



Sodium Chloride - Analytical Standard



Determination of Calcium and Magnesium Flame Atomic Absorption Spectrometric Method

EuSalt/AS 009-2005

Former numbering: ECSS/CN 185-1979 & ESPA/CN-E-114-1998

1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a flame atomic absorption spectrometric method for the determination of water-soluble calcium and magnesium in sodium chloride. The method is applicable to products of calcium and magnesium contents equal to or greater than

- 2.5 mg of calcium and 1 mg of magnesium per kilogram of salt when using an air/acetylene flame,
- 0.6 mg of calcium and 1 mg of magnesium per kilogram of salt when using a nitrous oxide/acetylene flame.

2. REFERENCE

International Standard - ISO 2479

Sodium chloride for industrial use - Determination of matter insoluble in water or in acid, and preparation of principal solutions for other determinations.

3. PRINCIPLE

Dissolution of the sample in water and, if necessary, filtration of insoluble matters.

Atomisation of the test solution in either a nitrous oxide-acetylene or an air-acetylene flame, after addition in the latter case of lanthanum ions to suppress potential interferences.

Measurement of the absorbance at wavelengths of 422.7 nm and 285.2 nm.

4. REAGENTS

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

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

4.2. Sodium chloride solution, $\beta_{(\text{NaCl})} \approx 100$ g/l

To prepare this solution, use a salt with element contents at least ten times lower than the limits given in section 1.

4.3. Lanthanum solution, $\beta_{(\text{La})} \approx 5$ g/l

Note: This solution is unnecessary when using a nitrous oxide/acetylene flame.

Dissolve 5.9 g of lanthanum oxide (La_2O_3) in a mixture of 15 ml of hydrochloric acid (4.1.) and 15 ml of water. Make up to 1000 ml in a one-mark volumetric flask and mix.

This solution should conform with the following test:

Dilute 20 ml of lanthanum solution to 100 ml in a volumetric flask and measure the absorbances as described in (7.5.).

The absorbances should be lower than those obtained with an aqueous solution containing respectively 30 μg Ca and 10 μg Mg per litre.

4.4. Calcium, stock solution I, $\beta_{(\text{Ca})} = 1000$ mg/l, commercial standard solution or to be prepared as follows.

Weigh, to the nearest 1 mg, 2497 mg of calcium carbonate previously dried for at least one hour at 250 °C and then cooled in a desiccator. Dissolve in a mixture of 20 ml hydrochloric acid (4.1.) and 20 ml of water, make up to 1000 ml in a one-mark volumetric flask and mix.

4.5. Calcium, stock solution II, $\beta_{(\text{Ca})} = 10$ mg/l

Transfer 10.0 ml of calcium stock solution I (4.4.) into a 1000 ml one-mark volumetric flask, make up to the mark and mix.

4.6. Magnesium, stock solution I, $\beta_{(\text{Mg})} = 1000$ mg/l, commercial standard solution or to be prepared as follows.

Dissolve 1.000 g of magnesium (metal 99.95 %) in a mixture of 20 ml hydrochloric acid (4.1.) and 20 ml of water

with care, make up to 1000 ml in a one-mark volumetric flask and mix.

4.7. Magnesium, stock solution II, $\beta_{(Mg)} = 10 \text{ mg/l}$

Transfer 10.0 ml of magnesium stock solution I (4.6.) into a 1000 ml one-mark volumetric flask, make up to the mark and mix.

5. APPARATUS

Usual laboratory equipment and:

5.1. Atomic absorption spectrometer fitted with a burner for acetylene-nitrous oxide flame or for acetylene-air flame.

5.2. Calcium hollow cathode lamp

5.3. Magnesium hollow cathode lamp

6. SAMPLING AND SAMPLES

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

7. PROCEDURE

7.1. Test portion

Weigh, to the nearest 0.1 g, about 100 g of the test sample.

7.2. Test solution

Prepare 1000 ml of a solution A (water solution) or of a solution B (acid solution) with the test portion (7.1.) as described in ISO 2479.

Transfer 20.0 ml of this solution A or B (see 9.2.), 2.00 ml of hydrochloric acid (4.1.) and, if using the air-acetylene

flame, 20.0 ml of lanthanum solution (4.3.) into a 100 ml volumetric flask. Make up to volume and mix.

7.3. Blank solution (see 9.1.)

Dilute to 1000 ml the same quantities of all the reagents used for the preparation of solution B (see 7.2.).

Transfer 20 ml of this solution, 20 ml of sodium chloride solution (4.2.), 2.00 ml of hydrochloric acid (4.1.) and, if using the air-acetylene flame, 20.0 ml of lanthanum solution (4.3.) into a 100 ml volumetric flask. Make up to volume and mix.

7.4. Calibration solutions

Transfer into a series of five 100 ml volumetric flasks, 20 ml of sodium chloride solution (4.2.), 2.0 ml of hydrochloric acid (4.1.), the volumes of calcium and magnesium stock solution II (4.5. and 4.7.) as shown in the following table and, if using the air-acetylene flame, 20.0 ml of lanthanum solution (4.3.). Make up to volume and mix.

Calibration solution No.	Stock solutions II, ml		Concentrations, mg/l	
	Ca (4.5.)	Mg (4.7.)	Ca	Mg
1(*)	0	0	0	0
2	2.0	0.4	0.20	0.04
3	5.0	1.0	0.50	0.10
4	10.0	2.0	1.00	0.20
5	20.0	4.0	2.00	0.40

(*) zero calibration solution

7.5. Determination

7.5.1. Apparatus setting

Equip the spectrometer (5.1.) with the calcium (magnesium) hollow cathode lamp (5.2. or 5.3.).

Set the lamp current, the slit and the pressure of acetylene and air (or nitrous oxide) according to the instruction manual of the instrument. Adjust the wavelength at the maximum of emission of the lamp at about 422.7 nm (285.2 nm).

7.5.2. Spectrometric measurements

Aspirate water after each measurement.

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

- the calibration solutions 1 to 5 (7.4.),
- the blank solution (7.3.),
- the test solution (7.2.),
- the calibration solutions.

7.6. Calibration curve

Subtract the absorbance of the zero calibration solution from that of each of the other calibration solutions and plot a graph showing the concentrations of calcium (or magnesium), in milligrams per litre, on the abscissa and the corresponding corrected absorbances on the ordinate.

The calibrations should be linear.

7.7. Control test

Samples of unknown composition should be tested for the presence of interference effects by the method of standard addition.

8. EXPRESSION OF RESULTS

8.1. Evaluation

The calcium (magnesium) content of the sample, $\omega_{(Ca)}$, ($\omega_{(Mg)}$), is given by the formula:

$$\omega_{(Ca \text{ or } Mg)} = 10^5 \times \frac{1}{m \times V} \times (\beta_1 - \beta_0)$$

where

- $\omega_{(Ca \text{ or } Mg)}$ is the calcium (magnesium) content, in milligrams per kilogram of salt,
- m is the mass, in grams, of the test portion (7.1.),
- V is the volume, in millilitres, of the test solution (7.2.),
- β_1 is the concentration, in milligrams of calcium (magnesium) per litre, of the test solution (7.2.),
- β_0 is the concentration, in milligrams of calcium (magnesium) per litre, of 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:

8.2.1. For calcium

	Rock salt	Vacuum salt	Sea salt
Number of laboratories after elimination of outliers	14	13	15
Results, mg Ca/kg salt			
Mean	1267	12	1054
Standard deviation for:			
- repeatability (s_p)	40	0.16	21
- reproducibility (s_R)	165	4.8	93

8.2.2. For magnesium

	Rock salt	Vacuum salt	Sea salt
Number of laboratories after elimination of outliers	14	13	14
Results, mg Mg/kg salt			
Mean	158	1.15	613
Standard deviation for:			
- repeatability (s_p)	3	0.08	17
- reproducibility (s_R)	16	0.91	28

Reference: European Committee for the Study of Salt, ECSS/CN 172-1978, Statistical evaluation of the Interlaboratory Study of Br, K, Ca, Mg, F.

9. REMARKS

- 9.1.** When salt is dissolved in water and not in acid according to ISO 2479 (usual case), the zero calibration solution (see 7.4.) may replace the blank solution (7.3.).
- 9.2.** If the estimated levels of calcium or magnesium in the test sample are greater than the maxima of the calibration curves, prepare the test solution (7.2.) with a smaller volume of solution A or B. The volume of sodium chloride (4.2.) used for the preparation of the calibration solutions must be modified accordingly.

The report should contain an account of all details relevant to the analysis.