eusalt
EUROPEAN SALT PRODUCERS'ASSOCIATION

Analytical Standard

Determination of Total Bromine and Iodine

Emission Spectrometric Method (ICP-OES)

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1. SCOPE AND FIELD OF APPLICATION

The present EUsalt Analytical Standard describes an inductively coupled plasma optical emission spectrometry method for the determination of bromine and iodine soluble in diluted hydrochloric acid, in sodium chloride. The limit of quantitation (LOQ) for each element, determined in an interlaboratory study is given in the following table:

Table 1: Limits of Quantitation (LOQ)

Element	Limit of quantitation (LOQ) (mg/kg of salt)
Br	5
I	10

2. REFERENCES

(1) ISO/CD 12235 – General guidelines for inductively coupled plasma emission spectrometry.

(2) Akzo Nobel – CAP F08004 (December 23, 2008) Determination of Br and I in NaCl.

3. PRINCIPLE

Dissolution of the sample in diluted hydrochloric acid and reduction of inorganic bromine and iodine with sodium sulfite solution added. Direct nebulization of the acid solution into an inductively coupled argon plasma sustained by a high frequency. Measurement of the radiation emitted at a specific wavelength of both elements using background correction.

NOTE: The use of a reference element (internal standard), such as scandium, yttrium or cobalt, may improve the quality of the results, especially using a simultaneous spectrometer. Every mention of this optional reagent (here *scandium*) is stated in *italics* and in brackets.

4. REAGENTS

All reagents shall be of recognized analytical grade and the water used shall conform to grade 2 purity in accordance with EN ISO 3696.

Store all prepared solutions in polyethylene or polytetrafluorethylene (PTFE) flasks to prevent contamination.

4.1. Hydrochloric acid, $\rho \approx 1.19$ g/ml, 35-37% (m/m) solution

4.2. Sodium chloride solution, $\beta_{(NaCl)}$ = 250 g/l
Dissolve 250 g of very pure NaCl (see note) in water and transfer to a 1000 ml volumetric flask. Make up to the mark and mix.

Note: A very pure salt is a salt with elemental impurities at least ten times lower than the respective limits of quantitation given in Table 1.

[4.3. Scandium (reference element) solution, $\beta_{(Sc)}$ *= 50 mg/l*

Transfer 50 ml of a scandium stock solution $\beta_{(Sc)}$ *= 1000 mg/l and 10 ml hydrochloric acid (4.1.) into a 1000 ml volumetric flask. Make up to the mark and mix.]*

4.4. Element stock solution, $\beta_{(each\ element)}$ = 1000 mg/l, certified commercial solutions.

Note: The stock solution has to be certified not only for the element itself but also for the other analyte elements (impurities).

4.5. Argon, pressure not less than 7 bar. The argon used may be compressed or liquefied gas.

4.6. Sodium sulfite solution, $\beta_{(SO_3^{2-})}$ = 100 g/l

Dissolve 15.8 g of $Na_2SO_3^{2-}$ in water and dilute to 100 ml.

5. APPARATUS

Usual laboratory equipment (see 9.1) and:

5.1. ICP, inductively coupled plasma emission spectrometer fitted with a nebulizer and a torch for high salt concentrations and with an argon humidifier filled with water. This instrument may measure simultaneously and/ or sequential. The specifications and operating conditions used with most spectrometers are given in appendix 1.

6. SAMPLING AND SAMPLES

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

7. PROCEDURE

Usual laboratory equipment (see 9.1) and:

7.1. Test portion (see 9.2)

Weigh, to the nearest 0.1 g, about 10 g of the test sample.

7.2. Test sample solution

Transfer the test portion (7.1.) and about 70 ml of water to a 100 ml volumetric flask. Add 1 ml hydrochloric acid (4.1.), *[5 ml of scandium solution (4.3.)]* and 0.5 ml of sodium sulfite solution (4.6.), stir to dissolve, make up to the mark and mix.

7.3. Calibration and verification solutions (see 9.2.)

Transfer 40 ml of sodium chloride solution (4.2.), (all reagents of the test solution without the test sample) and the volumes of each stock solution (4.4.) to obtain the concentrations indicated in table 2, into a series of further three 100 ml volumetric flasks to obtain the calibration solutions No. 1 + 2 + 3. Make up to the mark and mix.

Table 2: Calibration solutions

Calibration solution No.	Concentration of NaCl (g/l) (see 9.2)	Concentration of elements mg/l
1(1)	100	0
2(2)	100	10
3	100	20

(1) blank calibration solution
(2) linearity verification solution

7.4. Determination

7.4.1. Settings of the apparatus

Set all instrumental parameters of the optical emission spectrometer (5.1.) in accordance with the operating manual of the instrument's manufacturer.

Prepare the analytical procedure including the lines shown in appendix 2 (or lines with similar sensitivity and free from interferences), with background correction and concentrations of calibration solutions 1 and 3 described in (7.3.) *[and applying the reference technique].*

7.4.2. Spectrometric measurements

Repeat the measurements for at least five integration periods.

If necessary, rinse with the blank calibration solution (solution 1) after each solution.

Calibrate the instrument with the calibration solutions 1 and 3 (7.3.).

Control and check the linearity of the calibration curve by measurement of the following calibration solutions (7.3.) considered as unknown solutions:

- solution 3,
- solution 1,
- solution 1,
- solution 2,
- solution 3.

NOTE: If the calibration function does not appear to be a linear one, the corresponding calibration range should be decreased and/or the RF-power of the spectrometer should be adjusted.

Continue the measurements in the following order:

- solution 3 (7.3.),
- solution 1 (7.3.),
- solution 1 (7.3.),
- test sample solution(s) (7.2.),
- solution 3 (7.3.),
- solution 1 (7.3.),
- solution 1 (7.3.).

NOTE: Five to ten test sample solutions may be analysed consecutively, provided the stability of the measurements is sufficient.

8. EXPRESSION OF RESULTS

8.1. Evaluation

If necessary, correct the results obtained with the test sample solution for drift:

- for baseline drift by interpolating in time between both second measurements (the first may be cross-contaminated) of the blank calibration solution (solution 1),
- for sensitivity drift by interpolating in time between the corrected measurements for baseline drift of the control solution 3.

The element content of the sample, $\omega_{(\text{Element})}$ in milligrams per kilogram of sodium chloride is given by the formula:

$$\omega_{(\text{Element})} = \frac{100}{m} \times \beta_{(\text{Element})}$$

where

- m is the mass in grams of the test portion (7.1.),
- ß is the corrected concentration of element, in mg/l in the test sample solution (7.2.).

Report the result as given in chapter 8.3.

8.2. Repeatability and reproducibility

Analyses carried out on four samples, containing both elements in different concentrations, by 10 laboratories, gave the following statistical results. Each laboratory performed three replicates under repeatability conditions:

Table 3: Results of the interlaboratory study

(for details see (2))

	Bromine			Iodine		
Sample	ω	r	R	ω	r	R
Vacuum salt / KI	7.0	1.1	9.1	20	1.7	5.1
Sea salt / KI	130	6.4	17.5	82	5.1	12.1
Vacuum salt / KIO_3	49	2.5	5.6	17	3.2	8.2
Rock salt / KIO_3	125	6.4	11.4	19	4.3	9.3

where

- ω: mean value, in mg/kg,
- r: repeatability limit, in mg/kg,
- R: reproducibility limit, in mg/kg.

8.3 Expression of results

The limit of quantitation (LOQ) – the lowest concentration of the element, which can be determined with a coefficient of variation of 10% - is given below.

Table 4: Limits of Quantitation (LOQ)

Element	Limit of quantitation (LOQ) (mg/kg of salt)
Br	5
I	10

Report the results up to 10 mg Br /kg of salt to the nearest 0.1 mg/kg and >10 mg Br or I / kg of salt to the nearest 1 mg/kg.

9. REMARKS

9.1. All vessels (glassware, polyethylene-, polypropylene- and PTFE-flasks) should be washed successively with hydrochloric acid, $c_{(HCl)} \approx 6$ mol/l and water.

9.2. Use the highest concentration of NaCl acceptable to the spectrometer and correct the calibration- and verification-solutions accordingly.

Appendix 1

Typical operation conditions for most ICP spectrometers *)

Argon flows (l/min)	
- plasma	12 – 15
- auxiliary	≈ 1.5
- nebulizer	≈ 0.7
Sample flow (ml/min)	≈ 1.5
RF-power (W)	1250**)
Integration time (sec)	
- simultaneous	≈ 10
- sequential	≈ 3

*) Check for use with high salinity solutions
**) Use 1250 W or higher if necessary

Appendix 2

Typical wavelength per element

Element	Wavelength (nm)
Br	154.065
	163.040
I	161.760
Sc	424.683
(reference element)	361.384

NOTE: Other lines with similar sensitivity and free from interferences may be used.