

# International Standard



# 5934

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## Crude sodium borates for industrial use — Determination of alkali-soluble copper and manganese contents — Zinc bis(dibenzylidithiocarbamate) and formaldehyde oxime photometric methods

*Borates de sodium bruts à usage industriel — Dosage du cuivre et du manganèse solubles en milieu alcalin — Méthodes photométriques au bis(dibenzylidithiocarbamate) de zinc et à la formaldéhyde oxime*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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 5934 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in October 1978.

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

Australia	Germany, F. R.	Romania
Austria	Hungary	South Africa, Rep. of
Belgium	India	Switzerland
Brazil	Israel	Thailand
Bulgaria	Italy	United Kingdom
China	Korea, Rep. of	USSR
Czechoslovakia	Mexico	Yugoslavia
Egypt, Arab Rep. of	Philippines	
France	Poland	

The member body of the following country expressed disapproval of the document on technical grounds :

Netherlands

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

# Crude sodium borates for industrial use — Determination of alkali-soluble copper and manganese contents — Zinc bis(dibenzylthiocarbamate) and formaldehyde oxime photometric methods

## 1 Scope and field of application

This International Standard specifies zinc bis(dibenzylthiocarbamate) and formaldehyde oxime photometric methods for the successive determinations of the alkali-soluble copper and manganese contents in crude sodium borates for industrial use.

The methods are applicable to products in which the alkali-soluble copper and manganese contents exceed 0,25 and 0,5 mg/kg respectively.

## 2 Reference

ISO 2217, *Crude sodium borates for industrial use — Determination of matter insoluble in alkaline medium and preparation of test solutions.*

## 3 Principle

### 3.1 Determination of copper content

Formation of a coloured complex by reaction of zinc bis(dibenzylthiocarbamate) with the copper contained in an aliquot portion of solution A (see ISO 2217).

Extraction of this complex with carbon tetrachloride and photometric measurement of the coloured complex in the organic phase at a wavelength of about 435 nm.

Retention of the aqueous phase for the determination of manganese.

### 3.2 Determination of manganese content

Addition of potassium sodium tartrate, to assist in the subsequent separation of manganese, to the aqueous solution from the copper determination and then of sodium diethyldithiocarbamate, at pH 6 to 7, to form manganese bis(diethyldithiocarbamate) (and to react similarly with other metals).

Extraction of these complexes with carbon tetrachloride followed by evaporation of the organic phase, in the presence of hydrochloric acid, to destroy the diethyldithiocarbamates.

Addition of ascorbic acid to suppress interference by iron.

Addition of formaldehyde oxime in alkaline medium, to form the manganese-formaldehyde oxime coloured complex and photometric measurement at a wavelength of about 450 nm.

## 4 Reagents

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

### 4.1 Carbon tetrachloride.

**WARNING — Carbon tetrachloride is toxic. Avoid breathing the vapour and contact with eyes. Carry out all operations involving its use in a fume cupboard, away from intense heat.**

4.2 Hydrochloric acid, approximately 73 g/l solution.

4.3 Sodium hydroxide, approximately 80 g/l solution.

4.4 Ascorbic acid, 200 g/l solution, freshly prepared.

4.5 Potassium sodium tartrate, 200 g/l solution.

Discard the solution if it becomes cloudy.

4.6 Zinc bis(dibenzylthiocarbamate), 0,5 g/l solution in the carbon tetrachloride (4.1).

Discard the solution if it becomes cloudy.

4.7 Sodium diethyldithiocarbamate, 20 g/l solution.

Discard this solution after 1 week.

4.8 Formaldehyde oxime, approximately 5 mol/l solution.

Dissolve 350 g of hydroxylammonium chloride in about 500 ml of water, add 375 ml of 40 % (V/V) formaldehyde solution and dilute to 1 000 ml.

Discard the solution if it becomes cloudy.

**4.9 Copper**, standard solution corresponding to 0,100 g of copper (Cu) per litre.

Weigh to the nearest 0,000 1 g, exactly 0,1 g of electrolytic copper, add 10 ml of approximately 500 g/l nitric acid solution and stir until dissolution is complete. Transfer 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.

**4.10 Copper**, standard solution corresponding to 0,010 g of copper (Cu) per litre.

Transfer 10,0 ml of the standard copper solution (4.9) to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

1 ml of this standard solution contains 10 µg of Cu.

**4.11 Manganese**, standard solution corresponding to 0,100 g of manganese (Mn) per litre.

Transfer to a 250 ml conical flask 0,143 8 g, weighed to the nearest 0,000 1 g, of potassium permanganate. Add 100 ml of water, dissolve and add saturated sulphur dioxide solution, drop by drop, until the colour just disappears. Boil to remove excess sulphur dioxide and cool. Transfer quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

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

**4.12 Manganese**, standard solution corresponding to 0,010 g of manganese (Mn) per litre.

Transfer 10,0 ml of the standard manganese solution (4.11) to a 100 ml volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

1 ml of this standard solution contains 10 µg of Mn.

**4.13 Bromothymol blue**, 1 g/l ethanolic solution.

## 5 Apparatus

Ordinary laboratory apparatus and

**5.1 Spectrophotometer**, or

**5.2 Photoelectric absorptiometer**.

**5.3 Optical cells**.

**5.3.1 Cells**, having optical path lengths of 4 or 5 cm and of maximum capacity 7 to 8 ml, for the determination of copper.

**5.3.2 Cells**, having optical path lengths of 4 or 5 cm and of normal capacity, for the determination of manganese.

## 6 Procedure

### 6.1 Test portion

Transfer 100,0 ml of solution A (see ISO 2217) to a 250 ml separating funnel.

### 6.2 Blank tests

Carry out blank tests at the same time as the determinations, using the same procedures and the same quantities of all the reagents used in the determinations, but using 100,0 ml of solution B instead of solution A (see ISO 2217).

### 6.3 Preparation of the calibration graphs

#### 6.3.1 Preparation of standard colorimetric solutions and colour development

##### 6.3.1.1 Standard copper solutions

Into a series of five 250 ml separating funnels, each containing 20 ml of the hydrochloric acid solution (4.2), place the volumes of the standard copper solution (4.10) indicated in table 1.

Table 1

Standard copper solution (4.10)	Corresponding mass of copper
ml	µg
0,0*	0,0
0,25	2,5
0,50	5,0
0,75	7,5
1,00	10,0

\* Compensation solution.

Add 100 ml of water and, by means of a pipette, 10,0 ml of the zinc bis(dibenzylthiocarbamate) solution (4.6) to each funnel. Stopper the funnels, shake them vigorously for 1 min and allow the liquid phases to separate.

Allow the denser (organic) phase to run into a filter funnel fitted with a dry filter paper and collect the appropriate quantity of the filtrate in one of the cells (5.3.1).

##### 6.3.1.2 Standard manganese solutions

Into a series of four 25 ml one-mark volumetric flasks place the volumes of the standard manganese solution (4.12) indicated in table 2.

Table 2

Standard manganese solution (4.12)	Corresponding mass of manganese
ml	µg
0,0*	0
0,50	5,0
1,00	10,0
2,00	20,0

\* Compensation solution.

Add 10 ml of water and 2,5 ml of the ascorbic acid solution (4.4) to each flask. Then, flask by flask, add 1,0 ml of the formaldehyde oxime solution (4.8) and immediately afterwards, 5 ml of the sodium hydroxide solution (4.3). Dilute to the mark and mix.

After 5 min, transfer the solution to a filter funnel fitted with a dry filter paper and collect the appropriate quantity of the filtrate in one of the cells (5.3.2).

### 6.3.2 Photometric measurements

Using the spectrophotometer (5.1) at wavelengths of about 435 nm for copper and about 450 nm for manganese, or the photoelectric absorptiometer (5.2) fitted with suitable filters to give maximum transmissions of between 430 and 440 nm for copper and of about 450 nm for manganese, measure the absorbance of each solution after having adjusted the instrument to zero absorbance against carbon tetrachloride for copper and against water for manganese.

### 6.3.3 Plotting the graphs

Deduct the absorbance of the compensation solution from those of the corresponding standard colorimetric solutions (see 6.3.1.1 and 6.3.1.2).

Plot graphs having, for example, the masses, in micrograms, of copper or manganese in the standard colorimetric solutions as abscissae and the corresponding values of absorbance as ordinates.

## 6.4 Determination

### 6.4.1 Preparation of test solutions and colour development

#### 6.4.1.1 Copper

Add 3,0 ml of the hydrochloric acid solution (4.2) and 10,0 ml of the zinc bis(dibenzylthiocarbamate) solution (4.6) to the test portion (6.1). Stopper the funnel, shake vigorously for 1 min and allow the liquid phases to separate.

Allow the denser (organic) phase to run into a filter funnel fitted with a dry filter paper and collect the appropriate quantity of the filtrate in one of the cells (5.3.1). Retain the aqueous solution for the preparation of the manganese test solution (6.4.1.2).

#### 6.4.1.2 Manganese

Add 5 ml of the carbon tetrachloride (4.1) to the separating funnel containing the aqueous solution from which the copper has been removed (6.4.1.1). Shake the funnel vigorously for 1 min and allow the liquid phases to separate. Reject the denser (organic) phase.

Repeat this extraction and add to the aqueous solution, in the order given, shaking the separating funnel after each addition,

9,0 ml of the sodium hydroxide solution (4.3),

20 ml of the potassium sodium tartrate solution (4.5), and

5 drops of the bromothymol blue solution (4.13).

Add the sodium hydroxide solution (4.3), drop by drop, until the colour just changes from yellow to blue.

Add 10 ml of the sodium diethyldithiocarbamate solution (4.7) and 20 ml of the carbon tetrachloride (4.1). Stopper the separating funnel, shake for 5 min, allow the liquid phases to separate and allow the denser (organic) phase to run into a 250 ml beaker. Add a further 20 ml of the carbon tetrachloride (4.1), shake the funnel for 5 min and, after allowing the liquid phases to separate, transfer the denser (organic) phase to the 250 ml beaker.

Extract a third time with 10 ml of the carbon tetrachloride (4.1) and again transfer the denser (organic) phase to the 250 ml beaker.

Add 5 ml of the hydrochloric acid solution (4.2) to the combined extract and, taking suitable precautions, completely evaporate the carbon tetrachloride whilst retaining the aqueous residual solution. Cool, add 2,5 ml of the ascorbic acid solution (4.4), 1,0 ml of the formaldehyde oxime solution (4.8) and, immediately, 10,0 ml of the sodium hydroxide solution (4.3). Mix, transfer quantitatively to a 25 ml one-mark volumetric flask, dilute to the mark and mix.

After 5 min, transfer the solution to a filter funnel fitted with a dry filter paper and collect the appropriate quantity of the filtrate in one of the cells (5.3.2).

### 6.4.2 Photometric measurements

Measure the absorbances of the test solutions and the blank test solutions following the procedure specified in 6.3.2.

## 7 Expression of results

By reference to the appropriate calibration graph (6.3.3), determine the masses of copper and manganese corresponding to

the absorbances of the test solutions and the blank test solutions.

### 7.1 Copper content

The copper content, expressed in milligrams of Cu per kilogram, is given by the formula

$$\frac{m_1}{1\ 000} \times \frac{500}{100} \times \frac{1\ 000}{m_0} = \frac{5\ m_1}{m_0}$$

where

$m_0$  is the mass, in grams, of the test portion used for the preparation of solution A (see ISO 2217);

$m_1$  is the mass, in micrograms, of copper found in the test portion (6.1).

### 7.2 Manganese content

The manganese content, expressed in milligrams of Mn per kilogram, is given by the formula

$$\frac{m_2}{1\ 000} \times \frac{500}{100} \times \frac{1\ 000}{m_0} = \frac{5\ m_2}{m_0}$$

where

$m_0$  is the mass, in grams, of the test portion used for the preparation of solution A (see ISO 2217);

$m_2$  is the mass, in micrograms, of manganese found in the test portion (6.1).

## 8 Test report

The test report shall include the following particulars :

- a) an identification of the sample;
- b) the reference of the method used;
- c) the results and the method of expression used;
- d) any unusual features noted during the determination;
- e) any operation not included in this International Standard, or the International Standard to which reference is made, or regarded as optional.

## Annex

### ISO publications relating to crude sodium borates for industrial use

- ISO 1918 — Determination of sulphur compounds — Volumetric method.
- ISO 2216 — Determination of sodium oxide and boric oxide contents — Volumetric method
- ISO 2217 — Determination of matter insoluble in alkaline medium and preparation of test solutions.
- ISO 2218 — Determination of loss in mass after heating at 900 °C.
- ISO 2760 — Determination of total aluminium content — Titrimetric method.
- ISO 2761 — Determination of total titanium content — Photometric method.
- ISO 3120 — Determination of water content — Gravimetric method.
- ISO 3122 — Determination of iron content — 2,2'-Bipyridyl photometric method.
- ISO 3124 — Determination of iron soluble in alkaline medium — 2,2'-Bipyridyl photometric method.
- ISO 3125 — Determination of aluminium soluble in alkaline medium — EDTA titrimetric method.
- ISO 5933 — Determination of total nickel content of boric acid, boric oxide and *d*/sodium tetraborates and the alkali-soluble nickel content of crude sodium borates — Furl  $\alpha$ -dioxime photometric method.
- ISO 5934 — Determination of alkali soluble copper and manganese contents — Zinc bis(dibenzylidithiocarbamate) and formaldehyde oxime photometric methods.
- ISO 5935 — Determination of total silica content and content of silica soluble in alkaline medium — Photometric method.
- ISO 5936 — Determination of carbonate content — Gravimetric method.