International Standard 5993

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Sodium hydroxide for industrial use — Determination of mercury content — Flameless atomic absorption spectrometric method

Hydroxyde de sodium à usage industriel — Dosage du mercure — Méthode par spectrométrie d'absorption atomique sans flamme

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Foreword

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International Standard ISO 5993 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in September 1977.

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

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Sodium hydroxide for industrial use — Determination of mercury content — Flameless atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flameless atomic absorption spectrometric method for the determination of the mercury content of sodium hydroxide for industrial use.

The method is applicable to liquid or solid products having mercury (Hg) contents greater than 0,02 mg/kg.

NOTE — The alternative dithizone photometric method for the determination of mercury content, specified in ISO 5992, is intended for use in laboratories where flameless atomic absorption equipment is not available.

2 References

ISO 3195, *Sodium hydroxide for industrial use — Sampling — Test sample — Preparation of the main solution for carrying out certain determinations.*

ISO 5790, *Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method.*

ISO 5992, *Sodium hydroxide for industrial use — Determination of mercury content — Dithizone photometric method.*

3 Principle

Oxidation of the mercury contained in a test portion to mercury(II) ions by potassium permanganate in the presence of sulphuric acid. Reduction of the excess oxidant by hydroxylammonium chloride. Reduction of the mercury(II) ions to mercury by tin(II) chloride. Entrainment of the mercury in air or nitrogen and passage of the gaseous mixture through a measuring cell.

Measurement of the absorption at a wavelength of 253,7 nm, using an atomic absorption spectrometer.

4 Reagents

During the analysis, use only reagents of recognized analytical grade having the lowest possible mercury content, and only distilled water or water of equivalent purity.

4.1 Nitrogen, in a cylinder.

4.2 Sulphuric acid, approximately 490 g/l solution.

4.3 Potassium permanganate, 40 g/l solution.

4.4 Hydroxylammonium chloride ($NH_2OH.HCl$), 100 g/l solution.

4.5 Tin(II) chloride, 100 g/l solution in hydrochloric acid.

Dissolve 25 g of tin(II) chloride dihydrate ($SnCl_2.2H_2O$) in 50 ml of hot hydrochloric acid solution, ϱ approximately 1,19 g/ml. Transfer the solution quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer this solution to a glass flask and purge it by bubbling the nitrogen (4.1) through for 5 min, then add a few particles of granular metallic tin to assist stabilization. Discard when turbidity appears.

4.6 Iodine, 2,5 g/l solution.

Dissolve 2,5 g of iodine and 30 g of potassium iodide in water, dilute to the mark in a 1 000 ml one-mark volumetric flask and mix.

4.7 Mercury, standard solution corresponding to 1,000 g of Hg per litre.

Dissolve 1,354 g of mercury(II) chloride ($HgCl_2$) in 25 ml of hydrochloric acid, ϱ approximately 1,19 g/ml 38 % (m/m) solution. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Store this solution in a cool, dark place and renew after 2 months.

1 ml of this standard solution contains 1 mg of Hg.

4.8 Mercury, standard solutions corresponding to 1 and 0,1 mg of Hg per litre.

Prepare these solutions on the day of use by successive dilution of the standard solution (4.7) with an approximately 11 g/l hydrochloric acid solution. These solutions should be freshly prepared as their concentration can vary because of loss of mercury through evaporation or adsorption by the flask.

1 ml of each of these standard solutions respectively contains 1 µg and 0,1 µg of Hg.

NOTE — In order to prevent pollution of waste water, collect solutions containing mercury salts and remove mercury following the instruction given in annex B of ISO 5790.

5 Apparatus

All new glassware or glassware not previously used for this determination, including flasks used for reagents and samples, shall be washed as follows and rinsed with water after each operation :

- with a brush and soap if the walls are likely to be greasy;
- with nitric acid solution, ϱ approximately 1,42 g/ml;
- with a mixture, prepared at the time of washing, consisting of 4 volumes of sulphuric acid solution, approximately 100 g/l solution and 1 volume of the potassium permanganate solution (4.3).

Condition the glassware thus washed by carrying out several preliminary determinations of mercury using mercury standard solutions until satisfactory results are obtained before using it for actual determinations. Thereafter, use such glassware for mercury determination *only*.

A typical apparatus incorporating an open-circuit measuring system (see 9.1) is shown in the figure.

It includes the following items.

5.1 Atomic absorption spectrometer, fitted with a low-pressure mercury vapour lamp or a hollow-cathode lamp.

NOTES

1 Mercury hollow-cathode lamps have a relatively short life if used constantly. For this reason, but only with instruments which are not fitted with electrical source modulation, a low pressure mercury discharge lamp may be preferred as a cheaper alternative.

2 A suitable mercury vapour detector may be used as an alternative to the atomic absorption spectrometer.

5.2 Rapid-response recording instrument or **maximum-deflection indicator.**

5.3 Measuring cell, of length suitable for the spectrometer used (for example 1 or 10 cm) with windows transparent to ultraviolet light at a wavelength of about 253,7 nm.

The enclosure containing the cell may be heated slightly (by means of an electric lamp or a radiant heater run below its rated voltage, etc.) in order to prevent condensation.

5.4 Gas washing bottles, capacity approximately 100 ml, fitted with a pointed immersion tube and mark indicating a volume of 60 ml. Check that all such bottles give the same calibration graph.

5.5 Safety flask, capacity approximately 100 ml. The use of such a flask is optional.

5.6 Four-way stopcock.

5.7 Needle valve.

5.8 Pressure regulator.

5.9 Flowmeter, measuring range 0 to 150 l/h.

5.10 Absorber, containing the iodine solution (4.6) for treatment of the exhaust gases containing mercury vapour.

6 Sampling

Follow the procedure specified in ISO 3195, observing the additional precautions specified in 6.1 and 6.2.

6.1 Liquid products

As liquid products may contain small particles of metallic mercury, take a laboratory sample of about 1 litre at a place where the turbulence is sufficient to ensure, as far as possible, a representative sample.

Take the test sample immediately from the laboratory sample and oxidize, *at once*, following the procedure specified in 7.1.1 and 7.4.1.1 in order to avoid loss of mercury through evaporation or adsorption.

6.2 Solid products

The sampling of solid products involves no particular difficulty as such products are obtained by evaporation of sodium hydroxide solutions, which removes any volatile mercury. The only precautionary requirement is the immediate oxidation of the test solution prepared for the determination, in order to avoid loss of mercury.

Take and treat the test portion following the procedure specified in 7.1.2 and 7.4.1.2.

7 Procedure

WARNING — For safety reasons, the gases leaving the measuring cell (5.3) shall pass through the absorber (5.10) containing the iodine solution (4.6).

7.1 Test portion

7.1.1 Liquid samples

Weigh, to the nearest 0,1 g, a polyethylene flask of capacity 100 ml containing 10 ml of the potassium permanganate solution (4.3). Immediately after its preparation (see 6.1), transfer approximately 50 ml of the test sample (6.1) into the flask and again weigh the flask and contents to the nearest 0,1 g (see 9.2). Immediately follow the procedure specified in 7.4.1.1 (see 9.3).

7.1.2 Solid samples

Into a 400 ml beaker, weigh, to the nearest 0,1 g, about 20 g of the test sample. Immediately follow the procedure specified in 7.4.1.2.

7.2 Blank test

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

7.3 Preparation of the calibration graphs

Prepare calibration graphs for two series of standard matching solutions containing

- 0 to 1 µg of mercury;
- 0 to 10 µg of mercury.

7.3.1 Preparation of standard matching solutions

Into each of a series of twelve 100 ml beakers, place 40 ml of water, 1 ml of the sulphuric acid solution (4.2), 1 ml of the potassium permanganate solution (4.3) and the volumes of the appropriate standard mercury solutions (4.8) shown in the following table.

Calibration curve	**Standard mercury solution (4.8)**		**Corresponding mass of mercury**
µg Hg	concentration, mg/l	ml	µg
0 to 1,0	0,1	0*	0
	0,1	2,0	0,2
	0,1	4,0	0,4
	0,1	6,0	0,6
	0,1	8,0	0,8
	0,1	10,0	1,0
0 to 10,0	1,0	0*	0
	1,0	2,0	2,0
	1,0	4,0	4,0
	1,0	6,0	6,0
	1,0	8,0	8,0
	1,0	10,0	10,0

* Calibration blank solution.

Cover each beaker with a watch-glass, boil for a few seconds and allow to cool.

7.3.2 Spectrometric measurements

Connect one of the gas washing bottles (5.4) containing 60 ml of water in the circuit. Adjust the apparatus, ensuring particularly that the gas flow rate [air or the nitrogen (4.1)] is set to about 60 l/h.

Treat each standard matching solution separately and without interruption as follows.

Reduce the excess permanganate by adding, drop by drop, the hydroxylammonium chloride solution (4.4) until decoloration takes place. Transfer the solution to one of the gas washing bottle (5.4) and dilute to 60 ml. Divert the gas flow and replace the gas washing bottle containing water by that containing the standard matching solution. Add 2,0 ml of the tin(II) chloride solution (4.5), close the gas washing bottle immediately, shake it to mix the contents and restore the gas flow exactly 30 s after introducing the tin(II) chloride. Measure the peaks on the recording chart or note the maximum deflections indicated, converting the values into absorbances, if necessary.

7.3.3 Plotting the graphs

Plot two graphs corresponding to masses of mercury in the ranges 0 to 1,0 µg and 0 to 10 µg, having, for example, as abscissae the masses of mercury, expressed in micrograms, in the standard matching solutions and the corresponding values of the measured absorbances, less the measured value for the calibration blank solution (7.3.1 — 0 term), as ordinates.

7.4 Determination

7.4.1 Preparation of the test solution

7.4.1.1 Liquid samples

Transfer the test portion (7.1.1) to a 600 ml beaker, add approximately 150 ml of water and allow to cool. Rinse the flask which contained the test portion, using 25 ml of the sulphuric acid solution (4.2) to which 2 drops of the hydroxylammonium chloride solution (4.4) have been added, in order to dissolve any manganese hydroxide precipitate adhering to the walls of the flask. Pour this rinsing solution slowly and carefully into the 600 ml beaker, stirring continuously.

Then add, slowly and carefully, stirring continuously, a further 150 ml of the sulphuric acid solution (4.2), cover the beaker with a watch-glass and boil for about 10 min.

Allow to cool to room temperature and add, drop by drop, the hydroxylammonium chloride solution (4.4) until decoloration of the permanganate takes place, and add an excess of 0,5 ml of this solution. Transfer the contents of the beaker quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark, mix and immediately follow the procedure specified in 7.4.2.

7.4.1.2 Solid samples

Treat the test portion (7.1.2) in the beaker as follows.

Dissolve in 100 ml of water, allow to cool to room temperature, add 5 ml of the potassium permanganate solution (4.3) and, slowly and carefully, stirring continuously, 85 ml of the sulphuric acid solution (4.2). Cover the beaker with a watch-glass and boil for 10 min.

Allow to cool to room temperature and add, drop by drop, the hydroxylammonium chloride solution (4.4) until decoloration of the permanganate takes place, and add an excess of 0,25 ml of this solution to dissolve any manganese hydroxide precipitate adhering to the walls of the beaker. Transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark, mix and immediately follow the procedure specified in 7.4.2.

7.4.2 Spectrometric measurement

Introduce into one of the gas washing bottles (5.4) an aliquot portion of the test solution (7.4.1) not exceeding 60 ml and containing less than 10 µg of mercury. If necessary, dilute to 60 ml.

Adjust the apparatus as specified in the first paragraph of 7.3.2. Divert the gas flow and replace the gas washing bottle containing water by that containing the test solution. Add 2,0 ml of the tin(II) chloride solution (4.5), close the gas washing bottle immediately, shake it to mix the contents and restore the gas flow exactly 30 s after introducing the tin(II) chloride. Measure the peaks on the recording chart or note the maximum deflections indicated, converting the values into absorbances, if necessary. Determine the mercury content of the aliquot portion used for the determination from the calibration graph, taking into account the blank test.

7.4.3 Check test

Check for absence of interference by repeating the operations described in 7.4.2 on a further aliquot portion of the test solution (7.4.1) to which has been added a known quantity of the standard mercury solution (4.8). If interference is observed, use the remainder of the test solution (7.4.1) to repeat the calibration by the standard additions method. Ensure in this case that the operations are carried out in the linear section of the calibration graph.

8 Expression of results

8.1 Calculation

The mercury content, expressed as milligrams of mercury (Hg) per kilogram, is given by the formulae

— for liquid products

$$m_1 \times \frac{1}{1\,000} \times \frac{500}{V} \times \frac{1\,000}{m_0}$$

$$= \frac{500\, m_1}{V \times m_0}$$

— for solid products

$$m_1 \times \frac{1}{1\,000} \times \frac{250}{V} \times \frac{1\,000}{m_0}$$

$$= \frac{250\, m_1}{V \times m_0}$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_1 is the mass, in micrograms, of mercury found in the aliquot portion of the test solution (7.4.1) used for the determination;

V is the volume, in millilitres, of this aliquot portion of the test solution.

8.2 Repeatability and reproducibility

Comparative tests carried out on two samples by 27 and 16 laboratories respectively gave the following statistical data :

Characteristic		Sample 1	Sample 2
Average, mg/kg		0,021	0,201
Standard deviation	of repeatability, σ_r	0,001 7	0,011
	of reproducibility, σ_R	0,004 8	0,038

9 Notes on procedure

9.1 A closed-circuit measuring system may be used in which the mercury is recirculated by means of a pump. In this event, it is desirable to replace the heating device (see 5.3) by a drying tube containing magnesium perchlorate, placed between the gas washing bottle (5.4) and the measuring cell (5.3).

9.2 If it is not possible to take the test sample immediately, proceed as follows.

Record the mass of the laboratory sample. Shake the laboratory sample vigorously and then take the test sample. Empty the laboratory sample container and recover any mercury adhering to the walls by shaking mechanically for 1 h in the presence of a mixture of the potassium permanganate solution (4.3) and the sulphuric acid solution (4.2). Determine the mercury content of this mixture and correct the result (8.1) appropriately.

9.3 If it is not possible to carry out the determination immediately, some mercury may have been adsorbed by the walls of the flask. Under such conditions, apply a correction following the procedure specified in 9.2.

10 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 operations not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

11 Bibliography

BITC Standardization of methods for the determination of traces of mercury. Part 1. Determination of total inorganic mercury in inorganic samples. *Anal. Chem. Acta* (1974), pp. 37-48.