eusalt
EUROPEAN SALT PRODUCERS' ASSOCIATION

Sodium Chloride - Analytical Standard

Determination of Total Lead

Flame Atomic Absorption Spectrometric Method

EUsalt/AS 013-2005

Former numbering: ECSS/CN 313-1982 & ESPA/CN-E-108-1994

1. SCOPE AND FIELD OF APPLICATION

The present EUsalt Analytical Standard describes a flame atomic absorption spectrometric method for the determination of total lead in sodium chloride. The method is applicable to products of lead content (Pb) equal to or greater than 0.5 mg per kilogram of salt (see 8.5.).

2. PRINCIPLE

Dissolution of the sample in nitric acid for the total mineralization of lead.

Complexation of the metal by ammonium pyrrolidinedithiocarbamate.

Extraction of metal carbamates into chloroform and back-extraction into nitric acid.

Nebulization of the nitric acid solution into an acetyleneair flame and measurement of the absorbance at a wavelength of 283.3 nm.

Determination of the lead content using the standard addition method.

3. REAGENTS

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

3.1. Nitric acid, ρ ≈ 1.40 g/ml, 65% (m/m)

3.2. Chloroform, ρ ≈ 1.48 g/ml (see 8.6.)

3.3. APDC (ammonium pyrrolidinedithiocarbamate),

20 g/l solution, special reagent for AAS. Prepare this solution just before use.

Note: Solid APDC can decompose with loss of the ammonium group. The decomposition product results in a scum on the surface of the aqueous solution which can readily be separated by filtration.

3.4. Buffer solution

Dissolve 113 g of diammonium hydrogen citrate, $(NH_4)_2HC_6H_5O_7$, in about 500 ml of water and transfer this solution into a 1000 ml separating funnel.

Purify this solution as follows:

Shake with 50 ml of APDC solution (3.3.) and extract three times respectively with 50, 25 and 25 ml of chloroform (3.2.). Back-extract the combined three organic extracts first into only 5 ml of nitric acid (3.1.) and then after addition of 45 ml of water.

Repeat the extraction procedure until, aspirating the nitric extracts into the acetylene-air flame, the absorbance measured at 283.3 nm is lower than 10 times the absorbance of 20 ml chloroform extracted in 1 ml of nitric acid and 9 ml of water.

Transfer the purified solution into a 1000 ml one-mark volumetric flask and add 100 ml of ammonia solution, ρ ≈ 0.9 g/ml. Dilute to the mark and mix.

3.5. Lead stock solution I, $\beta_{(Pb)}$ = 1000 mg/l,

commercial standard solution or to be prepared as follows:

Dissolve 1.598 g of lead nitrate, $Pb(NO_3)_2$, in 10 ml of nitric acid (3.1.). Transfer quantitatively into a 1000 ml volumetric flask. Make up to volume and mix.

3.6. Lead stock solution II, $\beta_{(Pb)}$ = 10 mg/l

Transfer 10.0 ml of lead stock solution I (3.5.) and 1 ml of nitric acid (3.1.) into a 1000 ml one-mark volumetric flask. Make up to the mark and mix.

4. APPARATUS

Usual laboratory equipment (see 8.2.) and:

4.1. Atomic absorption spectrometer fitted with an acetylene-air burner

Note: In order to reduce the interferences of non atomic absorption, the use of background correction devices is recommended.

4.2. Lead hollow cathode lamp

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 1 g about 250 g of the test sample.

6.2. Test solution (see 8.3.)

Transfer the test portion (6.1.), 850 ml of water, 10.0 ml of nitric acid (3.1.) into a 2000 ml beaker. Stir to dissolve.
Add some glass beads, heat and keep boiling for 30 minutes. Take care that the total volume never becomes less than 800 ml and add water if required.
Allow to cool and transfer quantitatively into a 1000 ml one-mark volumetric flask. Dilute to the mark and mix.

6.3 Blank solution

Solution containing 10.0 ml of nitric acid (3.1.) per litre.

6.4. Calibration solutions (for the blank solution)

Transfer 0.5 ml of nitric acid (3.1.) and the volumes of lead stock solution II (3.6.) indicated in the following table into a series of four 50 ml volumetric flasks. Make up to volume and mix.

Calibration solution No.	Pb, stock solution II, ml	Corresponding mass of lead, µg
1(*)	0	0
2	0.5	5.0
3	1.0	10.0
4	2.0	20.0
(*) zero calibration solution		

6.5. Calibration solutions (for the test sample)

Transfer 200 ml of test solution (6.2.) and the volumes of lead stock solution II (3.6.) indicated in the table (6.4.) into a series of four 500 ml separating funnels. Solution No. 1 is the non spiked test solution.

6.6. Determination

6.6.1 Complexation and extractions

Transfer 200 ml of blank solution (6.3.) into a 500 ml separating funnel.

Proceed as follows with this separating funnel and the four solutions prepared in (6.5.).

Complexation:

Add 20.0 ml of buffer solution (3.4.), 5.0 ml of APDC solution (3.3.) and shake for 30 seconds.

Extraction:

Add 10.0 ml of chloroform (3.2.) and shake vigorously for 1 minute. Let the organic layer drain into a previously dried 100 ml separating funnel containing 1.0 ml of nitric acid (3.1.). Repeat this extraction procedure twice, using 5 ml of chloroform each time.

Combine the three organic extracts in the 100 ml separating funnel.

Back-extraction:

Shake vigorously the 100 ml separating funnel for

30 seconds. Add 9.0 ml of water and shake again vigorously for 1 minute.

Discard the lower organic layer when the layers have separated and collect the upper aqueous layer into a dry tube.

6.6.2 Apparatus setting

Equip the spectrometer (4.1.) with the lead hollow cathode lamp (4.2.).

Set the lamp current, the slit and the pressure of acetylene and air according to the instruction manual of the instrument. Adjust the wavelength at the maximum of emission at about 283.3 nm.

6.6.3. Spectrometric measurements

Aspirate water after each measurement.

Aspirate the solutions into the acetylene-air flame and determine the absorbance of each one in the following order:

- the four solutions prepared in (6.4.),
- the nitric extract obtained in (6.6.1.) for the blank solution (6.3.),
- the nitric extracts obtained in (6.6.1.) for the solutions prepared in (6.5.).

6.7. Calibration curves

6.7.1. For the blank solution

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 lead (Pb), in micrograms, on the abscissa and the corresponding corrected absorbances on the ordinate.

6.7.2. For the test solution

Subtract the absorbance of the nitric extract obtained for the solution No. 1 [non spiked test solution of (6.5.)] from that of each extract obtained for the solutions No. 2, 3 and 4 [spiked test solutions of (6.5.)] and plot a graph with the masses of lead (Pb), in micrograms, used to prepare these solutions on the abscissa and the corresponding corrected absorbances on the ordinate.

7. EXPRESSION OF RESULTS

7.1. Evaluation

The lead content of the sample, $\omega_{(Pb)}$, is given by the formula:

$$\omega_{(Pb)} = \frac{1}{m} \times (5\ m_1 - m_0)$$

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- $\omega_{(Pb)}$ is the total lead content, in milligrams per kilogram of salt,
- m is the mass, in grams, of the test portion (6.1.),
- m_1 is the mass of lead, in micrograms, analysed for the extract of the solution No. 1 prepared in (6.5.),
- m_0 is the mass of lead, in micrograms, analysed for the extract of blank solution (6.3.).

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	15	14	15
Results, mg Pb/kg salt			
Mean	0.045*)	0.025*)	0.808
Standard deviation for:			
- repeatability (s_r)	0.0566	0.0483	0.1254
- reproducibility (s_R)	0.1299	0.1566	0.4141
*) 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 lead is introduced during the sampling operations and during the analysis.

8.2. All new glassware used for this determination 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, $c(HNO_3) \approx 7$ mol/l.

8.3. In the special case of salt containing acid insoluble matter, the details of any operations not included in this standard, or regarded as optimal, together with any incidents likely to have had an influence upon the results should be reported.

8.4. If both lead and cadmium have to be determined in the same sample, it is possible to determine them jointly. In this case, prepare the calibration solutions and the spiked solutions according to the EUsalt documents EUsalt/AS 014-2005 and EUsalt/AS 013-2005.

8.5. The lower limit of determination, as stated in section 1, 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,
- pure reagents.

8.6. The use of chloroform is restricted under the Montreal Protocol because it is an ozone depleting substance.