International Standard 779

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Pulps — Determination of iron content — 1,10-Phenanthroline photometric and flame atomic absorption spectrometric methods

Pâtes — Détermination de la teneur en fer — Méthode photométrique à la phénanthroline-1,10 et méthode par spectrométrie d'absorption atomique de flamme

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries :

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No member body expressed disapproval of the document.

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Pulps — Determination of iron content — 1,10-Phenanthroline photometric and flame atomic absorption spectrometric methods

WARNING — The methods specified in this International Standard involve the use of some hazardous chemicals and of gases that can form explosive mixtures with air. Care shall be taken to ensure that the relevant safety precautions are observed.

0 Introduction

In ISO Recommendation 779, published in 1968, a colorimetric method was prescribed for the determination of the iron content of pulp. However, in practice, such determinations are frequently made by application of a flame atomic absorption procedure, if the equipment is available. As comparative tests have proved that similar results are obtainable by both methods, this International Standard provides guidance on the use of flame atomic absorption spectrometric equipment as an alternative procedure.

1 Scope and field of application

This International Standard specifies two methods for the determination of the iron content of pulp, namely

- a 1,10-phenanthroline photometric method (method A);
- a flame atomic absorption spectrometric method (method B).

These methods are applicable to all kinds of pulp.

2 References

ISO 638, *Pulps — Determination of dry matter content.*

ISO 1762, *Pulps — Determination of ash.*

3 Method A : 1,10-Phenanthroline photometric method

3.1 Principle

Ashing of the pulp and dissolution of the ash in hydrochloric acid. Reduction of the trivalent iron with hydroxylammonium chloride. Formation of a complex between iron(II) and 1,10-phenanthroline in a buffered medium and photometric measurement of the coloured complex at a wavelength of about 510 nm.

3.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.2.1 Sodium acetate trihydrate ($NaCOOCH_3.3H_2O$), 540 g/l solution.

3.2.2 Hydroxylammonium chloride [Hydroxylamine hydrochloride] ($HONH_3Cl$) 20 g/l solution.

3.2.3 1,10-phenanthroline hydrochloride monohydrate ($C_{12}H_8N_2.HCl.H_2O$), 10 g/l solution.

This reagent may be replaced by the corresponding quantity of 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$).

Store the solution away from light. Use only colourless solutions.

3.2.4 Hydrochloric acid, about 6 mol/l solution.

3.2.5 Iron, standard solution, corresponding to 0,1 g of Fe per litre.

Dissolve 0,100 g of pure iron wire in the smallest possible quantity of hydrochloric acid, ϱ 1,19 g/ml, in a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 0,1 mg of Fe.

3.2.6 Iron, standard solution corresponding to 0,01 g of Fe per litre.

Transfer 100 ml of the standard iron solution (3.2.5) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,01 mg of Fe.

This solution is not stable.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Spectrophotometer, or

3.3.2 Photoelectric absorptiometer, fitted with filters giving a maximum transmission between 500 and 520 nm and cells provided with lids.

3.3.3 pH meter.

3.4 Preparation of the sample

Tear the air-dry sample into pieces of a suitable size. Do not use cut or punched edges or other parts where metallic contamination may have occurred.

3.5 Procedure

3.5.1 Number of determinations and determination of dry matter content

The determination shall be carried out in duplicate.

Simultaneously with the determination, two 10 g test portions shall be taken to determine the dry matter content in accordance with ISO 638.

3.5.2 Test portion

Weigh, to the nearest 0,01 g, about 10 g of the sample.

NOTE — If the iron content of the sample is known to exceed 20 mg/kg, take a test portion of 5 g.

3.5.3 Ashing of the test portion

Carefully clean a dish of fused silica or platinum. Remove any spots in the platinum dish by rubbing with fine sand.

To check that the dish is free from iron, heat in the dish about 2 ml of the hydrochloric acid solution (3.2.4), diluted with about 10 ml of water. Allow to cool, and add 1 ml of the hydroxylamine hydrochloride solution (3.2.2), 1 ml of the 1,10-phenanthroline hydrochloride solution (3.2.3) and 10 ml of the sodium acetate solution (3.2.1). No red colour shall appear.

Ash the test portion in the dish as specified in ISO 1762.

3.5.4 Blank test

Carry out a blank test at the same time as the determination following the same procedure and using the same amounts of all reagents as used for the determination, but omitting the test portion.

3.5.5 Preparation of the calibration graph

3.5.5.1 Preparation of the standard colorimetric solutions for photometric measurements carried out in cells of 1 cm optical path length

Into each of a series of five 50 ml one-mark volumetric flasks, transfer respectively the volumes of the standard iron solution (3.2.6) shown in table 1.

Table 1

Standard iron solution (3.2.6)	Corresponding mass of Fe
ml	mg
0 *	0
5,0	0,05
10,0	0,10
15,0	0,15
20,0	0,20

* Compensation solution.

3.5.5.2 Colour development

Add to each flask 10 ml of the hydrochloric acid solution (3.2.4), 1 ml of the hydroxylammonium chloride solution (3.2.2), 1 ml of the 1,10-phenanthroline hydrochloride solution (3.2.3), 15 ml of the sodium acetate solution (3.2.1). Dilute to the mark, mix and allow to stand for 15 min.

3.5.5.3 Photometric measurements

Carry out the photometric measurements with the spectrophotometer (3.3.1) at a wavelength of about 510 nm or with the photoelectric absorptiometer (3.3.2) with suitable filters, after having adjusted the instrument to zero absorbance against a compensation solution, prepared as given in 3.5.5.1, 3.5.5.2 omitting the standard iron solution (3.2.6).

NOTE — Avoid exposure of the coloured solution to direct sunlight.

3.5.5.4 Plotting of the calibration graph

Plot a graph having, for example, the masses, in milligrams, of iron (contained in 50 ml of standard colorimetric solution) as abscissae and the corresponding values of absorbance as ordinates.

3.5.6 Determination

3.5.6.1 Dissolution of the ash and preparation of the test solution

To the ash (3.5.3), add 5 ml of the hydrochloric acid solution (3.2.4) and evaporate to dryness on a steam bath. Repeat this once and then treat the residue with another 5 ml portion of the hydrochloric acid and heat for 5 min on the steam bath.

With the aid of water, transfer the contents of the dish to a 50 ml one-mark volumetric flask. To ensure complete extraction, add a further 5 ml of the hydrochloric acid solution to the residue in the dish and heat on the steam bath. With the aid of water, transfer this last portion to the main quantity in the volumetric flask, dilute to the mark and mix.

3.5.6.2 Colour development

To the test solution (3.5.6.1), add, in the following order, 1 ml of the hydroxylammonium chloride solution (3.2.2), 1 ml of the

1,10-phenanthroline hydrochloride solution (3.2.3) and, to obtain a pH value of 3 to 6, 15 ml of the sodium acetate solution (3.2.1). Dilute to the mark and mix and allow to stand for 15 min. If the solution is turbid, filter through a glass filter or centrifuge.

3.5.6.3 Photometric measurement

Carry out the photometric measurement on the test solution after colour development, following the procedure specified in 3.5.5.3, after having adjusted the instrument to zero absorbance against the blank test solution (3.5.4).

3.5.7 Expression of results

The iron content, expressed in milligrams per kilogram, is given by the formula

$$1\,000 \times \frac{m_1}{m_0}$$

where

m_1 is the amount of iron, in milligrams, of the test solution, obtained from the calibration graph (3.5.5.4);

m_0 is the mass, in grams, of the test portion, calculated on an oven-dry basis in accordance with ISO 638.

Report the result as the mean of the two determinations to the first decimal place.

4 Method B : Flame atomic absorption spectrometric method

4.1 Principle

Ashing of the pulp and dissolution of the ash in hydrochloric acid. Aspiration of the test solution into an acetylene-air flame. Measurement of the absorption of the 248,3 nm line emitted by an iron hollow-cathode lamp.

4.2 Reagents

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

4.2.1 Hydrochloric acid, about 6 mol/l solution.

4.2.2 Iron, 0,01 g/l standard solution as specified in 3.2.6.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Atomic absorption spectrometer, fitted with an acetylene and air burner.

4.3.2 Iron hollow-cathode lamp.

4.4 Preparation of the sample

See 3.4.

4.5 Procedure

4.5.1 Number of determinations and determination of dry matter content

See 3.5.1.

4.5.2 Test portion

See 3.5.2.

4.5.3 Ashing of the test portion

See 3.5.3.

4.5.4 Blank test

See 3.5.4.

4.5.5 Preparation of the calibration graph

4.5.5.1 Preparation of the standard matching solutions

Into each of a series of five 50 ml one-mark volumetric flasks, place 10 ml of the hydrochloric acid solution (4.2.1) and then, respectively, the volumes of the standard iron solution (4.2.2) shown in table 2. Dilute to the mark and mix.

Table 2

Standard iron solution (4.2.2)	Corresponding mass of Fe
ml	mg
0 *	0
5,0	0,05
10,0	0,10
15,0	0,15
20,0	0,20

* Blank test on reagents for calibration graph.

4.5.5.2 Adjustment of the apparatus

Fit the hollow-cathode iron lamp (4.3.2) in the apparatus (4.3.1), switch on the current and allow to stabilize. Adjust the current, the sensitivity and the aperture of the slit according to the characteristics of the apparatus. Adjust the wavelength in the region of 248,3 nm to maximum absorbance. Adjust the pressure of the acetylene and of the air according to the characteristics of the burner. Adjust the aspiration rate to between 2 and 4 ml/min.

4.5.5.3 Spectrometric measurements

Aspirate the series of standard matching solutions (4.5.5.1) in succession into the flame and measure the absorbance for each. Take care to keep the aspiration rate constant throughout the preparation of the calibration graph. Spray water through the burner after each measurement.

4.5.5.4 Plotting the graph

Plot a graph having, for example, the masses, in milligrams (contained in 50 ml of the standard matching solutions) as abscissae and the corresponding values for the measured absorbance, reduced by the value of the absorbance measured in the blank test on the reagents for the calibration graph (table 2, term 0), as ordinates.

4.5.6 Determination

4.5.6.1 Dissolution of the ash and preparation of the test solution

See 3.5.6.1.

If the solution contains suspended matter, allow this to settle. Use the clear solution for the spectrometric measurements.

4.5.6.2 Spectrometric measurement

Carry out the spectrometric measurements on the test solution as specified in 4.5.5.3, after having adjusted the instrument to zero absorbance against the blank test solution (4.5.4).

4.5.7 Expression of results

The iron content, expressed in milligrams per kilogram, is given by the formula

$$1\,000 \times \frac{m_2}{m_0}$$

where

m_2 is the amount of iron, in milligrams, of the test solution, obtained from the calibration graph (4.5.5.4);

m_0 is the mass, in grams, of the test portion (4.5.2), calculated on an oven-dry basis in accordance with ISO 638.

Report the result as the mean of the two determinations to the first decimal place.

5 Test report

The test report shall include the following particulars :

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

b) reference to this International Standard and the method used (A or B);

c) the number of determinations, where this is greater than 2;

d) any variation of standard procedure, if applied;

e) the results, expressed as a numerical value only;

f) any unusual features observed during the course of the test;

g) any operation not specified in this International Standard or in the International Standards to which reference is made, or regarded as optional, which might have affected the results.