International Standard 778

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Pulps — Determination of copper content — Extraction-photometric and flame atomic absorption spectrometric methods

Pâtes — Détermination de la teneur en cuivre — Méthode par extraction et photométrie 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 778 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:

Australia	Hungary	Romania
Austria	India	South Africa, Rep. of
Belgium	Iran	Spain
Brazil	Italy	Sweden
Canada	Kenya	Switzerland
China	Korea, Dem. P. Rep. of	Turkey
Czechoslovakia	Korea, Rep. of	United Kingdom
Egypt, Arab Rep. of	Netherlands	USA
Finland	New Zealand	USSR
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Germany, F. R.	Poland	

No member body expressed disapproval of the document.

This International Standard cancels and replaces ISO Recommendation R 778-1968, of which it constitutes a technical revision.

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Pulps — Determination of copper content — Extraction-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 take to ensure that the relevant safety precautions are observed.

0 Introduction

In ISO Recommendation R 778, published in 1968, a colorimetric method was prescribed for the determination of the copper 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 copper content of pulp, namely

— an extraction-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 : Extraction-photometric method

3.1 Principle

Ashing of the pulp and dissolution of the ash in hydrochloric acid. Extraction of the copper with sodium diethyldithiocarbamate in carbon tetrachloride, followed by photometric measurement at 435 nm, interfering ions being masked by Na_2H_2edta.

3.2 Reagents

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

NOTE — The copper content of the distilled water must be below 0,01 mg/kg. If the absorbance of the blank test solution (3.5.4) compared with that of the carbon tetrachloride (3.2.1) exceeds 0,05, the quality of the water or of one or more of the reagents may be suspect.

3.2.1 Carbon tetrachloride (CCl_4).

3.2.2 Ammonia, concentrated solution, ϱ 0,91 g/ml.

3.2.3 *Di*sodiumdihydrogen [ethylene-dinitrilo] tetraacetate (Na_2H_2edta), 50 g/l solution.

Dissolve 50 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.

3.2.4 Sodium diethyldithiocarbamate trihydrate, about 1 g/l solution.

Dissolve 0,1 g of sodium diethyldithiocarbamate $[(C_2H_5)_2N.CSSNa.3H_2O]$ in 100 ml of water. Filter off any insoluble matter present.

Store the solution in a dark bottle. This solution can be kept unchanged for about 1 week.

3.2.5 Hydrochloric acid, about 6 mol/l solution.

3.2.6 Copper, standard solution corresponding to 0,1 g of Cu per litre.

Dissolve 0,100 g of pure electrolytic copper metal in the smallest quantity possible of nitric acid, ϱ 1,4 g/ml. Boil in order to expel nitrous fumes, allow to cool. 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 0,1 mg of Cu.

3.2.7 Copper, standard solution corresponding to 0,01 g of Cu per litre.

Transfer 100 ml of the standard copper solution (3.2.6) 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 Cu.

This solution is not stable.

3.2.8 Phenolphthalein indicator solution.

Dissolve 50 mg of phenolphthalein ($C_{20}H_{14}O_4$) in 50 ml of ethanol (C_2H_5OH) and dilute with 50 ml of water.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Spectrophotometer, or

3.3.2 Photoelectric absorptiometer, fitted with filters giving a maximum transmission at a wavelength of about 435 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 test sample.

NOTE — If the copper content of the sample is known to exceed 10 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.

Burners of brass or other material containing copper shall not be used.

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

Into a series of five 250 ml separating funnels, place 10 ml of the hydrochloric acid solution (3.2.5), 10 ml of the edta solution (3.2.3), 5 drops of the phenolphthalein ethanolic solution (3.2.8) and the volumes of the standard copper solution (3.2.7) shown in table 1.

Table 1

Standard copper solution (3.2.7)	Corresponding mass of Cu
ml	mg
0 *	0
2,0	0,02
5,0	0,05
7,0	0,07
10,0	0,10

* Compensation solution.

Neutralize the solution in each separating funnel with the ammonia solution (3.2.2) to a faint pink colour and allow to cool to ambient temperature. Add 5 ml of the sodium diethyldithiocarbamate solution (3.2.4) and, with a pipette, 20,0 ml of the carbon tetrachloride (3.2.1). Shake the funnels vigorously for at least 3 min and then leave the phases to separate. Filter into a cell (3.3.2) the carbon tetrachloride (lower) phase through a cotton plug, inserted in the outlet of the separating funnel, discarding the first 5 ml. Place the lid on the cell and immediately carry out the photometric measurements.

3.5.5.2 Photometric measurements

Carry out the measurement of the absorbance using either the spectrophotometer (3.3.1) at the wavelength of maximum absorption (about 435 nm) or the photoelectric absorptiometer (3.3.2), fitted with suitable filters, after having adjusted the instrument, in each case, to zero absorbance with reference to the compensation solution, prepared as given in 3.5.5.1, omitting the standard copper solution (3.2.7).

NOTE — Avoid exposure of the coloured carbon tetrachloride solutions to direct sunlight.

3.5.5.3 Plotting the calibration graph

Plot a graph having, for example, the masses of copper, in milligrams (contained in each 20 ml of the CCl_4 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

To the ash (3.5.3), add 5 ml of the hydrochloric acid solution (3.2.5) 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 separating funnel. 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 separating funnel.

3.5.6.2 Extraction

Add to the solution in the separating funnel 10 ml of the edta solution (3.2.3) and 5 drops of the phenolphthalein ethanolic solution (3.2.8). Neutralize the solution by adding the ammonia solution (3.2.2) till a faint pink colour persists and allow to cool to ambient temperature. Add 5 ml of the sodium diethyldithiocarbamate solution (3.2.4) and, using a bulb or safety pipette, 20,0 ml of the carbon tetrachloride (3.2.1). Shake the funnel vigorously for at least 3 min and allow the phases to separate. Filter into a cell (3.3.2) the carbon tetrachloride (lower phase) through a cotton plug inserted in the outlet of the separating funnel, discarding the first 5 ml.

3.5.6.3 Photometric measurement

Place the lid to the cell and immediately carry out the photometric measurement on the test solution as specified in 3.5.5.2, after having adjusted the instrument to zero absorbance against the blank test solution (3.5.4).

NOTE — Avoid exposure of the coloured carbon tetrachloride solutions to direct sunlight.

3.5.7 Expression of results

The copper 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 copper, in milligrams, of the test solution obtained from the calibration graph (3.5.5.3);

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 acetylene-air flame. Measurement of the absorption of the 324,7 nm line emitted by a copper 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.

NOTE — The copper content of the distilled water must be below 0,01 mg/kg.

4.2.1 Hydrochloric acid, about 6 mol/l solution.

4.2.2 Copper, 0,1 g/l standard solution as specified in 3.2.6.

4.2.3 Copper, 0,01 g/l standard solution as specified in 3.2.7.

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 Copper 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 100 ml one-mark volumetric flasks, place 5 ml of the hydrochloric acid solution (4.2.1) and the volumes of the standard copper solution (4.2.3) shown in table 2. Dilute to the mark and mix.

Table 2

Standard copper solution (4.2.3)	Corresponding mass of Cu
ml	mg
0 *	0
2,0	0,02
5,0	0,05
7,0	0,07
10,0	0,10

* Blank test on reagents for calibration graph.

4.5.5.2 Adjustment of the apparatus

Fit the hollow-cathode copper 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 324,7 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 copper (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 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 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.

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

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 copper 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 copper, 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.