Sodium Chloride – Analytical Standard

Determination of Arsenic

Silver Diethyldithiocarbamate Photometric Method

EUsalt/AS 011-2005
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1. SCOPE AND FIELD OF APPLICATION

The present Eusalt Analytical Standard describes a silver diethyldithiocarbamate photometric method for the determination of arsenic in sodium chloride. The method is applicable to products of arsenic content (As) equal to or greater than 0.1 mg per kilogram of salt.

2. REFERENCE

International Standard ISO 2590

General method for the determination of arsenic - Silver diethyldithiocarbamate photometric method.

3. PRINCIPLE (see 9.4.)

Dissolution of the sample in hydrochloric acid.

Reduction of arsenic by zinc in a hydrochloric acid medium with formation of arsine (AsH_3) and absorption of the arsine in a solution of silver diethyldithiocarbamate in pyridine.

Photometric measurement of the purplish-red colour produced by the colloidally dispersed silver at a wavelength around 540 nm.

Note: colloidal silver is formed according to the following equation

$$AsH_3 + 6\ Ag(DDTC) \rightarrow 6\ Ag + 3\ H(DDTC) + As(DDTC)_3$$

4. REAGENTS

Unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

All the reagents, and the zinc in particular, shall be free from arsenic or have a very low arsenic content.

4.1. Pyridine, $\rho \approx 0.980$ g/ml

WARNING : Because of the hazardous properties of pyridine, it is recommended to handle with care and in a well-ventilated fume cupboard.

4.2. Zinc pellets, 3 - 8 mm or any other form of zinc

Note: when zinc is used in any other form than pellets, ensure that the rate and time of evolution of hydrogen are sufficient to reduce and expel all arsenic present as arsine.

4.3. Hydrochloric acid, $\rho \approx 1.19$ g/ml, 37% (m/m)

4.4. Silver diethyldithiocarbamate, 5 g/l solution in pyridine

Dissolve 1 g of silver diethyldithiocarbamate [Ag(DDTC)] in pyridine (4.1.) and dilute to 200 ml with pyridine.

This solution remains stable for about 2 weeks, if stored in a tightly sealed dark glass bottle and protected from light.

4.5. Potassium iodide solution, $\beta_{(KI)} \approx 100$ g/l

Store this solution in a dark bottle.

4.6. Tin(II) chloride solution, $\beta_{(SnCl2.2H2O)} \approx 400$ g/l

Dissolve 40 g of tin (II) chloride dihydrate in a mixture of 25 ml of water and 75 ml of hydrochloric acid (4.3.).

4.7. Arsenic, stock solution I, $\beta_{(As)} = 1000$ mg/l,

commercial standard solution or to be prepared as follows.

Dissolve 1.320 g of arsenic trioxide, (As_2O_3), in about 20 ml of sodium hydroxide solution (50 g/l solution). Make up to 1000 ml in a one-mark volumetric flask and mix.

4.8. Arsenic, stock solution II, $\beta_{(As)} = 2.50$ mg/l

Transfer 2.50 ml of arsenic stock solution I (4.7.) into a 1000 ml one-mark volumetric flask, make up to the mark and mix.

Prepare this solution just before use.

4.9. Absorbent cotton wool, saturated with lead acetate

Dissolve 20 g of lead acetate trihydrate, $Pb(C_2H_3O_2)_2.3H_2O$, in 100 ml of water. Saturate the absorbent cotton wool with this solution, remove the excess solution by allowing it to drain and dry the cotton wool under vacuum at room temperature. Store it in an airtight container.

5. APPARATUS

Usual laboratory equipment (see 9.2.) and:

5.1. Glass apparatus, with ground glass joints, for the liberation and absorption of arsine

A suitable apparatus is shown in the figure in the appendix and includes:

5.1.1. Conical flask, 100 ml capacity

5.1.2. Connecting tube

5.1.3. Absorption vessel with 15 bulbs

5.2. Spectrophotometer or

5.3. Photocolorimeter fitted with a filter ensuring maximum transmission between 520 and 560 nm.

Note: Specify the type of apparatus used (spectrophotometer or photocolorimeter), the path length and the wavelength (or type of filter).

6. SAMPLING AND SAMPLES (see 9.1.)

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

7. PROCEDURE (see 9.1.)

7.1. Test portion

Weigh, to the nearest 0.1 g, about 10 g of the test sample containing a maximum of 20 µg of As (see 9.3.).

7.2. Test solution

Transfer the test portion (7.1.), 50 ml of water and 10 ml of hydrochloric acid (4.3.) into a 100 ml conical flask (5.1.1.).

7.3. Blank solution

Add 50 ml of water and 10 ml of hydrochloric acid (4.3.) into a 100 ml conical flask (5.1.1.).

7.4. Calibration

7.4.1. Calibration solutions

These preparations are used for photometric measurement in cuvettes of 1 cm optical path length. Transfer the volumes of arsenic stock solution II (4.8.) indicated in the following table into a series of six 100 ml conical flasks (5.1.1.). Add 10 ml of hydrochloric acid (4.3.) and the quantity of water necessary to make up to about 60 ml.

Calibration solution No.	Arsenic stock solutions II, ml	Corresponding mass of arsenic, µg
1(*)	0	0
2	1.0	2.5
3	2.0	5.0
4	4.°	10.0
5	6.0	15.0
6	8.0	20.0
(*) zero calibration solution		

7.4.2. Reduction and colour development

Proceed with each glass apparatus (5.1.) as follows.

Place a little of the absorbent cotton wool (4.9.) in the connecting tube in order to absorb any hydrogen sulphide which may be released with the arsine (see figure).

Transfer 5.0 ml of silver diethyldithiocarbamate solution (4.4.) into the absorption vessel and attach the connecting tube to the absorption vessel by means of a safety clip.

Proceed with the conical flask as follows.

Add 3 ml of potassium iodide solution (4.5.) and 2 ml of tin(II) chloride solution (4.6.), swirl and allow to stand for 15 minutes.

Add 5 g of zinc (4.2.), if necessary with the aid of a powder funnel, and rapidly assemble the apparatus as indicated in the figure.

Allow approximately 45 minutes for the reaction to take place.

Detach the absorption vessel, swirl in order to disperse the formed red deposit and to mix.

The colour of the solution is stable for about 2 hours in the absence of light, nevertheless, it is better to carry out the photometric measurements immediately.

7.4.3. Photometric measurements

Adjust the apparatus to zero absorbance with pyridine (4.1.).

Carry out the photometric measurements using a spectrophotometer (5.2.) set up at the maximum of absorption (wavelength around 540 nm) or a photocolorimeter (5.3.) fitted with the appropriate filter.

7.4.4. Calibration curve

Subtract the absorbance of the zero calibration solution from that of each calibration solution and plot a graph showing the quantities of arsenic (As), in micrograms, added to the calibration solutions (7.4.1.) on the abscissa and the corresponding corrected absorbances on the ordinate.

7.5. Determination

7.5.1. Reduction and colour development

Proceed with the test solution (7.2.) and the blank solution (7.3.) according to the procedure for calibration solutions described in paragraph (7.4.2.).

7.5.2. Photometric measurements

Carry out the photometric measurements of the two solutions (7.5.1.) according to the instructions given in paragraph (7.4.3.).

8. EXPRESSION OF RESULTS

8.1. Evaluation

The arsenic content of the sample, ω(As), of salt is given by the formula:

$$\omega_{(As)} = \frac{m_1 - m_0}{m}$$

where

- $\omega_{(As)}$ is the arsenic content, in milligrams per kilogram of salt,
- m is the mass, in grams, of the test portion (7.1.),
- m_1 is the mass of arsenic, in micrograms, analysed for the test solution (7.2.),
- m_0 is the mass of arsenic, in micrograms, analysed for the blank solution (7.3.).

8.2. 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	17	17	18
Results, mg AS/kg salt			
Mean*)	0.005	0.007	0.024
Standard deviation for:			
- repeatability (s_r)	0.0215	0.0236	0.0210
- reproducibility (s_R)	0.0340	0.0401	0.0506

(*) 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)

9. REMARKS

9.1. Ensure that no trace of arsenic is introduced during the sampling operations (e.g. by apparatus) or during the analysis.

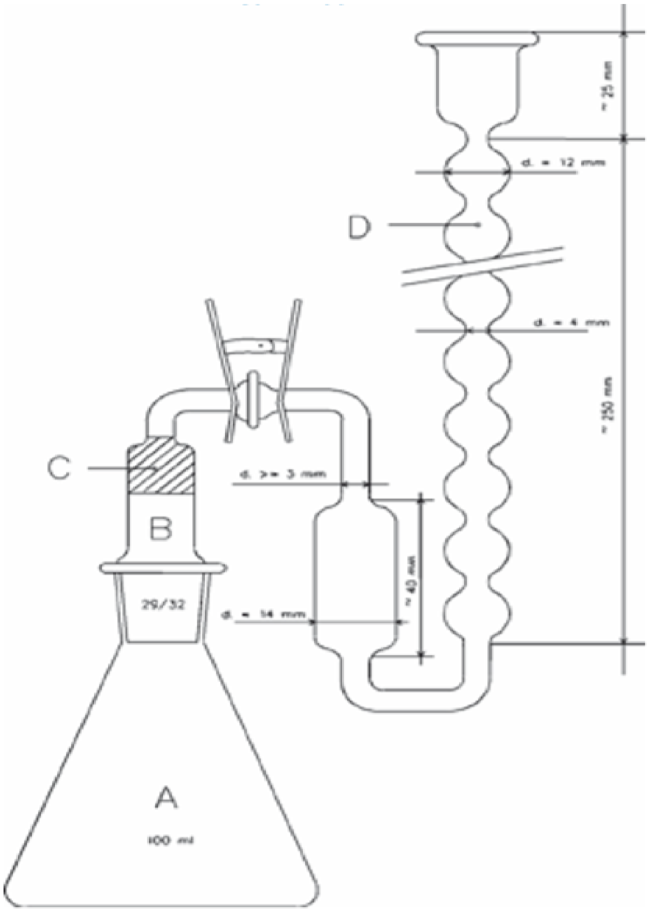
9.2. All the glass containers used for the determination of arsenic shall be washed with hot concentrated sulphuric acid, taking the necessary precautions, then rinsed thoroughly with water and dried in a drying cabinet.

9.3. In case of an arsenic content greater than 2 mg/kg of salt, the size of test portion (7.1.) must be reduced. Sodium chloride as a matrix does not influence the generation, evolution and determination of arsine.

9.4. Interferences of this method may be caused by nitrates, nitrites, antimony, mercury, chromium, cobalt, copper, molybdenum, nickel, platinum, silver and others. Generally there is no interfering effect at concentrations usually present in salt.

Appendix

Determination of arsenic - Silver Diethyldithiocarbamate Photometric Method Typical apparatus



A: 100 ml conical flask
B: connecting tube
C: absorbent cotton wool saturated with lead acetate
D: absorption vessel with 15 bulbs (total volume of the bulbs : ≈ 14 ml)