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EUROPEAN SALT PRODUCERS' ASSOCIATION

Sodium Chloride - Analytical Standard

Determination of Total Iodine Titrimetric Method with Sodium Thiosulphate

EUsalt/AS 002-2005

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1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a titrimetric method for the determination of total iodine (iodides and iodates) in sodium chloride. The method is applicable to products of iodine content (expressed as I) equal to or greater than 3.5 mg per kilogram of salt.

2. REFERENCES

H. Furrer, M. Staub, Mitteilungen aus dem Gebiet der

Lebensmitteluntersuchungen und Hygiene (1953), 44, 252

Gemeinschaftarbeit, Mitteilungen aus dem Gebiet der

Lebensmitteluntersuchungen und Hygiene (1964), 55, 43

3. PRINCIPLE

Dissolution of the sample in water.

Oxidation of iodide to iodate with bromine water and elimination of the excess bromine with formic acid. Addition of phosphoric acid and potassium iodide with formation of free iodine equivalent to the amount of iodate present.

Titration of free iodine with sodium thiosulphate using starch as indicator.

4. REAGENTS

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

4.1. Phosphoric acid, $\rho \approx 1.7$ g/ml, 85 % (m/m)

4.2. Formic acid, $\rho \approx 1.2$ g/ml, 90 % (m/m)

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

Prepare this solution on the day of use and store it in a dark bottle.

4.4. Bromine water, saturated at ambient temperature

4.5. Hydrochloric acid, $c_{(HCl)} = 0.1$ mol/l

4.6. Sodium thiosulphate, $c_{(Na2S2O3)} = 0.1$ mol/l, standard volumetric solution

4.7. Sodium thiosulphate, $c_{(Na2S2O3)} = 0.01$ mol/l, standard volumetric solution

Prepare this solution by dilution of the standard volumetric solution (4.6.).

Standardize with a potassium iodate solution, $c_{(1/6\ KIO3)} = 0.01$ mol/l.

4.8. Methyl red, 0.5 g/l solution in 95 % (v/v) ethanol

4.9. Starch solution, 2 g/l

Prepare this solution at the time of use from soluble starch.

5. APPARATUS

Usual laboratory equipment and:

5.1. Burette allowing the distribution and measurement of 0.01 ml

5.2. 500 ml conical flask with ground stopper

6. SAMPLING AND SAMPLES

A test sample of 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 50 g of the test sample.

7.2. Test solution

Transfer the test portion (7.1.) and 175 ml of water into a 500 ml conical flask (5.2.). Stir to dissolve.

7.3. Blank solution

Transfer 175 ml of water into a 500 ml conical flask (5.2.).

7.4. Determination

Proceed with the conical flasks prepared in (7.2.) and (7.3.) in the following way:

Add 4 drops of methyl red (4.8.) and hydrochloric acid 0.1 mol/l (4.5.) to the first colour change from yellow to orange and then add immediately 1.5 ml of bromine water (4.4.). Allow to stand for 3 minutes.

Add some glass beads, heat and keep boiling for 5 minutes, with swirling and avoiding crystallization of sodium chloride.

Allow to stand for 1 minute, add 1.0 ml of formic acid (4.2.) in such a way that the whole of the inside surface of the conical flask is wetted and swirl. After 1 minute, cool to about 20 °C, add 1.0 ml of phosphoric acid (4.1.) and 1.0 ml of potassium iodide solution (4.3.). Swirl, cork the conical flask and allow to stand in the dark for exactly 5 minutes.

Titrate with the sodium thiosulphate standard volumetric solution 0.01 mol/l (4.7.) using a burette (5.1.). When the solution is nearly discoloured, add 1 ml of starch solution (4.9.) and continue the titration until the blue color disappears for at least 3 seconds.

8. EXPRESSION OF RESULTS

8.1. Evaluation

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

$$\omega_{(I)} = 21.15 \times c_{(Na2S2O3)} \times \frac{1000}{m} \times (V_1 - V_0)$$

where

- $\omega_{(I)}$ is the total iodine content, expressed as milligrams of iodine per kilogram of salt,
- m is the mass, in grams, of the test portion (7.1.),
- V1 is the volume, in millilitres, of sodium thiosulphate (4.7.) used for the titration of the test solution (7.2.),
- V0 is the volume, in millilitres, of sodium thiosulphate (4.7.) used for the titration of the blank solution (7.3.),
- $c_{(Na2S2O3)}$ is the molar concentration of the sodium thiosulphate standard volumetric solution (4.7.).

The result is expressed to a single decimal place.

8.2. Repeatability and reproducibility

Analyses, carried out on six samples by 14 laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing three analyses per sample:

Product	$\omega_{(I)}$	k	p	n	S_r	S_R
Rock Salt	24.4	13	13	3	0.77	1.55
Sea Salt	11.6	13	13	3	0.65	1.05
	63.2	12	12	3	1.19	3.08
Vacuum salt	4.6	13	13	3	0.34	0.50
	15.2	13	13	3	0.49	0.70
	45.1	12	12	3	1.11	1.41

where

- ω(I) is the total iodine content, in mg I/kg,
- k is the number of analysts,
- p is the number of laboratories retained after eliminating outliers,
- n is the number of results per series,
- sr is the repeatability standard deviation, in mg of I/kg,
- sR is the reproducibility standard deviation, in mg of I/kg.

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

8.3. Limit of quantitation

The limit of quantitation (LOQ = 3.5 mg I/kg) is based on the formula:

$$LOQ = 10 \cdot s_r$$

where s_r is the repeatability standard deviation of a representative test sample having an iodine concentration near the expected LOQ (see Vacuum salt 4.6 mg I/kg).

This calculated value corresponds with a volume of titrant [$c(Na_2S_2O_3)$ = 0.01 mol/l] of 0.8 ml.

9. REMARKS

9.1. For iodine content greater than 20 mg per kilogram of salt, reduce the test portion (7.1.) accordingly.

9.2. The presence of oxidizing agents may lead to inaccurate results. The Fe3+ interference can be avoided by complexation with EDTA.

9.3. An automatic titrator provided with a platinum electrode and an Ag/AgCl reference electrode may be used. In this case, do not add starch solution (4.9.) during the determination (7.4.).