International Standard 777

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Pulps — Determination of calcium content — edta Titrimetric and flame atomic absorption spectrometric methods

Pâtes — Détermination de la teneur en calcium — Méthode titrimétrique à l'edta et méthode par spectrométrie d'absorption atomique de flamme

First edition — 1982-08-01

UDC 676.1 : 543.24 : 546.41 **Ref. No. ISO 777-1982 (E)**

Descriptors : pulps, tests, determination of content, calcium, volumetric analysis, atomic absorption spectroscopic analysis.

Price based on 5 pages

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 777 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.

This International Standard cancels and replaces ISO Recommendation R 777-1968, of which it constitutes a technical revision.

Printed in Switzerland

Pulps — Determination of calcium content — edta Titrimetric 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 777, published in 1968, a titrimetric method was prescribed for the determination of the calcium 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 calcium content of pulp, namely

— an edta titrimetric 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 : edta Titrimetric method

3.1 Principle

Ashing of the pulp and dissolution of the ash in hydrochloric acid. Titration of the test solution with a standard volumetric Na_2H_2edta solution at a pH in excess of 12, in the presence of a suitable indicator, interfering ions being masked by triethanolamine.

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 Hydrochloric acid, about 6 mol/l solution.

3.2.2 Hydrochloric acid, about 1 mol/l solution.

3.2.3 Potassium hydroxide, about 8 mol/l solution.

Store the solution in a polyethylene bottle.

3.2.4 2,2′,2″-Nitrilotriethanol [Triethanolamine] [$N(CH_2CH_2OH)_3$], 100 g/l solution.

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

3.2.6 Calcium, 0,01 mol/l standard reference solution.

Weigh 1,00 ± 0,01 g of calcium carbonate ($CaCO_3$), dried at a temperature not exceeding 200 °C, into a 500 ml beaker. Add 100 ml of water and from a burette add, drop by drop, the least amount (about 20 ml) of the hydrochloric acid solution (3.2.2) necessary to dissolve the calcium carbonate. Boil in order to expel the carbon dioxide, cool and, by rinsing with water, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

Store the solution in a polyethylene bottle.

3.2.7 Disodiumdihydrogen [ethylene-dinitrilo] tetraacetate (Na_2H_2edta), 0,01 mol/l standard volumetric solution.

3.2.7.1 Preparation of the edta solution

Dissolve 3,80 g of the Na_2H_2edta in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Store the solution in a polyethylene bottle.

3.2.7.2 Standardization of the solution

Place in a conical flask 20,0 ml of the standard reference calcium solution (3.2.6), 40 ml of water, 5 ml of potassium hydroxide solution (3.2.3), 2 ml of the hydroxylammonium chloride solution (3.2.5) and about 100 mg of the indicator (3.2.8). Titrate with the edta solution (3.2.7.1) until a colour change from wine-red to pure blue occurs.

3.2.7.3 Blank test

Carry out a blank test simultaneously with the standardization, using the same procedure and the same quantities of all the reagents used for the standardization, but replacing the standard reference calcium solution with an equal volume of water.

3.2.7.4 Calculation of the concentration

The equivalent concentration, expressed in moles per litre, of the edta solution is given by the formula

$$c_1 = \frac{0{,}01\ V_1}{V_2 - V_3}$$

where

V_1 is the volume, in millilitres, of the standard reference calcium solution (3.2.6) used for the standardization (3.2.7.2);

V_2 is the volume, in millilitres, of the edta solution (3.2.7.1) used for the standardization (3.2.7.2);

V_3 is the volume, in millilitres, of the edta solution (3.2.7.1) used for the blank test (3.2.7.3).

NOTE — If the concentration of the standard reference solution used is not exactly as specified in the list of reagents, an appropriate correction should be made.

3.2.8 Indicator.

Grind 100 mg of 3-hydroxy-4-[(2-hydroxy-4-sulfo-1-naphthyl) azo]-2-naphthoic acid (commercially available, for example, under the name of cal-red) in a mortar with 10 g of sodium sulfate (Na_2SO_4) to form a homogeneous mixture.

Store in a dark bottle.

NOTE — When the sample contains more than 0,03 mg of copper, the indicator is blocked. In this case, use calcein as the indicator, or mask the copper present by the addition of 5 ml of a 1 g/l solution of potassium cyanide.

3.3 Apparatus

Ordinary laboratory apparatus.

3.4 Preparation of the sample

Tear the air-dry sample into pieces of suitable size.

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 test sample.

NOTE — If method A (edta titrimetric method) is applied to pulps having a calcium content greater than 500 mg/kg, weigh a test portion corresponding to a maximum of 5 mg of calcium, or replace the edta solution specified in 3.2.7 by a 0,05 mol/l standard volumetric edta solution.

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 as specified in ISO 1762.

3.5.4 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, but omitting the test portion.

3.5.5 Determination

Rinse the inside wall of the dish, and add about 10 ml of water to the ash residue (3.5.3). Then add 3 ml of hydrochloric acid solution (3.2.1). Heat the dish on a steam bath for 5 to 10 min. If a brown precipitate of manganese dioxide is formed, filter the contents of the dish through a filter paper into a 300 ml conical flask, and wash with water. If no insoluble residue is visible, or if the residue is colourless, filtration is unnecessary. In this case, rinse the contents of the dish directly with water into a 300 ml conical flask, and adjust the volume to between 50 and 100 ml.

Add 5 ml of the potassium hydroxide solution (3.2.3) and after 5 min, with occasional shaking of the conical flask, add 5 ml of the triethanolamine solution (3.2.4), 2 ml of the hydroxylammonium chloride solution (3.2.5) and about 100 mg of the indicator (3.2.8). Titrate with the edta solution (3.2.7) until a colour change from wine-red to pure blue occurs.

When new reagents are being taken into use, check that they do not contain any calcium by titrating a blank solution containing all of the reagents, and with the sample solution replaced by an equal volume of water.

3.6 Expression of results

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

$$\frac{(V_4 - V_5) \times c_1 \times 40{,}08 \times 10^3}{m_0}$$

where

V_4 is the volume, in millilitres, of the edta standard volumetric solution (3.2.7), used in the determination (3.5.5);

V_5 is the volume, in millilitres, of the edta standard volumetric solution (3.2.7), used in the blank test (3.5.4);

c_1 is the concentration, in moles per litre, of the edta standard volumetric solution (3.2.7), calculated in accordance with 3.2.7.4;

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 calcium content as the mean of the results of the two determinations, as specified in table 1.

Table 1

Mean of results	Nearest unit of report
mg/kg	mg/kg
$\leqslant 100$	1
100 to 500	5
$\geqslant 500$	10

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 acetylene-air flame, after addition of lanthanum ions, to suppress certain interferences. Measurement of the absorption of the 422,7 nm line emitted by a calcium hollow-cathode lamp.

4.2 Reagents

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

4.2.1 Hydrochloric acid, about 6 mol/l solution.

4.2.2 Lanthanum, about 50 g/l solution.

Moisten 59 g of lanthanum oxide (La_2O_3) with water. Slowly and cautiously, add 250 ml of hydrochloric acid, ϱ 1,19 g/ml, to dissolve the lanthanum oxide. Dilute to the mark in a 1 000 ml one-mark volumetric flask and mix.

4.2.3 Calcium, standard solution corresponding to 500 mg of Ca per litre.

Weigh 1,249 ± 0,001 g of calcium carbonate, dried to a temperature not exceeding 200 °C, into a 1 000 ml one-mark volumetric flask. Add 50 ml of water. Add a minimum volume of hydrochloric acid (approximately 10 ml), drop by drop, to effect the complete dissolution of the calcium carbonate. Dilute to the mark and mix.

1 ml of this standard solution contains 0,500 mg of Ca.

4.2.4 Calcium, standard solution corresponding to 50 mg of Ca per litre.

Transfer 100 ml of the standard calcium solution (4.2.3) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,050 mg of Ca.

4.3 Apparatus

Ordinary laboratory apparatus and

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

4.3.2 Calcium 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

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

4.5.3 Ashing of the test portion

See 3.5.3.

4.5.4 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, but omitting the test portion.

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 100 ml one-mark volumetric flasks, place 20 ml of the lanthanum solution (4.2.2) and 10 ml of the hydrochloric acid solution (4.2.1), and then, respectively, the volumes of the standard calcium solution (4.2.4) shown in table 2. Dilute to the mark and mix.

Table 2

Standard calcium solution (4.2.4)	Corresponding mass of Ca
ml	mg
0 *	0
1,0	0,05
2,0	0,10
5,0	0,25
10,0	0,50

* Blank test on reagents for calibration graph.

4.5.5.2 Adjustment of the apparatus

Fit the hollow-cathode calcium 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 422,7 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 Ca^{2+} (contained in 100 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 basic 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 treat the residue with another portion of 5 ml 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 100 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.

4.5.6.2 Choice of dilution ratio

If the approximate content of calcium is known, choose a volume of 1,0 ml, 2,0 ml or 5,0 ml of the basic test solution for dilution so that the calcium concentration of the test solution, prepared as described in 4.5.6.3 falls within the range specified in table 2.

If the approximate content of calcium is not known, measure with a pipette a volume of 2,0 ml of the basic test solution into a 50 ml one-mark volumetric flask and test as specified in 4.5.6.3. If the calcium concentration so obtained does not fall within the range specified in table 2, carry out the test by choice of the correct volume according to the value of the calcium concentration so derived.

4.5.6.3 Spectrometric measurement

With a pipette, measure the chosen volume of the basic test solution (4.5.6.1) into a 50 ml one-mark volumetric flask. Add 10 ml of the lanthanum solution (4.2.2), 5 ml of the hydrochloric acid solution (4.2.1), and dilute to the mark with water. If the solution contains suspended matter, allow this to settle. Use the clear solution and carry out the spectrometric measurement 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 calcium content, expressed in milligrams per kilogram, is given by the formula

$$50\,000 \times \frac{m_1}{V_6 \times m_0}$$

where

m_1 is the amount of calcium, in milligrams, of the test solution, obtained from the calibration graph (4.5.5.4);

V_6 is the volume, in millilitres, of the basic test solution (4.5.6.1) taken for the determination;

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 calcium content as the mean of the results of the two determinations, as specified in table 3.

Table 3

Mean of results	Nearest unit of report
mg/kg	mg/kg
$\leqslant 100$	1
100 to 500	5
$\geqslant 500$	10