Food and Agriculture Organization of the United Nations

Standard operating procedure for soil total nitrogen

Dumas dry combustion method

GLOBAL SOIL PARTNERSHIP

Standard operating procedure for soil total nitrogen Dumas dry combustion method

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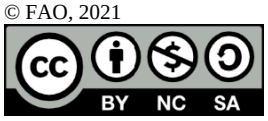

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SOIL TOTAL NITROGEN

Dumas dry combustion method

VERSION HISTORY

No.	Date	Description of the modification	Type of modification
01	12 January 2021	All comments by RESOLANs and reviewers to the draft SOP were addressed	Finalization of the SOP
02			
03			
04			

Contents

1. Brief introduction to total nitrogen

Nitrogen (N) is considered an essential macronutrient for plant development, playing a key role in the formation of proteins, DNA, RNA, etc. Analysis and quantification of soil total nitrogen (TN) is used to estimate nitrogen availability from the natural decay of organic materials. Testing for TN in arable soils is useful for making nitrogen fertilization management decisions if local mineralization rates are known.

Several methods are used to quantify soil nitrogen. The Dumas dry combustion method determines TN, representing all chemical forms of N in the soil. Other methods may be used to quantify the various forms of nitrogen. For example, the Kjeldahl method measures oxidizable organic nitrogen and also ammonium (it is also possible to include nitrites and nitrates, by adding reducing reagents before digestion).

An elemental analyzer is used for the analysis of TN by dry combustion. An advantage of using this equipment is the possibility of quantifying carbon, nitrogen and sulphur in the same sample, using a smaller amount of reagents and without generating hazardous waste. Disadvantages of its use are the initial cost of the equipment, the operating and maintenance costs, and the small number of laboratories using the autoanalyzer in the world. In addition, extra care must be taken during sample preparation if TN is quantified by the dry combustion method, as a very small sample is used, requiring it to be well homogenized. Nevertheless, some manufacturers already have equipment which use larger amounts of sample (up to 3 g), decreasing the risk of non-representative aliquots and increasing the determination accuracy in samples with very low C contents.

2. Scope and field of application

This Standard Operating Procedure (SOP) describes, in general terms, the quantification of TN content in soil samples by an elemental analyzer. The procedure measures both organic nitrogen and inorganic nitrogen together.

A typical limit of detection is 0,1 g kg^{-1} N, and a typical limit of quantification is 0,3 g kg^{-1} N, however this varies depending on the manufacturer and detector settings**.**

3. Principle

This method is based on the Dumas dry combustion principle. The sample is burned at high temperature (greater than 900 ºC) in an atmosphere of pure oxygen (O_2). Under these conditions, all nitrogen-containing compounds are completely decomposed and converted into nitrogen oxides and molecular nitrogen. After transforming all nitrogen into molecular nitrogen, the autoanalyzer measures the N content using thermal conductometry or other device specific detectors. Finally, it indicates the TN value as the concentration of elemental nitrogen present in the sample.

4. Apparatus

1. Elemental analyzer for N, with all specific accessories and consumables, including appropriate detection system.

The equipment must be well maintained, paying special attention to the saturation of the water trap.

Some apparatus has the option of allowing the operator to adjust the sample aliquot and detector settings to carry out the measurements.

Instrument precision can be optimized by using the largest sample aliquot for a given detector sensitivity range. Sample aliquot size is generally based on the anticipated analyte concentration.

The equipment might also analyse total carbon and total sulphur, depending on the manufacturer and model.

2. Analytical balance, ±0.0001 g, to weigh samples and reference materials.
3. Milling system that meets the requirements of the elemental analyzer manufacturer.

5. Materials

1. Certified Reference Material (CRM) with a known TN content to calibrate the elemental analyzer. (e.g. Ethylenediaminetetraacetic acid -EDTA, Aspartic acid - $C_4H_7NO_4$, acetanilide - C_8H_9NO or soils with certified N content)
2. Combustion gas (O_2) of very high purity (greater than 99.99 percent).
3. Reference or carrier gas (helium-He or argon-Ar), of very high purity (greater than 99.99 percent).

Thermal conductivity detectors work by detecting changes in the thermal conductivity of the analyte gas compared to the constant thermal conductivity of the reference/carrier gas. The greater the difference between the thermal conductivity of the carrier gas and the analyte gas, the greater the sensitivity response the detector will have. So, He used as a carrier gas, provides the highest sensitivity, and the best performance at the detection and quantification limit of nitrogen. Ar can also be used as a carrier gas, but the thermal conductivity difference between Ar and N is not as great as the thermal conductivity difference between He and N, therefore the detector is less sensitive when Ar is used as a carrier gas.

4. Consumables specific to the elemental analyzer.

6. Health and safety

This SOP does not imply the direct use of hazardous chemical reagents, however adequate safety precautions are necessary as some reagents and catalyst residues are toxic and must be disposed of properly. Gloves, lab coats, and safety glasses must be worn when handling reagents and samples. When a special reagent is used (for example, a reference material for equipment control), consult the material safety data sheet (MSDS) and conduct a risk assessment. Take the necessary precautions when handling compressed gasses and high-temperature equipment. Follow the manufacturer's safety guidelines when operating the elemental analyzer.

7. Sample preparation

The sample size varies from grams (g) to milligrams (mg), depending on the TN of the sample and the dynamic range of the analyzer. The smaller the sample size, the finer the grinding should be and the more homogeneous the sample. Then, a representative portion of the pre-treated soil sample (dried

and sieved to 2 mm) should be milled until the entire fraction passes through a sieve with a sufficiently fine mesh.

Note: All plant residues must be carefully removed before grinding the soil sample.

In general, if a mass greater than 1 g is weighed, a soil sample sieved by 2 mm can be used, but if a mass less than 1 g is used, it is recommended to mill the <2 mm fraction to 0.5 mm or less.

If supplied, follow the sample preparation instructions provided by the manufacturer to use the autoanalyzer.

Care must be taken to ensure that the milling equipment and the sieves do not introduce contamination into the samples.

8. Procedure

8.1. Calibration of the apparatus

Calibrate the equipment as described in the analyzer instruction manual. Use a CRM provided or recommended by the manufacturer (soil samples with certified total N content, aspartic acid, ethylenediaminetetraacetic acid - EDTA, acetanilide, etc.).

The calibration should cover the range of TN found in the batch samples.

Store and use all CRM as indicated on the manufacturer's label.

Fluctuations in TN may be caused by differences in nitrogen content of the carrier gases used. Therefore, a blank determination should be performed after changing the gas bottles. An increase in blank value may indicate chemical reagent failure or analyte carryover due to incomplete combustion.

Replicate blanks must also be analysed to determine the baseline according to the specific equipment procedure.

8.2. Determination of the total nitrogen (TN) content

As the analysis procedure varies between equipment and manufacturers, samples should be analyzed according to the manufacturer's guidelines for soil analysis.

The mass of the sample weighed is dependent on the TN of the sample and the dynamic range of the analyzer.

In general, it is recommended to weigh a mass between 50 mg and 2000 mg, considering the recommendations for sample preparation.

Samples must be weighed very precisely (for mg quantities, a highly sensitive balance is required - ± 0.0001 g), and scrupulous care is necessary to avoid contamination.

To check the elemental analyzer performance, CRM, control samples (Internal Reference Material – IRM), and blanks should be incorporated at regular intervals into each test batch. The number and frequency of control and check samples depends on the method used and the calibration stability of

the autoanalyzer. In general, it is recommended to perform daily calibration and controls with CRM and to use control samples (IRM) and blanks every 20-30 samples.

9. Calculation

Report TN using the International Units System as: milligrams of N per gram of soil (mg g^{-1}) or grams of N per kilogram of soil (g kg^{-1}). It is also possible to report results in percentage of N (percent), in which case, the result in mg g^{-1} or g kg^{-1} should be divided by ten.

Results should be reported based on air dry soil or oven dry soil (40 °C).

The number of decimals reported must conform to conventional rules of maintaining three digits:

- values greater than 100, no decimal reported;
- values between 10 and 100, 1 decimal (0.1) reported; and
- values less than 10, 2 decimals (0.01) reported.

10. Quality assurance/Quality control

10.1. Precision test

- At least five percent (5 percent) of the samples in a test batch must be replicates, ensuring at least one duplicate sample if the batch is small.

- Calculate the percentage relative standard deviation (RSD percentage) to determine precision.

$$\% \, RSD = \frac{s}{\bar{x}} \times 100$$

Where: s = standard deviation of the replicate result
$\bar{x}$ = mean

- Compare the result with the previously specified precision.

Acceptance requirements for precision testing must be defined by the equipment used, environmental conditions, and other testing factors, as well as specifications or requirements for the use of information and agronomic criteria.

If the precision test fails, the cause of the failure must be identified, and corrective or preventive actions must be developed.

10.2. Trueness test

10.2.1. **Recovery test**

- Perform triplicate analysis of CRM of the analysed matrix (soil) or an IRM, in accordance with the present SOP.

To assess instrument performance, this procedure should be replicated with different levels of TN.

The different levels can be selected by using a CRM with different concentrations of TN or by simply weighing different masses of the same CRM.

- Calculate the percentage recovery based on the equation below.

$$\% \text{ Recovery} = \frac{\text{mean of observed values}}{\text{true value}} \times 100$$

- Compare the result with the recovery target (percent), which is predefined for the usual range of work.

The recovery target must be defined for the usual range of work. The definition should take into account the working conditions (for example the characteristics of the equipment used and the environmental conditions). It should also consider the specifications or requirements for the given use of the information and any agronomic criteria. Recovery may also be considered acceptable if it is within the confidence interval reported for the certified value of CRMs.

If the recovery test fails, the cause of the failure must be identified and corrective or preventive actions must be developed.

10.2.2. **Interlaboratory comparison**

The laboratory must participate (at least once a year) in interlaboratory proficiency tests.

If the result obtained is questionable or unsatisfactory, it is necessary to; carry out an evaluation, identify the root cause of the problem, and develop corrective and preventive actions.

10.3. Control chart

- Perform the replicate analysis of a control sample or an IRM in a test batch of samples
- Plot the result in a control chart
- Monitor the results

If the results are out of specified limits (or tend to be so), an evaluation must be carried out. The cause of noncompliance must be identified, and corrective and preventive actions must be developed.

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12. Appendix I.—Acknowledgments

GLOSOLAN would like to thank Ms. Miriam Mabel Ostinelli for leading the harmonization of this SOP and Ms. Špela Velikonja Bolta, working group leader for Europe and Eurasia, for her contribution to the writing of this SOP. GLOSOLAN would also like to thank the experts who were part of the Review Panel and who ensured the finalization of the SOP, all laboratories that provided inputs for the harmonization of this method, all experts who technically reviewed this SOP and Mr. Christopher Lee from the Kellogg Soil Survey Laboratory, USDA-NRCS-NSSC, United States of America for proofreading it.

13. Appendix II. — List of authors

Leading author:

- Ms. Miriam Mabel Ostinelli, Laboratorio del Instituto de Suelos CIRN-CNIA-INTA**, Argentina**

Main authors (in alphabetical order):

- Ms. Špela Velikonja Bolta, Agricultural Institute of Slovenia, **Slovenia**

Members of the Review Panel (in alphabetical order):

- Mr. Alan Evans, A2 Análises Químicas, **Portugal**
- Ms. Aunthicha Phommuangkhuk, Soil and Plant Analysis Laboratory, Department of Soil Science, Faculty of Agriculture at Kamphaeng Saen, Kasetsart University, **Thailand**
- Mr. João Coutinho, Universidade de Trás-os-Montes e Alto Douro, **Portugal**
- Ms. Miriam Mabel Ostinelli, Laboratorio del Instituto de Suelos CIRN-CNIA-INTA**, Argentina**

14. Appendix III. — Contributing laboratories

GLOSOLAN would like to thank the following laboratories for completing the GLOSOLAN form on the method and providing information on their standard operating procedure for the soil total nitrogen - Dumas dry combustion method. This information was used as a baseline for the global harmonization.

From the Asian region:

- ICAR-Indian Institute of Soil Science, **India**
- Laboratory of Soil Science, Department of Plant and Soil Sciences, Faculty of Agriculture, Chiang Mai University, **Thailand**
- Department of soil science, Faculty of Agriculture, Kasetsart University, Kamphaeng Sean Campus, **Thailand**

From the Pacific region:

- DES - Chemistry Centre, **Australia**

From the Near East and North African region:

- Directorate of Plant wealth, Ministry of Works, Municipalities & Urban Planning, **Bahrain**
- Kuwait Institute for Scientific Research, **Kuwait**

From the African region:

- None

From the European region:

- Axe Echanges Eau-Sol-Plantes, GxABT, Liege University, **Belgium**
- University of Zagreb, Faculty of Agriculture, Department of General Agronomy, **Croatia**
- Central Institute for Supervising and Testing in Agriculture, **Czechia**
- Aarhus University, AGRO University laboratory, **Denmark**
- Natural Resources Institute Finland, **Finland**
- Laboratory of soil monitoring, Thuenen- institute, **Germany**
- Food Chain Safety Centre Non-profit Ltd., **Hungary**
- Latvian State Forest Research Institute "Silava", **Latvia**
- AgroCares Golden Standard Laboratory (Care4Agro BV), **Netherlands**
- Biologisch Laboratorium Bodem, Wageningen Universtiy, **Netherlands**
- A2 Analises Quimicas, Lda, **Portugal**
- National Research and Development Institute for Soil Science Agrochemistry and Environment – Department for physical and chemical analysis, **Romania**
- Soil Fertilizer and Water Resources Central Research Institute, **Turkey**
- Rothamsted Research, **United Kingdom of Great Britain and Northern Ireland**

From the Eurasian region:

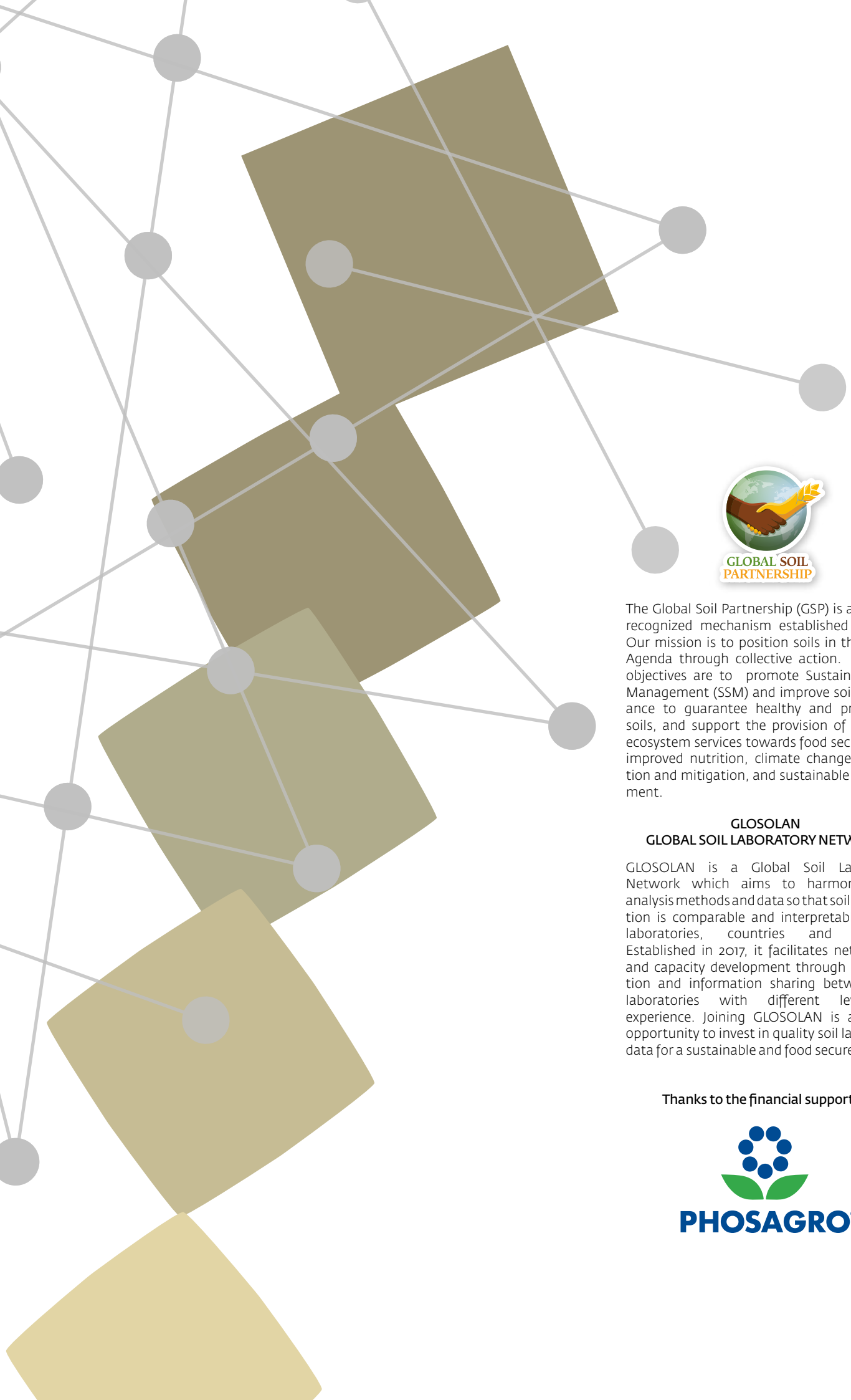
- None

From Latin America:

- Laboratorio del Instituto de Suelos. CIRN – CNIA - INTA. **Argentina**
- Laboratorio de Suelos y Tejidos Vegetales, Universidad de Concepción, **Chile**
- Agencia de Regulación y Control Fito y Zoosanitario. AGROCALIDAD, **Ecuador**
- Ministerio de Ganadería Agricultura y Pesca (MGAP), Laboratorio de Caracterización de suelos, **Uruguay**

From North America:

- None



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