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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**

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ISO/DTS 20917

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

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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 ethylenediamine 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.

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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

1 Scope

This document specifies an inductively coupled plasma-optical emission spectrometer (ICP-OES) method for the determination of the ammonium citrate, disodium-ethylenediamine 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, $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, with a molecular weight (MW) of 226,19 and a purity greater than 98 % or 980,0 g/kg.

5.2 EDTA, disodium salt, dehydrate, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, 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 28,0-30,0 % as NH_3 or $\rho = 0,91$ g/ml.

5.4 Nitric acid, HNO_3 , 67-70 %, 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/kg¹⁾.

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/kg²⁾.

5.8 Octyl phenol ethoxylate³⁾.

5.9 Beryllium, Be, stock solution of 10 000 $\mu\text{g}/\text{ml}$, commercially available.

5.10 Scandium, Sc, stock solution of 10 000 $\mu\text{g}/\text{ml}$, commercially available.

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 and 50 g dibasic ammonium citrate 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 ($\pm 0,02$) 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 $7,00 \pm$

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 0,5 % or 5 ml/l octyl phenol ethoxylate.

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 ml 10 000 µg/ml Sc stock standard, 3 g cesium chloride, 40 ml nitric acid, and 1 ml 0,5 % octyl phenol ethoxylate 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 Be is used as an internal standard, add 4 ml of 10 000 µg/ml Be stock standard to obtain a concentration of 40 µg/ml Be.

Alternatively, Li from LiNO_3 can be substituted for Cs as an ionization buffer at 7 g LiNO_3 per litre.

5.16 4 % nitric acid rinse solution.

Add 40 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.

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.

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**, with a readability to 0,1 mg.

6.2 **pH meter**, with a readability to pH 7,00.

6.3 **pH combination electrode**.

6.4 **Constant temperature water bath**, capable of maintaining a temperature of $65\text{ °C} \pm 2\text{ °C}$.

6.5 Heated shaking water bath, capable of maintaining a temperature of $65\text{ °C} \pm 2\text{ °C}$ 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 $65\text{ °C} \pm 2\text{ °C}$ 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 ISO 14820-1 or comparable (see References [8] and [9]).

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

8 Procedure

8.1 Extraction of P and K

For samples containing less than 45 % P_2O_5 or K_2O , weigh $0,5\text{ g} \pm 0,01\text{ g}$ 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 $0,45 \pm 0,01\text{ g}$ of ground fertilizer material and completely transfer to a 250 mL class A volumetric flask. Dispense 100 ml of $65\text{ °C} \pm 2\text{ °C}$ preheated ammonium citrate, disodium-EDTA extraction solution (5.13) into each flask and insert a rubber stopper. Shake test solutions in a $65\text{ °C} \pm 2\text{ °C}$ 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 ug/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 3 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 ₂ O ₅ µg/ml	P ₂ O ₅ solution %	P ₂ O ₅ fertilizer % ^e	K µg/ml	K ₂ O µg/ml	K ₂ O solution %	K ₂ O 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 PO₄ or 2,746 1 g of potassium dihydrogen phosphate KH₂PO₄ 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; 10 of Std 7 = 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 % P2O5 fertilizer material weighed at 0,45 g rather than 0,5 g results in a concentration of 46,8 % P2O5, which is a 2 % extrapolation from the top standard.

NOTE 2 A 62 % K2O fertilizer material weighed at 0,45 g rather than 0,5 g results in a concentration of 55,8 % K2O, which is a 3 % extrapolation from the top standard.