INTERNATIONAL STANDARD

ISO 15959

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Fertilizers — Determination of extracted phosphorus

Engrais — Dosage du phosphore extrait

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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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ISO 15959 was prepared by CEN/TC 260 as CEN/TS 15959:2009 and was adopted (without modification other than that stipulated below) by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*.

The following changes have been made:

- potassium dihydrogen phosphate has been added to the reagents (Clause 6);
- CEN/TS 15956, CEN/TS 15957 and CEN/TS 15958 have been updated to EN standards;
- other editorial changes.

Fertilizers — Determination of extracted phosphorus

1 Scope

This International Standard specifies a method for the determination of phosphorus in fertilizer extracts.

The method is applicable to all extracts of fertilizers for the determination of the different forms of phosphorus as phosphorus soluble in mineral acids, water soluble phosphorus, phosphorus soluble in solutions of ammonium citrate, phosphorus soluble in 2 % citric acid and phosphorus soluble in 2 % formic acid.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN 12944-1, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 apply.

4 Principle

After possible hydrolysis, phosphorus is precipitated in an acid media in the form of quinoline phosphomolybdate.

After filtering and washing, the precipitate is dried at 250 °C and weighed.

In the above mentioned conditions, no interfering action is exerted by the compounds likely to be found in the solution (mineral and organic acids, ammonium ions, soluble silicates, etc.) if a reagent based on sodium molybdate or ammonium molybdate is used in the precipitation.

5 Sampling and sample preparation

Sampling is not part of the method specified in this International Standard. A recommended sampling method is given in ISO 14820-1.

Sample preparation shall be carried out in accordance with ISO 14820-2. Grinding of the laboratory sample is recommended for homogeneity reasons.

6 Reagents

6.1 Water, distilled or demineralized.

6.2 Concentrated nitric acid, p = 1,40 g/ml.

6.3 Preparation of reagents

6.3.1 Preparation of the reagent based on sodium molybdate

Solution A: Dissolve 70 g of sodium molybdate dihydrate in 100 ml of distilled water.

Solution B: Dissolve 60 g of citric acid monohydrate in 100 ml of distilled water and add 85 ml concentrated nitric acid (6.2).

Solution C: Stir solution A into solution B to obtain solution C.

Solution D: To 50 ml of distilled water, add 35 ml of concentrated nitric acid (6.2), then 5 ml of freshly distilled quinoline. Add this solution to solution C, mix thoroughly and leave standing overnight in the dark. After this, make up to 500 ml with distilled water, mix again, and filter through a sintered glass funnel (7.7).

6.3.2 Preparation of the reagent based on ammonium molybdate

Solution A: In 300 ml of distilled water, dissolve 100 g of ammonium molybdate while heating gently and stirring from time to time.

Solution B: Dissolve 120 g of citric acid monohydrate in 200 ml of distilled water, add 170 ml of concentrated nitric acid (6.2).

Solution C: Add 10 ml of freshly distilled quinoline to 70 ml of concentrated nitric acid (6.2).

Quinoline can be purchased commercially and can be used instead of 'freshly distilled'. Also, the stock solution of quinolone should be examined periodically for colour degradation and replaced with a new stock when necessary.

Solution D: Slowly pour, stirring well, solution A into solution B. After thoroughly mixing, add solution C to this mixture and make up to 1 l. Leave standing for two days in a dark place and filter through a sintered glass funnel (7.7), or filter paper of similar porosity.

The reagents 6.3.1 and 6.3.2 may be used in the same way, both shall be kept in the dark in stoppered polyethylene bottles.

6.4 Potassium dihydrogen phosphate, that containing 0,01 g P_2O_5.

7 Apparatus

7.1 Standard laboratory equipment.

7.2 500 ml Erlenmeyer flask, with a wide neck.

7.3 Graduated pipettes, of 10 ml, 25 ml and 50 ml.

7.4 Filter crucible, with porosity of 5 µm to 20 µm.

7.5 Buchner flask.

7.6 Drying oven, regulated at (250 ± 10) °C.

7.7 Sintered glass funnel, with porosity of 5 µm to 20 µm or filter paper of similar porosity.

8 Procedure

8.1 Treatment of the solution

With a pipette (7.3), take an aliquot containing about 0,01 g of P_2O_5 as prescribed in Table 1 from the fertilizer prepared and previously extracted (see References [3], [4], [5], [6], [7], [8], [9], [10] and [11]). Place the aliquot in the Erlenmeyer flask (7.2). Add 15 ml of concentrated nitric acid (6.2) and dilute with water to about 100 ml. When the solution to be precipitated contains more than 15 ml of citrate solution (neutral citrate, Petermann, or Joulie alkaline citrate), an amount of 21 ml of concentrated nitric acid (6.2) shall be added.

Table 1 — Determination of the aliquot parts of the phosphate solutions

% P_2O_5 in the fertilizer	**% P in the fertilizer**	**Sample for analysis** g	**Dilution** to ml	**Sample** ml	**Dilution** to ml	**Sample to be precipitated** ml	**Quinoline phosphomolybdate conversion factor (*F*),** in % P_2O_5	**Quinoline phosphomolybdate conversion factor (*F′*),** in % P
5 to 10	2,2 to 4,4 {	1	500	—	—	50	32,074	13,984
		5	500	—	—	10	32,074	13,984
10 to 25	4,4 to 11,0 {	1	500	—	—	25	64,148	27,968
		5	500	50	500	50	64,148	27,968
>25	>11 {	1	500	—	—	10	160,370	69,921
		5	500	50	500	25	128,296	55,937

8.2 Hydrolysis

If the presence of metaphosphates, pyrophosphates, or polyphosphates is suspected in the solution, carry out the hydrolysis as follows.

Bring the content of the Erlenmeyer flask (7.2) to a boil slowly and keep at this temperature until hydrolysis is completed. This usually takes 1 h. Care shall be taken to avoid losses by splashing and excessive evaporation which could reduce the initial volume by more than half, by fitting a reflux condenser. After hydrolysis, make up to the initial volume with water (6.1).

8.3 Weighing the crucible

Dry the filter crucible (7.4) for at least 15 min in the drying oven (7.6) set at (250 ± 10) °C. Cool in a desiccator and weigh to the nearest 0,000 1 g.

8.4 Precipitation

Heat the acid solution contained in the Erlenmeyer flask (7.2) until it begins to boil. Then start the precipitation of the quinoline phosphomolybdate by adding 40 ml of the precipitating reagent (6.3.1 or 6.3.2) drop-wise, stirring continuously. To precipitate phosphate solutions containing more than 15 ml of citrate solution (neutral citrate, Petermann or Joulie) which have been acidified with 21 ml of concentrated nitric acid (see 8.1), an amount of 80 ml of the precipitating reagent shall be used. Place the Erlenmeyer flask in a hot water bath (temperature >80 °C), leave it there for 15 min, shaking it from time to time. Remove the flask from the water bath and allow to cool prior to filtering the solution

8.5 Filtering and washing

Filter the solution under vacuum by decantation. Wash the precipitate in the Erlenmeyer flask (7.2) with 30 ml of water (6.1). Decant and filter the solution. Repeat this process five times. Quantitatively transfer the rest of the precipitate into the crucible, washing it with water. Wash four times with 20 ml of water, allowing the liquid to drain from the crucible before each addition. Dry the precipitate thoroughly.

8.6 Drying and weighing

Wipe the outside of the crucible with a filter paper or cleaning tissue. Place this crucible in a drying oven (7.6) and keep it there until its mass remains constant, at a temperature of 250 °C (usually 15 min but not to exceed 30 min); leave it to cool in the desiccator at ambient temperature and weigh rapidly.

8.7 Blank test

For each series of determinations, carry out a blank test using only the reagents and solvents in the proportions used in the extraction (citrate solution, etc.) and allow for them in the calculation of the final result.

8.8 Verification

Carry out the determination using an aliquot part of a potassium dihydrogen phosphate solution containing 0,01 g of P_2O_5 (6.4).

9 Calculation and expression of the result

If the samples for analysis and dilutions are used according to Table 1, calculate the mass fraction, w_P, in percent, according to Formula (1):

$$w_P = (m_1 - m_2) \times F' \qquad (1)$$

If the samples for analysis and dilutions are used according to Table 1, calculate the mass fraction, $w_{P_2O_5}$, in percent, according to Formula (2):

$$w_{P_2O_5} = (m_1 - m_2) \times F \qquad (2)$$

where

m_1 is the mass, in grams, of the quinoline phosphomolybdate;

m_2 is the mass, in grams, of the quinoline phosphomolybdate obtained in the blank test;

F and F' are factors given in the last two columns of Table 1.

If the samples for analysis and dilutions differ from those of Table 1, calculate the mass fraction, w_P, in percent, according to Formula (3):

$$w_P = \frac{(m_1 - m_2) \times f' \times D \times 100}{M} \qquad (3)$$

If the samples for analysis and dilutions differ from those of Table 1, calculate the mass fraction, $w_{P_2O_5}$, in percent, according to Formula (4):

$$w_{P_2O_5} = \frac{(m_1 - m_2) \times f \times D \times 100}{M} \qquad (4)$$

where

m_1 is the mass, in grams, of the quinoline phosphomolybdate;

m_2 is the mass, in grams, of the quinoline phosphomolybdate obtained in the blank test;

f and f' are factors of quinoline phosphomolybdate into P_2O_5 = 0,032 074, (f) or into P = 0,013 984 (f');

D is the dilution factor;

M is the mass, in grams, of the test portion analyzed.

10 Precision

10.1 Interlaboratory tests

Interlaboratory tests have been carried out in 2008 based on extraction methods according to EN 15956, EN 15957 and EN 15958. The number of participating laboratories and different fertilizer extract samples are mentioned in Annex A and Tables A.1 to A.3. Repeatability and reproducibility were calculated according to ISO 5725-2.

The values derived from these interlaboratory tests may not be applicable to concentration ranges and matrices other than those given in Annex A.

10.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not, in more than 5 % of the cases, exceed the values of r given in Table 2.

10.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will not, in more than 5 % of the cases, exceed values of R given in Table 2.

Table 2 — Mean values, repeatability and reproducibility limits

Sample (extraction according to EN 15956)	$\bar{x}$ %	r %	R %
NP (DAP)	46,51	0,35	1,17
NPK (16 – 16 – 8 + 4S)	16,13	0,21	0,41
TSP	49,35	0,48	1,38
Sample (extraction according to EN 15957)	$\bar{x}$ %	r %	R %
NP (DAP)	46,22	0,24	1,07
NPK (16 – 16 – 8 + 4S)	16,08	0,18	0,41
TSP	48,34	0,33	1,09
Sample (extraction according to EN 15958)	$\bar{x}$ %	r %	R %
NP (DAP)	42,72	0,31	2,34
NPK (16 – 16 – 8 + 4S)	14,22	0,18	0,38
TSP	46,56	0,41	2,04

11 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 International Standard, i.e. ISO 15959, and the extraction method used;

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 International Standard, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Annex A
(informative)

Statistical results of the interlaboratory test

The precision of the method was established in 2008 by “Chemical analysis” of CEN/TC 260 *Fertilizers and liming materials* in an interlaboratory test evaluated in accordance with ISO 5725-2. The statistical results are given in Tables A.1, A.2 and A.3.

Table A.1 — Statistical results extraction according to EN 15956

Parameter	Sample		
	NP (DAP)	NPK (16-16-8+4S)	TSP
Number of participating laboratories	17	20	18
Number of laboratories after elimination of outliers (accepted test results)	16	20	18
Mean value, $\overline{x}$ (%)	46,51	16,13	49,35
Repeatability standard deviation, s_r (%)	0,12	0,08	0,17
RSD$_r$ (%)	0,27	0,50	0,30
Repeatability limit, r (%)	0,35	0,21	0,48
Reproducibility standard deviation, s_R (%)	0,42	0,15	0,49
RSD$_R$ (%)	0,90	0,90	1,00
Reproducibility limit, R (%)	1,17	0,41	1,38

Table A.2 — Statistical results extraction according to EN 15957

Parameter	Sample		
	NP (DAP)	NPK (16-16-8+4S)	TSP
Number of participating laboratories	17	20	18
Number of laboratories after elimination of outliers (accepted test results)	14	20	14
Mean value, $\overline{x}$ (%)	46,22	16,08	48,34
Repeatability standard deviation, s_r (%)	0,09	0,06	0,12
RSD$_r$ (%)	0,19	0,40	0,24
Repeatability limit, r (%)	0,24	0,18	0,33
Reproducibility standard deviation, s_R (%)	0,38	0,15	0,39
RSD$_R$ (%)	0,83	0,90	0,81
Reproducibility limit, R (%)	1,07	0,41	1,09