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Phosphoric acid and sodium phosphates for industrial use (including foodstuffs) — Determination of fluorine content — Alizarin complexone and lanthanum nitrate photometric method

Acide phosphorique et phosphates de sodium à usage industriel (y compris les industries alimentaires) — Dosage du fluor — Méthode photométrique au complexone d'alizarine et nitrate de lanthane

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FOREWORD

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It has been approved by the Member Bodies of the following countries :

Belgium	Hungary	Spain
Bulgaria	India	Switzerland
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Egypt, Arab Rep. of	Netherlands	United Kingdom
Finland	New Zealand	U.S.S.R.
France	Poland	Yugoslavia
Germany	South Africa, Rep. of	

No Member Body expressed disapproval of the document.

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Phosphoric acid and sodium phosphates for industrial use (including foodstuffs) — Determination of fluorine content — Alizarin complexone and lanthanum nitrate photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an alizarin complexone and lanthanum nitrate photometric method for the determination of the fluorine content of phosphoric acid and sodium phosphates for industrial use (including foodstuffs).

The method is applicable to products of which the fluorine content, expressed as F, is equal to or greater than 0,5 mg/kg.

2 PRINCIPLE

Separation of fluorine from a test portion by steam distillation in a phosphoric acid medium. Formation of a blue-coloured complex between the fluorine and the combined reagent alizarin complexone/lanthanum nitrate, at a controlled pH. Addition of acetone to increase the stability of the complex and the sensitivity of the method. Photometric measurement of the complex at a wavelength of about 600 nm.

3 REAGENTS

During the analysis, use only reagents of recognized analytical grade having as low a fluorine content as possible, and only distilled water or water of equivalent purity.

3.1 Phosphoric acid, approximately 1,70 g/ml, about 85 % (*m/m*) solution.

3.2 Silica, powdered, dried in an oven at about 150 °C for 2 h.

3.3 Acetone.

3.4 Nitric acid, approximately 0,02 N solution.

3.5 Sodium hydroxide, approximately 0,2 N solution.

3.6 Combined colour reagent.

3.6.1 Buffer solution, pH 4,6.

Dissolve 5,9 g of succinic (butanedioic) acid in approximately 300 ml of water and adjust the pH to 4,6 with 0,5 N sodium hydroxide solution, using a pH meter. Dilute to 500 ml with water.

3.6.2 Alizarin complexone, 0,88 g/l solution.

Suspend 0,44 g of alizarin complexone in 200 ml of water and add 0,5 N sodium hydroxide solution, in small portions, until the solid has just dissolved. Add 50 ml of the buffer solution (3.6.1). Check the pH of the solution using a pH meter and adjust, if necessary, to between 4,5 and 4,8. Dilute to 500 ml and store between 0 and 50 °C.

NOTE — This solution has a slightly higher equivalency than the lanthanum nitrate solution (3.6.3) in order to ensure that the trivalent lanthanum ions are fully complexed in the test.

3.6.3 Lanthanum nitrate, 0,86 g/l solution.

Dissolve 0,43 g of lanthanum(III) nitrate hexahydrate [$(La(NO_3)_3.6H_2O)$] in 500 ml of water.

3.6.4 Mix equal volumes of the alizarin complexone solution (3.6.2) and the lanthanum nitrate solution (3.6.3) when required for use.

3.7 Fluorine, standard solution, corresponding to 0,100 g of F per litre.

Weigh, to the nearest 0,000 1 g, 0,221 0 g of sodium fluoride, previously dried for 2 h at 105 °C and cooled in a desiccator. Place in a 250 ml beaker containing about 100 ml of water. After dissolution, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,100 mg of F.

Store the solution in a plastic flask.

3.8 Fluorine, standard solution, corresponding to 1,00 mg of F per litre.

Place 10,0 ml of the standard fluorine solution (3.7) in a 1 000 one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 1 μg of F.

Prepare this solution at the time of use.

3.9 Phenolphthalein, 1 g/l solution in 95 % (*V/V*) ethanol.

4 APPARATUS

Ordinary laboratory apparatus and

4.1 Steam-distillation apparatus, made of glass, capable of ensuring complete distillation and recovery of the fluorine.

An example of suitable apparatus is illustrated in the figure and comprises

4.1.1 Steam generator, for example a wide-neck flask of capacity approximately 3 000 ml, fitted with a stopper into which are inserted three glass tubes [4.1.1 a), b) and c)] of internal diameter about 6 mm.

a) **vertical recovery bend tube,** for introducing the steam into the distillation flask (4.1.2.1) (one limb dipping into the distillation flask);

b) **tube for regulating the flow of the steam,** fitted at its outer end with a rubber tube fitted with a screw clip,

c) **safety tube,** about 1 m long.

4.1.2 Apparatus of borosilicate glass, for steam distillation, with ground glass joints, consisting of

4.1.2.1 Distillation flask, of nominal capacity 250 ml, round bottomed with central neck and side neck, fitted with a thermometer pocket for introduction of a thermometer (glycerine in the pocket ensures thermal exchange).

4.1.2.2 Distillation column, Vigreux, column length between the first and last of the series of points 120 mm.

4.1.2.3 Condenser, Graham, with an effective length of about 400 mm.

4.1.3 Thermometer, including the range 0 to 200 °C.

NOTE – The efficiency of the apparatus used shall be previously checked by testing with known volumes of the standard fluorine solution (3.7).

It is necessary, especially when low levels of fluorine are to be determined, in order to condition a new apparatus, or a new component of apparatus, to carry out about twelve distillations with fluoride samples so as to bring the glass surfaces into a state of equilibrium with fluorine. For example, these distillations can be carried out with a mixture of 30 ml of the phosphoric acid (3.1), 0,75 g of the silica (3.2) and 1 g of a natural fluorapatite (Moroccan phosphates).

Before using an apparatus so treated for a determination, ensure, by means of two blank distillations in succession, that the assembly is in good condition. The quantity of fluorine found shall not be greater than that from a normal blank test, using an apparatus known to be in good condition.

4.2 Spectrophotometer, or

4.3 Photoelectric absorptiometer, fitted with filters allowing a maximum transmission at about 600 nm.

5 PROCEDURE

5.1 Test portion

Weigh, to the nearest 1 %, a mass of the test sample containing not more than 1 mg of F.

In the case of phosphoric acid, the mass of the test portion shall not exceed 50 g.

NOTE – If the concentration of fluorine (F) in the product is greater than 1 g/kg, prepare, from a suitable test portion, an appropriate dilution and take an aliquot portion containing not more than 1 mg of F.

5.2 Blank test

Carry out a blank test at the same time as the determination, under the same conditions, using the same quantities of all the reagents used for the determination and taking the same aliquot portion for colour development.

5.3 Fluorine distillation

Place 40 ml of water and 10 ml of the sodium hydroxide solution (3.5) in a 500 ml one-mark volumetric flask, for collecting the distillate.

Place the test portion (5.1) in the distillation flask (4.1.2.1). Add about 0,75 g of the silica (3.2) and either 30 ml of the phosphoric acid solution (3.1) in the case of a phosphate or, if the product to be analysed is phosphoric acid, a volume of the phosphoric acid (3.1) such that the total quantity of phosphoric acid present is equal to 45 g of orthophosphoric acid (H_3PO_4).

Using about 5 ml of water, rinse down the innner walls of the distillation flask (4.1.2.1). Place a few millimetres of glycerine in the thermometer pocket, put the thermometer (4.1.3) in place, assemble the apparatus (4.1) and start the water circulation in the condenser (4.1.2.3). Heat the distillation flask (4.1.2.1) and, if the apparatus described is used, the steam generation flask (4.1.1).

Do not pass steam into the distillation flask (4.1.2.1) until the temperature of the solution in the flask reaches 138 to 139 °C, at which point start the distillation. Maintain the temperature of the solution during distillation at 139 ± 3 °C.

Distil about 400 ml, collecting the distillate in the volumetric flask, dilute to the mark and mix.

NOTE – It has been shown that the presence of aluminium, which can complex the fluorine, does not interfere if the test portion contains up to 0,5 g of Al.

5.4 Preparation of the calibration graph

5.4.1 *Preparation of the standard colorimetric solutions,* for photometric measurements carried out using cells of optical path length 4 or 5 cm.

Into a series of five 50 ml one-mark volumetric flasks, place the volumes of the standard fluorine solution (3.8) indicated in the following table :

Standard fluorine solution (3.8)	Corresponding mass of fluorine
ml	µg
0*	0
5,0	5,0
10,0	10,0
15,0	15,0
20,0	20,0

* Compensation solution.

Add to each flask the quantity of water necessary to bring the volume to 20 ml and then 0,1 ml of the phenolphthalein solution (3.9). Adjust the colour of the solution to pink by addition of the sodium hydroxide solution (3.5) and then to colourless by addition of the nitric acid solution (3.4). Add 5 ml of the buffer solution (3.6.1), 10 ml of the combined colour reagent (3.6) and 10 ml of the acetone (3.3), dilute to the mark and mix.

5.4.2 *Photometric measurements*

After allowing the solutions (5.4.1) to stand for 20 min, carry out the photometric measurements with the spectrophotometer (4.2), at a wavelength of about 600 nm, or with the photoelectric absorptiometer (4.3) fitted with appropriate filters, after having adjusted the apparatus to zero absorbance against the compensation solution.

5.4.3 *Plotting the calibration graph*

Plot a graph having, for example, the masses, expressed in micrograms of F contained in 50 ml of the standard colorimetric solutions, as abscissae and the corresponding values of absorbance as ordinate.

5.5 Determination

5.5.1 *Colour development*

Place a volume of the solution obtained by the procedure specified in 5.3, containing not more than 20 µg of F and having a volume not greater than 20 ml, in a 50 ml one-mark volumetric flask. Add, if necessary, the quantity of water necessary to bring the volume to 20 ml and then 0,1 ml of the phenolphthalein solution (3.9). Adjust the colour of the solution to colourless by addition of the nitric acid solution (3.4). Add 5 ml of the buffer solution (3.6.1), 10 ml of the combined colour reagent (3.6) and 10 ml of the acetone (3.3), dilute to the mark and mix.

5.5.2 *Photometric measurement*

Carry out the photometric measurement on the test solution by the procedure specified in 5.4.2, after having adjusted the instrument to zero absorbance against the compensation solution.

6 EXPRESSION OF RESULTS

By means of the calibration graph (5.4.3), determine the masses of fluorine (F) corresponding to the values of the photometric measurements on the test solution (5.5.2) and on the blank test solution (5.2).

The fluorine (F) content, expressed as milligrams per kilogram, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times \frac{500}{V}$$

where

m_0 is the mass, in grams, of the test portion (5.1);

m_1 is the mass, in micrograms, of fluorine (F) found in the aliquot portion of the test solution taken for the colour development;

m_2 is the mass, in micrograms, of fluorine (F) found in the aliquot portion of the blank test solution taken for the colour development.

V is the volume, in millilitres, of the aliquot portion of the test and blank solutions taken for the colour development.

7 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

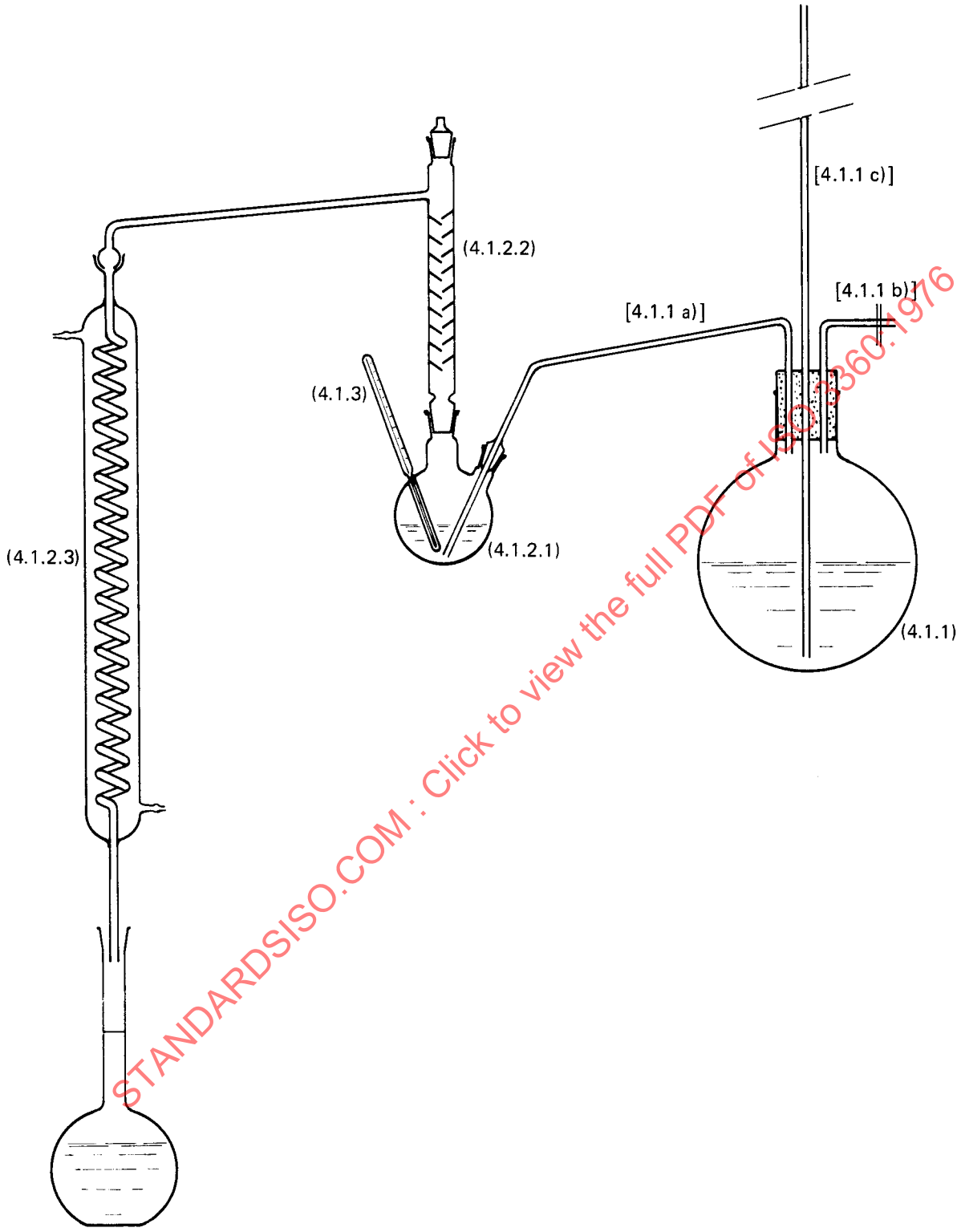

FIGURE — **Distillation apparatus (4.1)**