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Boric acid, boric oxide and *Disodium* tetraborates for industrial use — Determination of manganese content — Formaldehyde oxime photometric method

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FOREWORD

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Boric acid, boric oxide and Disodium tetraborates for industrial use — Determination of manganese content — Formaldehyde oxime photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a formaldehyde oxime method for the photometric determination of the manganese content of boric acid, boric oxide and disodium tetraborates for industrial use.

2 PRINCIPLE

Removal of the boron by evaporation with methanol and separation of manganese and other metals from the residue, by extraction with chloroform, as their diethyldithiocarbamates. Wet destruction of the diethyldithiocarbamates with a sulphuric acid/hydrogen peroxide mixture. Removal of any interfering iron by extraction as the thiocyanate.

Formation of the coloured manganese formaldehyde oxime complex in alkaline solution and photometric measurement at a wavelength of approximately 450 nm.

3 REAGENTS

Distilled water or water of equivalent purity shall be used in the test.

3.1 Organic extraction solvent

Mix equal volumes of amyl alcohol (mixed isomers) and amyl acetate.

3.2 Chloroform, redistilled.

3.3 Methanol, redistilled.

3.4 Hydrochloric acid, ρ 1.19 g/ml approximately, 38 % (m/m) solution or approximately 12 N.

3.5 Ammonia solution, ρ 0.88 g/ml approximately, 35 % (m/m) solution or approximately 18 N.

3.6 Sulphuric acid, approximately 16 N solution.

3.7 Sodium hydroxide, approximately 6 N solution.

3.8 Ammonium thiocyanate, 100 g/l solution.

3.9 Formaldehyde oxime hydrochloride, 60 g/l solution.

3.10 Hydrogen peroxide, 500 g/l solution.

3.11 Hydroxylammonium chloride, 100 g/l solution.

NOTE — Solid hydroxylammonium chloride should not be allowed to come into contact with the skin. The solution shall be dispensed from a burette or safety pipette.

3.12 Potassium sodium tartrate, 100 g/l solution.

3.13 Sodium diethyldithiocarbamate, 10 g/l solution.

Dissolve 1 g of sodium diethyldithiocarbamate in 100 ml of water and filter before use.

3.14 Manganese standard solution, containing 0.10 g/l of Mn.

Measure by means of a burette 45.51 ml of exactly 0.1 N potassium permanganate solution into a 250 ml conical flask.

NOTE — If the normality of the potassium permanganate solution used is not exactly 0.1 N, use a volume of solution calculated to be equivalent to 45.51 ml of 0.1 N solution.

Add to the flask, drop by drop, a saturated solution of sulphur dioxide until the contents are clear and colourless. Boil the solution to remove excess sulphur dioxide and then cool. Transfer quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 100 μ g of manganese.

3.15 Manganese standard solution, containing 0.01 g/l of Mn.

Transfer 10.0 ml of the manganese standard solution (3.14) to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 10 μ g of manganese.

Prepare this solution just before use.

3.16 Cresol red, 0.2 g/l solution.

4 APPARATUS

Ordinary laboratory apparatus and

4.1 Spectrophotometer, with 4 cm cells, or

4.2 Photoelectric absorptiometer, with 4 cm cells.

NOTE — It is essential that the glassware used in this determination be scrupulously clean; beakers etc. shall be cleaned with boiling approximately 6 N hydrochloric acid solution and rinsed with water.

5 PROCEDURE

5.1 Test portion

Weigh, to the nearest 0.1 g, a quantity of the test sample, up to 10.0 g, containing not more than 25 µg of manganese.

5.2 Blank test

Transfer 30 ml of the hydrochloric acid solution (3.4) to a beaker, heat until the volume is reduced to about 10 ml and carry out a blank test following the instructions given in 5.4.

5.3 Preparation of calibration curve

5.3.1 Preparation of standard colorimetric solutions for photometric measurements with 4 cm cells.

Into a series of six 25 ml one-mark volumetric flasks transfer the quantities of the manganese standard solution (3.15) indicated in the following table :

Volume of manganese standard solution (3.15)	Corresponding mass of manganese
ml	µg
0 ¹⁾	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25

1) Compensation solution.

5.3.2 Development of the colour

Add to each flask approximately 10 ml of water, 2.0 ml of the hydroxylammonium chloride solution (3.11) and 0.5 ml of the formaldehyde oxime hydrochloride solution (3.9). Mix, add 5 ml of the ammonia solution (3.5) and dilute to the mark. Mix thoroughly and allow to stand for 10 min.

5.3.3 Photometric measurements

Using the spectrophotometer (4.1) at a wavelength of

approximately 450 nm or the photoelectric absorptiometer (4.2) with suitable filters, carry out the photometric measurements, adjusting the instrument to zero absorbance against water. Deduct the absorbance of the compensation solution from those of the standard colorimetric solutions.

5.3.4 Plotting of the calibration curve

Prepare a graph having, for example, the quantities in micrograms of manganese in 25 ml of the standard colorimetric solution as abscissae and the corresponding values of the absorbance as ordinates.

5.4 Determination

5.4.1 Preparation of the test solution

Transfer the test portion (5.1) to a 250 ml beaker. Add 20 ml of water and 20 ml of the hydrochloric acid solution (3.4) and evaporate carefully to dryness on a boiling water bath. Mix 5 ml of the hydrochloric acid solution (3.4) and 50 ml of the methanol (3.3). Add this mixture to the beaker and, in so doing, wash down any solid matter adhering to the inner walls of the beaker. Evaporate to dryness on the boiling water bath. Repeat this evaporation with methanol twice more, adding the methanol-hydrochloric acid mixture in the manner described. To the residue add 1.0 ml of the hydrochloric acid solution (3.4) and 100 ml of water. Stir to dissolve the contents of the beaker.

To the boiling solution, add 50 ml of water and 2 ml of the hydroxylammonium chloride solution (3.11). Boil the solution for a further 5 min and allow to cool slightly. Add 5.0 ml of the potassium sodium tartrate solution (3.12) and 5 drops of the cresol red solution (3.16). Cautiously add the ammonia solution (3.5) with continual mixing until the indicator colour turns yellow, and then drop by drop until the purple indicator colour just appears.

Cool the solution and immediately add 5 ml of the sodium diethyldithiocarbamate solution (3.13), mix carefully and allow to stand for 10 min.

Transfer the solution quantitatively to a 250 ml separating funnel and extract with 10 ml portions of the chloroform (3.2) until the final extract is colourless. Collect the extracts in a conical flask containing 2 ml of the sulphuric acid solution (3.6).

Heat the flask on a hot plate until white fumes are evolved. To the fuming residue, carefully add a few drops of the hydrogen peroxide solution (3.10) from a dropping pipette. Cool the solution, carefully add 5 ml of water and cool again. Add 5.0 ml of the sodium hydroxide solution (3.7) and 5.0 ml of the ammonium thiocyanate solution (3.8). Mix well, transfer to a 100 ml separating funnel and extract with 10 ml portions of the organic extraction solvent (3.1) until the extract is colourless.

5.4.2 *Development of the colour*

Transfer the test solution (5.4.1) to a 25 ml one-mark volumetric flask, and proceed with the colour development, following the instructions given in 5.3.2.

5.4.3 *Photometric measurements*

Carry out the photometric measurements on the test solution and on the blank solution following the instructions given in 5.3.3, adjusting the instrument to zero absorbance against water.

6 EXPRESSION OF RESULTS

By reference to the calibration curve (see 5.3.4) determine the mass of manganese corresponding to the absorbance of the test solution and that of the blank test.

The manganese content (Mn), expressed in parts per million by mass, is given by the formula :

$$\frac{m_1 - m_2}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in micrograms, of manganese found in the test solution;

m_2 is the mass, in micrograms, of manganese found in the blank test.

7 TEST REPORT

The test report shall include the following particulars :

- a) the reference of the method used;
- b) the results and the method of expression used;
- c) any unusual features noted during the determination;
- d) any operation not included in this International Standard or regarded as optional.