) Indicator titration.

Transfer a suitable aliquot of sample (see Note 1) to a 100 or 200 ml Erlenmeyer flask and add 0.2 - 0.4 ml cresol red - thymol blue indicator according to preference. Transfer to a similarly sized flask a volume of buffer solution (pH 8.4) equal to the sample aliquot taken and add a volume of indicator equal to that added to the sample. Titrate the sample with 0.020 N hydrochloric acid until the colour matches the colour of the buffer solution, under the same lighting conditions. (see Note 3) Record the volume of acid needed.

8.E. CALCULATIONS.

Let

V be the volume in ml of the aliquot taken for analysis

T be the volume in ml of 0.020 N acid needed in the titration

Since the carbonate is converted just to bicarbonate, it is only half neutralized and full neutralization would need 2T ml of acid.

Thus, the volume V ml of sample contains (2T x 0.02) milliequivalent of carbonate and the concentration is

$$\frac{40\ T}{V}$$ milliequivalent per litre

8.F. NOTES.

(1) For natural waters, 50 ml is a suitable aliquot since the carbonate concentration is normally low. Soils containing sodium carbonate are difficult to extract with water since clay is deflocculated and organic matter is partially soluble; thus the volume of colourless clear water extract obtainable is often small and rarely is it possible to take 50 ml for this determination. 20 ml or 10 ml must be used, even though this may give only very low titrations. Small aliquots may be diluted to provide sufficient liquid to cover the electrodes (in potentiometric titration) without sensibly affecting the pH value, althouth it is better to use micro-electrodes if these are available.

(2) pH values may be affected by the stirring motion and they should be checked when the liquid is still.

(3) Carbonate concentrations are normally low and colour matching in the indicator titration is not affected by the dilution due to the small amount of added acid.

8.G. REFERENCES.

BLACK. Chapter 62, Section 62-3.4. (C.A. BOWER and L.V. WILCOX)

JACKSON. Chapter 10, Section 10-87 to 10-93.

KOLTHOFF and STENGER. Chapter IV, Section IV.5. (pp. 131 to 133)

VOGEL. Chapter III, Section III.15.

WILSON. Vol. I.B. Chapter VII. (4.f.(vii) - C. AYERS)

IV. 9. BICARBONATE

9.A. PRINCIPLE.

Bicarbonate ion reacts with mineral acid and releases carbon dioxide into the solution -

$$HCO_3^- + H^+ = H_2O + CO_2$$

the pH value at complete neutralization being about 3.8. Thus, bicarbonate may be measured by titration with mineral acid to a pH of 3.8, either potentiometrically or using an indicator unaffected by carbon dioxide. Methyl orange is suitable and, if screened with a blue dye such as indigo carmine or xylene cyanol FF, gives a good colour change from green through grey (end-point) to red, which obviates the need for a matching buffer solution.

If carbonate is present, it also reacts with the acid but the amount of acid reacting with the bicarbonate only can be calculated. As in the determination of carbonate, standard hydrochloric acid is used in preference to sulphuric acid.

9.B. APPARATUS

Pipettes, 20 or 50 ml, as required for aliquots
Burette, 10 or 25 ml, with 0.05 ml divisions

Plus, either, for potentiometric titration -

Beakers, 50 or 100 ml
pH meter and electrodes (see III.1.or IV.2.)
Magnetic stirrer and followers

or, for indicator titration -

Erlenmeyer flasks, 100 or 200 ml
Graduated pipette, 1 ml, with 0.01 ml divisions

9.C. REAGENTS.

Hydrochloric acid, 0.020 N
Screened methyl orange
Dissolve 0.05 g methyl orange and 0.125 g indigo carmine in 100 ml water or
Dissolve 0.1 g methyl orange and 0.14 g xylene cyanol FF in 100 ml of 50 per cent ethanol - water.

9.D. PROCEDURES.

(a) Potentiometric titration.

Transfer a suitable aliquot of natural water or water extract of soil (see Note 1) to a small beaker, place on the platform of a magnetic stirrer and insert a "follower". Calibrate the pH meter with phthalate and phosphate buffers (see III.I.) and then insert the electrodes in the sample for analysis. With the pH meter switched on, start the stirrer and add 0.020 N hydrochloric acid until the pH falls to 3.8. Stop the stirrer and check the pH, adding more acid and stirring again

if necessary (see Note 2). Record the volume of acid needed.

When carbonate is present and is determined potentiometrically, (see IV.8.) the determination of bicarbonate can conveniently follow in the same sample. In this case, the pH meter performance should be checked initially with phthalate, phosphate and borate buffers.

(b) Indicator titration.

Transfer a suitable aliquot of sample (see Note 1) to a 100 or 200 ml Erlenmeyer flask and add 0.2 - 0.4 ml screened methyl orange according to preference. Titrate with 0.020 N hydrochloric acid until the green colour of the indicator changes to a neutral grey with the faintest tinge of pink. Record the volume of acid needed.

9.E. CALCULATIONS.

Let

V be the volume in ml of the aliquot taken for analysis

(a) Carbonate absent.

Let

T be the volume in ml of 0.020 N acid needed in the titration

Then, the volume V ml of sample contains (T x 0.02) milliequivalent bicarbonate and the concentration is

$$\frac{20\ T}{V} \text{ milliequivalent per litre}$$

(b) Carbonate present.

(i) Potentiometric titration following carbonate determination.

Let

X be the volume in ml of 0.020 N acid needed in the determination of carbonate by titration to pH 8.4

Y be the volume in ml of 0.020 N acid needed in the subsequent determination of bicarbonate in the same aliquot by titration from pH 8.4 to pH 3.8

After addition of X ml acid, the solution contains bicarbonate, derived from the carbonate, equivalent to X ml 0.020 N acid.

Thus, the bicarbonate in the original aliquot consumes (Y - X) ml 0.020 N acid and its concentration is

$$\frac{20(Y - X)}{V} \text{ milliequivalent per litre}$$

(ii) Titration of carbonate and bicarbonate together.

Let

X be the volume in ml of 0.020 N acid needed in the determination of carbonate by titration to pH 8.4 (of V ml of sample)

Z be the volume in ml of 0.020 N acid needed in the determination of carbonate plus bicarbonate by titration to pH 3.8 of a separate aliquot, also of V ml of sample (but see Note 3)

Then, as in IV.8.E, the carbonate consumes 2X ml of 0.020 N acid in the titration to pH 3.8.

Thus, the bicarbonate consumes (Z - 2X) ml of 0.020 N acid and its concentration is

$$\frac{20(Z - 2X)}{V} \text{ milliequivalent per litre}$$

9.F. NOTES.

(1) For natural waters, a 50 ml aliquot is suitable except in the case of hard waters from limestone areas, when 20 ml gives a more convenient titration value. For water extracts of soils, the largest aliquot (up to 50 ml) which is possible should be taken, as soluble bicarbonate levels are normally low.

(2) pH values may be affected by the stirring motion and they should be checked when the liquid is still.

(3) If, for any reason, the aliquot taken for carbonate determination (say, A ml) is different from that taken for carbonate plus bicarbonate determination (say, B ml), then the concentrations of carbonate and carbonate plus bicarbonate are calculated separately and the bicarbonate obtained by difference. The result (using the symbols of calculation (b)(ii)) is

$$\left(\frac{20\ Z}{B} - \frac{40\ X}{A}\right) \text{ milliequivalent per litre}$$

9.G. REFERENCES

BLACK. Chapter 62, Section 62-3.4. (C.A. BOWER and L.V. WILCOX)

JACKSON. Chapter 10, Section 10-87 to 10-93

VOGEL. Chapter III, Section III.15

WILSON. Vol. I.B. Chapter VII. (4.f.(vii) - C. AYERS)

IV. 10. CHLORIDE

10.A. PRINCIPLE

Chloride ion combines with mercuric ion in acid solution to form mercuric chloride, which is soluble but almost completely unionized. Thus, if a chloride solution is titrated with mercuric nitrate in the presence of a little nitric acid, the mercuric ion is complexed by the chloride ion until no chloride ion is left. The end-point of the titration is denoted by the presence of free mercuric ion which is detected by its sensitive reaction with diphenylcarbazone to form a violet compound.

The optimum acidity for the reaction is about pH 3. Since the amount of carbonate and bicarbonate present is known from determinations IV.8 and IV.9, this optimum pH - or one near it - may easily be obtained by adding a calculated volume of standard nitric acid.

10.B. APPARATUS.

Pipettes, 5, 10, 20 or 50 ml, as required for aliquots
Graduated pipette, 1 ml, with 0.1 ml divisions
Erlenmeyer flasks, 100 or 150 ml
Burettes (two), 25 ml, with 0.05 ml divisions

10.C. REAGENTS.

Nitric acid, 0.05 N
Mercuric nitrate, 0.020 N
Dissolve about 7 g mercuric nitrate, $Hg(NO_3)_2.H_2O$ in 2 litres of approximately 0.05 N nitric acid. Standardize by titration with a standard chloride solution (magnesium, sodium or potassium, as convenient - usually 0.050 N solutions as used in determinations IV.4, IV.6 or IV.7.) and adjust to exactly 0.020 N. (see Note 3)

Diphenylcarbazone
0.5 per cent in ethanol

10.D. PROCEDURE.

Transfer a suitable aliquot of natural water or water extract of soil (see Note 1) to a 100 or 150 ml Erlenmeyer flask and add a volume of 0.05 N nitric acid sufficient to neutralize the bicarbonate or carbonate plus bicarbonate (to pH 3.8) and provide 1 ml in excess (see Note 2). Add 0.5 ml diphenylcarbazone solution and titrate with 0.020 N mercuric nitrate to the first permanent pink-violet tinge. Record the volume of mercuric nitrate needed.

10.E. CALCULATION.

Let

V be the volume in ml of the aliquot taken for analysis

T be the volume in ml of 0.020 N mercuric nitrate needed in the titration.

Then, as in previous similar calculations, the concentration of chloride is

$$\frac{20\ T}{V} \text{ milliequivalent per litre}$$

10.F. NOTES.

(1) 20 ml is a suitable aliquot in most cases, having the advantage that the desired concentration of chloride in milliequivalent per litre is numerically equal to the titration value in ml. Natural waters are often low in chloride and 50 ml may be taken if preferred. Water extracts of saline soils may be high in chloride and 10 ml (or even 5 ml) may then be more appropriate aliquots.

(2) If V ml of sample requires M ml of 0.020 N acid for neutralization of bicarbonate or carbonate plus bicarbonate (see IV.9.), the volume of 0.05 N nitric acid needed is

$$(\frac{2\ M}{5} + 1) \text{ ml}$$

(3) The sharpness of the colour change at the end-point tends to fall off as the amount of chloride increases, probably due to an inhibiting effect of the mercuric chloride. There is no difficulty in detecting the end-point with small amounts of chloride (titrations less than 5 ml) but with larger amounts it is advisable to use a colour standard for matching. This is conveniently made by titrating 5 or 10 ml of 0.050 N chloride solution (magnesium, sodium or potassium - as used in determinations IV.4, IV.6 or IV.7.) The titrations should be performed in good lighting conditions and the volume of the test solution should be the same as that of the matching solution, in the same sized flask. It may be better, in some cases, to titrate to a constant (slightly deeper) shade of pink-violet, as produced by (say) 0.1 ml 0.020 N mercuric nitrate in excess and then use this volume as a "blank" correction; with such a procedure, the amount of chloride in the matching solution should be roughly the same as that in the test solution.

(4) A mixture of 0.5 per cent diphenylcarbazone and 0.05 per cent bromo-phenol blue may be used in place of diphenylcarbazone alone when the degree of alkalinity of the sample is not known. 0.05 N nitric acid is run in until the solution turns yellow and then 1 ml more is added. Some analysts claim that the background yellow colour makes it easier to see the end-point.

10.G. REFERENCES.

RICHARDS. Chapter 7. Method 59.

VOGEL. Chapter III, Section III.43.

IV. 11-1. SULPHATE - GRAVIMETRIC

11-1.A. PRINCIPLE.

Sulphate ion reacts quantitatively with barium ion in a dilute hydrochloric acid solution (optimum concentration about 0.05 N) to form insoluble barium sulphate, the acid preventing the precipitation of barium carbonate, hydroxide and phosphate. Precipitation of barium sulphate is carried out by the addition of barium chloride very slowly in boiling solution to avoid supersaturation and to promote formation of large crystals, which are again encouraged to grow larger by a period of digestion in hot solution (see Note 1).

$$SO_4^{2-} + BaCl_2 = BaSO_4 + 2Cl-$$

The precipitate is filtered off, washed, ignited and weighed as barium sulphate, $BaSO_4$.

The optimum amount of sulphate for an accurate determination lies between 0.2 and 1.2 milliequivalents.

11-1.B. APPARATUS

Pipettes, 10, 20, 25, 50 or 100 ml, as required for aliquots
Measuring cylinder, 200 ml
Burette, 10 ml, with 0.05 ml divisions
Beakers, 400 ml
Watch glasses, 100 mm diameter
Hot plate
Beaker (appropriate volume) and pipette, 10 ml, for barium chloride
Glass rods, fitted with rubber 'policemen'
Water bath
Wash bottle, glass, for hot water
Drying oven
Muffle furnace
Desiccator
Analytical balance, accurate to 0.1 mg

Plus, either -

Funnels, 75 mm diameter
Filter papers, 11.0 cm diameter, (e.g. Whatman No 42)
Crucibles, porcelain or silica, 32 mm diameter

or -

Filter crucibles, porcelain or silica, fine porosity
Filter flasks, with adapters for crucibles
Vacuum pump

11-1.C. REAGENTS.

Hydrochloric acid, 5 N
Barium chloride, 10 per cent
Dissolve 100 g barium chloride, $BaCl_2.2H_2O$, in about 500 ml water, filter and make to 1 litre.

Bromo-cresol green
0.2 per cent in ethanol

11.1.D. PROCEDURE.

Transfer an aliquot of natural water or water extract of soil containing between 0.2 and 1.2 milliequivalent sulphate (see Note 2) to a 400 ml beaker and add water to approximately 200 ml. Add 0.2 - 0.3 ml bromo-cresol green and then 5 N hydrochloric acid from a burette until the colour changes to yellow-green (see Note 3); then add 2 ml more acid.

Heat to boiling on a hot plate, at the same time heating an appropriate volume of 10 per cent barium chloride solution. While still hot, add 10 ml barium chloride solution very slowly, stirring constantly. Cover the beaker with a watch glass and digest on a nearly boiling water bath for two to three hours.

Filter through a fine filter paper or a tared filtering crucible (see Note 4, cleaning the beaker thoroughly with a rubber 'policeman', and wash the precipitate with the minimum quantity of hot water (see Note 5) until the washings are free of chloride (test with silver nitrate). If a filter paper is used, fold it carefully round the precipitate and place it in a tared porcelain or silica crucible. Dry this - or the filtering crucible (if used) - in an oven at 105°C. Transfer to a muffle furnace and ignite slowly, finally increasing the temperature to 800°C for one hour. Remove the crucible from the furnace, cool somewhat, place in a desiccator, cool to room temperature and weigh to 0.1 mg.

11-1.E CALCULATION

Let

V be the volume in ml of the aliquot taken for analysis

W be the weight in gram of barium sulphate

1 gram barium sulphate = 8.567 milliequivalents

Thus, V ml of sample contains (8.567 x W) milliequivalent of sulphate and the concentration is

$$\frac{8567\ W}{V} \quad \text{milliequivalent per litre}$$

11-1.F. NOTES.

(1) Certain metals may coprecipitate with barium sulphate. In samples of natural water or water extracts of soil, calcium, magnesium and possibly sodium may be present in amounts sufficient to cause a slight error. This is reduced by slow precipitation and by digestion of the precipitate. No errors arise from the anions normally present in the samples under analysis.

(2) An assessment of the concentration of sulphate must be made before starting this analysis. The total salt concentration is either estimated from the conductivity (see IV.6.E.(a)) or taken as the sum of the cations calcium plus magnesium and sodium (potassium being neglected) where these analyses have been done. The sum of the chloride and bicarbonate concentrations (carbonate can usually be neglected) is then subtracted to give the probable sulphate concentration. For water extracts of soil, chloride alone may be subtracted, since bicarbonate is normally low.

If possible, choose an aliquot containing 0.5 - 1.0 milliequivalent sulphate. For very low concentrations, take up to 200 ml if this amount of sample is available.

(3) If preferred, a calculated volume of 5 N acid may be added (omitting the bromo-cresol green) when the alkalinity of the sample is known (from determination IV.9.). For many water extracts of soil, this calculated volume comes to one drop or less and then just 2 ml of 5 N acid can be added to adjust the acidity to the required level.

(4) When the barium sulphate is ignited in the presence of filter paper, there is some danger of its reduction by the carbon from the paper, unless the temperature of the muffle furnace is raised slowly. Porcelain or silica crucibles with porous bases are preferable.

(5) Washing of the precipitate should not be prolonged after it is free of chloride because of the slight solubility of barium sulphate in water.

11-1.G. REFERENCES.

BLACK. Chapter 62, Section 62-3.1. (C.A. BOWER and L.V. WILCOX)

CHAPMAN and PRATT. Chapter 21, Sections 21-1 and 21-3.

RICHARDS. Chapter 8. Method 83.

VOGEL. Chapter V, Section V.6

WILSON. Vol. I.C. Chapter IX. (6.b.(a) - L.A. HADDOCK

IV. 11-2. SULPHATE - COLORIMETRIC

11-2.A. PRINCIPLE.

In the gravimetric method, barium sulphate is precipitated by the addition of barium chloride in approximately 0.05 N hydrochloric acid. If barium chromate is used in place of barium chloride, the reaction effectively involves the production of yellow chromate ion in an amount equivalent to the sulphate ion.

$$SO_4^{2-} + BaCrO_4 = BaSO_4 + CrO_4^{2-}$$

In fact, in the acid solution of barium chromate used for the precipitation, chromate ion is converted temporarily into dichromate ion

$$2\ CrO_4^{2-} + H^+ = Cr_2O_7^{2-} + OH^-$$

Then, after precipitation of barium sulphate, the excess barium reagent is rendered insoluble by making the solution ammoniacal, when the dichromate ion is converted back to chromate ion. The combined precipitates of barium sulphate and barium chromate are filtered off to give a yellow solution whose depth of colour is related directly to the amount of sulphate in the original sample.

Thus, by making the mixture, after precipitation of barium sulphate and barium chromate, to a constant volume, the concentration of chromate in the filtered solution can be measured colorimetrically and related to the original sulphate concentration.

11-2.B. APPARATUS.

Pipettes and volumetric flasks, as required for dilution of samples
Pipette, 5 ml (automatic, if possible) or burette, 50 ml
Burette, 25 ml, with 0.1 ml divisions
Volumetric flasks, 100 ml
Funnels, 75 mm diameter
Filter papers, 12.5 cm diameter (e.g. Whatman No 42)
Erlenmeyer or flat-bottom flasks, 150 ml
Spectrophotometer, with appropriate cells or tubes (see Note 1)

11-2.C. REAGENTS.

Barium chromate, 0.1 N in 1.5 N hydrochloric acid
Dilute 130 ml concentrated hydrochloric acid, s.g. 1.18, to about 650 ml, add 12.7 g barium chromate and make the volume to 1 litre. Stand overnight and filter if turbid.

Ammonium hydroxide, 5 N

Sodium sulphate, 0.200 N (200 milliequivalent per litre)
Dissolve 7.1025 g anhydrous sodium sulphate to 500 ml

Sodium sulphate standard solutions containing 1.0, 2.0, 3.0, 4.0 and 5.0 milliequivalents per litre
Dilute 5, 10, 15, 20 and 25 ml of 0.200 N solution each to 1 litre.

11-2.D. PROCEDURE.

Estimate the sulphate concentration of the natural water or water extract of soil as described in IV.11-1.F.(2). If this is more than 5 milliequivalent per litre, dilute the sample, preparing 50 or 100 ml of solution containing between 0 and 5 milliequivalent sulphate per litre.

Transfer 5 ml acid barium chromate solution to each of a series of 100 ml volumetric flasks, sufficient to cover the number of samples under test, five standards and one blank. Add to each, from a burette, 1.2 ml 5 N ammonium hydroxide (see Note 2). Then add 25 ml of sample, or 25 ml of standard sulphate solution, or 25 ml water (for the blank) respectively. Stopper the flasks, shake well and allow to stand for a convenient time (see Note 3). Add 1.0 ml 5 N ammonium hydroxide to each flask, make to 100 ml, stopper, shake and filter through fine filter papers into dry 150 ml flasks.

Transfer the yellow filtrates to appropriate tubes or cells and measure the absorbance or transmittance of light of wavelength 410 millimicron against water.

11-2.E. CALCULATION.

Plot absorbance or transmittance values against concentration of sulphate in milliequivalent per litre (range 0 - 5)

From this graph, record the concentration of sulphate in the solution used for analysis.

Hence record the concentration of sulphate in the original sample, multiplying by the appropriate dilution factor, where necessary.

11-2.F. NOTES.

(1) The procedure is adapted to spectrophotometers in which light of 410 millimicron wavelength can be produced and using cells or tubes of 1.0 to 1.5 cm light path. Modifications may have to be made for instruments using coloured filters (violet or deep blue) or if cells of longer light path are used.

(2) The barium chromate solution is made up in 1.5 N acid to keep it reasonable clear during storage (although it may have to be filtered from time to time). The acidity is too great for the accurate precipitation of barium sulphate, even after the dilution resulting from the addition of 25 ml of water. Thus a calculated amount of ammonium hydroxide is added to reduce the acidity of the solution in which barium sulphate is precipitated to near the required optimum level (0.05 N).

A very alkaline water may give rise to an acidity rather less than 0.05 N but this does not affect the precipitation.

(3) The time of standing after precipitation does not seem to be critical. Any convenient period from 30 minutes to overnight may be adopted.

(4) The usual difficulties found in the quantitative precipitation of barium sulphate - slight solubility, coprecipitation, etc. - are

avoided by analysing standard solutions of sulpahte and sample of natural water or water extracts of soil under the same conditions so that any errors are common to both.

11-2.G. REFERENCE.

NEMETH, (Journal paper)

IV. 12. NITRATE

12.A. PRINCIPLE.

If the reagent phenol 2:4 disulphonic acid in concentrated sulphuric acid is added to a dry nitrate, nitration of the reagent takes place at room temperature and phenol 6 nitro 2:4 disulphonic acid is formed. The alkaline salts of this acid are an intense yellow and thus addition of ammonia or sodium or potassium hydroxide to a definite volume produces a yellow solution whose depth of colour depends on the amount of nitrate originally present. Ammonia is usually preferred for producing the alkaline salt.

Samples of natural water and water extracts of soil may be analysed for nitrate by this method provided they contain no organic matter, no nitrite and only traces of chloride (less than one part per million). Organic matter may impart yellow to brown colours to the sample and also give rise to brown oxidation products during nitration; nitrite, as well as nitrate, causes nitration of phenol 2:4 disulphonic acid; and chloride can react with nitrate in concentrated sulphuric acid to give volatile oxides of nitrogen.

Natural waters which have been clarified for chemical analysis as described in the introduction (Section 1.4-3.) should contain negligible quantities of organic matter; and nitrite is also negligible in most cases, although it is advisable to test for it (see Note 1). Chloride, however, is sometimes present in high amounts and this must be removed as silver chloride by the addition of the calculated quantity of silver sulphate. Water extracts of soil prepared as described in Section III.6 may also be used for determining soluble nitrate, although it is more usual to make special extracts for this purpose (see III.11.). Water extracts of soil normally contain negligible amounts of organic matter and nitrite but chloride often has to be removed. A qualitative test for nitrite should be carried out as a precaution (see Note 1). With all samples, particular care should be taken to ensure that activated carbon, which may have been used to remove soluble organic matter, does not absorb nitrate ion. (see Note 2)

The sample solution, free of organic matter and nitrite and containing less than 1 ppm chloride, should be neutral or slightly alkaline (pH 7.0 - 8.5) when evaporated to dryness before nitration. Most samples under analysis come within this range; acidic samples may be treated with calcium hydroxide solution and very alkaline samples with sulphuric acid.

12.B. APPARATUS

Pipette, 50 or 100 ml
Beakers, 250 ml
Watch glasses and glass rods, for beakers
Burettes, (two) 25 or 50 ml
Evaporating basins, porcelain or glass, 100-125 ml and 25-30 ml
Water bath
Centrifuge, with 50 ml tubes
Balance, for centrifuge
Wash bottles, plastic
Dispensing burette with coarse jet, 10 or 25 ml
Small glass rods

Volumetric flasks, 100 ml
Erlenmeyer flasks, 125 ml
Funnels and filter papers (e.g. Whatman No 42)
Spectrophotometer, with cells or tubes

12.C. REAGENTS

Sulphuric acid, 0.1 N
Calcium hydroxide, saturated (see III.14-3)

Silver sulphate, 0.04 N
Dissolve 3.12 g silver sulphate to 500 ml

Phenol 2:4 disulphonic acid
Treat 25 g pure phenol crystals with 150 ml concentrated sulphuric acid and, when dissolved, add 75 ml fuming sulphuric acid (13-15 per cent sulphur trioxide). Digest for two hours on a boiling water bath or immersed in boiling water. Cool and transfer to an amber glass bottle and store in the dark, well stoppered. (see Note 3)

Ammonia solution, 5 N

Potassium nitrate, 500 ppm nitrogen
Dissolve 3.61 g dry potassium nitrate to 1 litre with nitrate-free water.

Potassium nitrate, 10 ppm nitrogen
Dilute 10 ml of 500 ppm solution to 500 ml with nitrate-free water.

12.D. PROCEDURE

Transfer 100 ml (see Note 4) of natural water or water extract of soil to a 250 ml beaker and, if the pH is not between 7.0 and 8.5, adjust to this range with 0.1 N sulphuric acid or saturated calcium hydroxide solution, using pH indicator paper or a pH meter with a calomel reference electrode of negligible leak. For a chloride concentration in the sample (method IV.10) of X milliequivalent per litre, add 2.5 X ml 0.04 N silver sulphate solution, stir well, cover the beaker and allow the mixture to stand in the dark for some hours (overnight is convenient).

Decant the clear liquid into a 100-125 ml evaporating basin and start heating on a water bath. Transfer the silver chloride precipitate and remaining solution to a 50 ml centrifuge tube and wash out the beaker with a small quantity of water. Centrifuge at 2500 rpm for 10 minutes and add the supernatant liquid to the evaporating basin. When the volume has been reduced to about 10 ml, transfer the liquid to a 25-30 ml evaporating basin, washing out the larger basin with a minimum amount of water, and continue the evaporation to dryness.

Remove the basin from the water bath and dry the outside. Add 2 ml phenol 2:4 disulphonic acid reagent from a dispensing burette, bringing all the residue rapidly into contact with the reagent. Stir with a small glass rod to help the solids to dissolve. After about 10 minutes, add 10-15 ml cold water and stir to dissolve any remaining solids; then add 5 N ammonia solution from a dispensing burette until the solution turns yellow, followed by 2 ml more. Transfer the liquid quantitatively to a 100 ml volumetric flask and make to 100 ml. Filter (if turbid) through a fine filter paper into a clean, dry Erlenmeyer flask. (see Note 5)

Prepare a set of standards by evaporating to dryness 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 ml (or other appropriate volumes in this range) of potassium nitrate solution, containing 10 ppm nitrogen, and treating each with phenol 2:4 disulphonic acid and ammonia as described above.

Transfer the yellow standard solutions and the test solutions to 1 cm cells or tubes and read the absorbance or transmittance of light of 410 millimicron wavelength.

12.E. CALCULATION.

Plot the absorbance or transmittance values obtained with the standard nitrate solutions against microgram nitrogen. With the volumes suggested above, the nitrogen range is 25-200 microgram.

From this graph, record the microgram nitrogen present in each of the test solutions. Divide each value by 100 (volume in ml of aliquot taken) to give the concentration of nitrate nitrogen in the original sample in parts per million.

If a different aliquot is taken (say, V ml), divide the migrogram value by V. If the result is required in milliequivalent per litre, divide the ppm value by 14.

12.F. NOTES

(1) To test for the presence of nitrite, make a solution containing 0.1 g sulphanilic acid and 0.08 g 1-naphtol in 100 ml of acetic acid solution containing 75 ml glacial acetic acid. Add 5 ml of this reagent to 20 ml of the water or water extract and note if any pink colour develops. When nitrite is detected, estimate the amount by comparing the colour produced in the above test with that produced with 20 ml portions of standard sodium nitrite solutions containing 0-100 microgram nitrogen per litre.

In many cases, even if nitrite is detected, the amount is too small to affect the nitrate value seriously. When the amount of nitrite nitrogen is greater than 0.1 ppm, the aliquot taken for nitrate determination may be treated with 1 ml 1 N sulphuric acid and a little hydrogen peroxide (20-volume) for about 15 minutes, to oxidize the nitrite to nitrate, before proceeding with the determination of nitrate as above. The total nitrate nitrogen figure is then corrected for the nitrite nitrogen.

(2) If activated carbon is used to remove organic matter colours, it should be tested for its possible effect on nitrate. Shake 20 or 25 ml standard potassium nitrate solution (containing 10 ppm nitrogen) with a little activated carbon and filter into a dry flask. Determine the nitrate in 10 ml of the filtrate and compare it with the amount in 10 ml of untreated potassium nitrate solution. If there is a significant reduction, the activated carbon is unsuitable for removal of soluble organic matter. In this case, the organic matter may be oxidized with hydrogen peroxide, using a period of digestion on a water bath (depending on the amount of organic matter present) before evaporation to dryness.

(3) If fuming sulphuric acid is not available, 25 g phenol may be digested with 225 ml concentrated sulphuric acid for 6 hours. The reagent can also be bought ready prepared but it must be fresh.

(4) Nitrate concentrations are normally low enough in the samples Under examination to need 100 ml of liquid for analysis. Other volumes can, of course, be taken but the amount of nitrate nitrogen present should lie between 25 and 200 microgram.

(5) When nitrate is very low, the appearance of a yellow colour to denote formation of the alkaline salt of phenol 6 nitro 2:4 disulphonic acid is not easily seen. The amount of 5 N ammonia solution needed is usually 15-20 ml; if preferred, a constant volume of ammonia solution, based on experience, may be added.

When small evaporating basins are used, the nitrated acid may be transferred to a 100 ml volumetric flask before adding the ammonia solution.

12.G. REFERENCES.

BLACK. Chapter 84, Section 84-5. (J.M. BREMNER)

BOLTZ. Chapter IV. Nitrate, I.A. pp. 135 to 152. (M.J. TARAS)

CHAPMAN and PRATT. Chapter 17, Section 17-3.

JACKSON. Chapter 8, Sections 8-48 to 8-66

RICHARDS. Chapter 6. Method 15.

WILSON. Vol. I.C. Chapter IX. (5.a.(c) - A.F. WILLIAMS)

IV. 13. AMMONIA

13.A. PRINCIPLE

An alkaline solution of potassium iodide and mercuric iodide in the correct proportions contains potassium mercuri-iodide, K_2HgI_4, known as Nessler's reagent. This reacts with small quantities of ammonia to form a reddish-brown colloidal compound (given the empirical formulae $NH_2Hg_2I_3$ and $HgO.(NH_2I)$ in the literature) which is the basis of a sensitive colorimetric method for ammonia, applicable when micro distillation and titration is not accurate enough. The amount of ammonia nitrogen should preferably lie between 0 and 250 microgram in a test volume of about 50 ml, if the amount of ammonia nitrogen is more than this (near 1 milligram), the stronger colours can still be measured with light of a different wavelength but there is danger of opalescence developing fairly rapidly as the ammonia compound precipitates and it is preferable to adjust the amount of sample so that less than 250 microgram nitrogen is present - or to use distillation and titration of the ammonia with 0.01 N acid.

The formation of the coloured compound with ammonia is affected by alkalinity, temperature and time; and also by the method of preparation and age of the Nessler reagent. Therefore it is necessary to keep closely to a standard procedure for both ammonium salt standards and test solutions. Interferences may arise in the test solutions from cations which form insoluble hydroxides; in the case of waters and water extracts of soil, calcium, magnesium, manganese and iron should be removed. Soluble organic matter must also be absent.

A common method of separating ammonia from interfering substances is to distil it from slightly alkaline solutions, this procedure also serving to concentrate the ammonia. An alternative method, suitable for most waters and water extracts of soil, is to form a flocculent precipitate of zinc hydroxide which carries down with it calcium, magnesium, manganese, iron and organic matter and any insoluble material. Remaining traces of magnesium can be complexed with tartrate by adding a little Rochelle salt solution. Choice of method depends mainly on the concentration of ammonia present, the volume of sample available and the accuracy required.

13.B. APPARATUS.

Preliminary assessment.

Measuring cylinder, 50 ml
Pipettes, 1 and 25 ml
Erlenmeyer flasks, 125 ml

Direct method.

Pipettes, 5, 10, 20, 25 and 50 ml
Volumetric flasks, 100 ml
Graduated pipettes, 5 ml with 0.05 ml divisions
Centrifuge, with 50 ml tubes
Balance for centrifuge
Erlenmeyer flasks, 125 ml
Pipette, 1 ml
Spectrophotometer, with cells and tubes

Distillation method.

Distillation apparatus, preferably all-glass and fitted for steam distillation, capacity of distilling flask 750 ml

Measuring cylinders, 250 and 500 ml
Pipettes, 1 and 10 ml
Volumetric flask, 50 ml - or Nessler tubes
Spectrophotometer, with cells and tubes
Burette, 10 ml with 0.02 ml divisions, if ammonia is titrated

13.C. REAGENTS.

Zinc sulphate, $ZnSO_4.7H_2O$, 10 per cent
Sodium hydroxide, 25 per cent

Rochelle salt solution, 50 per cent
Dissolve 50 g potassium sodium tartrate (tetrahydrate) in 100 ml water, boil off about 20 ml to remove ammonia, cool and make to 100 ml

Phosphate buffer, pH 7.4
Dissolve 14.3 g potassium dihydrogen phosphate, KH_2PO_4 and 68.8 g dipotassium hydrogen phosphate, K_2HPO_4 to 1 litre.

Nessler's reagent (see Note 1)
Dissolve 100 g mercuric iodide and 70 g potassium iodide in about 100 ml water. Dissolve 160 g sodium hydroxide in about 700 ml water and cool. Add the iodides slowly to the alkali, stirring all the time, then make to 1 litre.
Allow to stand for a few days before use. A precipitate settles and continues to be formed slowly; the clear supernatant liquid is used and the mixture is not disturbed.

Ammonium chloride, 500 ppm nitrogen
Dissolve 1.908 g anhydrous ammonium chloride to 1 litre

Ammonium chloride, 10 ppm nitrogen
Dilute 20 ml of 500 ppm solution to 1 litre.

13.D. PROCEDURE.

Obtain a rough assessment of the probable ammonia content of the sample under analysis by adding 1 ml Nessler reagent to 50 ml, at the same time adding 1 ml Nessler reagent to 50 ml ammonium chloride solution containing 250 microgram nitrogen. If the colour developped shows nitrogen in the range 20-250 microgram or above per 50 ml sample, either use the direct method or distillation and titration of the ammonia with 0.01 N acid. If the colour is very faint and an accurate determination is required, use distillation of a large volume of sample, followed by colorimetric determination of ammonia.

(a) Direct method.

Transfer a suitable volume of the natural water or water extract of soil (usually between 50 and 90 ml - see Note 2) to a 100 ml volumetric flask, add 1 ml zinc sulphate solution and 0.5 ml sodium hydroxide, make to 100 ml and mix. After standing for a few minutes, transfer most of the liquid and precipitate to two 50 ml centrifuge tubes, balance the tubes and centrifuge at 2500 rpm for 5 minutes. Collect 50 ml of the clear supernatant liquid in a 125 ml Erlenmeyer flask by pipetting 25 ml out of each centrifuge tube and add two drops of Rochelle

salt solution.

Prepare a set of ammonia nitrogen standards by transferring 5, 10, 15, 20 and 25 ml ammonium chloride solution (10 ppm nitrogen) to 125 ml Erlenmeyer flasks, making each to 50 ml and adding two drops Rochelle salt solution. Then add 1 ml Nessler reagent to all standards and test solutions and mix well. After 15 minutes, transfer the solutions to 1 cm cells or tubes and read the absorbance or transmittance of light of 400-425 millimicron wavelength. Carry out a blank determination on 50 ml ammonia-free water to test for traces of ammonia in the reagents.

(b) Distillation method.

Steam out the distillation apparatus until the distillate gives no colour with Nessler reagent. Transfer a suitable volume of sample (up to 500 ml - see Note 2) to the distilling flask, adjust the volume to about 500 ml and add 10 ml phosphate buffer (see Note 3). Distil gently, collecting the distillate in 50 ml portions by means of volumetric flasks or Nessler tubes.

After the second 50 ml has been collected, develop and measure the ammonia colour in the first two portions of distillate by adding 1 ml Nessler reagent and proceeding as in the direct method, meanwhile leaving the distillation to continue. If there is a measurable amount of ammonia nitrogen in the second portion of distillate, collect a third portion and continue until no more ammonia distils over.

Alternatively, distil over about 150 ml liquid, add bromocresol green methyl red indicator and titrate the ammonia with 0.01 N acid described in Section III.4. (see Note 4)

13.E. CALCULATIONS

(a) Colorimetry.

Plot the absorbance or transmittance values obtained with the standard ammonia solutions against microgram nitrogen. With the volumes suggested above, the nitrogen range is 50-250 microgram.

From this graph record the microgram nitrogen present in each of the test solutions.

Let an individual value be G microgram

(i) Direct method.

Let
V be the volume in ml of sample taken

Then, the volume of sample analysed for nitrogen is 0.5 V ml and this contains G microgram

Thus, the concentration is

$$\frac{2\,G}{V} \text{ parts per million}$$

(ii) Distillation.

Let
V be the volume in ml of sample distilled

G_1 G_2 G_3 - - be the amounts of ammonia nitrogen in microgram in the successive 50 ml portions of distillate

Then, V ml sample contains $(G_1 + G_2 + G_3 + —)$ microgram nitrogen

and the concentration is

$$\frac{G_1 + G_2 + G_3 + - -}{V} \text{ parts per million}$$

(b) Distillation and titration.

Let

V be the volume in ml of sample distilled

T be the volume in ml of 0.01 N acid needed to titrate the ammonia distilled, after correction for the blank

Then, V ml sample contains 0.01 T milliequivalent nitrogen and the concentration is

$$\frac{10\ T}{V} \text{ milliequivalent per litre}$$

$$\text{or } \frac{140\ T}{V} \text{ parts per million}$$

13.F. NOTES.

(1) Various procedures for making Nessler's reagent appear in the literature. That given is one of the simplest; it contains a slight excess of mercuric iodide over the amount needed to react with the potassium iodide and this tends to increase the sensitivity.

The clear supernatant liquid may be separated from the precipitate by decantation or centrifugation immediately before use.

(2) Amounts of ammonia nitrogen in water samples are usually very small (less than 0.1 ppm) and distillation of 500 ml is often necessary to obtain an accurate figure. If this volume of sample is not available, the sensitivity of the colorimetric method may be increased by using 5 or 10 cm cells for measuring the light absorption and working over a lower range of standards (e.g. 0-50 or 0-25 microgram). When only small volumes of sample are available, the direct method is preferable to distillation.

(3) The precaution of using a mild alkaline buffer is necessary for waters containing organic matter, which may be decomposed during boiling with stronger alkalies. For waters or water extracts containing much calcium, more buffer is needed and a secondary test should be made to establish the correct volume of phosphate buffer needed to maintain the pH of the sample near 7.4 during distillation.

(4) 1 ml of 0.01 N acid corresponds to 140 microgram ammonia nitrogen. It is preferable to have at least 100 microgram nitrogen present in the volume of sample distilled. If more than 250 microgram ammonia nitrogen is distilled over, it is advisable to trap the

ammonia in dilute boric acid (see Section III.4.).

(5) All water used for reagents and dilutions should be ammonia-free. Deionized water is usually satisfactorily pure; distilled water may have to be redistilled from alkaline permanganate (see Section I.1-4.).

Filter paper may contain traces of ammonia; if a centrifuge is not available and the zinc hydroxide (in the (direct method) is filtered off, the first 20-25 ml of filtrate should be discarded

13.G. REFERENCES.

BLACK. Chapter 84, Section 84-3. (J.M. BREMNER)

BOLTZ. Chapter IV. Ammonia. pp. 75 to 124. (M.J. TARAS)

CHAPMAN and PRATT. Chapter 17, Section 17-5.

VOGEL. Chapter X, Section X.10.

IV. 14. BORON

14.A. PRINCIPLE

Borate ion reacts with the red dye carmine or carminic acid in nearly concentrated sulphuric acid (about 90-91 per cent by volume) to form, at normal room temperatures, a blue compound, the concentration of which may be measured colorimetrically at 585 millimicron wavelength. The reaction proceeds slowly and about one hour is needed for full colour development, after which the colour very gradually fades. Nitrate ion interferes but its effect can be prevented by adding hydrochloric acid; oxidizing agents should be absent.

Amounts of boron suitable for determination range from 1 to 10 microgram in a total volume of about 20 ml, of which about 10 per cent (i.e. 2 ml) is the volume of the sample under test. The method may thus be applied directly to natural waters, unless the amount of boron is very low, when concentration of the sample may be necessary to obtain a reliable figure (see Note 2). However, the determination is normally carried out to detect toxic levels of boron (greater than 2-3 parts per million) and an accurate knowledge of the lowest levels (below 1 part per million) is not often required.

Boron determination in water extracts of soils is dealt with separately (see Section III.16-6).

14.B. APPARATUS.

Dispensing burettes (two), 100 ml, with coarse jets, fitted with moisture traps

Pipette, 2 ml
Erlenmeyer flasks, capacity 50 ml, stoppered, boron-free if possible
Spectrophotometer, with cells or tubes which can be stoppered or covered

14.C. REAGENTS.

Hydrochloric acid, concentrated
Sulphuric acid, concentrated, sp.gr. 1.84
Carmine solution, 0.025 per cent in sulphuric acid
Stir 0.125 g powdered carmine (or carminic acid) rapidly into 500 ml concentrated sulphuric acid and store immediately in a boron-free glass bottle.

Boric acid, 500 ppm boron
Dissolve 2.860 g boric acid, H_3BO_3, to 1 litre

Boric acid, 50 ppm boron
Dilute 25 ml of 500 ppm solution to 250 ml

Boric acid, standards containing 1, 2, 3, 4 and 5 ppm boron
Dilute 5, 10, 15, 20 and 25 ml of 50 ppm solution each to 250 ml

(NOTE. store all standard boron solutions in boron-free glass bottles; do not use borosilicate glass or polythene or plastic - see Note 1.)

14.D. PROCEDURE.

Transfer 2 ml water sample to a 50 ml Erlenmeyer flask. Also transfer 2 ml of each of the standard boron solutions (containing 1, 2, 3, 4 and 5 ppm boron) and 2 ml pure water to six other 50 ml Erlenmeyer flasks.

Add one drop concentrated hydrochloric acid to each, followed by 10 ml concentrated sulphuric acid, added slowly and with shaking. Stopper the flasks and allow to cool. Add 10ml carmine solution, mix well, stopper and leave for one hour.
Transfer the solutions to the tubes or cells supplied with the spectrophotometer and determine the absorbance or transmission of light of 585 millimicron wavelength, using the red liquid obtained with 2 ml pure water for the reference solution.

14.E. CALCULATION

Plot the absorbance or transmission values obtained with the standard boron solutions against microgram boron (2, 4, 6, 8 and 10).

From this graph, record the microgram boron present in the waters taken for analysis. Divide each by 2 to give the boron concentration in parts per million. (see also Note 2)

14.F. NOTES.

(1) Borosilicate glass is obviously unsuitable for storage of standard solutions of boron and it is claimed that polythene and plastic material can absorb borate ion. Thus boron-free glass bottles must be used.

Although boron-free glassware should strictly be used for the determination, borosilicate glassware is allowable if standards and blank and test solutions are all subjected to the same treatment at the same time. Sometimes the tubes or cells supplied with a particular spectrophotometer may be used for the colour development; this is preferable.

(2) If the water sample contains less than 1.0 ppm boron and an accurate figure is required, concentrate the water sample as described for soil extracts in Section III.16-6.D. Using a five times concentration, the final microgram boron figure must be divided by 10 to give the boron concentration in the water sample in parts per million.

14.G. REFERENCES.

BLACK. Chapter 75. (J.I. WEAR)

BOLTZ. Chapter XI. (II.B). (G. PORTER and R.C. SHUBERT)

CHAPMAN and PRATT. Chapter 6, Section 6-2.

JACKSON. Chapter 14.

RICHARDS. Chapter 8, Method 73(b).

APPENDIX I

DATA ON CONCENTRATED ACIDS AND AMMONIA SOLUTION

Concentrated acid solutions and ammonia solution are supplied for analysis with precise values or ranges of values for specific gravity and percentage composition by weight. These tend to vary according to the source and the figures given below are approximate only.

It is useful to prepare stocks or 5 N solutions of the common acids and ammonia and store them in borosilicate glass or polythene bottles. These are very convenient for general qualitative work and for the preparation of more dilute solutions for quantitative analysis.

Solution	Specific gravity	Percentage composition by weight	Approximate normality	Millilitre needed to make 1 litre of 5 N solution
Sulphuric acid	1.84	98	37	135
Hydrochloric acid	1.18	36	12	435
Nitric acid	1.42	72	16	310
Acetic acid	1.05	99	17	300
Phosphoric acid	1.75	90	48	-
Ammonia (for use in hot countries)	0.91	25	13	375

REFERENCES.

JACKSON. Chapter 1, Section 1-5

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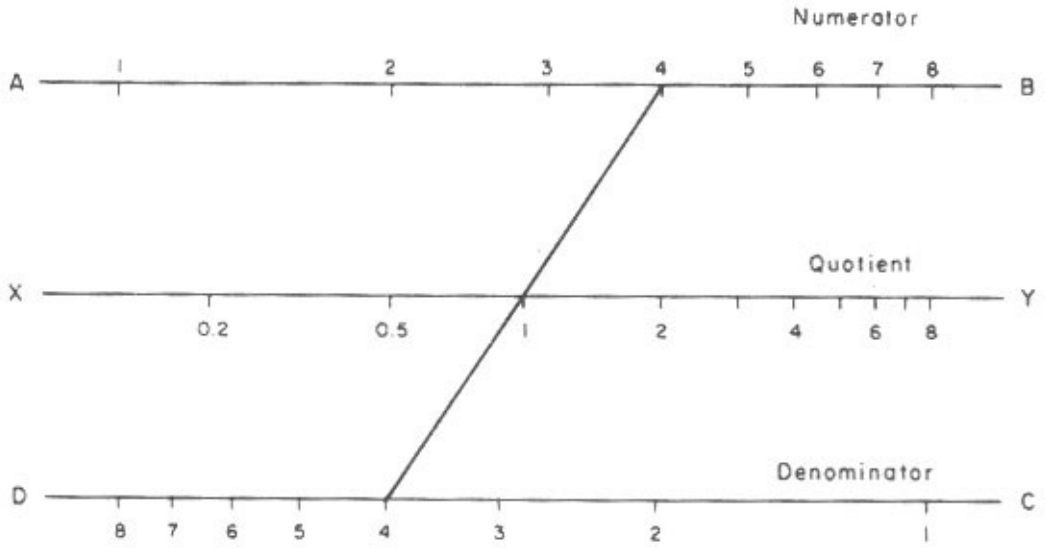
VOGEL. Appendix A.6

Catalogues of Chemical Manufacturers.

APPENDIX 2

USE OF NOMOGRAMS

A - NOMOGRAM FOR DIVISION SUMS - GENERAL CASE.



Let two parallel lines, AB and CD be drawn at a convenient distance from each other.

On line AB, let a logarithmic scale be marked covering values expected for the numerator of a division sum.

On line CD, let a logarithmic scale be marked, in the opposite direction, covering values expected for the denominator of a division sum.

Then, the answer (quotient) to any sum involving these expected values appears on a logarithmic scale on a third parallel line XY, between AB and CD, the quotient being at the point where a straight line joining numerator and denominator cuts XY.

If the scales for numerator and denominator are equal, the quotient line lies midway between the two scales. If they are not equal, the position of the quotient line must be found by construction or calculation.

B - NOMOGRAM FOR SATURATION PERCENTAGE CALCULATIONS.

Method II.4 leads to a division sum

$$\frac{100\ W}{D}$$

where W gram is the weight of water

and D gram is the weight of oven-dry soil

in (W + D) gram of saturated soil paste.

By the procedures advocated, values for W may lie between 4 and 25; and values for D may lie between 12 and 30.

Now, the difference between log 30 and log 12 is 0.3979 and 100 times this figure (39.8) makes a suitable scale length, in centimetres, for a nomogram chart.
Measure this distance on a line to denote oven-dry soil values and mark the first point "12" (origin) and the last point "30".

The point for value "13" is at a distance

100(log 13 - log 12) cm from the origin (i.e. 3.47 cm)

The point for value "14" is at a distance

100(log 14 - log 12) cm from the origin (i.e. 6.69 cm)

and so on.

Intermediate points for 0.1 g are marked in the same way.

Similarly, since the difference between log 25 and log 4 is 0.7958, a suitable length for the water scale is 50 times this figure (also 39.8).

Measure this distance on a line parallel to the oven-dry soil line and mark the first point "4" (origin) and the last point "25", working in the opposite direction to the oven-dry soil scale.

The point for value "5" is at a distance

50(log 5 - log 4) cm from the origin (i.e. 4.84 cm)

The point for value "6" is at a distance

50(log 6 - log 4) cm from the origin (i.e. 8.80 cm)

and so on.

Intermediate points for 0.1 g are marked in the same way.

Now draw a pencil line between the points D = 12 and W = 6 and a second pencil line between the points D = 30 and W = 15. These lines intersect at a point representing a saturation percentage value of 50.

Draw a line through this intersection point parallel to the water and oven-dry soil lines. All saturation percentage values fall on this line and, in this particular case, its distance from the oven-dry soil line is twice its distance from the water line.

Taking the probable lowest saturation percentage value as 20, mark off this point (origin) by joining W = 5 to D = 25. The distances of other saturation percentage values from the origin are

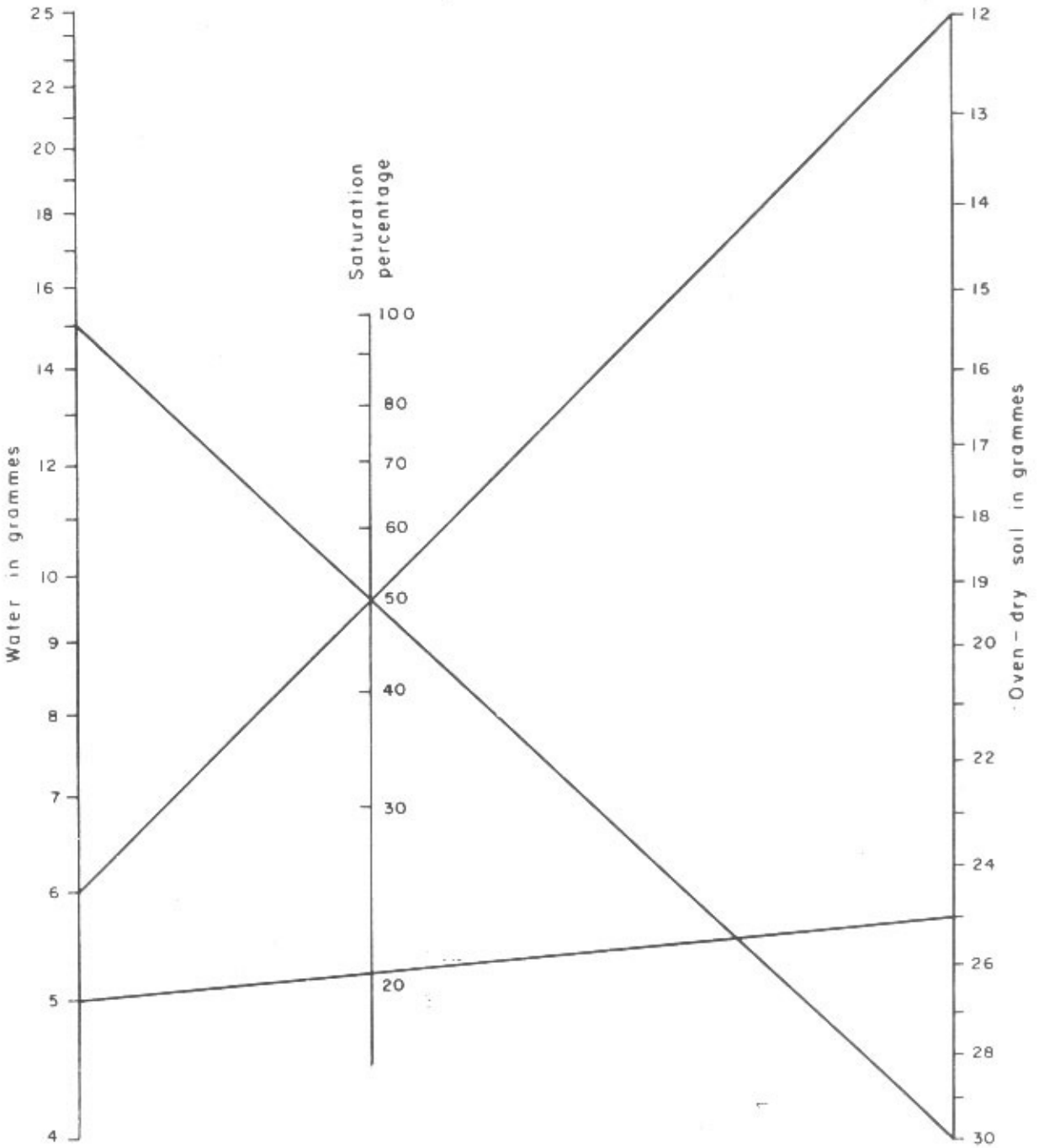
For value "21" $\frac{100(\log 21 - \log 20)}{3}$ (i.e. 0.71 cm)

For value "22" $\frac{100(\log 22 - \log 20)}{3}$ (i.e. 1.38 cm)

and so on.

The illustrative diagram below is drawn to half size and only the main points on the scales are included, so that the construction is clear.

SUGGESTED NOMOGRAM FOR SATURATION PERCENTAGE CALCULATIONS
(half-size)



APPENDIX 3

EXAMPLES OF WORK-SHEETS - I

Project: _____ FAO Laboratory: _____

Soil Analysis — Work Sheet II.3.C.

PARTICLE SIZE DISTRIBUTION — SAND FRACTIONS

Fraction Sizes in microns	100 to 50	250 to 100	500 to 250	1000 to 500	2000 to 1000
Laboratory Number 2468					
Weight of soil (M) 19.20 g					
Basin plus Total Sand through LARGER Sieve g	24.16	26.63	30.38	31.95	32.42
Basin plus Total Sand through SMALLER Sieve g	22.74	24.16	26.63	30.38	31.95
Sand Fraction g	1.42	2.47	3.75	1.57	0.47
SAND FRACTION per cent	7.4	12.9	19.5	8.2	2.4
Laboratory Number _____					
Weight of Soil (M) _____	etc.				
Sand Fraction g	_____	_____	_____	_____	_____
SAND FRACTION per cent	_____	_____	_____	_____	_____

If the basin weight is W and the sand fraction weights ("very fine" first) are P, Q, R, S and T, then the weights recorded above are -

Basin plus Total Sand through LARGER Sieve	W+P	W+P+Q	W+P+Q+R	W+P+Q+R+S	W+P+Q+R+S+T
Basin plus Total Sand through SMALLER Sieve	W	W+P	W+P+Q	W+P+Q+R	W+P+Q+R+S

Original weight of oven-dry, organic-free soil is M g (from Work Sheet II.3.A.)

Sand Fraction per cent is $\frac{100\ P}{M}$, $\frac{100\ Q}{M}$, etc.

Comments:

Sheet Sequence: _____

Analyst: _____

Date completed: _____

APPENDIX 3

EXAMPLES OF WORK-SHEETS - II

Project: _____ FAO Laboratory: _____

Soil Analysis Work Sheet II.3.D.

	PARTICLE SIZE DISTRIBUTION		CLAY LESS THAN 2 MICRONS		
	Laboratory Number	123	124	____	____
	Beaker Number	6	7	____	____
	Cylinder Number	1	2	____	____
	Dish Number	1	2	____	____
	Settling times Start	10.05	10.15	____	____
	for 6 cm depth Finish	14.13	14.23	____	____
D + R	Dish + Residue g	20.4184	21.9423	____	____
D	Dish g	20.2488	21.8517	____	____
R	Residue g	0.1696	0.0906	____	____
50R	Residue per litre g	8.48	4.53	____	____
C = 50R-S	Clay per litre g	7.48	3.53	____	____
M	Original wt. of Soil g	18.55	18.75	____	____
100 C / M	CLAY per cent	40.3	18.8	____	____
	Laboratory Number	____	____	____	____
	Beaker Number etc	____	____	____	____
100 C / M	CLAY per cent	____	____	____	____

M g oven-dry, organic-free soil suspended in 1 ~~litre~~ of dispersing solution.
Residue (R) is clay plus dispersing salts in 20 ml of this suspension.
S is weight of dispersing salts per litre of dispersing solution (1.00 g).

Values of M appear in Work-Sheet II.3.A.

Comments:

Sheet Sequence: _____

Analyst: _____

Date completed: _____

APPENDIX 4

PARTICLE SIZE DISTRIBUTION (MECHANICAL ANALYSIS)

TABLE A - SETTLING TIMES FOR SILT PARTICLES OF 20 MICRON DIAMETER

Temperature Degrees Centigrade.	Viscosity Milli-poises.	Settling Times for Sampling Depths of 4 cm mins. secs.	6 cm mins. secs.	8 cm mins. secs.	10 cm mins. secs.
16	11.11	2 04	3 05	4 07	5 09
17	10.83	2 00	3 01	4 01	5 01
18	10.56	1 57	2 56	3 55	4 54
19	10.30	1 54	2 52	3 49	4 46
20	10.05	1 52	2 48	3 44	4 39
21	9.81	1 49	2 44	3 38	4 33
22	9.58	1 46	2 40	3 33	4 26
23	9.36	1. 44	2 36	3 28	4 20
24	9.14	1 42	2 32	3 23	4 14
25	8.94	1 39	2 29	3 19	4 08
26	8.74	1 37	2 26	3 14	4 03
27	8.54	1 35	2 22	3 10	3 57
28	8.36	1 33	2 19	3 06	3 52
29	8.18	1 31	2 16	3 02	3 47
30	8.01	1 29	2 14	2 58	3 43

Based on Stokes' Law (see Section II.3.-3.D.(a), using -

Density of particles (D_1) = 2.65.

Density of liquid (D_2) = 1.00

Gravity (G) = 981 cm per $(sec)^2$

Laboratories situated above sea level must use different (lower) values for G and prepare their own table.

REFERENCE. (Viscosity values)

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APPENDIX 4

PARTICLE SIZE DISTRIBUTION (MECHANICAL ANALYSIS)

TABLE B - SETTLING TIMES FOR CLAY PARTICLES OF 2 MICRON DIAMETER

Temperature Degrees Centigrade	Viscosity Milli-poises.	Settling Times for Sampling Depths of 4 cm hrs. mins.	6 cm hrs. mins.	8 cm hrs. mins.	10 cm hrs. mins.
16	11.11	3 26	5 09	6 52	8 34
17	10.83	3 21	5 01	6 41	8 22
18	10.56	3 16	4 54	6 31	8 09
19	10.30	3 11	4 46	6 22	7 57
20	10.05	3 06	4 39	6 12	7 46
21	9.81	3 02	4 33	6 04	7 34
22	9.58	2 58	4 26	5 55	7 24
23	9.36	2 53	4 20	5 47	7 14
24	9.14	2 49	4 14	5 39	7 04
25	8.94	2 46	4 08	5 31	6 54
26	8.74	2 42	4 03	5 24	6 45
27	8.54	2 38	3 58	5 17	6 36
28	8.36	2 35	3 52	5 10	6 27
29	8.18	2 32	3 47	5 03	6 19
30	8.01	2 28	3 43	4 57	6 11

Based on Stokes' Law (see Section II.3.-3.D.(a), using -

Density of particles (D_1) = 2.65

Density of liquid (D_2) = 1.00

Gravity (G) = 981 cm per $(sec)^2$

Laboratories situated above sea level must use different (lower) values for G and prepare their own table.

REFERENCE: (Viscosity values)

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APPENDIX 4

PARTICLE SIZE DISTRIBUTION (MECHANICAL ANALYSIS)

TABLE C - SAMPLING DEPTHS FOR SILT PARTICLES OF 20 MICRON DIAMETER

Temperature Degrees Centigrade.	Viscosity Milli-poises.	Sampling Depths in cm for Settling Times of 2 minutes	3 minutes	4 minutes	5 minutes
16	11.11	3.9	5.8	7.8	9.7
17	10.83	4.0	6.0	8.0	10.0
18	10.56	4.1	6.1	8.2	10.2
19	10.30	4.2	6.3	8.4	10.5
20	10.05	4.3	6.4	8.6	10.7
21	9.81	4.4	6.6	8.8	11.0
22	9.58	4.5	6.8	9.0	11.3
23	9.36	4.6	6.9	9.2	11.5
24	9.14	4.7	7.1	9.4	11.8
25	8.94	4.8	7.2	9.6	12.1
26	8.74	4.9	7.4	9.9	12.3
27	8.54	5.0	7.6	10.1	12.6
28	8.36	5.2	7.7	10.3	12.9
29	8.18	5.3	7.9	10.6	13.2
30	8.01	5.4	8.1	10.8	13.5

Based on Stokes' Law (see Section II.3-3.D.(a)), using -

Density of particles (D_1) = 2.65

Density of liquid (D_2) = 1.00

Gravity (G) = 981 cm per $(sec)^2$

Laboratories situated above sea level must use different (lower) values for G and prepare their own table.

REFERENCE. (Viscosity values)

LANGE. page 1680

APPENDIX 4

PARTICLE SIZE DISTRIBUTION (MECHANICAL ANALYSIS)

TABLE D - SAMPLING DEPTHS FOR CLAY PARTICLES OF 2 MICRON DIAMETER

Temperature Degrees Centigrade.	Viscosity Milli-poises.	Sampling Depths in cm for Settling Times of 4 hours	5 hours	6 hours	7 hours
16	11.11	4.7	5.8	7.0	8.2
17	10.83	4.8	6.0	7.2	8.4
18	10.56	4.9	6.1	7.4	8.6
19	10.30	5.0	6.3	7.5	8.8
20	10.05	5.2	6.4	7.7	9.0
21	9.81	5.3	6.6	7.9	9.2
22	9.58	5.4	6.8	8.1	9.4
23	9.36	5.5	6.9	8.3	9.7
24	9.14	5.7	7.1	8.5	9.9
25	8.94	5.8	7.2	8.7	10.1
26	8.74	5.9	7.4	8.9	10.4
27	8.54	6.1	7.6	9.1	10.6
28	8.36	6.2	7.7	9.3	10.8
29	8.18	6.3	7.9	9.5	11.1
30	8.01	6.5	8.1	9.7	11.3

Based on Stokes' Law (see Section II.3-3.D.(a)), using -

Density of particles (D_1) = 2.65

Density of liquid (D_2) = 1.00

Gravity (G) = 981 cm per $(sec)^2$

Laboratories situated above sea level must use different (lower) values for G and prepare their own table.

REFERENCE. (Viscosity Values)

LANGE. page 1680

APPENDIX 5

pH VALUES OF STANDARD BUFFER SOLUTIONS AT ROOM TEMPERATURES

Temperature in °C	Phathalate	Phosphate	Borate
15	4.00	6.90	9.27
20	4.00	6.88	9.22
25	4.00	6.86	9.18
30	4.01	6.85	9.14
35	4.02	6.84	9.10

Phathalate is Potassium hydrogen phthalate, 0.05 M

Phosphate is Potassium dihydrogen phosphate + Disodium hydrogen phosphate, each 0.025 M

Borate is Sodium borate, 0.01 M

prepared as described in Section III.1.

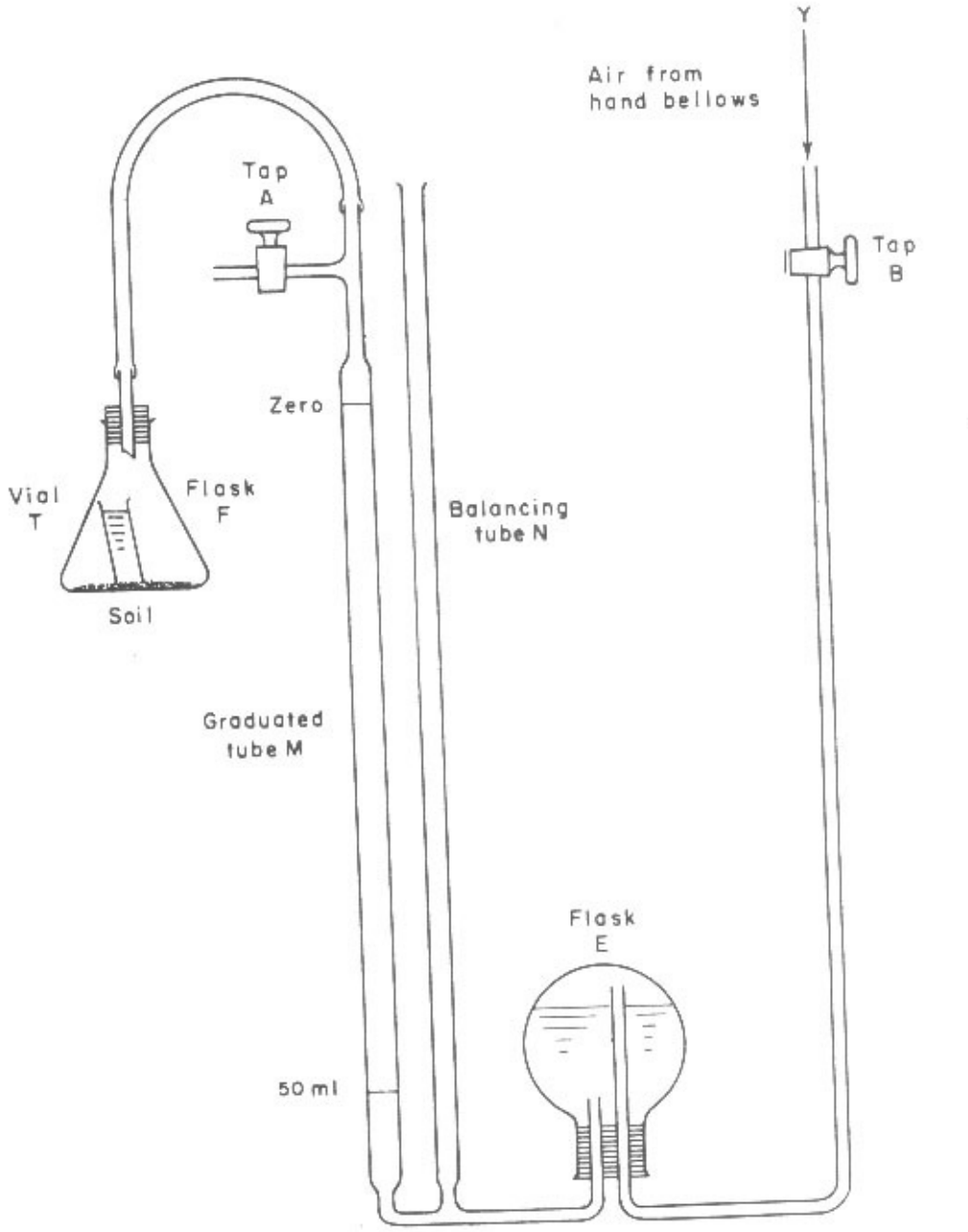
REFERENCES.

BATES Chapter 4, Table 4-6 (p.76)
Chapter 5, pp. 123-130

VOGEL Chapter XVI, Table 1. (p.910)

APPENDIX 6

DIAGRAM OF CALCIMETER



NOT TO SCALE

APPENDIX 7

SPECIFIC CONDUCTIVITY VALUES OF POTASSIUM CHLORIDE SOLUTIONS

Micromhos

Temperature in °C	0.002 N	0.005 N	0.01 N	0.05 N
15	239	585	1,147	5,404
16	244	598	1,173	5,527
17	249	611	1,199	5,651
18	255	625	1,225	5,775
19	260	638	1,251	5,889
20	266	651	1,278	6,024
21	271	665	1,305	6,149
22	276	678	1,332	6,275
23	282	692	1,359	6,402
24	287	706	1,386	6,529
25	293	720	1,413	6,656
26	299	734	1,440	6,784
27	304	748	1,468	6,912
28	310	763	1,496	7,041
29	316	777	1,524	7,170
30	321	792	1,552	7,300
31	327	807	1,580	7,430
32	333	821	1,609	7,561
33	339	837	1,637	7,692
34	345	852	1,666	7,824
35	351	867	1,695	7,956

REFERENCE.

LANGE. page 1222

APPENDIX 8

FACTORS FOR CONVERSION OF CONDUCTIVITY VALUES TO 25°C

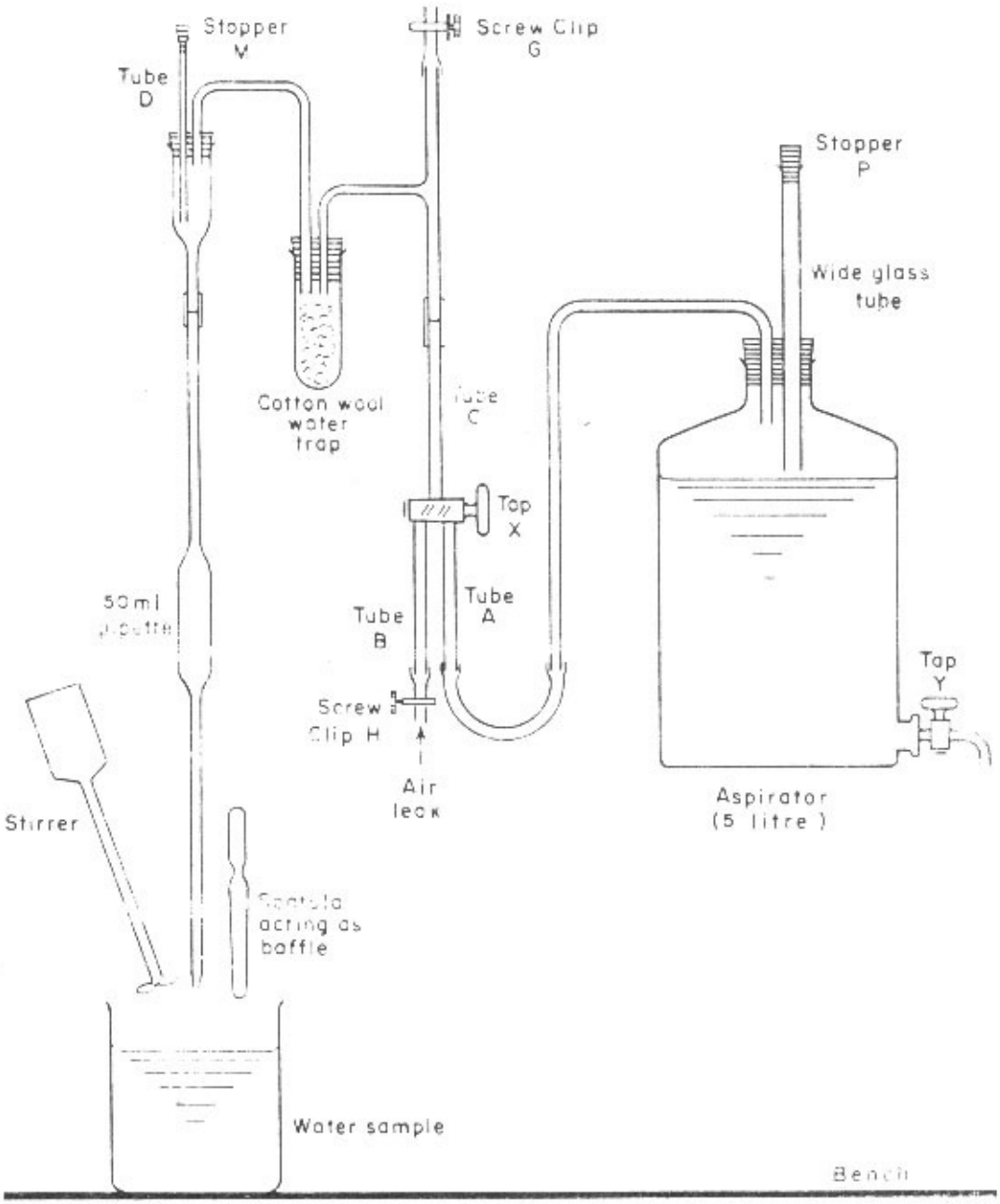
Temperature in °C	Factor
15	1.25
16	1.22
17	1.19
18	1.16
19	1.14
20	1.11
21	1.09
22	1.06
23	1.04
24	1.02
25	1.00
26	0.98
27	0.96
28	0.94
29	0.93
30	0.91
31	0.89
32	0.87
33	0.86
34	0.84
35	0.83

REFERENCE.

RICHARDS, Chapter 6, Table 15.

APPENDIX 9

SAMPLING APPARATUS FOR INSOLUBLE MATTER IN WATERS



NOT TO SCALE

9.A. CONSTRUCTION OF APPARATUS.

Set up the apparatus shown in the diagram, using a Grade B 50 ml pipette and holding the parts in position on laboratory scaffolding. A firm base is needed for the aspirator. The tip of the 50 ml pipette should be about 12 cm above bench level, thus allowing a 600 ml beaker to be placed conveniently underneath. In addition to the parts shown, a block of wood about 8 cm high is needed to support the beaker during sampling.

9.B. DIRECTIONS FOR USE.

1. Initial Preparation.

To fill the aspirator with water, close tap Y, remove stopper P and insert a large funnel in the wide glass tube. Allow a free passage for excluded air by turning tap X so that tube A connects with tube C and opening the screw clip G. Pour clear tap water into the aspirator until the level is near the shoulder. Remove the funnel and insert stopper P tightly. Close screw clip G and tap X.

2. Adjustment of Air Leak.

Start with all taps and screw clips closed and stoppers M and P in position. Place a 600 ml beaker containing about 500 ml water under the pipette and raise on the wood block so that the pipette tip is about 4 cm from the bottom of the beaker and 4-5 cm below the surface of the water. Open tap Y and turn tap X to connect tube A with tube C. Water runs out of the aspirator and, correspondingly, water is drawn out of the beaker into the 50 ml pipette. When the level reaches just above the 50 ml mark, close taps X and Y.

Lower the beaker to the bench and turn tap X to connect tube B with tube C. Gently open screw clip H until air slowly leaks in, allowing the liquid level in the pipette to fall. Adjust screw clip H carefully so that good control over the fall of liquid can be obtained with tap X only; it is essential that the fall of liquid can be stopped exactly at the 50 ml mark by operating tap X.

Remove stopper M allow the pipette to empty. Wash down the pipette (through tube D) and allow it to drain. Replace stopper M.

3. Taking a 50 ml aliquot from a Water Sample

Raise the beaker (containing about 500 ml of water sample) on the wood block and switch on the stirrer, making sure the spatula baffle is preventing any centrifuging effect on the particles of insoluble matter. Open tap Y and turn tap X to connect tube A with tube C. When liquid has risen in the pipette just above the 50 ml mark, close taps X and Y.

Switch off the stirrer and lower the beaker to the bench. Turn tap X to connect tube B with tube C, allow the liquid level to fall to the 50 ml mark and close tap X. Replace the beaker with a tared evaporating basin. Remove stopper M, allow the 50 ml aliquot to run into the basin and wash down the pipette with water, through tube D. Drain the pipette and replace stopper M.

9.C. NOTES.

(1) When the apparatus described is used for taking aliquots from a batch of water samples, a reduced pressure forms above the water in the aspirator and, if this is allowed to build up, a bubble of air may enter through the water when tap Y is opened. Thus, after about two aliquots have been taken, it is best, when the sample beaker is in position, to turn tap X to connect tube A with tube C before opening tap Y. For the same reason, tap Y may be closed before tap X as liquid rises near the 50 ml mark on the pipette.

(2) Although the water trap is essential to prevent water getting into the finely-adjusted air leak, the air space between tap X and the 50 ml pipette must not be too large or responses of the liquid level in the pipette to movements of tap X will be sluggish. Thus cotton wool is used to pack the trap.

(3) Ideally, during adjustment of the liquid level to the 50 ml mark, the tip of the pipette should just touch the level of liquid in the beaker. If this is not convenient, remove any drop of sample on the pipette tip with filter paper before transferring the aliquot to the evaporating basin.

APPENDIX 10

RELATION BETWEEN CONDUCTIVITY AND SOLUBLE SALTS FOR WATERS

TABLE A. For natural waters containing mainly bicarbonates and sulphates of calcium and magnesium

Conductivity micromhos at 25°C	Soluble Salts g per litre	Conductivity micromhos at 25°C	Soluble Salts g per litre
10 - 20	0.01	510 - 520	0.36
25 - 35	0.02	525 - 535	0.37
40 - 45	0.03	540 - 550	0.38
50 - 60	0.04	555 - 560	0.39
65 - 75	0.05	565 - 575	0.40
80 - 90	0.06	580 - 590	0.41
95 - 105	0.07	595 - 605	0.42
110 - 120	0.08	610 - 620	0.43
125 - 135	0.09	625 - 635	0.44
140 - 150	0.10	640 - 645	0.45
155 - 160	0.11	650 - 660	0.46
165 - 175	0.12	665 - 675	0.47
180 - 190	0.13	680 - 690	0.48
195 - 205	0.14	695 - 705	0.49
210 - 220	0.15	710 - 720	0.50
225 - 235	0.16	725 - 735	0.51
240 - 245	0.17	740 - 750	0.52
250 - 260	0.18	755 - 760	0.53
265 - 275	0.19	765 - 775	0.54
280 - 290	0.20	780 - 790	0.55
295 - 305	0.21	795 - 805	0.56
310 - 320	0.22	810 - 820	0.57
325 - 335	0.23	825 - 835	0.58
340 - 350	0.24	840 - 845	0.59
355 - 360	0.25	850 - 860	0.60
365 - 375	0.26	865 - 875	0.61
380 - 390	0.27	880 - 890	0.62
395 - 405	0.28	895 - 905	0.63
410 - 420	0.29	910 - 920	0.64
425 - 435	0.30	925 - 935	0.65
440 - 445	0.31	940 - 950	0.66
450 - 460	0.32	955 - 960	0.67
465 - 475	0.33	965 - 975	0.68
480 - 490	0.34	980 - 990	0.69
495 - 505	0.35	995 - 1005	0.70

Based on the relation - 1000 micromhos = 0.70 g salts per litre

APPENDIX 10

RELATION BETWEEN CONDUCTIVITY AND SOLUBLE SALTS FOR WATERS

TABLE B. For natural saline waters containing sodium and chloride in addition to bicarbonates and sulphates of calcium and magnesium

Conductivity micromhos at 25°C	Soluble Salts g per litre	Conductivity micromhos at 25°C	Soluble Salts g per litre
10 - 20	0.01	510 - 520	0.31
25 - 40	0.02	525 - 540	0.32
45 - 55	0.03	545 - 555	0.33
60 - 75	0.04	560 - 575	0.34
80 - 90	0.05	580 - 590	0.35
95 - 105	0.06	595 - 605	0.36
110 - 120	0.07	610 - 620	0.37
125 - 140	0.08	625 - 640	0.38
145 - 155	0.09	645 - 655	0.39
160 - 175	0.10	660 - 675	0.40
180 - 190	0.11	680 - 690	0.41
195 - 205	0.12	695 - 705	0.42
210 - 220	0.13	710 - 720	0.43
225 - 240	0.14	725 - 740	0.44
245 - 255	0.15	745 - 755	0.45
260 - 275	0.16	760 - 775	0.46
280 - 290	0.17	780 - 790	0.47
295 - 305	0.18	795 - 805	0.48
310 - 320	0.19	810 - 820	0.49
325 - 340	0.20	825 - 840	0.50
345 - 355	0.21	845 - 855	0.51
360 - 375	0.22	860 - 875	0.52
380 - 390	0.23	880 - 890	0.53
395 - 405	0.24	895 - 905	0.54
410 - 420	0.25	910 - 920	0.55
425 - 440	0.26	925 - 940	0.56
445 - 455	0.27	945 - 955	0.57
460 - 475	0.28	960 - 975	0.58
480 - 490	0.29	980 - 990	0.59
495 - 505	0.30	995 - 1005	0.60

Based on the relation -

1000 micromhos = 0.60 g salts per litre

APPENDIX 11

ATOMIC ABSORPTION SPECTROPHOTOMETRY

During the time taken for preparation of this Guide, the use of atomic absorption spectrophotometry has increased considerably in the general field of soil and water analysis. Thus, at various appropriate points in the script, the possibility of using this technique has been mentioned.

If a soil and water laboratory possesses or acquires an atomic absorption spectrophotometer, it should certainly be used experimentally in the determination of calcium, magnesium, iron, manganese, copper, zinc and molybdenum to establish whether it gives more accurate results - or results of similar accuracy more quickly or more easily - than the procedures included in this Guide. In this experimental work, it is necessary to take note of possible interferences and either measure them or eliminate them. Although interferences are often less than in flame emission photometry, they can still exist; thus phosphate can reduce the atomization of calcium, and aluminium that of magnesium.

For each individual element being determined, a full programme of experimental tests should be conducted, similar to those suggested in Section IV.B.D.(a) for sodium by flame emission photometry, making full use of the literature normally supplied by the manufacturers of atomic absorption spectrophotometers to assess possible interfering ions or salts. It is emphasized that soil extracts can vary a great deal in composition according to the type of soil being analysed and care must be taken to allow for this in the study of these interference effects.

One type of atomic absorption spectrophotometer, using one kind of mixed fuel, may not be equally suitable for determination of all the elements mentioned above. Thus, a hot flame (air-acetylene) may reduce chemical interferences in the determination of calcium and magnesium but be less suited to the determination of copper, zinc and manganese. Many considerations of this kind have to be taken into account in deciding whether to employ atomic absorption spectrophotometry in preference to other methods. At present (1969) it seems likely that this new technique will eventually supercede the use of EDTA in the determination of calcium and magnesium in soils and waters, just as flame emission photometry has completely replaced the old chemical methods for sodium and potassium. Atomic absorption spectrophotometry also has obvious advantages in the determination of minor elements on a large scale. However, the chemical methods included in this Guide are still useful as standard methods for comparison purposes and may even be more suited to the working conditions of some laboratories.

LIST OF REFERENCES

I -- BOOKS

The following books have been consulted in writimg the Guide and developing the procedures suggested. Detailed references to appropriate sections are given at the end of each method; these sections may provide more explanation of the principles involved or alternative methods or modifications which may be mentioned in the Guide.

References.	Year.	Titles, Authors and Publishers.
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AKROYD.	1957	LABORATORY TESTING IN SOIL ENGINEERING by T.N.W. Akroyd. Soil Mechanics Limited, U.K.
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VOGEL	1962	A TEXT-BOOK OF QUANTITATIVE INORGANIC ANALYSIS, INCLUDING ELEMENTARY INSTRUMENTAL ANALYSIS by A.I. Vogel. Third edition. Longmans, Green and Company, Ltd., London.
WILSON	1959 1960 1962	COMPREHENSIVE ANALYTICAL CHEMISTRY, VOLUMES I.A, I.B and I.C. by various authors under the joint editorship of C.L.Wilson and D.W.Wilson. Elsevier Publishing Company, Amsterdam, London, New York.

The following books will provide useful additional information.

DEAN	1960	FLAME PHOTOMETRY by J.A. Dean. McGraw-Hill Book Company, Inc., New York.
DUCHAFOUR	1960	PRECIS DE PEDOLOGIE by P. Duchafour Masson et Cie, Paris, France.
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II -- ANNOTATED BIBLIOGRAPHIES

These bibliographies are prepared by the Commonwealth Bureau of Soils, Rothamsted Experimental Station, Harpenden, England from abstracts originally printed in its journal "Soils and Fertilizers", published by Commonwealth Agricultural Bureaux, Farnham Royal, Bucks, England. The bibliographies cover world literature on soil science and fertilizer use; and short summaries provide information on the papers quoted.

The following are referred to in this Guide.

Serial Number	Years Covered	Title
508	-	Mechanical analysis of soil.
652	1951-1962	The determination of soil pH.
661	1956-1963	Phosphate determination in relation to crop response.
668	1956-1963	Fertilizer response in relation to some chemical and physical soil test values. Production functions.
689	1950-1962	Determination of manganese in soil.
690	1950-1962	Determination of zinc in soil.
719	1956-1963	Soil deficiencies in Zn and Cu.
720	1955-1963	Potash fixation.
751	1950-1963	Determination of bulk density and compaction.
766	-	Nitrogen determination in relation to crop responses.
779	1963-1964	Phosphate determination in relation to crop response.
789	1961-1964	Determination of cation exchange capacity.
852	1950-1964	Determination of boron in soil.
854	1957-1964	Effects of soil storage and pre-treatment on nitrogen determination.
860	1956-1964	Sampling variation in soil nitrogen, carbon and bulk density.
869	1931-1964	Tolerance of forage crops, cereals and potatoes to aluminium.
870	1945-1964	Determination of lime requirement and exchange acidity.
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885	1951-1964	Effects of soil storage and treatment on nitrogen transformations.
890	1956-1963	Soil sampling for soil analysis.
922	1956-1965	Aluminium in plant nutrition.
963	1956-1965	Mechanical analysis of soil.
966	1951-1964	Methods of measuring nitrogen mineralization.

979	1945-1965	Aluminium and soil acidity.
983	1956-1964	Phosphorus determination in tropical soils.
1004	1964-1965	Phosphate determination in relation to crop response.
1005	1957-1965	Potassium determination in relation to crop responses.
1006	1957-1965	Nitrogen determination in relation to crop responses
1012	1958-1965	Effect of soil moisture on availability of P.
1067	1957-1966	Molybdenum in soils.
1077	1953-1966	Determination of zinc in soil.
1080	1943-1966	Variability of soil samples taken for chemical analysis
1086	1957-1965	Chemical methods of assessing available potassium in soils
1090	1962-1966	Availability of copper and zinc in soils
1093	1958-1965	Effect of drying and storage on exchangeable K in soil

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III -- JOURNAL OR REPORT PAPERS

The books and bibliographies quoted above give extensive references to papers in journals covering the subject matter of this Guide. These may be consulted if more information is needed on historical development of individual methods or on details of theory or procedure.

Eight papers are quoted in the references as having appropriate information not appearing (as far as is known) in the books used.

These are -

DEB	1966	A NEW METHOD FOR ESTIMATING GYPSUM IN SALINE AND ALKALI SOILS by B.C. Deb. United Arab Republic - High Dam Soil Survey (Special Subjects and Investigations). Report of United Nations Special Fund Project FAO/SF/16/UAR, Appendix I, pp 3-9.
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Clay Mineral Bulletin, Vol. 3, No. 15.

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Z. Pfl. Brnährr. Düng., Vol 103, pp. 193-196.
Abstract 1378, Soils and Fertilizers, Vol XXVII, p. 198.

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