



Sodium Chloride - Analytical Standard



Determination of Total Bromine and Iodine (Expressed as Bromine) Titrimetric Method with Sodium Thiosulphate

EuSalt/AS 006-2005

Former numbering: ECSS/CN 182-1979 & ESPA/CN-E-113-1998

1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a titrimetric method for the determination of total bromine and iodine in sodium chloride. The method is applicable to products of bromine and iodine content (expressed conventionally as Br) equal to or greater than 3 mg bromine per kilogram of salt.

2. PRINCIPLE

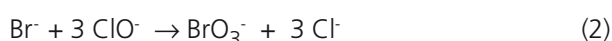
Dissolution of the sample in water.

Oxidation of iodide to iodate and bromide to bromate with hypochlorite in a buffered medium and elimination of the excess oxidant with formic acid. Addition of hydrochloric acid and potassium iodide to form free iodine equivalent to the amount of iodate and bromate present.

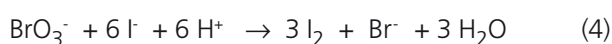
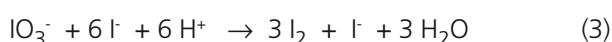
Titration of free iodine with sodium thiosulphate using starch as indicator.

3. REACTIONS

Oxidation of the iodide and bromide follows the reactions:



Titration of the iodate and bromate follows the reactions:



Note: Reactions (1) and (2) require the presence of chloride ions for completion.

4. REAGENTS

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

4.1. Calcium carbonate, solid

4.2. Hydrochloric acid, $c_{(\text{HCl})} \approx 4 \text{ mol/l}$

4.3. Formic acid, $c_{(\text{HCOOH})} \approx 3 \text{ mol/l}$

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

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

4.5. Sodium hypochlorite solution, $\beta_{(\text{NaClO})} \approx 19 \text{ g/l}$

Prepare this solution by dilution of a concentrated technical sodium hypochlorite solution.

Renew the solution each week.

Note: Do not use commercial household solutions, which may contain interfering additives.

4.6. Buffer solution

Dissolve 50 g of sodium dihydrogen orthophosphate dihydrate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 50 g of disodium hydrogen orthophosphate dodecahydrate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 50 g of tetrasodium pyrophosphate decahydrate, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, and 150 g of sodium chloride (see note) in 650 ml of water.

Note: As the same quantity of buffer solution is used for the sample and for the blank solution, it is not necessary to use products completely free of iodine and bromine.

4.7. Sodium thiosulphate, $c_{(\text{Na}_2\text{S}_2\text{O}_3)} = 0.01 \text{ mol/l}$,

standard volumetric solution

Prepare this solution by dilution of a standard volumetric solution $c_{(\text{Na}_2\text{S}_2\text{O}_3)} = 0.1 \text{ mol/l}$ and standardize with a potassium iodate solution [$c_{(1/6 \text{ KIO}_3)} = 0.01 \text{ mol/l}$].

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 delivery and measurement of 0.01 ml

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 40 g of the test sample.

7.2. Test solution

Transfer the test portion (7.1.) and 150 ml of water into a 500 ml conical flask. Stir to dissolve.

7.3. Blank solution

Transfer 150 ml of water into a 500 ml conical flask.

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 (4.2.) until the solution turns red. Neutralize by addition of calcium carbonate (4.1.) to a permanent slight cloudiness.

Add 6.0 ml of buffer solution (4.6.) and 5.0 ml of sodium hypochlorite solution (4.5.). Heat to 90 ± 2 °C with agitation to avoid local overheating and keep at this temperature for 20 minutes.

Add 10 ml of formic acid (4.3.) and swirl. When CO₂ ceases to evolve, cool to about 20°C, add 2.0 ml of potassium iodide solution (4.4.) and 25 ml of hydrochloric acid (4.2.). Swirl and allow to stand for 1 minute.

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 colour disappears for at least 30 seconds.

8. EXPRESSION OF RESULTS

8.1. Evaluation

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

$$\omega_{(Br)} = 13.318 \times c_{(Na_2S_2O_3)} \times \frac{1000}{m} \times (V_1 - V_0)$$

where

- $\omega_{(Br)}$ is the total bromine plus iodine content, expressed as milligrams of bromine per kilogram of salt,
- m is the mass, in grams, of the test portion (7.1.),
- V_1 is the volume, in millilitres, of sodium thiosulphate (4.7.) used for the titration of the test solution (7.2.),
- V_0 is the volume, in millilitres, of sodium thiosulphate (4.7.) used for the titration of the blank solution (7.3.),
- $c_{(Na_2S_2O_3)}$ is the molar concentration of the sodium thiosulphate standard volumetric solution (4.7.).

8.2. Repeatability and reproducibility

Analyses, carried out on three samples by 14 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	13	12
Results, mg Br/kg salt			
Mean	141	85	135
Standard deviation for:			
- repeatability (s_r)	4	1	1
- reproducibility (s_R)	14	4	8

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. For bromine plus iodine content greater than 200 mg per kilogram of salt, reduce the test portion (7.1.) accordingly.
- 9.2. The presence of oxidising agents may lead to inaccurate results. The Fe^{3+} 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.).