Food and Agriculture Organization of the United Nations

GLOSOLAN
GLOBAL SOIL LABORATORY NETWORK

Analytical Method Validation for Soil Testing Laboratories

Noorunisha Abdool

July '25

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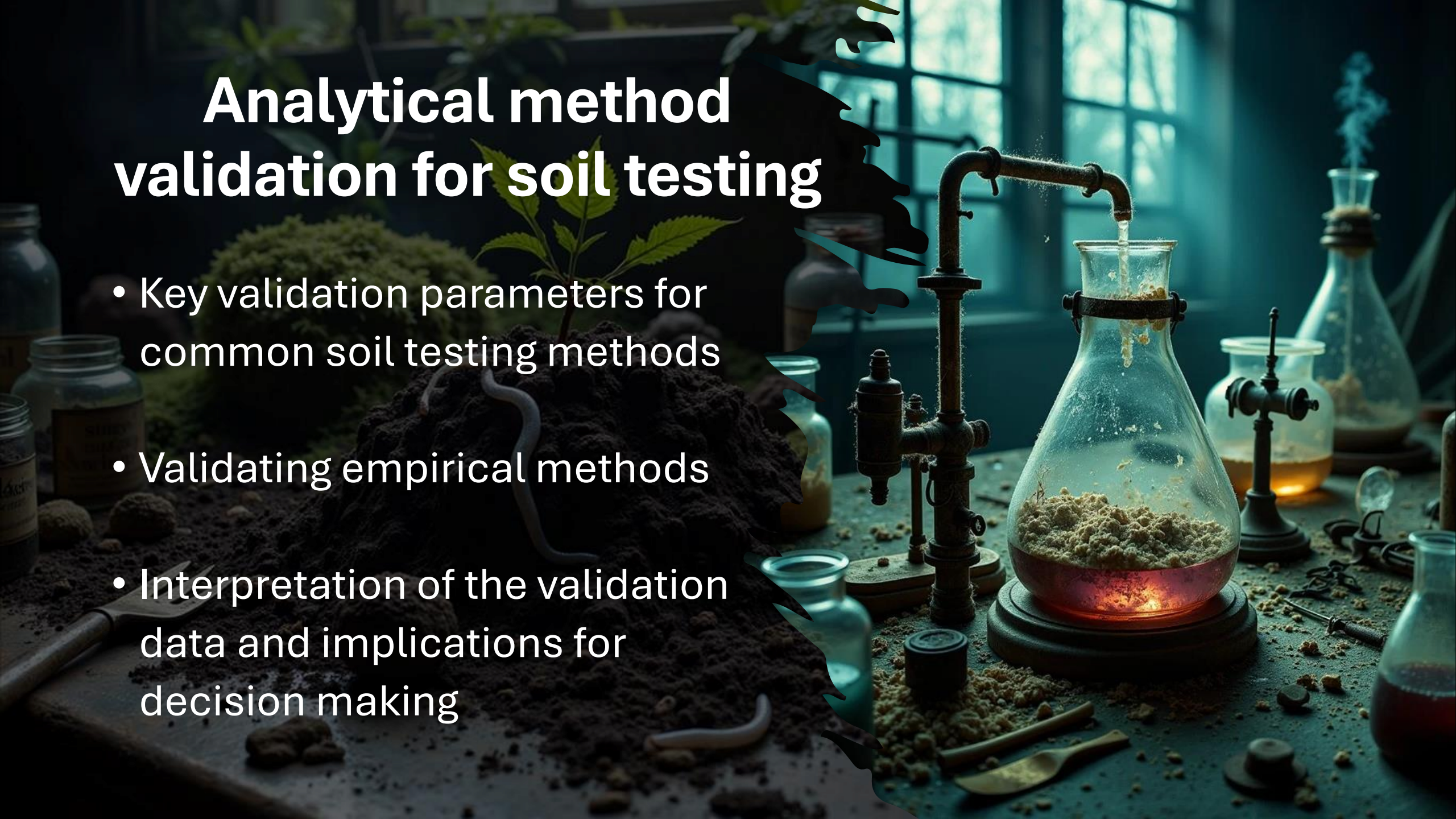
Analytical method validation for soil testing

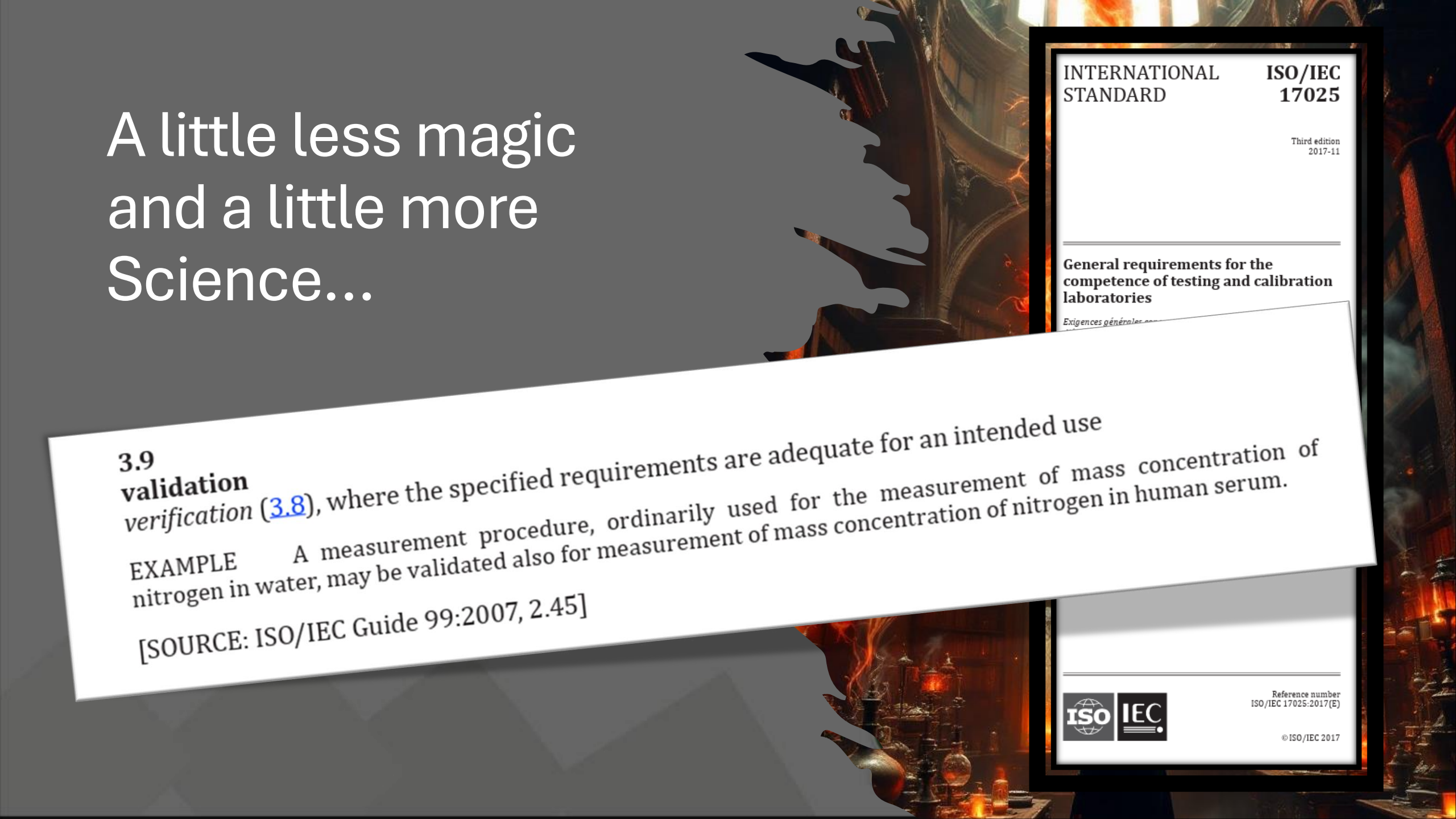
- Key validation parameters for common soil testing methods
- Validating empirical methods
- Interpretation of the validation data and implications for decision making



A little less magic and a little more Science…

Analytical Method Validation

A little less magic and a little more Science…



3.9
validation
verification (3.8), where the specified requirements are adequate for an intended use

EXAMPLE A measurement procedure, ordinarily used for the measurement of mass concentration of nitrogen in water, may be validated also for measurement of mass concentration of nitrogen in human serum.

[SOURCE: ISO/IEC Guide 99:2007, 2.45]

Analytical Method Validation

3.8
verification
provision of objective evidence that a given item fulfils specified requirements

Method Validation is the process where the laboratory proves that their method is fit for purpose.

Fit for purpose means the method is performed while taking the customer's analytical requirements, uncertainty of measurement, cost, time, laboratory requirements and methods performance characteristics etc. into consideration for both the laboratory and the client.

Method validation includes evaluating performance characteristics and comparing them with the analytical requirements.

When should a Soil laboratory validate a method?

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A few days before th auditor is scheduled to arrive.....

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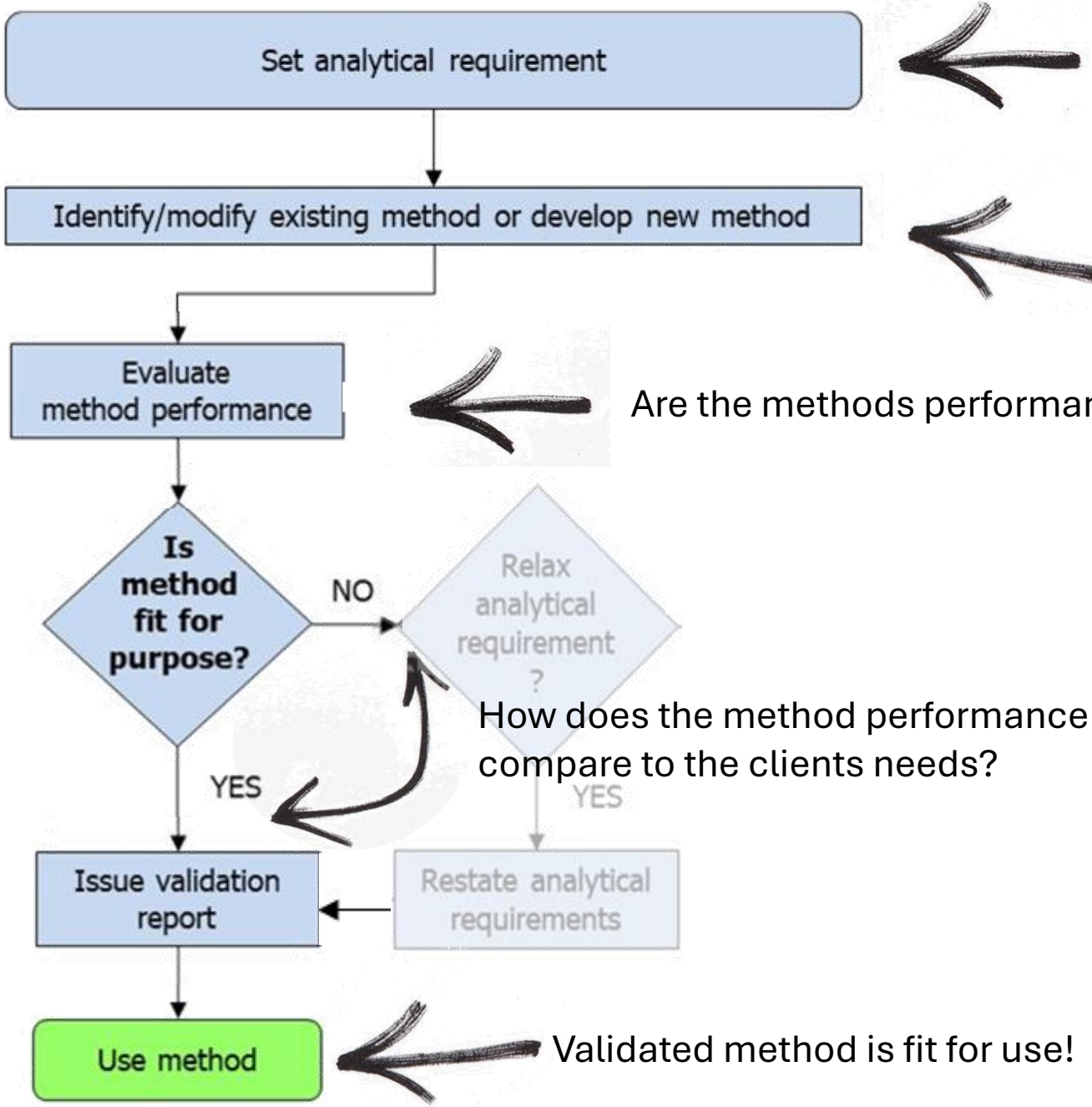
A few days before th auditor is scheduled to arrive.....

- A need to verify the method's performance characteristics are fit for use
- Development of a new method
- Revision of the method to address a new customer requirement
- Laboratory QC shows the method is changing with time
- A new laboratory space, or new instruments are being used



What does your client need?

What method can your laboratory offer?

Are the methods performance characteristics as you expected?

How does the method performance characteristics compare to the clients needs?

Validated method is fit for use!

Referenced from:
Eurachem MV Leaflet
Produced by the Eurachem Method Validation Working Group
First English edition, January 2021
www.eurachem.org

Where to begin?

Documents:

ISO 17025

TR-26

Validation Plan

Internal Quality Management System

Soil samples:

Certified Reference Material

Proficiency testing samples

Internal Soil Control samples*

Proficiency testing samples

Agromat AG-1 & Agromat AG-2

ALP
Agricultural Laboratory
Proficiency Program

AGRI ALASA
N P K Ca Mg S Zn Fe Mn Cu
AGRILABORATORY ASSOCIATION OF SOUTHERN AFRICA
AGRILABORATORIUM ASSOSIASIE VAN SUIDELIKE AFRIKA

Alpha Resources
Synthetic Soils

Sigma Aldrich Montana Soil I

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Certified Reference Material

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The South African National Accreditation System (SANAS) is the only national body responsible for carrying out accreditations in respect of conformity assessment, as mandated through the Accreditation for Conformity Assessment, Calibration and Good Laboratory Practice Act (Act 19 of 2006)

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NOTIFICATION OF B-BBEE RATING AGENCY WITHDRAWALS

2025-05-22 | Trending News

At times, the Accreditation of a B-BBEE Rating Agency can be withdrawn voluntarily or involuntarily or may even expire, and in order to assist the end user of a B-BBEE Verification Certificate to ensure that the B-BBEE Verification Certificate is valid and has not been fraudulently issued, please take note of the attached announcement: B-BBEE Rating Agency Withdrawals - May 2025.pdf

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List of Publications

Document No. tr26

tr26

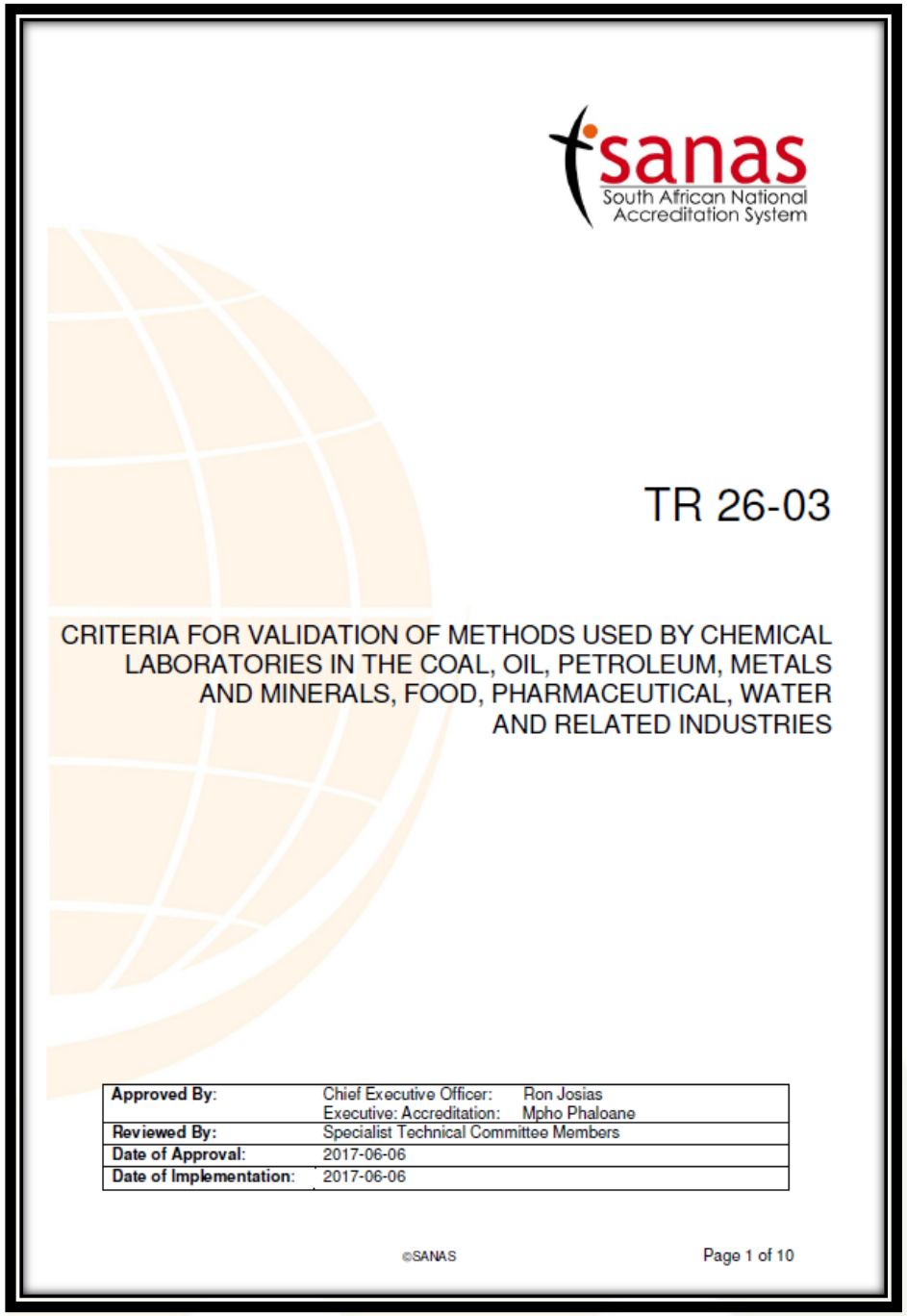
Document Title

Category Select Value

Search..

Document No.	Issue	Date of Publication	Title	Category	Document Link
TR 26	3	2017-06-06	Criteria for Validation of Methods used by Chemical Laboratories in the Coal, Oil, Petroleum, Metals and Minerals, Food, Pharmaceutical, Water and Related Industries	Testing, Pharmaceutical	TR 26-03

whether products, services, or systems meet specified standards and requirements. These bodies play a crucial role in ensuring quality, safety, and compliance in various industries. Read more on attached: SANAS Statement - Suspension of Laboratories.pdf


sanas
South African National Accreditation System

TR 26-03

CRITERIA FOR VALIDATION OF METHODS USED BY CHEMICAL LABORATORIES IN THE COAL, OIL, PETROLEUM, METALS AND MINERALS, FOOD, PHARMACEUTICAL, WATER AND RELATED INDUSTRIES

Approved By:	Chief Executive Officer: Ron Josias Executive: Accreditation: Mpho Phaloane
Reviewed By:	Specialist Technical Committee Members
Date of Approval:	2017-06-06
Date of Implementation:	2017-06-06

The purpose of this document is to define the concepts and processes of method validation, and to provide technical requirements in order to facilitate a uniform approach. This document amplifies ISO/IEC 17025 requirements and lists SANAS requirements applicable to chemical laboratories.

The following do not form part of this document: sampling, sample handling and transportation.

- References, Definitions, Abbreviations
- Performance characteristics and criteria for a test method
- Validation Plan
- Implementation and Review
- Summary Report
- Revalidation

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Validation Plan = Blueprint

Validation Criteria

Which analytes are being determined and why?

What is the sample matrices?

Are there potential interferences?

Are there legal requirements?

How robust must the method be?

What are the expected concentration levels of the analytes?

Are there environmental conditions to be considered?

What instrumentation is being used?

* Is there a method available that covers sample preparation, sub-sampling, etc.? *

Performance Characteristics

Accuracy

Bias

Precision

Reproducibility

Linearity

Working Range

Limit of Detection

Limit of Quantification

Sensitivity

Specificity

Uncertainty of Measurement

Robustness

Performance Characteristics?

Parameters which define how well an analytical method performs its intended purpose

Identification	What is being measured ?
Working range	What is a valid range for the result ?
Precision	How do repeated results compare to each other ?
Accuracy	How far off the true value is the result ?
Uncertainty	How far off the true value could the result be ?
Stability	Do the results degrade over time ?
Robustness	What could become a problem ?

Identification

What is being measured, and where?

Instruments

The method validation report MUST specify which instrument the method was validated on.

If there are multiple instruments of the same kind e.g. ICP-OES each unit must have a unique identifier/name. When validating a method on an ICP-OES or similar, all the details and specifications of the instrument must be recorded including the positions of the wavelengths.

Interferences

List all known and important interferences.

These interferences will be addressed when determining selectivity/specificity.

Accuracy

How close the measured value is to the true value?

<u>Four ways to determine accuracy:</u>

Spiked Recovery Test ❌

Alternative Method ❌

Proficiency Testing Scheme/ Interlaboratory testing samples ✔

Certified Reference Materials  ✔

Accuracy should be determined by performing 10 different analyses - a reduced number of analyses can be run; however, it is not recommended.

<u>Two ways to report accuracy:</u>

MS Excel ✔

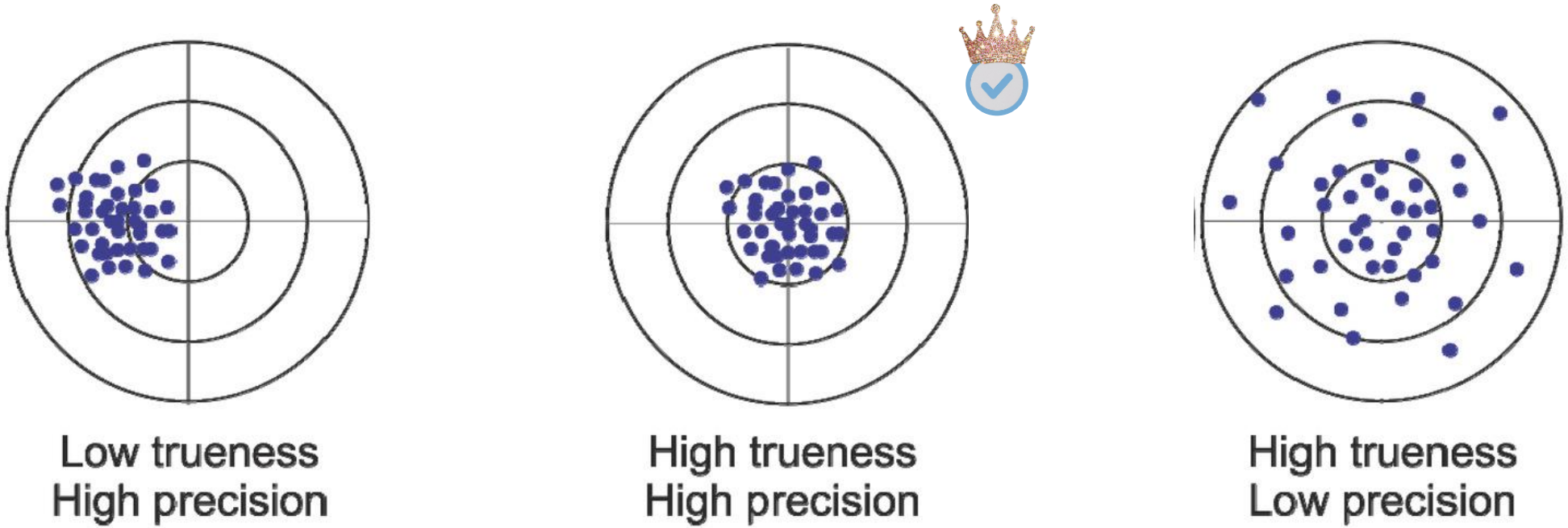
Validation Report Template ✔

The result is expressed as absolute difference and relative error, for a specific concentration.

For certified reference materials, the consensus value and uncertainty is given by the certificate of the material.
For PT Schemes or Interlaboratory testing, it is calculated by the scheme and reported.

Accuracy Includes Precision and Trueness

Trueness: How close is the mean of the TEST results compared to the result of the CRM?



Precision: How similar are the TEST results when compared to the result of the CRM?

The result is expressed as standard deviation, relative standard deviation (RSD) or RSD%

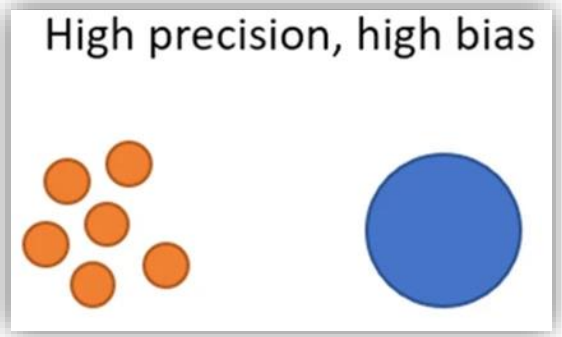
Accuracy

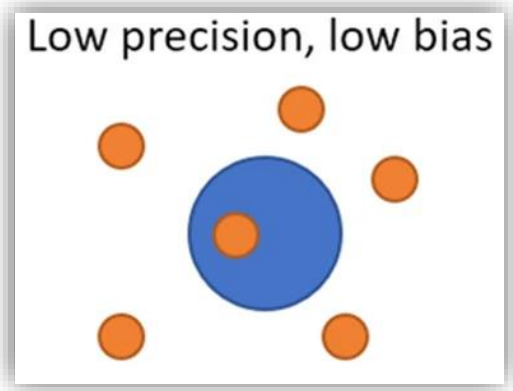
Results can be used to determine a Bias in the analytical method

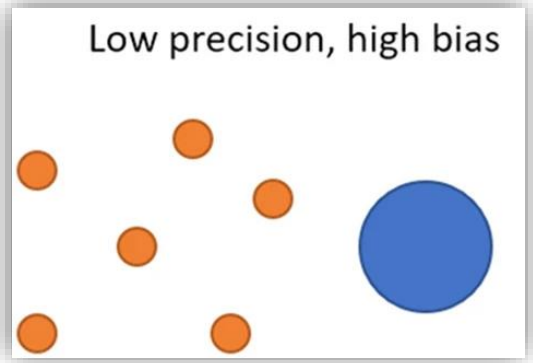
Determined by comparing the mean of the TEST results to the certified result of the CRM ***= Trueness***

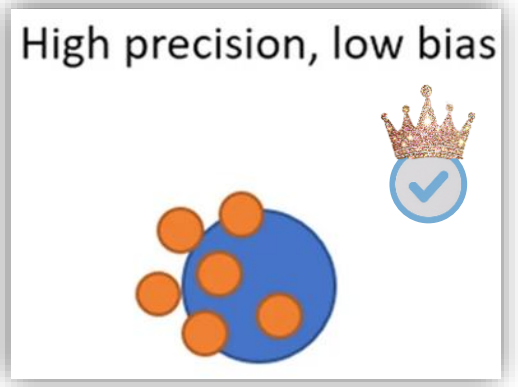
Bias?

A measure of systematic measurement error









Determined by comparing the mean of the TEST results to the certified result of the CRM ***= Trueness***

Performance Characteristics

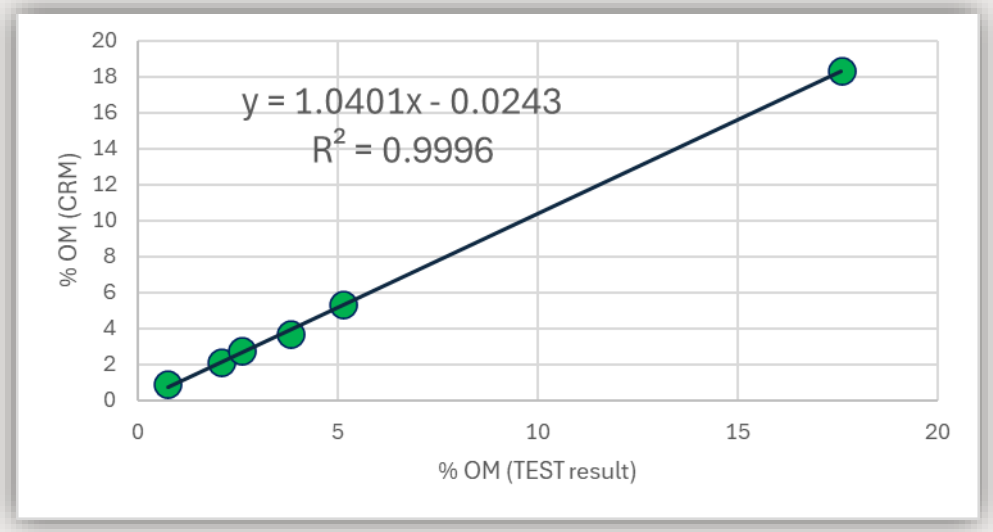
Parameters which define how well an analytical method performs its intended purpose

- **Accuracy**
- **Bias**
- **Precision**
- **Reproducibility & Repeatability**
- **Linearity**
- **Working Range**
- **Limit of Detection**
- **Limit of Quantification**
- **Sensitivity**
- **Specificity**
- **Uncertainty of Measurement**
- **Robustness**

Linearity

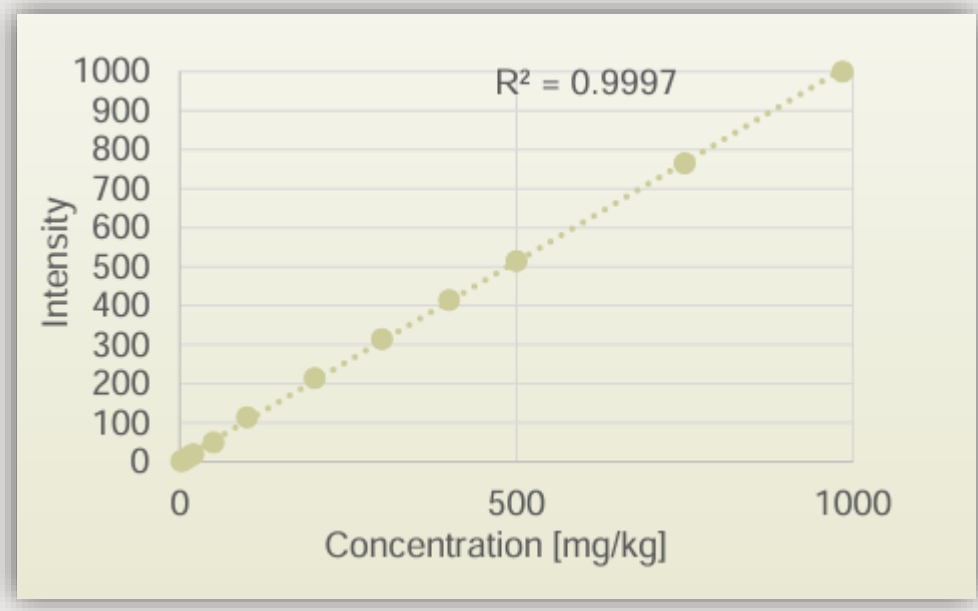
The ability of the method to accurately measure an analyte across a given range

The TEST results are directly proportional to the concentration of the analyte, most quantitative analytical methods are based on a linear calibration



A given analyte e.g. Carbon in soils; determined by titration via Walkley Black; shall be analysed at several concentrations. Each concentration must have at least six determinations

Minimum acceptable $R^2 > 0.999$ covering a concentration range of 80 – 120% of the target analyte concentration



Determination of the working range can be dependent on the composition of the soil.
On an ICP-OES a presence of large amount of Na can limit the working range of other elements like Ca.

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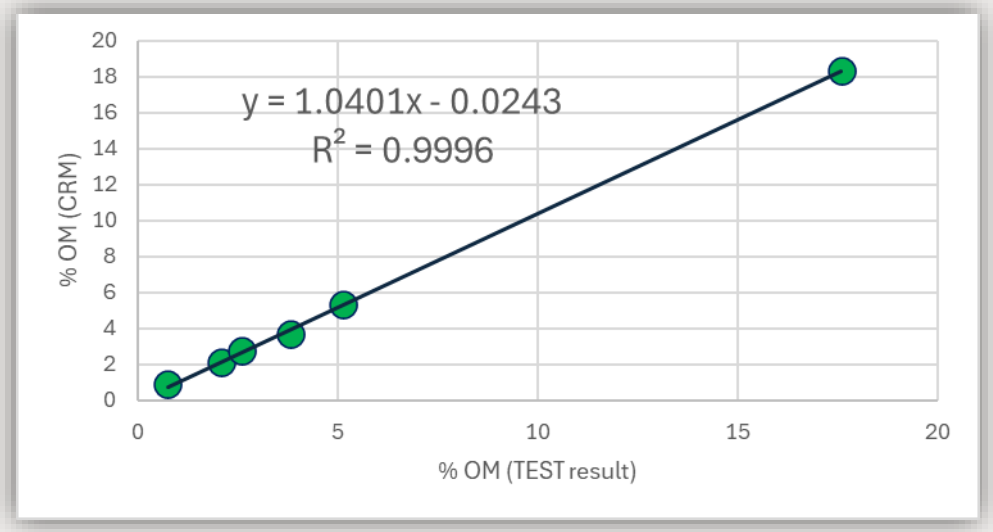

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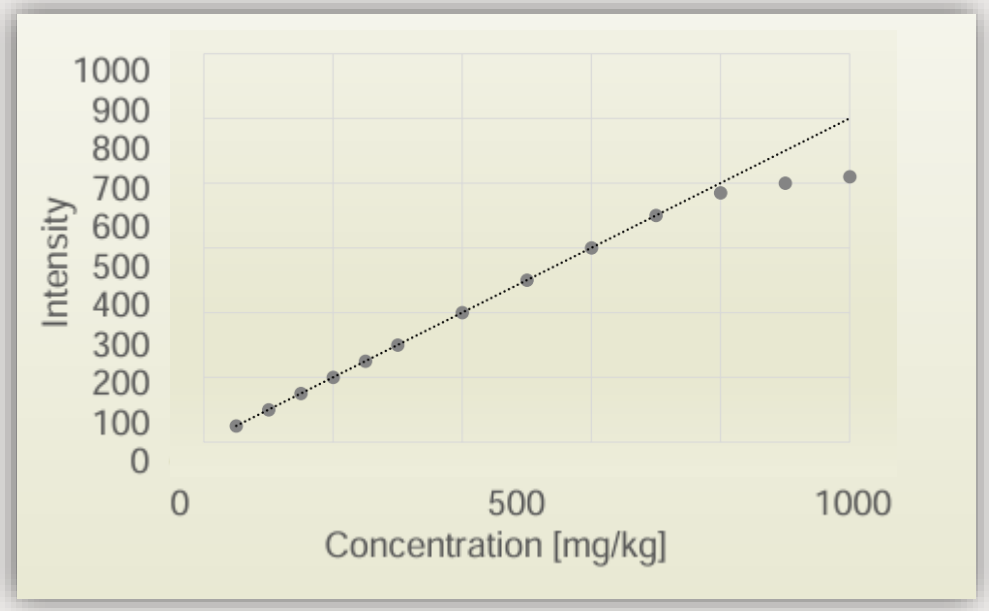


Determination of the working range can be dependent on the composition of the soil.
On an ICP-OES a presence of large amount of Na can limit the working range of other elements like Ca.

Working Range

What is a valid range for the result ?

The defined interval from the Minimum (Quantification Limit) to the Maximum (Linearity determination)

The working range is expressed in the same units as the TEST results obtained by the analytical method

Analyse a set of standards, covering the expected sample analyte concentration. Each standard concentration must be determined no less than six times

e.g. to determine % Organic Material and % Carbon determined by Carbon Walkley Black titration a concentration range of ± 0.1-14% was considered.

Standard concentration levels: 0.1; 0.3; 0.5, 1, 5 ,10, 14*

CRM's are not widely available for Carbon or Organic Material therefore PT/Interlaboratory testing samples were used

Limit of Detection (LOD)

The lowest concentration of an analyte that can be consistently detected

Limit of Quantification (LOQ)

The lowest concentration of an analyte that can be consistently measured

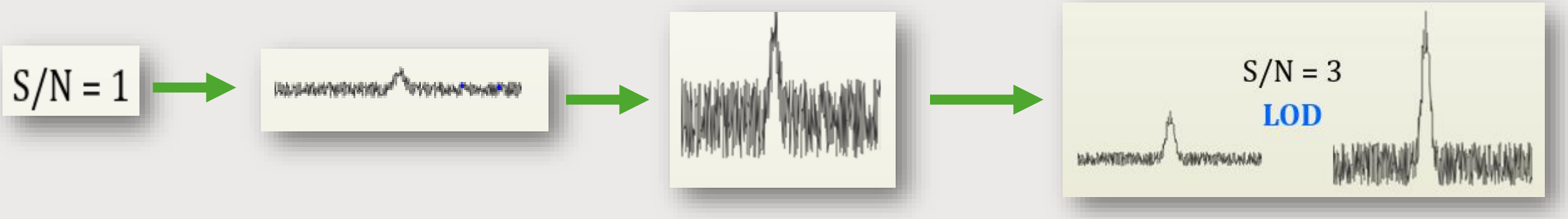
The Detection Limit is calculated as three times the standard deviation $LOD = 3*\sigma$

The Quantification Limit is calculated as three times the LOD $LOQ = 3*LOD$

When different matrixes are used in the method, limits must be reported for all matrices, or the absence of matrix influence must be validated.

Limit of Detection

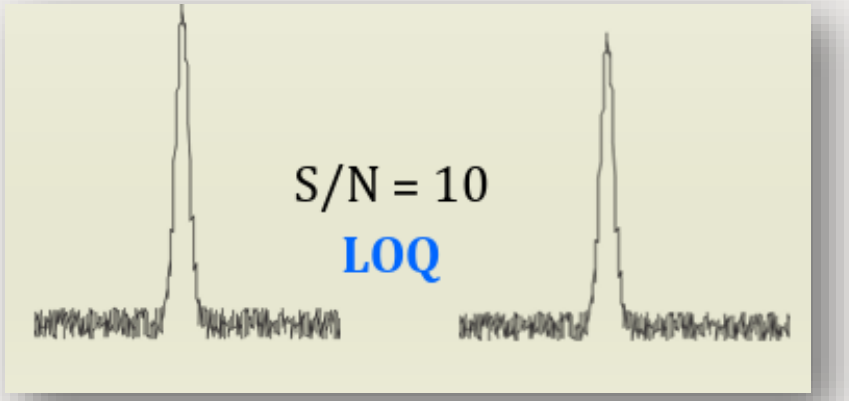
Is the signal larger than the noise ?



Lowest amount of an analyte that can be distinguished from a blank (signal > its uncertainty)

Limit of Quantification

Quantity of the analyte that provides a S/N = 10



Using an ICP – BLANK measurements are the easiest way to determine LOD and LOQ

For titrations – Make use of the WORKING RANGE to determine LOD and LOQ

Calculating Standard Deviation

	AVERAGE, SD & RSD - Agromat AG-2					
	K	Na	Ca	Mg	S	TRACKING DETAILS
	ppm	ppm	ppm	ppm	ppm	
1	332	43	1092	113	17	**Week One - 2025 03 04**
2	316	78	1969	213	27	**Week Two - 2025 03 12**
3	348	46	1085	103	16	**Week Three - 2025 03 18**
4	348	45	1209	114	21	**Week Four - 2025 03 26**
AVERAGE	**335.9**	**53.0**	**1338.8**	**135.9**	**20.3**	
SD	**17.2**	**22.1**	**466.4**	**56.7**	**7.0**	
%RSD	**5.1**	**41.7**	**34.8**	**41.7**	**34.7**	
True Value	337.0	71.3	2030.0	214.0	22	
3S	51.6	66.4	1399.2	170.0	21.1	
MAX	670.0	63.5	2186.0	224.0	41.4	
MIN	356.0	36.9	1250.0	114.0	-0.8	

Upper Limit	547.0	53.2	1818.0	181.0	169.4
Defined Concentration	513.0	50.2	1718.0	169.0	20.3
Lower Limit	480.0	47.1	1618.0	157.0	30.6

* Sulphur is not a certified value on the Agromat COA - the values used are calculated from the establishment data

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Analysis Report

1.0 DESCRIPTION: Matrix Reference Material *Agro***MAT - Sandy Soil (AG-2)**
Catalogue Number: 140-025-102
Lot Number: S220425004
Expiration Date: 2 years from date of shipment (See Ship Date label on bottle) Jul 2024

2.0 CONSENSUS VALUES (See section 8 for additional details):

Parameters	Extraction Method	Units	Consensus Value	Uncertainty (+/-)	Confidence Interval	Tolerance Interval
Phosphorus	Mehlich III	mg/kg	69.9	9.5	60.4 – 79.4	10.9 – 129
	Olsen	mg/kg	51.5	2.8	48.7 – 54.3	37.1 – 66.0
Potassium	Ammonium Acetate pH 7	mg/kg	513	33	480 – 547	356 – 670
	Mehlich III	mg/kg	525	30	495 – 555	326 – 723
Calcium	Ammonium Acetate pH 7	mg/kg	1718	100	1618 – 1818	1250 – 2186
	Mehlich III	mg/kg	1666	88	1578 – 1754	1083 – 2250
Magnesium	Ammonium Acetate pH 7	mg/kg	169	12	157 – 181	114 – 224
	Mehlich III	mg/kg	254	11	243 – 266	184 – 325
Sodium	Ammonium Acetate pH 7	mg/kg	50.2	3.0	47.1 – 53.2	36.9 – 63.5
	Mehlich III	mg/kg	57.1	3.9	53.2 – 61.0	36.5 – 77.7
Zinc	DTPA	mg/kg	(1.11)			
	Mehlich III	mg/kg	4.0	0.3	3.7 – 4.3	2.0 – 6.1
	Amm. Ace. pH 7 + EDTA	mg/kg	(2.5)			
Manganese	DTPA	mg/kg	(22.9)			
	Mehlich III	mg/kg	155	11	144 - 165	89.4 - 220
	Amm. Ace. pH 7 + EDTA	mg/kg	(43.3)			
Copper	DTPA	mg/kg	(1.3)			
	Mehlich III	mg/kg	1.2	0.1	1.0 – 1.3	0.4 – 1.9
	Amm. Ace. pH 7 + EDTA	mg/kg	(2.8)			
Iron	DTPA	mg/kg	(100)			
	Mehlich III	mg/kg	969	101	869 - 1070	345 – 1594
	Amm. Ace. pH 7 + EDTA	mg/kg	(221)			
Boron	Hot Water	mg/kg	0.44	0.08	0.36 – 0.51	0.14 – 0.73
	Mehlich III	mg/kg	0.67	0.12	0.55 – 0.79	0.10 – 1.25
Sulfur	Mehlich III	mg/kg	25.1	1.2	23.8 – 26.3	19.2 – 30.9
Aluminum	Mehlich III	mg/kg	1502	93	1409 - 1596	932 – 2072
pH	1 :1 (Soil:Water)	-----	6.94	0.07	6.87 – 7.01	6.50 – 7.39
	1 :2 (Soil:Water)	-----	6.99	0.11	6.88 – 7.10	6.42 – 7.57
	1 :5 (Soil:Water)	-----	(7.15)			
	Saturated Paste	-----	6.78	0.11	6.67 – 6.89	6.33 – 7.23
	Buffer SMP	-----	7.06	0.03	7.02 – 7.09	6.90 – 7.22
Organic Matter	LOI	%	3.5	0.2	3.3 – 3.7	2.3 – 4.8
	Walkley Black	%	2.6	0.3	2.3 – 2.9	1.2 – 4.0
Nitrogen as Nitrate	KCl	mg/kg	143	2	141 - 145	129 - 156
Soluble Salts	1 :2 Soil :Water	uS/cm	643	53	591 - 696	389 - 898
	Saturated Paste	uS/cm	(1177)			

Note : Values in bracket are not certified. They are listed for information only.

3.0 APPROVAL AND REVISION:

Approval: Daniel Boisvert, Chemist
Date of Issue of Report: August 25th, 2022
Date of revision: December 15th, 2022

Daniel Boisvert

4.0 DESCRIPTION AND INTENDED USE:

The Matrix Reference Material (MRM) AG-2 is a naturally agricultural sandy soil (not spiked or fortified) with a particle size of -200 mesh. It is designed to be used for quality control verification, internal standards validation or methods development for the analysis of the listed parameters using the indicated extraction methods. Not intended for calibration.

5.0 INSTRUCTIONS FOR USE AND STABILITY:

Instructions for use: Before weighing, mix the material by shaking the container to avoid segregation in the bottle. In order to have a representative sample, the minimum use quantity must be 1 g to conform to previous homogeneity testing. Analysis has been performed on a dry weight basis.

Stability: This MRM is guaranteed to be stable up to 2 years from the shipping date provided the material is kept sealed, stored under normal laboratory conditions and used according to good laboratory practices. Shipping date will be stamped on container at time of shipping. **SCP SCIENCE** will monitor the stability of representative samples regularly and if any changes occur that invalidate the reported results, **SCP SCIENCE** will notify purchasers.

Date of last verification: **N/A**

6.0 HAZARDOUS INFORMATION:

Please refer to the associated Safety Data Sheet (SDS) for information regarding this product (available at http://www.scpscience.com/ecert).

7.0 PREPARATION METHOD AND HOMOGENEITY:

Preparation Method: The initial sample has been dried, crushed and sieved through a 0.5 inch sieve. The "fines" portion has been further crushed and sieved with 80% of the material passing through a 200 mesh screen. This portion has been re-pulverized and sieved through a 200 mesh sieve to obtain 100% less than 200 mesh. The final material has then been packaged in 175 g containers and tested for homogeneity.
Homogeneity: The homogeneity of the material has undergone third party verification by Particle Size Analysis and by metals oxides analysis using X-ray fluorescence spectrometer. The method used for material homogeneity determination is based on ISO Guide 35.

8.0 ANALYSIS AND DETERMINATION OF CONSENSUS VALUES:

These values were the result of an inter-laboratory study involving thirteen laboratories. Each laboratory was asked to supply analysis data for a specific list of parameters employing specific extraction methods. Not all the laboratories supplied data for the different parameters. Consensus Values are based on an average of 19 values per parameter (36 values being the highest and 6 values being the lowest). Values in brackets are not certified as less than 9 values were received. They are provided for information only.

Several extraction methods have been used by lab participants. Mehlich III, Olsen, Ammonium and Acetate at pH 7 are methods that we had enough results to do statistical calculation. Almost all labs did their sampling by weight rather than by calibrated scoop. Extraction method soil ratio used by most labs is: Mehlich III (1:10), Olsen (1:20), Ammonium acetate pH 7 (1:10), DTPA (1:2).

Agricultural extraction methods for all elements are listed on section 2.0 of this certificate. Most participating labs used ICP or AA to test metals. ICP and colorimetric method have been used for phosphorus testing: Colorimetric for Olsen extraction methods, ICP for Mehlich III extraction method. For nitrates analysis, cadmium reduction with colorimetric method, ionic chromatography or segmented flow analyser have been used by most participating laboratories.

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Parameters	Extraction Method	Units	Consensus Value	Uncertainty (+/-)	Confidence Interval	Tolerance Interval
Potassium	Ammonium Acetate pH 7	mg/kg	513	33	480 – 547	356 – 670
	Mehlich III	mg/kg	525	30	495 – 555	326 – 723
Calcium	Ammonium Acetate pH 7	mg/kg	1718	100	1618 – 1818	1250 – 2186
	Mehlich III	mg/kg	1666	88	1578 – 1754	1083 – 2250
Magnesium	Ammonium Acetate pH 7	mg/kg	169	12	157 – 181	114 – 224
	Mehlich III	mg/kg	254	11	243 – 266	184 – 325
Sodium	Ammonium Acetate pH 7	mg/kg	50.2	3.0	47.1 – 53.2	36.9 – 63.5
	Mehlich III	mg/kg	57.1	3.9	53.2 – 61.0	36.5 – 77.7

The Tolerance Interval is an indication of the lowest possible value and the highest possible value based on the complete set of data, exclusive of outliers, used to calculate the Consensus Value.

The following table is a guideline on how to interpret the results:

Results within Confidence Interval	Method working properly
Results outside Confidence Interval but within Tolerance Interval	Method may need improvement
Results outside Tolerance Interval	Method not working properly

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Parameters	Extraction Method	Units	Consensus Value	Uncertainty (+/-)	Confidence Interval	Tolerance Interval
Potassium	Ammonium Acetate pH 7	mg/kg	513	33	480 – 547	356 – 670
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	Mehlich III	mg/kg	1666	88	1578 – 1754	1083 – 2250
Magnesium	Ammonium Acetate pH 7	mg/kg	169	12	157 – 181	114 – 224
	Mehlich III	mg/kg	254	11	243 – 266	184 – 325
Sodium	Ammonium Acetate pH 7	mg/kg	50.2	3.0	47.1 – 53.2	36.9 – 63.5
	Mehlich III	mg/kg	57.1	3.9	53.2 – 61.0	36.5 – 77.7

	K	Na	Ca	Mg	S
	ppm	ppm	ppm	ppm	ppm
1	332	43	1092	113	17
2	316	78	1969	213	27
3	348	46	1085	103	16
4	348	45	1209	114	21
AVERAGE	**335.9**	**53.0**	**1338.8**	**135.9**	**20.3**
SD	**17.2**	**22.1**	**466.4**	**56.7**	**7.0**
%RSD	**5.1**	**41.7**	**34.8**	**41.7**	**34.7**
True Value	337.0	71.3	2030.0	214.0	22
3S	51.6	66.4	1399.2	170.0	21.1
MAX	670.0	63.5	2186.0	224.0	41.4
MIN	356.0	36.9	1250.0	114.0	-0.8
Upper Limit	547.0	53.2	1818.0	181.0	169.4
Defined Concentration	513.0	50.2	1718.0	169.0	20.3
Lower Limit	480.0	47.1	1618.0	157.0	30.6

Average = `=AVERAGE(B4:B203)`

SD = `=STDEV(B4:B203)`

%RSD = `=B205/B204*100`

True Value = CONSENSUS value

3S (LOD) = `=B205*3`

Max Limit = Upper value of TOLERANCE value

Min Limit = Lower value of TOLERANCE value

Upper Limit = Upper value of CONFIDENCE interval

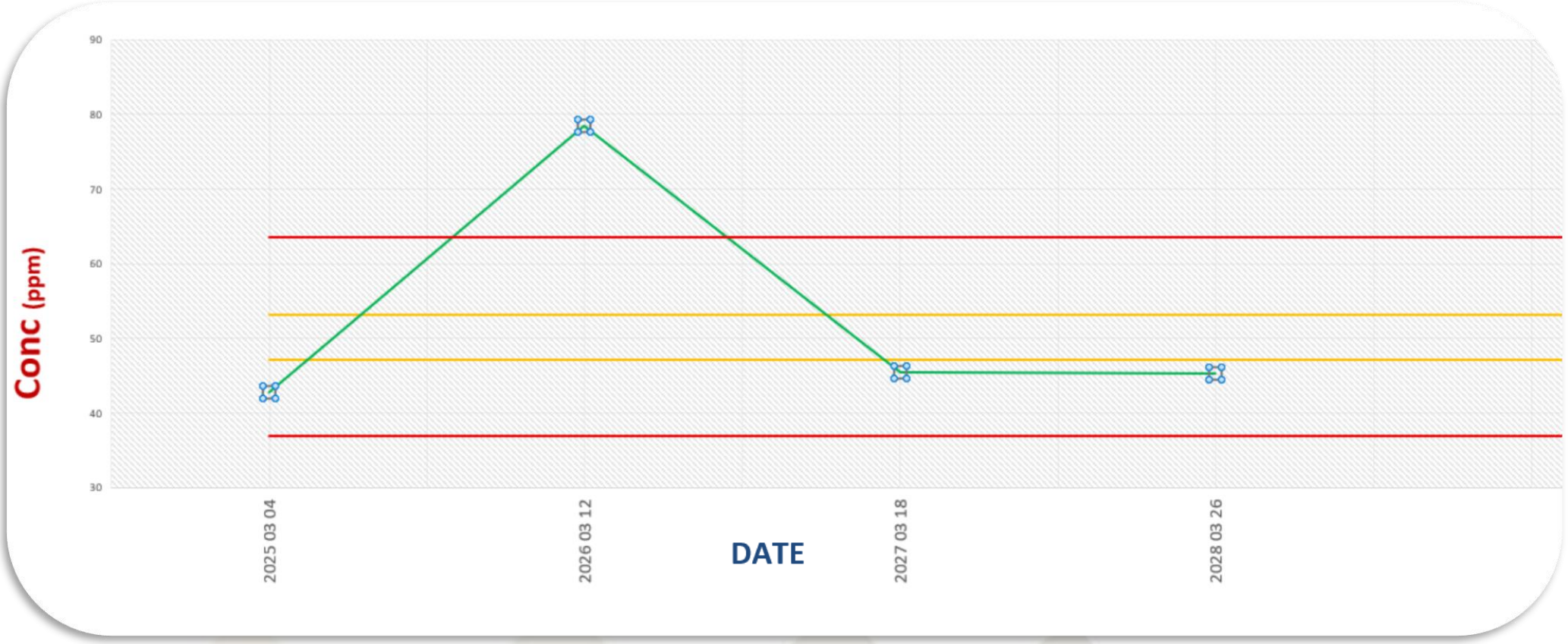
Defined concentration = CONSENSUS value (TRUE value)

Lower Limit = Lower value of CONFIDENCE interval

ICP QC CHART

Element: Na

Based on Confidence Level & Tolerance Limit



Performance Characteristics

Parameters which define how well an analytical method performs its intended purpose

- **Accuracy**
- **Bias**
- **Precision**
- **Reproducibility & Repeatability**
- **Linearity**
- **Working Range**
- **Limit of Detection**
- **Limit of Quantification**
- **Sensitivity**
- **Specificity**
- **Uncertainty of Measurement**
- **Robustness**

Sensitivity

The method can differentiate between small differences of concentrations of the analyte measured

Specificity

The method can detect the analyte measured even in the presence of interferences

Sensitivity

Can be determined from the WORKING RANGE

Different concentrations of analyte were determined – make sure there are at least two concentration values close to each other

For analytes determined by ICP – specific concentrations can be made and used to determine the working range

Lab number	Consensus value %OM	% OM	%C	Range %OM	Analyst	Date
SMP 2403	2.09	2.14	1.24	1.465 - 2.716	Analyst 1	22.10.24
SMP 2403	2.09	2.08	1.21			
SMP 2403	2.09	2.20	1.28			
SMP 2403	2.09	2.11	1.23			
SMP 2403	2.09	2.10	1.22			
SMP 2403	2.09	2.10	1.22			
SMP 2403	2.09	2.12	1.23			
SMP 2403	2.09	2.05	1.19			
SMP 2403	2.09	2.07	1.21			
SMP 2403	2.09	2.09	1.22			
Avg	**2.09**	**2.11**	**1.22**			
sd		**0.04083264**	**0.023739909**			
%rsd		**1.93804602**	**1.938046021**			

Lab number	Consensus value %OM	% OM	%C	Range %OM	Analyst	Date
Agromat AG2	2.6	2.66	1.54	2.3 - 2.9	Analyst 2	22.10.24
Agromat AG2	2.6	2.72	1.58			
Agromat AG2	2.6	2.81	1.63			
Agromat AG2	2.6	2.76	1.61			
Agromat AG2	2.6	2.79	1.62			
Agromat AG2	2.6	2.72	1.58			
Agromat AG2	2.6	2.70	1.57			
Agromat AG2	2.6	2.76	1.60			
Agromat AG2	2.6	2.76	1.61			
Agromat AG2	2.6	2.77	1.61			
Avg	**2.60**	**2.74**	**1.60**			
sd		**0.044874103**	**0.02609**			
%rsd		**1.635459156**	**1.635459**			

Specificity

Analyse a CRM that represents the sample matrix.

Alternatively spike samples with high, medium, and low concentrations of the analyte being measured.

Spiking samples is possible for analytes measured by ICP, but spiking samples is not always possible, eg, Carbon content in soils

To determine Carbon content in soil Agromat AG-1 and AG-2 CRM's are used to represent different matrices; Sandy soils and Clay soils

Lab number	Consensus value %OM	% OM	%C	Range %OM	Analyst	Date
Agromat AG1	2.21	2.15	1.25	2.02 - 2.40	Analyst 1	22.10.24
Agromat AG1	2.21	2.19	1.27			
Agromat AG1	2.21	2.21	1.29			
Agromat AG1	2.21	2.19	1.27			
Agromat AG1	2.21	2.24	1.30			
Agromat AG1	2.21	2.17	1.26			
Agromat AG1	2.21	2.13	1.24			
Agromat AG1	2.21	2.15	1.25			
Agromat AG1	2.21	2.13	1.24			
Agromat AG1	2.21	2.22	1.29			
Avg	**2.21**	**2.18**	**1.27**			
sd		**0.03789895**	**0.022034272**			
%rsd		**1.73990962**	**1.73990962**			

Lab number	Consensus value %OM	% OM	%C	Range %OM	Analyst	Date
Agromat AG2	2.6	2.68	1.56	2.3 - 2.9	Analyst 3	22.10.24
Agromat AG2	2.6	2.77	1.61			
Agromat AG2	2.6	2.79	1.62			
Agromat AG2	2.6	2.83	1.65			
Agromat AG2	2.6	2.78	1.61			
Agromat AG2	2.6	2.80	1.63			
Agromat AG2	2.6	2.81	1.63			
Agromat AG2	2.6	2.81	1.63			
Agromat AG2	2.6	2.71	1.57			
Agromat AG2	2.6	2.74	1.59			
Avg	**2.60**	**2.77**	**1.61**			
sd		**0.049529165**	**0.028796026**			
%rsd		**1.787571399**	**1.787571399**			

Robustness

What could become a problem ?

The methods ability to detect the analyte measured despite small, deliberate changes made to the method parameters

Can also be considered Intermediate Precision, and is the laboratory variability in the short term

Small changes can occur:

- Single or different analysts
- Single or different instruments
- Within a single day

Temperatures

Reagent Supplies

Dilutions

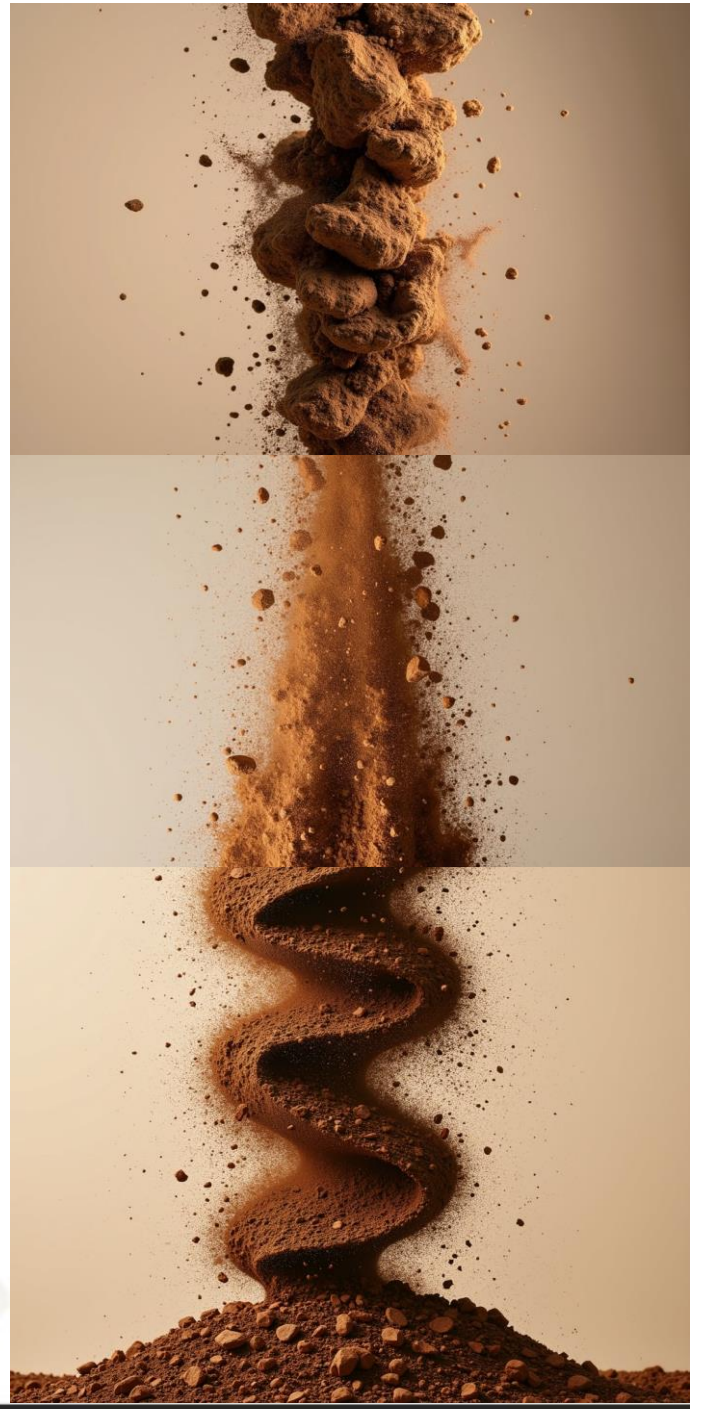
Weighing

Plasma Stability

Injection

Flow variation

Sample stability



Easiest way to determine TEST values?
Run control samples over an extended period of time

Reproducibility

The ability of the method to accurately determine the analyte despite changing conditions

Conditions that must be changed include:

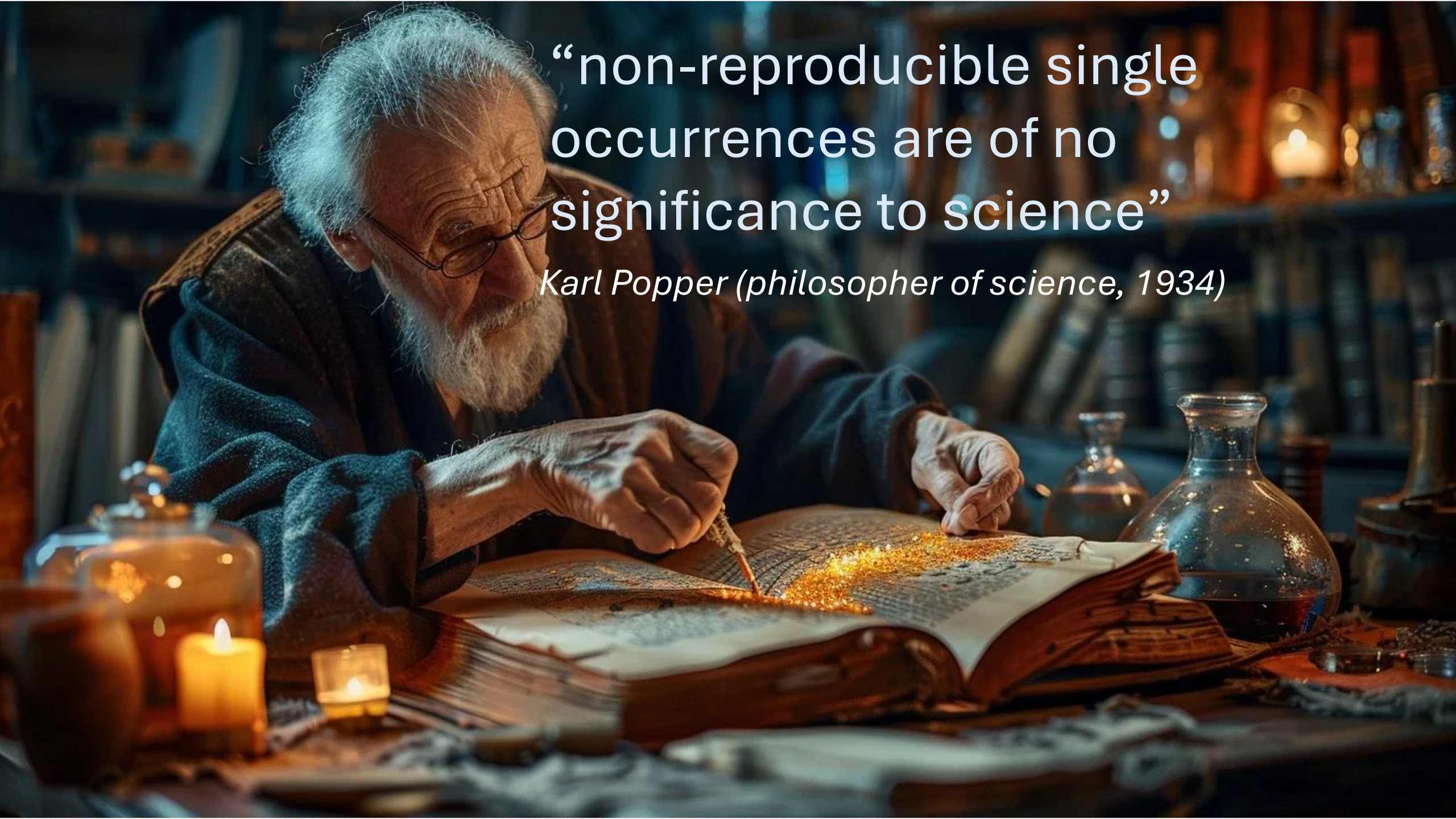
- Different locations
- Different operators
- Different instruments
- Replicate measurements on the same instrument on different days
- Replicate measurements on the different instrument on different days

Repeatability

The ability of the method to accurately determine the analyte with no changing conditions

All conditions stay the same:

- Same location
- Same operator
- Same instrument
- Replicate measurements on the same instrument on the same day


“non-reproducible single occurrences are of no significance to science”
Karl Popper (philosopher of science, 1934)

Performance Characteristics

Parameters which define how well an analytical method performs its intended purpose

- Accuracy
- Bias
- Precision
- Reproducibility & Repeatability
- Linearity
- Working Range
- Limit of Detection
- Limit of Quantification
- Sensitivity
- Specificity
- Uncertainty of Measurement
- Robustness

Uncertainty of Measurement

How far off the true value could the result be ?

Uncertainty of Measurement

How far off the true value could the result be ?

Uncertainty MUST be reported if a customer requests it

Uncertainty MUST be evaluated for ISO 17025 accreditation

Uncertainty is associated with the result of an analysis – not the method

Uncertainty characterises the distribution of the values that could reasonably be attributed to the result of an analysis

Four ways to approach Uncertainty of Measurement

Single laboratory

Statistical approach

Component evaluation
ISO GUM

Inter-laboratory

Statistical approach
ISO 5725

Proficiency Testing
ISO/IEC 17043
ISO 13528

Uncertainty of Measurement

Statistical Approach

The analyte of interest is determined in the following manner:

3 operators
3 balances
3 instruments
Multiple days

90 TEST results

mean	75.42%
standard deviation	0.112%
expanded uncertainty (k=2)	0.224%

TEST result = 75.42 ± 0.22% (k=2)

Calculating Uncertainty

Standard Uncertainty from Certified Reference Materials

Analyte	CRM Identity	Certified	Expanded Uncertainty (U)	Unit	Coverage Factor (k)	Standard Uncertainty u	Supplier
OM	AG-1	2.21	0.19	%	2	0.095	SCP Science
OM	AG-2	2.6	0.3	%	2	0.15	SCP Science

Mass and volume	**Weights in g**		
Balance 2	**0.5**	**Balance 28**	**20**
AL 24_1	0.501	RO Water_1	20.0
AL 24_2	0.509	RO Water_2	20.0
AL 24_3	0.502	RO Water_3	20.0
AL 24_4	0.5	RO Water_4	20.0
AL 24_5	0.498	RO Water_5	20.0
AL 24_6	0.505	RO Water_6	20.0
AL 24_7	0.503	RO Water_7	20.0
AL 24_8	0.5	RO Water_8	20.0
AL 24_9	0.499	RO Water_9	20.0
AL 24_10	0.502	RO Water_10	20.0

Balance 2	**0.5**	**Balance 28**	**20**
Avg	***0.5020***		***20.0000***
SD	***0.0032***		***0.0000***
(s/x)	***0.0064***		***0.0000***
(s/x)^2	***0.0000***		***0.0000***

Pipette volumes

	Volume of Sulphuric Acid	Volume of phosphoric acid	Volume of potassium dichromate	Volume of AFS	Volume of RO Water	Volume of RO Water	Volume of RO Water	Volume of RO Water
	Dispenser 4	**Dispenser 6**	**Micro pipette 5**	**Burette 2**	**Dispenser 493**	**Dispenser 6**	**Micro pipette 5**	**Burette 2**
	20ml	10ml	10ml	20ml	20ml	10ml	10ml	20ml
	mass (g)	mass (g)	mass (g)	mass (g)	mass (g)	mass (g)	mass (g)	mass (g)
1	36.99	16.74	10.17	20.01	19.95	10.3	10.03	20
2	36.92	16.73	10.11	20	19.96	10.12	9.89	20
3	37.07	16.79	10.17	20	19.99	10.05	9.9	20
4	37.02	16.76	10.18	20.01	19.92	10.15	9.87	20
5	36.91	16.79	10.16	20	20.04	10.02	9.91	20
6	36.67	16.93	10.19	20	20.02	10.01	9.83	20
7	36.81	16.98	10.17	20	19.96	10.21	9.96	20
8	36.68	16.89	10.19	20	20	10.19	9.85	20
9	36.83	16.96	10.19	20	19.95	10.1	9.86	20
10	36.77	16.98	10.20	20	20.02	10.12	9.94	20
Avg	***36.8533***	***16.8550***	***10.1730***	***20.0020***	***19.9810***	***10.1270***	***9.9040***	***20.0000***
SD	***0.1314***	***0.0977***	***0.0241***	***0.0040***	***0.0367***	***0.0856***	***0.0566***	***0.0000***
(s/x)	***0.0036***	***0.0058***	***0.0024***	***0.0002***	***0.0018***	***0.0084***	***0.0057***	***0.0000***
(s/x)^2	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0000***	***0.0001***	***0.0000***	***0.0000***

Uncertainty of measurement for % OM

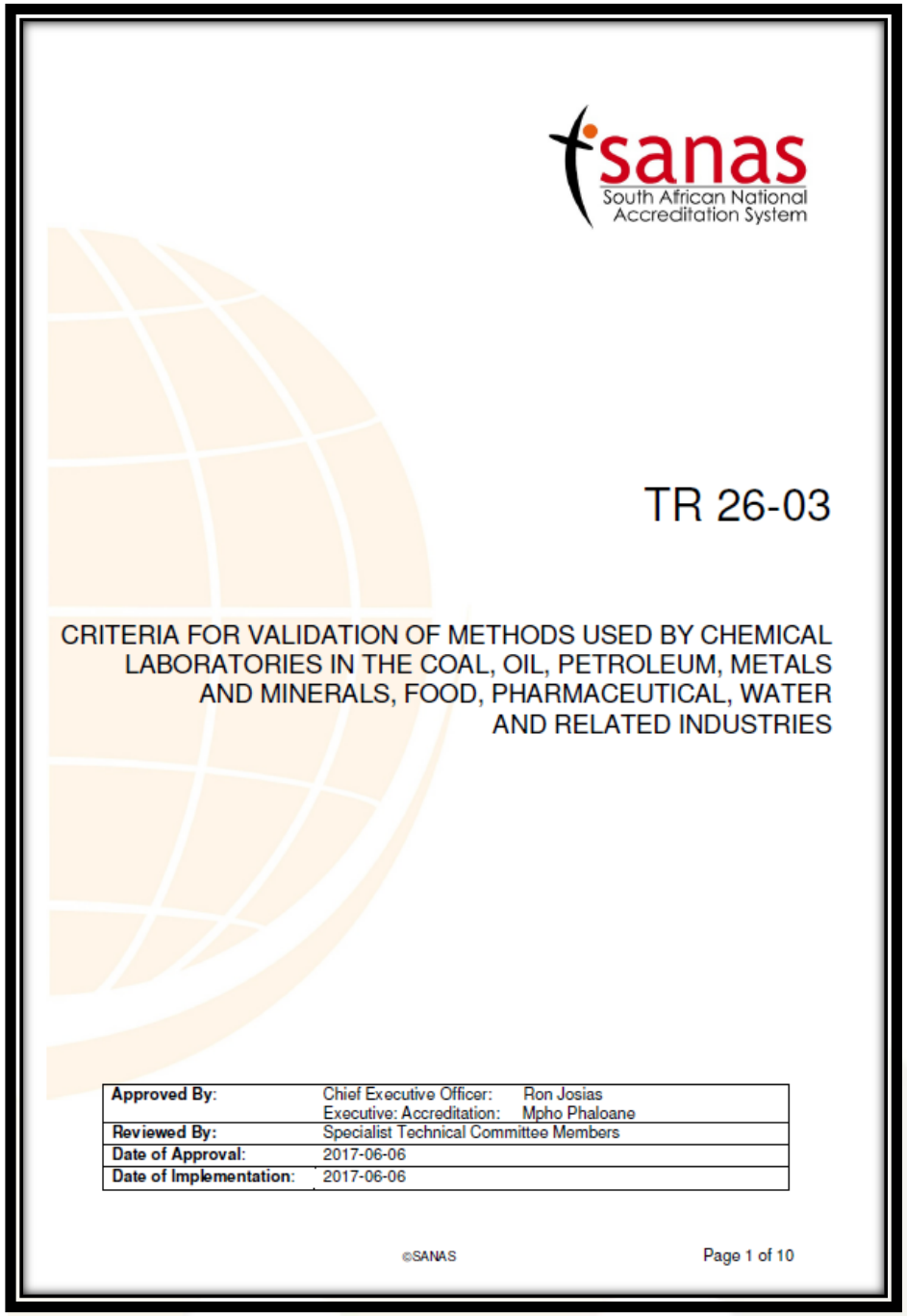
Contributor	Instrument	x Value	Standard uncertainty	Relative Std Uncertainty	Rel U^2	% Contribution	Combined uncertainty	Expanded uncertainty	Total % Rel expanded uncertainty
Stock Unc		2.2100	0.0950	0.0430	0.0018478	58.98	0.22	0.45	11.19
Regression Uncertainty		3.6459	0.0743	0.0204	0.0004157	13.27			
Mass U 0.5	Balance 2	0.5020	0.0032	0.0064	0.0000406	1.29			
Mass U 20	Balance 2	20.0000	0.0000	0.0000	0.0000000	0.00			
Vol of Sulphuric Acid	Dispenser 4	36.8533	0.1314	0.0036	0.0000127	0.41			
Vol of phosphoric acid	Dispenser 6	16.8550	0.0977	0.0058	0.0000336	1.07			
Vol of potassium dichromate	Micro pipette 5	10.1730	0.0241	0.0024	0.0000056	0.18			
Vol of AFS	Burette 2	20.0020	0.0040	0.0002	0.0000000	0.00			
Volume of RO Water	Dispenser 4	19.9810	0.0367	0.0018	0.0000034	0.11			
Volume of RO Water	Dispenser 6	10.1270	0.0856	0.0084	0.0000714	2.28			
Volume of RO Water	Micro pipette 5	9.9040	0.0566	0.0057	0.0000327	1.04			
Volume of RO Water	Burette 2	20.0000	0.0000	0.0000	0.0000000	0.00			
Intermediate precision		3.9813	0.10299	0.0259	0.0006692	21.36			

% Relative expanded uncertainty with k=2 will be reported (k=2; 95% confidence level)

Report TEST result 3.98 ± 0.45 %OM

Uncertainty from Certified Reference Materials - Typical Example of ICP-OES Standards used for multiple analytes

Compound	CRM Identity	Company	Certified	%U	Expanded Uncertainty (U)	Unit	Coverage Factor (k)	Standard Uncertainty
Al	N 23	Supplier A	10018		35	µg/ml	2	18
Al	V 45	Supplier B	10000	2.4	240	µg/ml	2	120
B	N 63	Supplier A	99.99		0.90	µg/ml	2	0
B	V 21	Supplier B	1000	2.4	24	µg/ml	2	12
Ca	N 3	Supplier A	10013		34	µg/ml	2	17
Co	V0 4	Supplier B	100.04		0.47	µg/ml	2	0
Cr	N 29	Supplier A	1000	2.4	24	µg/ml	2	12
Cu	V 11	Supplier B	100.02		0.49	µg/ml	2	0
Cu	N 10	Supplier A	1000	2.4	24	µg/ml	2	12
Fe	V 49	Supplier B	1000	2	24	µg/ml	2	12
Fe	N 04	Supplier A	1001		4	µg/ml	2	2
K	V 74	Supplier B	10006		30	µg/ml	2	15
K	V 50	Supplier A	10000	2.4	240	µg/ml	2	120
Mg	N 17	Supplier B	10022		30	µg/ml	2	15
Mg	V 97	Supplier A	10000	2.4	240	µg/ml	2	120
Mn	N 76	Supplier B	1000	2.4	24	µg/ml	2	12
Mn	V 36	Supplier A	1000		4	µg/ml	2	2
Mo	N 12	Supplier B	100.04		0.58	µg/ml	2	0
Mo	V 84	Supplier A	1000	2.4	24	µg/ml	2	12
Na	N 77	Supplier B	10033		30	µg/ml	2	15
Na	V 244	Supplier A	10000	2.4	240	µg/ml	2	120
Ni	N 46	Supplier B	1000	2.4	24	µg/ml	2	12
P	V 27	Supplier A	10000	2.4	240	µg/ml	2	120
S	N 80	Supplier B	10014		35	µg/ml	2	18
S	V 246	Supplier A	10000	2.4	240	µg/ml	2	120
Si	V 644	Supplier B	1000	2.4	24	µg/ml	2	12
Si	N 491	Supplier A	1001		7	µg/ml	2	4
Zn	N 78	Supplier B	100.03		0.62	µg/ml	2	0
Zn	V 82	Supplier A	1000	2.4	24	µg/ml	2	12



sanas
South African National Accreditation System

TR 26-03

CRITERIA FOR VALIDATION OF METHODS USED BY CHEMICAL LABORATORIES IN THE COAL, OIL, PETROLEUM, METALS AND MINERALS, FOOD, PHARMACEUTICAL, WATER AND RELATED INDUSTRIES

Approved By:	Chief Executive Officer: Ron Josias Executive: Accreditation: Mpho Phaloane
Reviewed By:	Specialist Technical Committee Members
Date of Approval:	2017-06-06
Date of Implementation:	2017-06-06

The purpose of this document is to define the concepts and processes of method validation, and to provide technical requirements in order to facilitate a uniform approach. This document amplifies ISO/IEC 17025 requirements and lists SANAS requirements applicable to chemical laboratories.

The following do not form part of this document: sampling, sample handling and transportation.

- References, Definitions, Abbreviations
- Performance characteristics and criteria for a test method
- Validation Plan
- Implementation and Review
- Summary Report

GLOBAL SOIL PARTNERSHIP

Other Important Requirements

- Traceability
- Proficiency Testing
- Equipment Calibration and Maintenance
- Documented Procedures
- Internal Audits

Validation Report

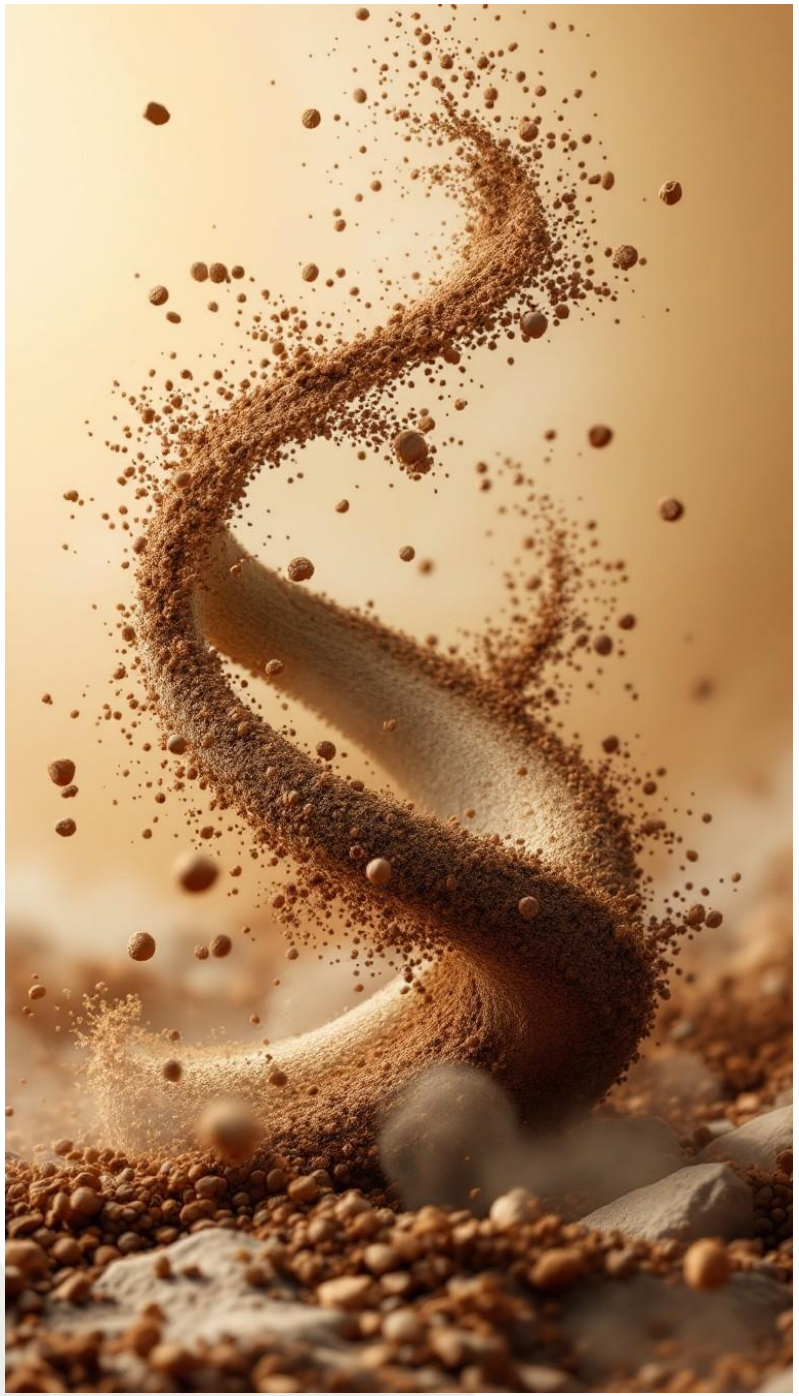
Validation Report

Excel Workbook

Word Document

Validation Template

Internal Laboratory Template



Cover Page

Aboo's Laboratory

Validation Report

DOC NO. ABC 123

TITLE Validation of organics

	NAME	SIGNATURE	DATE
PREPARED	Marmaduke	Marmaduke	01-Nov-24

- Laboratory Name
- Validation Report
- Document Control Number
- Name of Method
- Person preparing the document
- Date of preparation

- **Validation Summary**

	Criteria	OM	C
Sensitivity (slope) Area/µg/L	NR	0.91747	0.91969
correlation coefficient	NR	0.99994	0.99995
Coefficient of determination	NR	0.99989	0.99991
Standard error of a regression	NR	0.06820	0.03602
Relative limit of detection %	NR	0.22	0.12
Relative Limit of Quantitation %	NR	0.74	0.39
Uncertainty in sample analysis Sx0 %	NR	0.07	0.04
T calc	T calc > T crit	19642	23801
Tcrit		2.57	2.57
Working Range in %		0.4 - 10	0.23 - 5.8
Accuracy as % recovery at 1% OM	90-110	100.5	100.5
Precision (Repeatability)at 1% OM as %RSD	<5	2.78	2.78
% Bias at 1 % OM	± 10	-7.0	-7.0
Reproducibility / Selectivity	Z Score <2	Z Score <1	Z Score <1
Ruggedness	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$
Robustness	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$
Intermediate precision	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$	$F_{calc}<F_{crit}$
Expanded uncertainty (95% Confidence)	NR	11%	7%

1.TABLE OF CONTENTS

- Table of Contents
- Validation Plan & Formulas
- Method Summary
- Validation Summary

2. Validation plan and formulas used

Use the same definitions as is described in TR26-03

Organic matter (%) = Total organic carbon (%) x 100/58
OM (%) = TOC (%) x 1.724138

Performance characteristic	Criteria
Linearity	$t_{calc} > t_{crit}$
% RSD	<5
% Recovery	90 - 110%

Parameter	How	Formulas	Explanation
Limit of Detection (LOD)	**Analyse a set of standards, covering the expected sample analyte concentration (calibration curve)**	LOD=(3*$S_{y/x}$)/b	LOD and LOQ is calculated from the calibration data and regression statistics instead. The slope standard error of the regression ($S_{y/x}$) is used to calculate LOD. This is a method recommended by the US EPA and is an ISO method, namely, ISO11843. $S_{y/x}$= standard error of the regression. b= slope
Limit of Quantification (LOQ)	From calibration curve	LOQ=(10*$S_{y/x}$)/b	
Linearity	*From calibration curve*	significance of R^2	R^2 = Coefficient of determination or coefficient of
Linearity	*If tcalc > tcrit then there is significant linearity*	$t_{calc} = r\sqrt{\frac{n-2}{1-r^2}}$	r = correlation coefficient, n = the number of measurements and r2 is the coefficient of determination. Df=n-2
Sensitivity	From calibration curve	Sensitivity can be viewed as the slope of a response curve (b)	
Accuracy	**Analyse CRM**	%Relative accuracy=[x̄/μ]*100	x̄ = the measured mean value and
Bias	Analyse CRM	$\%\,Bias = \left[\frac{\bar{x}-\mu}{\mu}\right]100$	x̄ = the measured mean value and μ= the expected or true value
Precision	Analyse CRM/(Std) each prepared and analysed once a day over an extended period	%RSD= (s / x̄)x 100	x̄ = the measured mean value and s = Standard deviation
Reproducibility	Analyse CRM/(Std) each prepared and analysed once a day over an extended period	%RSD= (s / x̄)x 100	

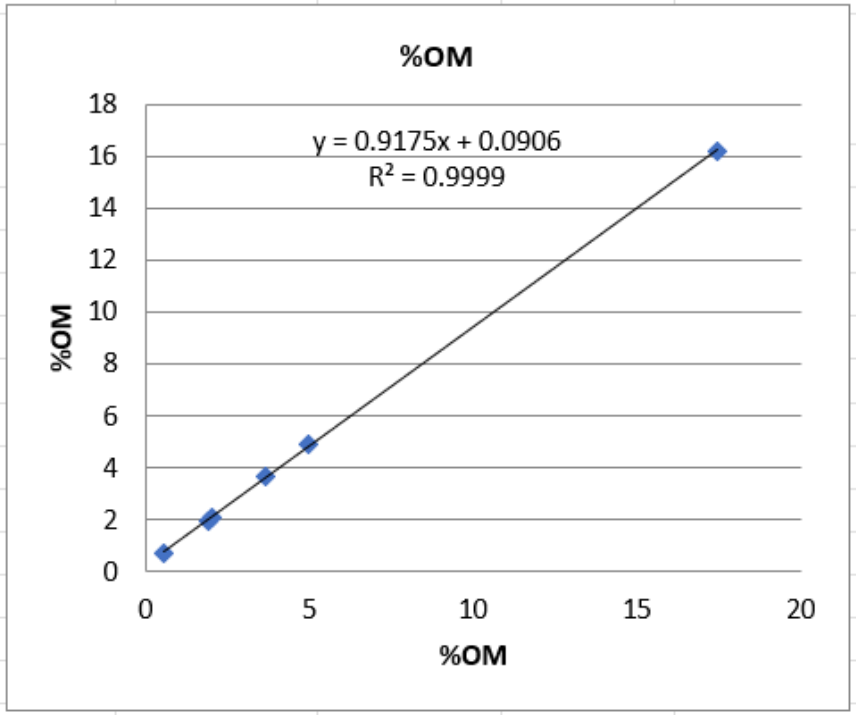
Validation Plan & Formulas

Parameter	How	Formulas	Explanation
Repeatability	**Analyse an extended range (standards below and above calibration curve) standards from another supplier 8 times back as samples**	%RSD= (s / $\bar{x}$)x 100	
Working Range	The range of an analytical method is the interval between the upper and lower levels of an analyte, including these levels that have been demonstrated to be determined with a suitable and defined level of precision, accuracy and linearity, using the method as written. Use data obtained from accuracy, precision and linearity against set criteria		
Specificity	**Analyse CRM that represent the labs matrix. Accuracy and precision must comply against set criteria**		Reproducibility - The conditions include different operators, measuring
Ruggedness	Analyse CRM/(Std) each prepared and analysed once a day over an extended period. **Use different analysts. Each analyst must have at least 5 results**	Accuracy and %RSD must comply against set criteria	systems and replicate measurements on the same or similar objects.
Uncertainty of Measurement	**Uncertainty - All of the Uncertainty components are calculated/referred to here from their respective fields. Al certificates for calibration standards, balances, pipettes, diluters etc. Volume: Weigh and note each dilution volume 10X**	$u_c = \sqrt{a^2 + b^2 + c^2}$	Where a, b and c for example are: mass, precision and purity and U_c is the combined uncertainty

Validation Plan & Formulas

Regression of % OM (Linearity, Limit of Detection, Limit of Quantification, Sensitivity)

Standards	% OM concensus value	%OM	%C
ALP 2405	0.74	0.74	0.43
ALP 2403	2.09	1.93	1.12
Agro AG1	2.21	2.10	1.22
ALP 2407	3.817	3.65	2.12
ALP 2401	5.133	4.89	2.83
ALP 2406	17.6	16.21	9.43



SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99994308
R Square	0.999886163
Adjusted R Square	0.999857704
Standard Error	0.068202889
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	163.4304932	163.430493	35133.996	4.85975E-09
Residual	4	0.018606536	0.00465163		
Total	5	163.4490997			

- Each tab contains all the calculations and data generated throughout the Validation testing
- A statement of Purpose MUST be included

Validation Report

- Regression
  (Linearity) for each analyte determined
- Working range, Accuracy, Bias, and Precision (Repeatability)
- Reproducibility and Selectivity
- Ruggedness and Intermediate precision
- Robustness
- Standard Uncertainty from Certified Reference Materials
- Standard Uncertainty from Mass and volume
- Uncertainty of measurement for each analyte determined

STATEMENT OF PURPOSE!
This method is fit for use

Performance Characteristics

Parameters which define how well an analytical method performs its intended purpose

- Accuracy
- Bias
- Precision
- Reproducibility & Repeatability
- Linearity
- Working Range
- Limit of Detection
- Limit of Quantification
- Sensitivity
- Specificity
- Uncertainty of Measurement
- Robustness

References

Principles and framework for assessing the risk of bias for studies included in comparative quantitative environmental systematic reviews; Geoff Frampton, Paul Whaley, et. al, *Environmental Evidence* volume 11, Article number: 12 (2022)

SANAS TR 26-03; Criteria for validation of methods used by chemical laboratories in the coal, oil, petroleum, metals and minerals, food, pharmaceutical, water and related industries

ISO/IEC 17025:2017; General requirements for the competence of testing and calibration laboratories

A Guide to Method Validation ; A Reagecon guide; www.reagecon.com

An auditor's perspective on Method Validation; Jonathan J. Jodry; LBMA Assaying & Refining Conference March 2023

Soil Analysis; Vossie Wilsnach; FERTASA Soil Fertility and Plant Nutrition Symposium; 21 August 2019


Congratulations!
Ladies & Gentlemen, you have successfully completed your online method validation

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I am adept and knowledgeable in ISO standards and requirements, having successfully accredited soil testing methods in my career. I am currently a SANAS approved technical signatory on 12 soil and plant methodologies.

I am most passionate about conserving the environment and am committed to developing young minds through education and training.

When not working or training, I enjoy TNR for community cats, am active in animal rescue and an avid wildlife photographer.

I hold a Chemical Sciences qualification from the University of Johannesburg , and my latest achievement is having a soil pH article published in the People's Library Of Science journal.

Since 2005, I have worked in different laboratory environments and industries, focusing on technological advancements and their implementation in everyday laboratory work to enhance quality control, and improve laboratory turnaround time and capacity.

Never one to shy away from a challenge, I am often pushing boundaries and disrupting the status quo, having recently designed and opened a commercial agricultural laboratory in Lusaka Zambia using Lean Laboratory Principles and employing a hybrid mix of traditional wet chemistry and rapid-analysis technologies for the testing of soil and plant materials across Southern Africa.

Food and Agriculture Organization of the United Nations

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Thank you

GLOBAL SOIL PARTNERSHIP