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Fertilizers, soil conditioners and beneficial substances — Determination of ammonium citrate, disodium-EDTA soluble phosphorus and potassium by ICP-OES in inorganic fertilizers

Engrais, amendements et substances bénéfiques – Détermination de la teneur en phosphore et potassium solubles dans le citrate d'ammonium et l'EDTA disodique par ICP-OES dans les engrais inorganiques

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 134, *Fertilizers, soil conditioners and beneficial substances*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Inductively coupled plasma-optical emission spectrometer (ICP-OES) instrumentation is becoming increasingly popular in fertilizer testing laboratories (see References [1], [2] and [3]). Because these instruments are automated and can determine multiple elements simultaneously, they offer significant productivity gains. Also, the method does not generate hazardous wastes. The ammonium citrate disodium etheylenediamine tetraacetic acid (EDTA) organic solvent and samples containing high phosphorus and/or potassium concentrations pose some analytical challenges for the instrumentation, which must be addressed. Due to the increasing use of this technology, this document was created.

For organic fertilizers and for liquid fertilizers containing phosphorous acid (H_3PO_3 or phosphite), an alternative method that specifically measures PO_4 is preferred since the ICP-OES measures all elemental phosphorus, which can result in a high bias for these types of fertilizer materials (see Reference [1]).

Due to the inability of the ICP-OES to differentiate between phosphorus species, under normal operating conditions, this method is primarily intended for fertilizer materials in which the source(s) of phosphorus is known. While this document can be used with minimal bias, the repeatability and reproducibility is not consistent with other standards routinely used for inspection at this time, such as EN 15959[4], EN 15477[5] or ISO 22018[6].

As a result, this document is intended for screening purposes, where a large number of fertilizer phosphorus and potassium results must be obtained as efficiently as possible.

Fertilizers, soil conditioners and beneficial substances — Determination of ammonium citrate, disodium-EDTA soluble phosphorus and potassium by ICP-OES in inorganic fertilizers

1 Scope

This document specifies an inductively coupled plasma-optical emission spectrometer (ICP-OES) method for the determination of the ammonium citrate, disodium-etheylenediamine tetraacetic acid (EDTA) soluble phosphorus and potassium content in fertilizer extract solutions.

This document is applicable to all inorganic fertilizer products, whether compound or complex fertilizer products or blends thereof, and straight concentrated fertilizer products.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8157, *Fertilizers, soil conditioners and beneficial substances — Vocabulary*

ISO 14820-1, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

ISO 14820-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8157 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Phosphorus and potassium contained in inorganic fertilizers that is soluble in a heated, dilute ammonium citrate and disodium-EDTA solvent is determined. The neutral ammonium citrate is the primary solvent for phosphate, while the EDTA is mainly included to chelate calcium, magnesium and other soluble metallic cations to minimize their interaction with phosphate and eliminate the water-wash step (see Reference [7]). Also, since this solvent is a relatively weak solution, it extracts primarily the highly soluble potassium compounds and has been used for fertilizer potassium determination since 1993. It compares very favourably with other soluble potash solvents such as ammonium oxalate. The user of this document is not obligated to determine both phosphorus and potassium; however, one of the main advantages of this approach is to measure both simultaneously in a single extract in a more productive, cost-effective way.

The resulting extract solution is tested by ICP-OES to quantify the levels of phosphorus and potassium, which can be converted to their equivalent P_2O_5 and K_2O concentrations. The extract solution is nebulized to produce a fine aerosol, which is introduced to a plasma or high energy source to ionize or excite electrons to higher energy orbitals. As these electrons return to ground state, they emit characteristic ultraviolet or visible wavelengths that are unique to each element. The intensity of the wavelength emission is proportionate to the concentration, which can be quantified by various detector types including a photomultiplier tube (PT), a charge injection device (CID) or a charge coupled device (CCD).

5 Reagents

5.1 Ammonium citrate, dibasic, $(NH_4)_2HC_6H_5O_7$, with a molecular weight (MW) of 226,19 and a purity greater than 98 % or 980,0 g/kg.

5.2 EDTA, disodium salt, dihydrate, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, with a MW of 372,24 and a purity greater than 98 % or 980,0 g/kg.

5.3 Ammonium hydroxide, NH_4OH, with a MW of 35,05 and a purity equal to 28,0 % to 30,0 % as NH_3 or $\rho = 0{,}91$ g/ml.

5.4 Nitric acid, HNO_3, 67 % to 70 %, with a $\rho = 1{,}40$ g/ml.

5.5 Potassium dihydrogen phosphate, KH_2PO_4, with a MW of 136,09, with a purity greater than 99 % or 990,0 g/kg[1].

5.6 Potassium chloride, KCl, with a MW of 74,55 and a purity greater than 99 % or 990 g/kg.

5.7 Potassium nitrate, KNO_3, with a MW of 101,10 with a purity greater than 99 % or 990,0 g/kg[2].

5.8 Octyl phenol ethoxylate[3].

5.9 Beryllium stock solution, of 10 000 µg/ml.

5.10 Scandium stock solution, of 10 000 µg/ml.

5.11 Cesium chloride, CsCl, MW of 168,36, with a purity greater than 99,99 % or 999,99 g/kg.

5.12 Lithium nitrate, $LiNO_3$, MW of 68,95, with a purity greater than 99 % or 990,0 g/kg.

5.13 Citrate-EDTA extraction solution (0,11 M ammonium citrate and 0,033 M disodium-EDTA).

Weigh and transfer 25 g disodium-EDTA (5.2) and 50 g dibasic ammonium citrate (5.1) to a 2 l volumetric flask containing approximately 500 ml of deionized (or equivalent) water. Adjust the pH to near neutral by adding 30 ml of ammonium hydroxide and water (1:1, volume fraction) solution in a fume hood. Adjust the final pH to 7,00 (±0,02) using a pH electrode and meter while adding the ammonium hydroxide and water (1:1, volume fraction) solution drop-by-drop and stirring. After obtaining a stable pH of 7,00 ±

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[1] SRM 194a is the trade name of a product supplied by National Institute of Standards and Technology (NIST). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

[2] SRM 193 is the trade name of a product supplied by NIST. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

[3] Triton X-100 is the trade name of a product supplied by Sigma-Aldrich. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

0,02, bring the flask to volume with deionized water (or equivalent) and mix. Larger volumes of this solution can be prepared; however, it is susceptible to microbial degradation resulting in a shelf life of no more than three weeks, if stored in a dark location.

5.14 Octyl phenol ethoxylate, 0,5 % or 5 ml/l.

Add 1 ml of octyl phenol ethoxylate (5.8) to a 200 ml volumetric flask and dilute to volume with deionized water.

5.15 Internal standard/ionization buffer (10 µg/ml Sc in 0,018 M CsCl and 4 % nitric acid).

Add 1,00 ml of 10 000 µg/ml scandium stock standard, 3 g cesium chloride, 40 ml nitric acid, and 1 ml of 0,5 % octyl phenol ethoxylate (5.14) to a 1 l volumetric flask containing approximately 500 ml of deionized (or equivalent) water. Bring flask to volume with deionized (or equivalent) water and mix. If beryllium is used as an internal standard, add 4,00 ml of 10 000 µg/ml beryllium stock standard to obtain a concentration of 40 µg/ml beryllium.

Alternatively, lithium from $LiNO_3$ can be substituted for cesium as an ionization buffer at 7 g/l $LiNO_3$.

5.16 Nitric acid rinse solution, 1 %.

Add 10 ml of nitric acid (5.4) to approximately 500 ml of deionized or equivalent water contained in a 1 l volumetric flask and bring to volume.

5.17 2 500 µg/ml phosphorus from phosphate (PO_4).

Add 2,746 1 g of potassium dihydrogen phosphate (5.5) to a 250 ml volumetric flask, then bring to volume with deionized (or equivalent) water. This standard also contains 3 156,5 µg/ml K; also, this standard can take several hours to solubilize and stabilize. This standard should be prepared fresh each time. Alternatively, a commercial custom standard from a phosphate source prepared in a water matrix and preserved with a biocide is acceptable.

The weight added should be adjusted for the purity of the reagent used.

NOTE A commercial stock standard preserved in acid is not acceptable as the acid changes the matrix of the pH neutral ammonium citrate EDTA solution and produces erroneous results.

5.18 7 500 µg/ml potassium from potassium chloride.

Add 1,430 0 g of potassium chloride (5.6) to a 100 ml volumetric flask, then bring to volume with deionized (or equivalent) water. Alternatively, 1,939 4 g of potassium nitrate (5.7) can be used rather than potassium chloride. This standard should be prepared fresh each time. Alternatively, a commercial custom standard from a potassium source prepared in a water matrix and preserved with a biocide is acceptable.

The weight added should be adjusted for the purity of the reagent used.

NOTE A commercial stock standard preserved in acid is not acceptable as the acid changes the matrix of the pH neutral ammonium citrate EDTA solution and produces erroneous results.

6 Apparatus

6.1 Analytical balance, capable of weighing to 0,1 mg.

6.2 pH meter, with a readability to 0,01.

6.3 pH combination electrode.

6.4 Constant temperature water bath, capable of maintaining a temperature of 65 °C ± 2 °C.

6.5 Shaking water bath, capable of maintaining a temperature of 65 °C ± 2 °C and set to approximately 200 reciprocations/min.

A water bath is preferred, but alternatively an enclosed heated air shaker is also acceptable; however, ensure the added citrate-EDTA solution (5.13) is at 65 °C ± 2 °C before starting.

6.6 ICP-OES instrument.

A radial view instrument is preferred for potassium, while phosphorus can be determined in either radial or axial view.

6.7 Rotating riffle splitter, or comparable**.**

6.8 Grinding mill, capable of grinding fertilizer material to pass a 0,50 mm screen or sieve**.**

7 Sampling and sample preparation

7.1 Collect a field sample using a recognized sampling procedure such as that given in ISO 14820-1 or another comparable one (see References [8] and [9]).

7.2 Prepare solid and liquid fertilizer materials using a recognized sample preparation procedure such as that given in ISO 14820-2 or another comparable one.

8 Procedure

8.1 Extraction of P and K

For samples containing less than 45 % P_2O_5 or K_2O, weigh 0,5 g ± 0,01 g of material and completely transfer to a 250 ml class A volumetric flask. For samples containing 45 % or more P_2O_5 or K_2O, weigh 0,45 g ± 0,01 g of ground fertilizer material and completely transfer to a 250 ml class A volumetric flask. Dispense 100 ml of 65 °C ± 2 °C preheated (6.4) ammonium citrate, disodium-EDTA extraction solution (5.13) into each flask and insert a rubber stopper. Shake test solutions in a 65 °C ± 2 °C preheated water bath set to approximately 200 reciprocations per minute for exactly 60 min. Then, remove from the water bath; allow to cool to room temperature; bring to volume with deionized (or equivalent) water; stopper and mix. Filter any test solution containing suspended debris using P and K free filters. Some slowly soluble phosphate compounds can continue to solubilize over time resulting in a high bias, so test solutions should be run as soon as possible, but no more than 24 h after extraction.

8.2 Instrument conditions

Optimal instrument conditions identified during robustness testing are listed in Table 1. ICP-OES' differ in their design and options, so adjustment to the conditions listed in Table 1 can be necessary; however, any adjustments to these conditions must be performance-based and validated. Special attention should be paid to the recovery of P in fertilizer concentrates such as concentrated superphosphate, diammonium phosphate (46 % of P_2O_5), and monoammonium phosphate (50 % or 52 % of P_2O_5), since these materials require optimal instrument performance.

Table 1 — Recommended ICP-OES conditions[a]

Factor	Setting
Power, kW	1,4
Plasma flow, l/min	18,0
Auxiliary flow, l/min	2,25
Nebulizer pressure, l/min	0,7
Nebulizer	Concentric type
Spray chamber	Double path cyclonic
Sample pump tube	black/black
Buffer/internal standard pump tube	gray/gray
CsCl ionic buffer concentration, M	0,018
Buffer matrix	4 % nitric acid
Exposure length, s	10
Number of exposures	2
Rinse time, s	35
Total analysis time, min	2

[a] Other instrument conditions that produce equivalent test results are an option provided the test conditions are validated.

8.3 Preparation of standards

8.3.1 Standards from reagent salts

Calibration standards can be made from potassium dihydrogen phosphate (5.17) and potassium chloride (5.18). Several calibration standards are required for the following reasons:

a) multiple ICP-OES wavelengths are utilized to expand the dynamic calibration range,

b) some wavelengths are split into multiple calibration segments, and

c) a minimum of 5 points per curve is recommended.

The standards used and their P and K concentrations expressed as µg/ml and as their percent oxide forms are listed in Table 2. These standards are susceptible to microbial degradation and have a shelf life of no more than three weeks, if stored in the dark.

8.3.2 Standards from commercial stock solutions

Alternatively, custom stock standards can also be purchased but must be in a water matrix and preserved with a biocide as standards preserved in acid will change the pH of the matrix and produce erroneous results.

Table 2 — ICP P and K calibration standards

Standard ID	Volume ml	Citrate-EDTA ml	Volume of P standard ml[a]	Volume of K standard ml[b]	P µg/ml	P_2O_5 µg/ml	P_2O_5 solution %	P_2O_5 fertilizer %[e]	K µg/ml	K_2O µg/ml	K_2O solution %	K_2O fertilizer %[e]
Blank	250	100	0	0	0	0	0,000 00	0	0	0	0,000 00	0
1	250	100	10 of Std 7[d]	NA[c]	12	27,5	0,002 75	1,4	15,2	18,3	0,001 83	0,9
2	250	100	20 of Std 7[d]	NA[c]	24	55,0	0,005 50	2,7	30,3	36,5	0,003 65	1,8
3	250	100	5	NA[c]	50	114,6	0,011 46	5,7	63,1	76,0	0,007 60	3,8
4	250	100	10	NA[c]	100	229,1	0,022 91	11,5	126,3	152,1	0,015 21	7,6
5	250	100	15	NA[c]	150	343,7	0,034 37	17,2	189,4	228,1	0,022 81	11,4
6	250	100	22 (15+7)	NA[c]	220	504,1	0,050 41	25,2	277,8	334,6	0,033 46	16,7
7	250	100	30	NA[c]	300	687,4	0,068 74	34,4	378,8	456,3	0,045 63	22,8
8	250	100	40	NA[c]	400	916,5	0,091 65	45,8	505	608,4	0,060 84	30,4
9	250	100	NA[c]	20	NA[c]	NA[c]	NA[c]	NA[c]	600	722,7	0,072 27	36,1
10	250	100	NA[c]	25	NA[c]	NA[c]	NA[c]	NA[c]	750	903,4	0,090 34	45,2
11	250	100	NA[c]	30	NA[c]	NA[c]	NA[c]	NA[c]	900	1 084,1	0,108 41	54,2

[a] P standard concentration is equal to 2 500 µg/ml P as PO_4 or 2,746 1 g of potassium dihydrogen phosphate KH_2PO_4 is brought to 250 ml, which also contains 3 156,5 µg/ml K.

[b] K standard concentration is equal to 7 500 µg/ml K from KCl or 1,430 0 g of potassium chloride or 1,939 4 g of potassium nitrate is brought to 100 ml.

[c] NA : not applicable.

[d] Serial dilution from another standard; i.e. 10 of Std 7 signifies: pipet 10 ml from standard 7.

[e] Equivalent final result when based upon a 0,5 g sample brought to a final volume of 250 ml.

NOTE 1 A 52 % P_2O_5 fertilizer material weighed at 0,45 g rather than 0,5 g results in a concentration of 46,8 % P_2O_5, which is a 2 % extrapolation from the top standard.

NOTE 2 A 62 % K_2O fertilizer material weighed at 0,45 g rather than 0,5 g results in a concentration of 55,8 % K_2O, which is a 3 % extrapolation from the top standard.

8.3.3 Calibration and wavelength splitting

As the higher points on the calibration curve have a much greater influence, this can adversely impact the accuracy of the lower points. It is therefore recommended that the broad calibration range be split into two segments, which are listed in Table 3. By splitting the same wavelength into two separate curves (see Reference [1]) or a low and high concentration range and/or by using two separate wavelengths, the quality of the lower P and K concentrations will improve.

Table 3 — Calibration criteria for ammonium citrate, disodium-EDTA soluble P and K by ICP-OES[a]

Element	Wavelength nm[b]	Preferred view	Calibration range µg /ml	Standards used (see Table 1)	Curve fit	Spectral deconvolution
P	213,618 (1)	Radial or axial	0 to 100	Blank, 1, 2, 3, 4	Linear	Cu 213,598
P	213,618 (2)	Radial or axial	100 to 400	4, 5, 6, 7, 8	Linear	Cu 213,598
P	214,914 (1)	Radial or axial	0 to 100	Blank, 1, 2, 3, 4	Linear	Cu 214,898
P	214,914 (2)	Radial or axial	100 to 400	4, 5, 6, 7, 8	Linear	Cu 214,898
P	177,434 (1)[c]	Axial	0 to 100	Blank, 1, 2, 3, 4	Linear	None
P	177,434 (2)[c]	Axial	100 to 400	4, 5, 6, 7, 8	Linear	None
P	178,222 (1)[c]	Axial	0 to 100	Blank, 1, 2, 3, 4	Linear	None
P	178,222 (2)[c]	Axial	100 to 400	4, 5, 6, 7, 8	Linear	None
K	766,485 (1)	Radial	0 to 126	Blank, 1, 2, 3, 4	Linear	None
K	766,485 (2)	Radial	126 to 505	4, 5, 6, 7, 8	Linear	None
K	766,485 (3)	Radial	379 to 900	7, 8, 9, 10, 11	Linear	None

[a] Other instrument conditions that produce equivalent test results are an option provided the test conditions are validated.

[b] (1), (2) and (3) are used to distinguish between the same wavelength used multiple times to cover separate concentration ranges.

[c] Optional, less intense wavelengths without any spectral interference that can be considered.

8.3.4 Analysis

A test portion is prepared as described in Clause 7 and extracted as described in 8.1 and presented to the ICP-OES configured according to Tables 1 and 3 using calibration standards outlined in Table 2.

8.4 Quality control

8.4.1 Reference material

Within each analytical batch of samples, inclusion of one or more certified or consensus fertilizer materials for quality assurance purposes is recommended, especially for the fertilizer concentrates (i.e. P_2O_5 and K_2O greater than 40 %).

8.4.2 Duplicates

Duplicate pours from each extract solution are recommended. Duplicate phosphate results that agree within 0,183 and duplicate potash results that agree within 0,148 are recommended as outlined in Tables A.27 and A.28.

9 Calculations and expression of results

9.1 Calculations

Several options exist in the instrument software to assist with data reporting, including test portion weight, test solution volume, dilution factor and reporting units.

The ammonium citrate, disodium-EDTA soluble phosphorus (w_1) and potassium (w_2) content are expressed as mass fraction of P_2O_5 and K_2O according to the formulas as follows:

— for the mass fraction of P_2O_5:

$$w_1 = [P \times (250 / m) \times 142 / (30{,}97 \times 2)] / 10\,000$$

where

w_1	is the percentage of P_2O_5 in fertilizer;
P	is the ICP-OES phosphorus reading, in µg/ml;
250	is the final volume, in ml;
m	is the test portion weight, in g;
142	is the MW of P_2O_5;
30,97	is the MW of P;
2	is the mole ratio of P_2O_5/P;
10 000	is the conversion of µg/ml to %;

— for the mass fraction of K_2O:

$$w_2 = [K \times (250 / m) \times 94{,}2 / (39{,}1 \times 2)] / 10\,000$$

where

w_2	is the percentage of K_2O in fertilizer;
K	is the ICP-OES potassium reading, in µg/ml;
250	is the final volume, in ml;
m	is the test portion weight, in g;
94,2	is the MW of K_2O;
39,1	is the MW of K;
2	is the mole ratio of K_2O/K;
10 000	is the conversion of µg/ml to %.

Alternatively, the standards can be entered with their theoretical percent P_2O_5 and K_2O in solution values, as listed in Table 2. By entering the sample weight, setting the volume to 250 ml and setting the dilution factor to 1 in the instrument software, final percentages of P_2O_5 and K_2O in the fertilizer material are generated.

9.2 Precision

9.2.1 General

A complete description of the sample types with additional information on the study collaborators is included in Annex A. The mean equivalent values for P_2O_5 and K_2O and their targeted values are listed in Annex A, Tables A.1 and A.2.

9.2.2 Repeatability, *r*

Repeatability standard deviation (s_r), repeatability variance (s_r^2), repeatability (r) and repeatability percent (r_{percent}) are expressed in Table 4 for phosphorus and in Table 5 for potassium.

9.2.3 Reproducibility, *R*

Reproducibility standard deviation (s_R), reproducibility variance (s_R^2), reproducibility (R) and reproducibility percent (R_{percent}) are given in Table 4 for phosphorus and in Table 5 for potassium.

Table 4 — ICP-OES repeatability and reproducibility results for phosphorus

ID	Number of labs	Number outliers removed[a]	P_2O_5 mean	Target[b]	s_r	s_r^2	s_R	s_R^2	r	R	r_{percent}	R_{percent}
180911	8	1	2,75	2,73	0,060 6	0,003 7	0,115 3	0,013 3	0,170	0,323	6,17	11,74
180611	9	1	3,15	3,11	0,047 2	0,002 2	0,088 4	0,007 8	0,132	0,247	4,20	7,86
181111	8	1	6,80	6,64	0,058 2	0,003 4	0,193 5	0,037 4	0,163	0,542	2,40	7,97
181211	10	2	10,80	10,69	0,036 1	0,001 3	0,160 6	0,025 8	0,101	0,450	0,94	4,16
190311	10	0	12,43	12,34	0,090 2	0,008 1	0,375 1	0,140 7	0,253	1,050	2,03	8,45
171211	9	0	15,12	15,12	0,183 6	0,033 7	0,243 4	0,059 2	0,514	0,681	3,40	4,51
170911	7	0	38,99	39,37	0,679 4	0,461 6	0,813 1	0,661 2	1,902	2,277	4,88	5,84
190911	7	1	44,81	45,06	0,332 3	0,110 4	0,972 6	0,945 9	0,930	2,723	2,08	6,08
171012	7	1	45,92	45,72	0,543 2	0,295 1	0,770 5	0,593 6	1,521	2,157	3,31	4,70
191011	11	0	45,64	46,05	0,523 5	0,274 0	0,707 3	0,500 2	1,466	1,980	3,21	4,34
170111	7	0	46,03	46,51	0,193 7	0,037 5	0,671 5	0,450 9	0,542	1,880	1,18	4,08
190811	7	0	51,78	52,11	0,550 1	0,302 6	0,913 6	0,834 6	1,540	2,558	2,97	4,94

[a] Of the number of labs reporting, the number of outliers removed based upon Cochran's and Grubb's tests for outliers.

[b] Consensus value based upon all methods used to determine available phosphate.

$r_{\text{percent,ave}}$ = 3,06 %; $R_{\text{percent,ave}}$ = 6,22 %

Table 5 — ICP-OES repeatability and reproducibility results for potassium

ID	Number of labs	Number outliers removed[a]	K_2O mean	Target[b]	s_r	s_r^2	s_R	s_R^2	r	R	r_{percent}	R_{percent}
170511	7	0	1,76	1,73	0,079 5	0,006 3	0,087	0,007 5	0,223	0,243	12,68	13,83
180911	10	1	3,78	3,73	0,053 7	0,002 9	0,160	0,025 7	0,150	0,449	3,97	11,87
160811	8	0	4,02	3,96	0,044 8	0,002 0	0,168	0,028 3	0,125	0,471	3,12	11,71
170811	10	1	5,10	5,10	0,117 4	0,013 8	0,173	0,030 0	0,329	0,485	6,44	9,50
161111	9	0	10,01	10,13	0,130 4	0,017 0	0,342	0,116 7	0,365	0,956	3,62	9,48
160711	8	0	12,43	12,26	0,123 9	0,015 4	0,249	0,061 9	0,347	0,697	2,79	5,61
190211	9	1	14,49	14,38	0,145 0	0,021 0	0,468	0,219 2	0,406	1,311	2,80	9,05
180211	11	1	14,45	14,55	0,239 9	0,057 5	0,470	0,220 9	0,672	1,316	4,65	9,11
181111	10	1	17,89	17,96	0,248 0	0,061 5	0,4959	0,245 9	0,694	1,389	3,88	7,76
190411	10	1	25,30	25,22	0,294 9	0,087 0	0,421	0,177 3	0,826	1,179	3,26	4,66
171211	10	0	30,84	30,49	0,302 0	0,091 2	0,823	0,678 0	0,845	2,306	2,74	7,48
180812	10	1	60,65	60,32	0,725 4	0,526 2	1,076	1,157 1	2,031	3,012	3,35	4,97

[a] Of the number of labs reporting, the number of outliers removed based upon Cochran's and Grubb's tests for outliers.

[b] Consensus value based upon all methods used to determine soluble potash.

$r_{\text{percent,ave}}$ = 4,44 %; $R_{\text{percent,ave}}$ = 8,75 %

CAUTION — Due to the organic solvent, the dynamic concentration range of phosphorus and potassium, and the lower ionization potential of phosphorus, this document poses some analytical challenges that are outlined in Annex B. Failure to address these challenges can result

in erroneous results, so deviation from this document is not recommended without further validation.

10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this document (i.e. ISO/TS 20917:2023);

c) test results obtained;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which can have influenced the test results.

Annex A
(informative)

Ring test background and results

A.1 General

The source of the ring study data used for method performance evaluation and validation was the Magruder fertilizer proficiency testing program (see Reference [10]). The data was mined from laboratory results reported to this program. The Magruder proficiency program is an association of 139 participating laboratories representing 21 different countries. It is open to any laboratory worldwide that would like to participate and is a nonprofit organization. Ground and homogenized fertilizer materials representing a broad range of fertilizer products and matrices are included in the program, and one or more samples are sent to all participating laboratories on a monthly basis. Duplicate test results from separate days and calibrations for the individual labs for the method(s) they performed are reported to the Magruder proficiency program administrator through a secure data reporting website. Data for each method is processed using internationally harmonized statistics (see ISO 13528[11]) and data for the mean, range, standard deviation and z-score for each sample for all reporting laboratories is downloadable. Each laboratory is assigned a unique number known only to them, so the data is anonymous, except to the program administrator. For the data used in this validation study, 18 different labs reported data; however, not all labs reported data for all samples. The program administrator indicated participating labs for this ring study included regulatory, commercial and private labs, with three different countries represented, namely the United States, Canada and Coast Rica.

A.2 Ring study samples

Samples selected for the evaluation were based upon three main criteria. First, a minimum of seven labs reporting data was important for statistical analysis and potential removal of any outliers. Second, samples representing low, medium and high concentrations of phosphorus and potassium were targeted. Third, a variety of matrices including, solid, liquid, inorganic and organic fertilizers were sought. Samples used for ICP-OES phosphate and potash method performance assessment are included in Tables A.1 and A.2. These tables provide the assigned Magruder proficiency program ID, the fertilizer type or matrix, the listed grade and the consensus value based upon the mean value from all analytical methods used to determine reported P_2O_5 and K_2O results.

Table A.1 — Phosphate samples used in ring study

Number	Sample ID[a]	Fertilizer type	Grade	Analyte P_2O_5 value[b]
1	180911	Organic solid	3-1-3	2,73
2	180611	Lawn	18-3-6	3,11
3	181111	Compound with micronutrients	17-6-18	6,64
4	181211	Compound with micronutrients	11-11-21	10,69
5	190311	Organic solid	12-12-2.5	12,34
6	171211	Compound	14-14-14	15,12
7	170911	Monoammonium phosphate + sulfur	12-40-0	39,37
8	190911	Water-soluble	10-45-10	45,06
9	171012	Concentrated superphosphate	0-45-0	45,72
10	191011	Diammonium phosphate	18-46-0	46,05
11	170111	Diammonium phosphate	18-46-0	46,51
12	190811	Monoammonium phosphate	11-52-0	52,11

[a] Sample identification from the Magruder Proficiency Testing Program, see Reference [10].

[b] Mean value from all analytical methods, including gravimetric, spectrophotometric and ICP-OES.

Table A.2 — Potash samples used in ring study

Number	Sample ID[a]	Fertilizer type	Grade	Analyte K_2O value[b]
1	170511	Complex	16-1-0	1,73
2	180911	Organic solid	3-1-3	3,73
3	160811	Organic liquid	5-20-4	3,96
4	170811	Compound	21-0-5	5,10
5	161111	Compound	32-0-10	10,13
6	160711	Compound with micronutrients	12-12-12	12,26
7	190211	Compound	14-14-14	14,38
8	180211	Compound with micronutrients	14-14-14	14,55
9	181111	Compound with micronutrients	17-6-18	17,96
10	190411	Potassium thiosulfate, liquid	0-0-25	25,22
11	171211	Compound	5-15-30	30,49
12	180812	Muriate of potash	0-0-60	60,32

[a] Sample identification from the Magruder Proficiency Testing Program, see Reference [10].

[b] Mean value from all analytical methods, including STPB, flame photometric, atomic absorption spectrophotometry and ICP-OES.

A.3 Test results

Results for all phosphate and potash samples along with the data identified as outliers are reported in Tables A.3 to A.26. They are listed in order of lowest-to-highest mean result. ISO 13528[11] and Reference [12] were used as a reference document for statistical analysis.

Table A.3 — Percentage of P_2O_5 results for sample 180911

Participating lab	Value 1	Value 2	Mean value
0423	2,53	2,60	2,57
0117	2,61	2,74	2,67
0040	2,70	2,70	2,70
0377	2,73	2,78	2,76
0043	2,72	2,81	2,77
0025	2,76	2,79	2,78
0360	2,84	2,92	2,88
0023	2,82	2,96	2,89
0494[a]	2,39	2,83	2,61 (76,7 %)
P_2O_5 mean	2,75		

[a] Lab 0494 was significant for Cochran's test (69,3 %).

Table A.4 — Percentage of P_2O_5 results for sample 180611

Participating lab	Value 1	Value 2	Mean value
0233[a]	2,38	2,52	2,45 (65,0 %)
0043	3,01	3,06	3,04
0360	3,01	3,08	3,05
0117	3,09	3,12	3,10
0377	3,06	3,21	3,14
0423	3,11	3,18	3,15
0025	3,14	3,18	3,16
0040	3,20	3,20	3,20
0368	3,24	3,28	3,26
0023	3,24	3,28	3,26
P_2O_5 mean	3,15		

[a] Lab 0233 was significant for single Grubb's test (42,0 %).

Table A.5 — Percentage of P_2O_5 results for sample 181111

Participating lab	Value 1	Value 2	Mean value
0423	6,41	6,48	6,45
0037	6,66	6,75	6,70
0040	6,70	6,80	6,75
0377	6,76	6,80	6,78
0043	6,76	6,87	6,82
0360	6,86	6,88	6,87
0025	6,90	7,02	6,96
0072	7,06	7,11	7,09
0494[a]	6,51	7,02	6,77 (82,8 %)
P_2O_5 mean	6,80		

[a] Lab 0494 was significant for Cochran's test (69,3 %).

Table A.6 — Percentage of P_2O_5 results for sample 181211

Participating lab	Value 1	Value 2	Mean value
0025[a]	8,37	8,43	8,40 (42,1 %)
0423[b]	9,28	9,47	9,38 (65,3 %)
0486	10,55	10,60	10,58
0037	10,60	10,62	10,61
0040	10,60	10,70	10,65
0377	10,73	10,81	10,77
0117	10,78	10,80	10,79
0043	10,81	10,82	10,82
0023	10,88	10,92	10,90
0072	10,89	10,94	10,92
0368	10,92	10,96	10,94
0360	11,06	11,08	11,07
P_2O_5 mean	10,80		

[a] Lab 0025 was significant for first single Grubb's test (36,1 %).

[b] Lab 0423 was significant for second single Grubb's test (38,8 %).

Table A.7 — Percentage of P_2O_5 results for sample 190311

Participating lab	Value 1	Value 2	Mean value
0117	11,85	11,96	11,91
0368	11,80	12,08	11,94
0423	12,06	12,18	12,12
0040	12,20	12,30	12,25
0043	12,48	12,50	12,49
0486	12,49	12,60	12,55
0494	12,51	12,67	12,59
0025	12,60	12,70	12,65
0377	12,78	12,82	12,80
0360	13,03	13,03	13,03
P_2O_5 mean	12,43		

Table A.8 — Percentage of P_20_5 results for sample 171211

Participating Lab	Value 1	Value 2	Mean value
0368	14,73	14,77	14,75
0423	14,85	15,00	14,93
0072	14,84	15,04	14,94
0037	14,95	15,25	15,10
0025	15,00	15,39	15,20
0377	15,14	15,30	15,22
0117	15,23	15,29	15,26
0360	15,26	15,40	15,33
0040	15,10	15,60	15,35
P_20_5 mean	15,12		

Table A.9 — Percentage of P_20_5 results for sample 170911

Participating lab	Value 1	Value 2	Mean value
0025	37,51	38,82	38,17
0233	37,26	39,27	38,27
0360	38,52	39,05	38,79
0377	38,81	38,88	38,85
0494	39,40	39,46	39,43
0423	39,50	39,64	39,57
0117	39,56	40,19	39,88
P_20_5 mean	38,99		

Table A.10 — Percentage of P_20_5 Results for Sample 190911

Participating lab	Value 1	Value 2	Mean value
0136	43,20	43,60	43,40
0486	43,87	43,88	43,88
0377	44,52	44,63	44,58
0025	44,70	45,10	44,90
0043[a]	43,88	46,16	45,02 (77,1 %)
0117	45,28	45,51	45,40
0023	45,10	45,80	45,45
0360	45,69	46,51	46,10
P_20_5 mean	44,81		

[a] Lab 0043 was significant for Cochran's test (73,6 %).

Table A.11 — Percentage of P_2O_5 results for sample 171012

Participating lab	Value 1	Value 2	Mean value
0423	44,68	44,78	44,73
0023	45,17	46,24	45,71
0117	45,61	45,89	45,75
0360	45,55	46,17	45,86
0494	45,36	46,70	46,03
0377	46,57	46,68	46,63
0025	46,32	47,16	46,74
0233[a]	42,53	46,51	44,52 (79,3 %)
P_2O_5 mean	45,92		

[a] Lab 0233 was significant for Cochran's test (73,6 %).

Table A.12 — Percentage of P_2O_5 results for sample 191011

Participating lab	Value 1	Value 2	Mean value
0136	44,00	45,50	44,75
0423	44,45	45,28	44,87
0117	44,63	45,36	45,00
0377	45,07	45,38	45,23
0025	45,50	45,70	45,60
0043	45,42	45,91	45,67
0040	45,60	46,10	45,85
0360	45,94	46,24	46,09
0494	45,55	46,88	46,22
0486	46,17	46,40	46,29
0023	46,40	46,50	46,45
P_2O_5 mean	45,64		

Table A.13 — Percentage of P_2O_5 results for sample 170111

Participating lab	Value 1	Value 2	Mean value
0423	44,56	44,90	44,73
0040	45,40	45,90	45,65
0117	45,95	46,06	46,01
0037	46,23	46,52	46,38
0494	46,38	46,41	46,40
0377	46,40	46,64	46,52
0023	46,51	46,58	46,55
P_2O_5 mean	46,03		

Table A.14 — Percentage of P_2O_5 results for sample 190811

Participating lab	Value 1	Value 2	Mean value
0043	49,62	51,32	50,47
0377	50,76	50,82	50,79
0360	51,69	51,97	51,83
0040	51,90	52,10	52,00
0117	52,27	52,39	52,33
0023	52,45	52,46	52,46
0025	52,00	53,10	52,55
P_2O_5 mean	51,78		

Table A.15 — Percentage of K_2O results for sample 170511

Participating lab	Value 1	Value 2	Mean value
0494	1,58	1,75	1,67
0354	1,61	1,77	1,69
0423	1,73	1,75	1,74
0360	1,76	1,76	1,76
0117	1,72	1,84	1,78
0377	1,80	1,84	1,82
0137	1,78	1,92	1,85
K_2O mean	1,76		

Table A.16 — Percentage of K_2O results for sample 180911

Participating lab	Value 1	Value 2	Mean value
0494	3,48	3,55	3,52
0354	3,54	3,58	3,56
0025	3,66	3,68	3,67
0485	3,80	3,80	3,80
0377	3,72	3,89	3,81
0423	3,78	3,86	3,82
0117	3,78	3,90	3,84
0360	3,89	3,90	3,90
0043	3,96	3,97	3,97
0486	3,96	3,97	3,97
0023[a]	3,21	4,06	3,64 (92,6 %)
K_2O mean	3,78		

[a] Lab 0023 was significant for Cochran's test (62,2 %).

Table A.17 — Percentage of K_2O results for sample 160811

Participating lab	Value 1	Value 2	Mean value
0025	3,79	3,84	3,81
0360	3,91	3,93	3,92
0377	3,91	3,93	3,92
0117	3,89	3,96	3,93
0023	3,99	4,10	4,05
0486	4,00	4,10	4,05
0494	4,17	4,20	4,19
0354	4,31	4,34	4,32
K_2O mean	4,02		

Table A.18 — Percentage of K_2O results for sample 170811

Participating lab	Value 1	Value 2	Mean value
0117	4,62	5,00	4,81
0494	4,88	5,12	5,00
0025	4,89	5,12	5,00
0377	4,97	5,05	5,01
0486	5,07	5,15	5,11
0354	5,12	5,15	5,13
0023	5,12	5,17	5,15
0360	5,21	5,23	5,22
0423	5,20	5,25	5,23
0137	5,32	5,38	5,35
0543[a]	5,74	5,84	5,79 (39,9 %)
K_2O mean	5,10		

[a] Lab 0543 was significant for single Grubb's test (38,8 %).

Table A.19 — Percentage of K_2O results for sample 161111

Participating lab	Value 1	Value 2	Mean value
0117	9,46	9,62	9,54
0025	9,68	9,99	9,84
0485	9,88	9,99	9,94
0423	9,95	10,17	10,06
0023	10,02	10,27	10,15
0360	10,12	10,18	10,15
0354	10,20	10,21	10,20
0494	10,24	10,25	10,25
0486	10,63	10,86	10,75
K_2O mean	10,10		

Table A.20 — Percentage of K_2O results for sample 160711

Participating lab	Value 1	Value 2	Mean value
0117	12,08	12,20	12,14
0354	12,21	12,23	12,22
0377	12,26	12,29	12,28
0025	12,22	12,40	12,31
0494	12,47	12,49	12,48
0360	12,42	12,61	12,52
0486	12,46	12,86	12,66
0423	12,80	12,83	12,82
K_2O mean	12,43		

Table A.21 — Percentage of K_2O results for sample 190211

Participating lab	Value 1	Value 2	Mean value
0377	14,06	14,08	14,07
0486	14,05	14,11	14,08
0117	14,11	14,17	14,14
0043	14,15	14,18	14,17
0485	14,20	14,40	14,30
0354	14,50	14,80	14,65
0360	14,65	14,65	14,65
0494	14,73	15,22	14,98
0072	15,37	15,37	15,37
0025[a]	13,90	15,00	14,45 (76,2 %)
K_2O mean	14,49		

[a] Lab 0025 was significant for Cochran's test (65,5 %).

Table A.22 — Percentage of K_2O results for sample 180211

Participating lab	Value 1	Value 2	Mean value
0486	13,62	13,85	13,74
0485	13,84	14,06	13,95
0494	14,01	14,39	14,20
0037	14,31	14,37	14,34
0117	14,10	14,58	14,34
0023	14,08	14,87	14,48
0360	14,48	14,55	14,52
0043	14,52	14,55	14,54
0377	14,52	14,65	14,59
0354	14,80	14,90	14,85
0025	15,21	15,57	15,39
0423[a]	18,13	18,35	18,24 (62,6 %)
K_2O mean	14,45		

[a] Lab 0423 was significant for single Grubb's test (36,1 %).

Table A.23 — Percentage of K_2O results for sample 181111

Participating lab	Value 1	Value 2	Mean value
0543[b]	14,13	15,18	14,65 (56,6 %)
0072[b]	15,81	16,59	16,20 (56,6 %)
0423	17,17	17,23	17,20
0037	17,15	17,31	17,23
0025[a]	16,50	18,00	17,25 (69,6 %)
0043	17,61	18,13	17,87
0377	17,93	17,94	17,94
0354	18,00	18,10	18,05
0494	18,11	18,15	18,13
0360	18,13	18,14	18,14
0486	18,15	18,97	18,56
K_2O mean	17,89		

[a] Lab 0025 was significant for Cochran's test (69,3 %).

[b] Lab 0543 & 0072 were significant for double Grubb's (LL, 52,1 %).

Table A.24 — Percentage of K_2O results for sample 190411

Participating lab	Value 1	Value 2	Mean value
0485	24,87	24,96	24,91
0117	24,41	25,43	24,92
0377	24,86	25,14	25,00
0354	25,00	25,10	25,05
0025	25,00	25,40	25,20
0494	25,11	25,49	25,30
0360	25,29	25,66	25,48
0023	25,44	25,53	25,49
0486	25,41	25,73	25,57
0423	25,97	26,19	26,08
0233[a]	23,60	27,20	25,40 (88,2 %)
K_2O mean	25,30		

[a] Lab 0233 was significant for Cochran's test (62,2 %).

Table A.25 — Percentage of K_2O results for sample 171211

Participating lab	Value 1	Value 2	Mean value
0072	29,08	29,83	29,46
0486	29,75	29,90	29,83
0043	30,15	30,55	30,35
0423	30,55	30,95	30,75
0037	30,76	31,17	30,97
0360	30,94	31,11	31,03
0354	30,90	31,24	31,07
0025	31,00	31,37	31,19
0117	31,33	31,99	31,66
0377	32,01	32,20	32,11
K_2O mean	30,84		

Table A.26 — Percentage of K_2O results for sample 180812

Participating lab	Value 1	Value 2	Mean value
0486[a]	48,64	48,70	48,67 (74,6 %)
0423	58,95	59,69	59,32
0023	59,56	59,98	59,77
0043	60,08	60,33	60,21
0360	60,14	60,52	60,33
0354	60,30	60,60	60,45
0494	60,52	60,54	60,53
0377	60,68	60,99	60,84
0485	59,84	61,93	60,89
0117	60,54	62,37	61,46
0025	62,10	63,40	62,75
K_2O mean	60,65		

[a] Lab 0486 was significant for single Grubb's test (38,8 %).

A.4 Precision

Repeatability (r) and reproducibility (R) are reported in 9.2, Tables 4 and 5. Short term precision both from one-sample-to-the-next and from one-day-to-the-next are listed in Tables A.27 and A.28.

Table A.27 — Short-term precision for phosphorus

Concentration	Day 1, rep 1	Day 1 rep 2	s	Day 2 rep 1	Day 2 rep 2	s
47,1	46,862	47,169	0,217	47,320	47,305	0,004
23,6	23,557	23,535	0,016	23,715	23,573	0,100
11,8	11,759	11,807	0,034	11,815	11,693	0,086
5,9	5,779	5,901	0,086	5,933	5,963	0,021
2,9	2,984	2,937	0,033	2,955	2,937	0,013

Key

s : standard deviation

s_{ave} : standard deviation average

$s_{ave} = 0,061$

Recommend replicates agree within ±3*s or 0,183.

Table A.28 — Short-term precision for potassium

Concentration	Day 1, Rep 1	Day 1 Rep 2	s	Day 2 Rep 1	Day 2 Rep 2	s
60	60,020	59,660	0,255	59,900	59,880	0,014
30	29,970	30,110	0,099	30,000	30,060	0,042
15	15,020	15,030	0,007	15,050	15,050	0,035
7,5	7,544	7,529	0,011	7,603	7,602	0,001
3,8	3,784	3,761	0,016	3,767	3,750	0,012

Key

s : standard deviation

s_{ave} : standard deviation average

$s_{ave} = 0,049$

Recommend replicates agree within ±3*s or 0,148.