International Standard 1830

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Pulps — Determination of manganese content — Sodium periodate photometric and flame atomic absorption spectrometric methods

Pâtes — Détermination de la teneur en manganèse — Méthode photométrique au périodate de sodium 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.

International Standard ISO 1830 was developed by Technical Committee ISO/TC 6, *Paper, board and pulps*, and was circulated to the member bodies in March 1981.

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 manganese content — Sodium periodate 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 R 1830, published in 1970, a colorimetric method was prescribed for the determination of the manganese 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 manganese content of pulp, namely

- a sodium periodate photometric method (method A);
- a flame atomic absorption spectrometric method (method B).

These two 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 : Sodium periodate photometric method

3.1 Principle

Ashing of the pulp and dissolution of the ash in hydrochloric acid. Oxidation of manganese(II) to manganese(VII) by means of sodium periodate in the presence of phosphoric acid. Photometric measurement at a wavelength of about 525 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 sulfite (Na_2SO_3), 50 g/l solution.

3.2.2 Hydrochloric acid, about 6 mol/l solution.

3.2.3 Sodium periodate-phosphoric acid, solution, containing 50 g of sodium periodate ($NaIO_4$) and 200 ml of phosphoric acid (H_3PO_4), ϱ 1,70 g/ml, per litre.

3.2.4 Manganese, standard solution corresponding to 0,1 g of Mn per litre.

Weigh 0,274 9 g of manganese sulphate ($MnSO_4$), dried at 300 °C, and transfer to a 1 000 ml one-mark volumetric flask. Dissolve in water, dilute to the mark and mix.

1 ml of this solution contains 0,1 mg of Mn.

3.2.5 Manganese, standard solution corresponding to 0,01 g of Mn per litre.

Transfer 100 ml of the standard manganese solution (3.2.4) 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 Mn.

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 515 and 535 nm and cells provided with lids.

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 manganese content of the sample is known to exceed 5 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.

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 25 ml one-mark volumetric flasks, transfer respectively the volumes of the standard manganese solution (3.2.5) shown in table 1.

Table 1

Standard manganese solution (3.2.5)	Corresponding mass of Mn
ml	mg
0 *	0
1,0	0,01
2,0	0,02
5,0	0,05
10,0	0,10

* Compensation solution.

3.5.5.2 Colour development

Without any further dilution, heat the solutions by placing the flasks in a steam bath and add 1 ml of the sodium periodate-phosphoric acid solution (3.2.3) to each flask. Leave the flasks in the steam bath for a further 5 min. Dilute to the mark and mix. Allow to cool to 20 ± 2 °C and adjust the volumes. The temperatures of the solutions in the flasks shall not differ by more than ± 3 °C.

3.5.5.3 Photometric measurements

Carry out the photometric measurements with the spectrophotometer (3.3.1) at a wavelength of about 525 nm or with the photoelectric absorptiometer (3.3.2) with suitable filters after having adjusted the instrument to zero absorbance against the compensating solution, prepared as described in 3.5.5.2, omitting the standard manganese solution (3.2.5).

3.5.5.4 Plotting of the calibration graph

Plot a graph having, for example, the masses, in milligrams, of manganese (contained in 25 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 3 drops of the sodium sulfite solution (3.2.1) and dissolve in a maximum of 5 ml of the hydrochloric acid solution (3.2.2). Place the dish on a steam bath and evaporate to dryness. Add a few drops of the hydrochloric acid and transfer the contents of the dish to a 25 ml one-mark volumetric flask with water.

3.5.6.2 Colour development

Heat the contents by placing in a steam bath. Add 1 ml of the sodium periodate-phosphoric acid solution (3.2.3). Leave the flasks in the steam bath for a further 5 min. Dilute to the mark and mix. Allow to cool to 20 ± 2 °C and adjust the volume. The temperature of the solution shall not differ from that of the standard colorimetric solutions by more than ± 3 °C. If the solution is turbid, the turbidity can be removed by centrifuging. Do not filter the solution.

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 manganese 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 manganese, 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 (3.5.2), 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.

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-dinitrogen monoxide or air-acetylene flame. Measurement of the absorption of the 279,5 nm line emitted by a manganese hollow-cathode lamp.

4.2 Reagents

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

4.2.1 Hydrochloric acid, about 6 mol/l solution.

4.2.2 Manganese, standard solution corresponding to 0,1 g of Mn per litre.

Weigh 0,274 9 g of manganese sulphate ($MnSO_4$), dried at 300 °C, and transfer to a 1 000 ml one-mark volumetric flask. Dissolve in water, dilute to the mark and mix.

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

4.2.3 Manganese, standard solution corresponding to 0,01 g of Mn per litre.

Transfer 100 ml of the standard manganese solution (4.2.2) 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 Mn.

This solution is not stable.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Atomic absorption spectrometer, fitted with either an acetylene and dinitrogen monoxide or an acetylene and air burner.

4.3.2 Manganese 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 5 ml of the hydrochloric acid solution (4.2.1) and then respectively, the volumes of the standard manganese solution (4.2.3) shown in table 2. Dilute to the mark and mix.

Table 2

Standard manganese solution (4.2.3)	Corresponding mass of Mn
ml	mg
0 *	0
1,0	0,01
2,0	0,02
5,0	0,05
10,0	0,10

* Blank test on reagents for calibration graph.

4.5.5.2 Adjustment of the apparatus

Fit the manganese hollow-cathode 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 279,5 nm to maximum absorbance. Adjust the pressure of the acetylene, the air, and the dinitrogen monoxide, according to the characteristics of the burner. To avoid explosion, it is necessary to light the burner with air-acetylene, before switching to acetylene-dinitrogen monoxide.

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, of Mn^{2+} (contained in 50 ml of the standard matching solutions) as abscissae, and the corresponding values of 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

To the ash (4.5.3), add 5 ml of the hydrochloric acid solution (4.2.1), 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 solution 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.

If the solution contains suspended matter, allow this to settle.

4.5.6.2 Spectrometric measurement

Carry out the spectrometric measurement 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 manganese 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 manganese, 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 to the International Standards to which reference is made, or regarded as optional, which might have affected the results.