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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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Technical Specification

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this ~~proposed technical specification 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 ~~proposed technical specification document~~ was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this ~~proposed technical specification document~~ may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this ~~proposed technical specification document~~ is information given for the convenience of users and does not constitute an endorsement.

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 ~~the following URL:-~~.

This ~~proposed technical specification 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 (4,4,5) ~~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, ~~a Technical Specification this document~~ was created ~~at this time~~ with the goal of generating a Final Draft International Standard.

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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 Technical Specification specifies an ICP-OES method for the determination of the ammonium citrate, disodium-EDTA soluble phosphorus and potassium content in fertilizer extract solutions. This specification is suitable for all inorganic fertilizer products, whether compound or complex fertilizer products or blends thereof, and straight concentrated fertilizer products. 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 (4)—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 the trueness of this technical specification is good, document can be used with minimal bias, the repeatability and reproducibility is not consistent with other standards routinely used for governative inspection at this time, such as EN15959, EN15477, EN 15959^[4], EN 15477^[5] or ISO 22018^[6].

As a result, this technical specification document is intended for screening purposes, where a large number of fertilizer phosphorus and potassium results must be obtained as efficiently as possible. Where governative inspection is critical, such as where fertilizer tolerances or desired statistical certainty criteria have been exceeded by this technical specification, then standards such as EN15959, EN15477 or ISO 22018 can be used for confirmation.

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 ~~proposed technical specification document~~. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

~~EN 15959:2014~~ ISO 8157, *Fertilizers — Determination of extracted phosphorus, soil conditioners and beneficial substances — Vocabulary*

~~EN 15477:2009~~, *Fertilizers — Determination of the water-soluble potassium content*.

~~ISO 14820-1:2016~~, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

~~ISO 14820-2:2016~~, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

~~ISO 22018:2021~~ Fertilizers, soil conditioners and beneficial substances — Determination of EDTA soluble phosphorus content in inorganic fertilizers.

~~ISO 13528:2015~~, *Statistical methods for use in proficiency testing by interlaboratory comparison*.

3 Terms and definitions

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

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

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~~IEC Electropedia: available at~~ — ISO Online browsing platform: available at <https://www.iso.org/obp>

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

5.4 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 (~~6~~—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 favorably/favourably with other soluble potash solvents such as ammonium oxalate. The user of this technical standard/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). ~~S 20917~~

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5.5 Reagents

5.1 Ammonium citrate, dibasic, $(NH_4)_2HC_6H_5O_7$, ~~Formula Weight (FW) 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, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, ~~FW with a MW of 372,24, and a~~ purity >greater than 98 % or 980,0 g/kg.

5.3 Ammonium hydroxide, NH_4OH ; ~~FW, with a MW of 35,05; and a~~ purity =equal to 28,0-30,0 % as NH_3 or ρ = 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 , ~~FW with a MW of 136,09, certified at 26,93% P or 269,3 with a purity greater than 99 % or 990,0 g/kg¹; National Institute of Standards and Technology (NIST) SRM 194a (Gaithersburg, MD), or comparable.~~

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

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.

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5.7 Potassium nitrate, KNO_3 , ~~FW with a MW of 101,10; NIST SRM 193 with a purity greater than 99 % or comparable, certified at 38,66% K or 386,6-990,0 g/kg².~~

~~Triton X-100~~, 5.8 Octyl phenol ethoxylate³.

5.9 Beryllium, Be , stock solution ~~—10000 of 10 000~~ $\mu\text{g/ml}$; commercially available.

5.10 Scandium, Sc , stock solution ~~—10000 of 10 000~~ $\mu\text{g/ml}$; commercially available.

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

5.12 Lithium nitrate, LiNO_3 , ~~FW 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 ~~4500–500~~ ml of deionized (or equivalent) water. Adjust the pH to near neutral by adding 30 ml of ~~(1+1, v/v)~~ 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, v/v volume fraction)~~ solution drop-by-drop and stirring. After obtaining a stable pH of 7,00 (~~$\pm 0,02$~~), 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 ~~3~~ weeks, if stored in a dark location.

5.14 0,5 % or 5 mL/L Triton X— ml/l octyl phenol ethoxylate.

Add ~~1 mL Triton X-100 ml of octyl phenol ethoxylate (5.8-~~above~~)~~ to a 200 ml volumetric flask and dilute to volume with deionized water.

5.15 Internal standard/ionization buffer (10 $\mu\text{g/ml}$ Sc in 0,018 M CsCl and 4 % nitric acid).

~~—Add 1 mL 10000- ml 10 000~~ $\mu\text{g/ml}$ Sc stock standard, 3 g cesium chloride, 40 ml nitric acid, and 1 ml 0,5% ~~Triton X-% 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 ~~40000 10 000~~ $\mu\text{g/ml}$ Be stock standard to obtain a concentration of 40 $\mu\text{g/ml}$ Be.

~~5.15.1~~ Alternatively, Li from LiNO_3 ~~may can~~ be substituted for Cs as an ionization buffer at 7 g LiNO_3 per ~~liter—litre.~~

~~2% Nitric Acid Rinse Solution—5.16 4 % nitric acid rinse solution.~~

Add ~~20–40~~ 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.

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.

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~~2500~~ 5.17 2 500 µg/ml phosphorus from phosphate (PO₄)~~—~~].

Add ~~2,7464~~ 746 1 g of potassium dihydrogen phosphate (5.5~~—above~~) to a 250 ml volumetric flask, then bring to volume with deionized (or equivalent) water. This standard also contains ~~34563~~ 156,5 µg/ml K; also, this standard ~~may~~ 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 ~~will~~ change~~changes~~ the matrix of the pH neutral ammonium citrate EDTA solution and ~~produce~~ produces erroneous results.

~~7500~~ 5.18 7 500 µg/ml potassium from potassium chloride~~—~~].

Add ~~1,4300~~ 430 0 g of potassium chloride (5.6~~—above~~) to a 100 ml volumetric flask, then bring to volume with deionized (or equivalent) water. Alternatively, ~~1,9394~~ 939 4 g of potassium nitrate (5.7~~—above~~) 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 ~~will~~ change~~changes~~ the matrix of the pH neutral ammonium citrate EDTA solution and ~~produce~~ produces erroneous results.

7 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 ~~temperatures~~ a temperature of 65 ± 2 °C ± 2 °C.

6.5 Heated shaking water bath, capable of maintaining ~~bath temperatures~~ a temperature of 65 ± 2 °C; ± 2 °C and set to approximately 200 reciprocations/min. ~~NA~~

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.

8 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])).

~~7.1-7.2~~ ~~3)~~

Prepare solid and liquid fertilizer materials using a recognized sample preparation procedure such as ISO 14820-42 or comparable.

98 Procedure

9.18.1 Extraction of P and K

For samples containing less than 45 % P_2O_5 or K_2O , weigh $0,5 \pm 0,01$ 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 $0,45 \pm 0,01$ g of ground fertilizer material and completely transfer to a 250 mL class A volumetric flask. Dispense 100 ml of 65 ± 2 °C preheated ammonium citrate, disodium-EDTA extraction solution (5.13-~~above~~) into each flask and insert a rubber stopper. Shake test solutions in a 65 ± 2 °C preheated water bath set to approximately 200 reciprocations per minute for exactly 60 min; ~~then~~. 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 ~~may~~ 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 hours after extraction.

NOTE: If a homogeneous ground laboratory sample is not attainable, the weights and volumes listed should be at least doubled to improve representation.

9.58.2 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 ~~may~~ 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 MAP + S (40% concentrated superphosphate, diammonium phosphate (46 % of P_2O_5), TSP and DAP (46% P_2O_5), and MAP monoammonium phosphate (50 % or 52% of P_2O_5), since these materials require optimal instrument performance.