EUsalt
EUROPEAN SALT PRODUCERS'ASSOCIATION

Sodium Chloride – Analytical Standard

Determination of Total Mercury
Flameless Atomic Absorption Spectrometric Method

1.SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a cold vapour atomic absorption spectrometric method for the determination of total mercury in sodium chloride. The method is applicable to products of mercury content (Hg) equal to or greater than 20 µg per kilogram of salt (see 8.6.).

2. PRINCIPLE

Dissolution of the sample in a mixture of water, sodium chlorate and hydrochloric acid.

Oxidation with the nascent chlorine, converting all forms of mercury to ionic mercury (II).

Reduction of the excess of oxidant by hydroxylammonium chloride and of mercury (II) to atomic mercury by tin (II) chloride.

Entrainment of the mercury in a stream of gas and measurement of the absorbance at a wavelength of 253.7 nm.

3. REAGENTS

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

Store all reagents in glass bottles.

3.1. Sodium chloride with a mercury content less than 20 µg/kg (check against water)

3.2. hydrochloric acid, $c_{(HCl)} \approx 6$ mol/l (azeotropic mixture)

Purify this solution as follows.

Add 500 ml of water and 5 ml of sulphuric acid, $\rho \approx 1.84$ g/ml, 96% (m/m), to 500 ml of hydrochloric acid $\rho \approx 1.19$ g/ml, 37% (m/m). Distil the azeotropic mixture.

3.3. Sodium chlorate solution, $\beta_{(NaClO3)} \approx 100$ g/l

3.4. Potassium dichromate solution, $\beta_{(K2Cr2O7)} \approx 4$ g/l

Dissolve 4 g of potassium dichromate in 500 ml of water. Add 500 ml of nitric acid, $\rho \approx 1.40$ g/ml, 65% (m/m), and mix.

3.5. Tin(II) chloride solution, $\beta_{(SnCl2.2H2O)} \approx 100$ g/l

Dissolve 25 g of tin (II) chloride dihydrate in 50 ml of warm hydrochloric acid, $\rho \approx 1.19$ g/ml, 37% (m/m). Allow to cool and add 1-2 g of metallic tin. Dilute to 250 ml and mix.

Prepare this solution just before use and slowly pass nitrogen through for 30 minutes to remove any mercury.

Note: Prevent oxidation of solid tin (II) chloride by air.

3.6. hydroxylammonium chloride solution,

$\beta_{(NH2OH.HCl)} \approx 100$ g/l

3.7. Mercury, stock solution I, $\beta_{(Hg)} = 1000$ mg/l,

commercial standard solution or to be prepared as follows.

Dissolve 1.354 g of mercury (II) chloride ($HgCl_2$) in 50 ml of hydrochloric acid (3.2.) and add 50 ml of potassium dichromate solution (3.4.). Transfer into a 1000 ml onemark volumetric flask, dilute to the mark with water and mix.

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

3.8. Mercury, stock solution II, $\beta_{(Hg)} = 1$ mg/l

Prepare this solution just before use by successive dilutions of the stock solution I (3.7.). Add 50 ml of potassium dichromate solution (3.4.) for preparing 1000 ml of final solution.

3.9. Air or nitrogen

Use a gas containing no mercury or other components capable of absorbing radiations at a wavelength of 253.7 nm. Any mercury present can be removed by a charcoal filter.

4. APPARATUS

Usual laboratory equipment (see 8.2.) and an apparatus allowing the determination of mercury.

An example of suitable apparatus is shown in the figure in the appendix. This applies to an open-circuit measuring system and includes principally the following:

4.1. Atomic absorption spectrometer

4.2. Mercury hollow cathode lamp or

4.3. Low-pressure mercury vapour lamp

4.4. Measuring cell, minimum path length 10 cm with windows transparent to radiation of 253.7 nm.

4.5. Reaction bottle

Use, for example, a 100 ml gas washing bottle with sintered gas inlet or pointed immersion tube and 60 ml mark.

Note: Fill the bottle with water when not in use.

If different bottles are used, check that the results are identical. Traces of tin (IV) oxide which may have settled onto the walls have to be removed by hydrochloric acid, $\rho \approx 1.19$ g/ml, 37% (m/m).

5. SAMPLING AND SAMPLES (see 8.1.)

A test sample of about 500 g should be taken for analysis, ensuring it is representative of the whole batch.

6. PROCEDURE (see 8.1.)

6.1. Test portion

Weigh, to the nearest 0.1 g, about 10 g of the test sample.

6.2. Test solution (see 8.3.)

Transfer the test portion (6.1.) into a 100 ml conical flask and add 30 ml of water.

6.3. blank solution

Transfer 30 ml of water in a 100 ml conical flask.

6.4. Calibration solutions (see 8.4.)

Dissolve in a series of six 100 ml conical flasks 10 g of sodium chloride (3.1.) in 30 ml of water and add the volumes of mercury stock solution II (3.8.) indicated in the following table:

Calibration solution No.	Hg, stock solution II, ml	Corresponding mass of mercury, µg
1(*)	0	0
2	0.5	0.5
3	1.0	1.0
4	1.5	1.5
5	2.0	2.0
6	3.0	3.0
(*) zero calibration solution		

6.5. Determination

6.5.1. Mineralization

Proceed as follows with the conical flasks prepared in (6.2.), (6.3.) and (6.4.).

Add some glass beads, 4 ml of hydrochloric acid (3.2.) and 3 ml of sodium chlorate solution (3.3.). Heat and keep boiling for 5 minutes.

Allow to cool and transfer quantitatively into a 100 ml onemark volumetric flask. Dilute to the mark and mix.

6.5.2. Apparatus setting

Equip the spectrometer (4.1.) with the mercury lamp (4.2.) or (4.3.). Set the lamp current, the slit and the flow of air or nitrogen according to the instruction manual of the instrument. Adjust the wavelength at the maximum of emission at about 253.7 nm.

6.5.3. Spectrometric measurements (see 8.5.)

Proceed with the solutions prepared in (6.5.1.) in the following way.

Transfer 10.0 ml of solution (6.5.1.) and 3.0 ml of hydroxylammonium chloride solution (3.6.) into the reaction bottle (4.5.). Fill to the mark (60 ml) with water, add 2 ml of tin (II) chloride solution (3.5.) and place the flask immediately into the device. Swirl to mix and allow to stand for a few minutes.

Pass air or nitrogen through the reaction bottle and determine the maximum of absorbance. Stop the gas flow and remove the reaction bottle.

Wash the bottle with potassium dichromate solution (3.4.) to oxidize any traces of tin (II) and rinse thoroughly with water.

6.5.4. Calibration curve

Subtract the absorbance of the zero calibration solution from that of each other calibration solution (6.4.) and plot a graph with the masses of mercury (Hg), in micrograms, used to prepare the calibration solutions on the abscissa and the corresponding corrected absorbances on the ordinate.

7. EXPRESSION OF RESULTS

7.1. Evaluation

The mercury content of the sample, $\omega(Hg)$, is given by the formula:

$$\omega_{(Hg)} = \frac{1000}{m} \times (m_1 - m_0)$$

where

- $\omega_{(Hg)}$ is the total mercury content, in micrograms per kilogram of salt,
- m is the mass, in grams, of the test portion (6.1.),
- m_1 is the mass of mercury (Hg), in micrograms, analysed in the test solution (6.5.3.),
- m_0 is the mass of mercury (Hg), in micrograms, analysed in the blank solution (6.5.3.).

7.2. Repeatability and reproducibility

Analyses, carried out on three samples by several laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing two analyses per sample:

	Rock salt	Vacuum salt	Sea salt
Number of laboratories after elimination of outliers	14	12	12
Results, µg Hg/kg salt Mean*) Standard deviation for :	6.2	3.3	4.6
- repeatability (s_r)	3.98	2.78	3.12
- reproducibility (s_R)	24.10	11.42	15.98
*) Mean values are below Limit of Quantitation			

Reference: European Committee for the Study of Salt, ECSS/CN 287-1982, Statistical Study of Inter-Laboratory Analysis of Sodium Chloride (As, Cd, Hg, Pb)

8. REMARKS

8.1. Ensure that no trace of mercury is introduced during the sampling operations and during the analysis.

8.2. All new glassware used for this determination, including flasks used for reagents or samples should be washed as follows and thoroughly rinsed with water after each operation :

- with a brush and detergent if the walls are greasy
- with diluted nitric acid, $c_{(HNO3)} \approx 7$ mol/l.

Check the glassware by carrying out several blank tests until satisfactory results are obtained before using it for actual determinations. Thereafter use such glassware for mercury determination only.

8.3. Test solutions described in ISO 2479 (Sodium chloride for industrial use - Determination of matter insoluble in water or in acid and preparation of principal solutions for other determinations) should not be used, as mercury losses may occur.

8.4. To take into account the influence of sodium chloride on mercury evolution, a quantity of sodium

chloride equal to the test portion (6.1.) should be taken for the preparation of calibration solutions.

Samples of unknown composition should be tested for the presence of matrix effects, caused by components present other than sodium chloride, by the method of standard addition.

8.5. A maximum signal is obtained only under optimum conditions. For instance, the gas flow and the waiting time between tin (II) chloride addition and start of stripping have great influence on the peak height. A typical waiting time will be in the order of 5 minutes. Therefore those parameters have to be established experimentally for any individual apparatus and matrix.

The maximum absorbance also depends very strongly upon the temperature of the solution during aeration (ΔA = 3% per °C at room temperature). Therefore, all solutions have to be allowed to cool to about the same temperature ($\pm$ 1° C).

Test and blank solutions have to be analysed at the same time and with the same reagents.

8.6. The lower limit of determination, as stated here, can only be achieved if the procedure is carried out under optimum conditions:

- skilled operators experienced with this method,
- clean glassware, only used for such determination,
- optimum apparatus settings,
- very low mercury level of the ambient air,
- pure reagents.

Apendix

Determination of mercury by atomic absorption spectrometry Typical apparatus
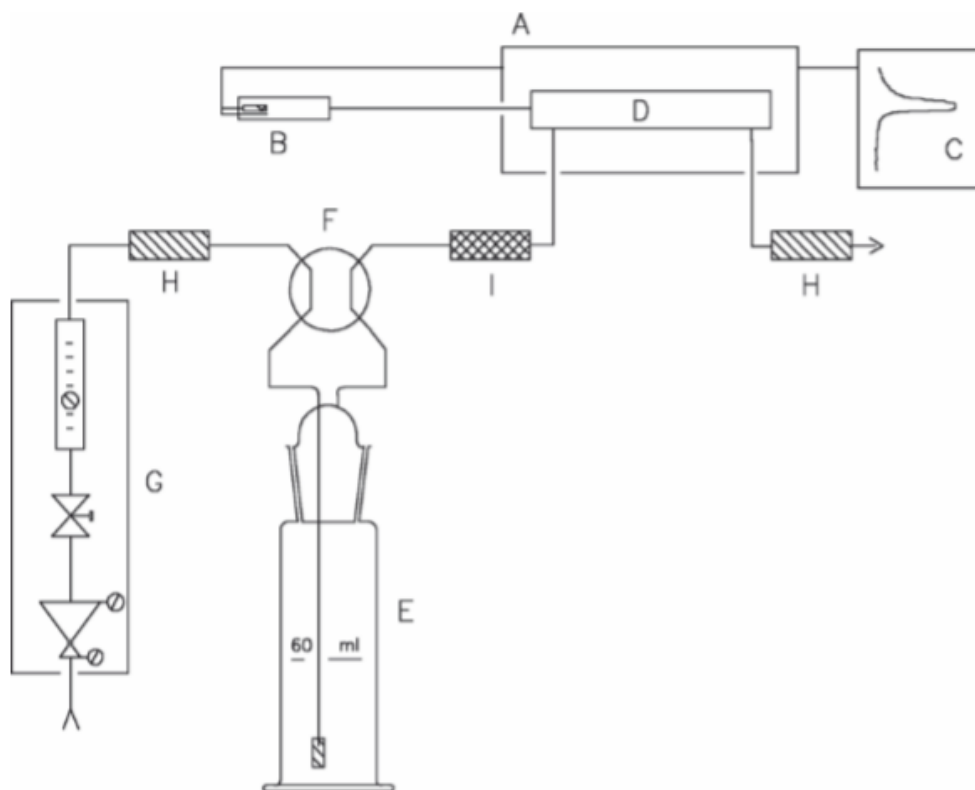
A : atomic absorption spectrometer or mercury vapour meter

B : mercury hollow cathode lamp or low-pressure mercury vapour lamp

C : recorder or maximum deflection indicator

D : measuring cell

E : reaction bottle with sintered glass inlet or pointed immersion tube

F : four-way stopcock

G : flow control system (e.g. pressure regulator, needle valve and flow meter)

H : absorption tube with charcoal

I : absorption tube with drying agent