Sodium Chloride - Analytical Standard

Determination of Anions

High Performance Ion Chromatography (HPIC)

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1. SCOPE AND FIELD OF APPLICATION

The present EUsalt Analytical Standard describes a High Performance Ion Chromatography (HPIC) method for the determination of five anions in sodium chloride. The limit of quantitation for each anion is given in table 1:

Table 1: Limit of quantitation (LOQ) for each anion

Anion	LOQ, mg/kg of salt
F^-	15
Br^-	15
NO_3^-	15
PO_4^{3-}	35
SO_4^{2-}	35

Note: The performance of HPIC varies from instrument to instrument and the limit of quantitation may be affected by the quality of the used material (eluents, separator columns, suppressor device, pressures, flows, conductivity cells and electronic integrator).

2. REFERENCES

(1) EN ISO 10304 Determination of dissolved anions by liquid chromatography of ions.

(2) Akzo Nobel – CGS-AW F01054 (December 2001): Final Research Report: The determination of F^-, Br^-, NO_3^-, PO_4^{3-} , SO_4^{2-} in NaCl.

3. PRINCIPLE

Dissolution of the sample in water. Separation of the anions on a column using a High Performance Ion Chromatograph and a suitable eluent. Determination of the content in the sample by calculation of the peak area (or peak height) of the chromatogram.

4. REAGENTS

All reagents shall be of recognized analytical grade and the water must conform to ISO 3696, Grade 1 (ultra pure water).

Store all solutions in glass flasks except the fluoride solutions which need to be stored in PE-, PP- or PTFE-flasks. All vessels shall be washed before use with hydrochloric acid, $c_{(HCl)} \approx 6$ mol/l, and ultra pure water successively.

4.1. Sodium chloride solution, $\beta_{(NaCl)} = 100$ g/l

Dissolve 100 g of very pure NaCl (high purity grade) with ultra pure 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 LOQ's given in Table 1.

4.2. F^-, Br^-, NO_3^-, PO_4^{3-} or SO_4^{2-}, stock solutions I, $\beta_{(element)} = 1000$ mg/l Commercial standard solutions

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

4.3. F^-, Br^-, NO_3^-, PO_4^{3-} or SO_4^{2-}, mixed stock solution II, $\beta_{(element)} = 10$ mg/l

A mixed solution of these different elements at 10 mg/l is prepared as follows.

Transfer 1 ml of each stock solution (4.2.) into a 100 ml volumetric PTFE flask, make up to the mark and mix. Prepare this solution on the day of use.

4.4. Helium and nitrogen

The helium and nitrogen pressures shall be no less than 1 and 6 bar respectively to push the eluent through the column and operate the high pressure valves.

Note: Always degas and store all eluents in glass or PTFE eluent bottles pressurised with helium. Only helium can be used to purge and degas ionic eluents containing solvents, since nitrogen is soluble in some solvents present in eluents.

4.5. Eluent

Preparation of a 100-times concentrate eluent: dissolve 95.36 g of Na_2CO_3 (MW = 106.00 g/mol) in 700 ml of degassed, ultra pure water in a 1000 ml volumetric flask. Make up to the mark and mix. Filter the concentrate eluent before using with a membrane filter (0.45 µm). Dilute 10 ml of this solution to 1000 ml to make the final eluent (9 mmol Na_2CO_3/l).

5. APPARATUS

Ordinary laboratory equipment and glassware together with the following:

- Dilutor to obtain a solution at precisely the desired concentration.
- High Performance Ion Chromatograph:

1. a system injection loop, 10-50-100 µl to inject no more than 10 nanomol (100-200 mg/kg) of any of the analytes into the analytical column,
2. a constant pressure/constant flow pump,
3. a guard column placed in line prior to the analytical column to prevent sample contaminants from eluting and prolong the life of the analytical column,
4. an analytical column, suitable for the required separation with the specified eluent,
5. a conductivity detector,
6. a suppressor device,
7. an electronic integrator with peak evaluation software,
8. an automatic sampler (optional).

Note: Suitable equipment for this separation is the «IonPac AG9-HC» Guard column, the «IonPac AS9HC» analytical column (dimensions 250 x 4 mm) and the Peak Net software from DIONEX. Equipment from other suppliers can be used as well, provided its' performance is verified.

Set the ion chromatograph parameters and general operating conditions in accordance with the manufacturers manual. Typical values are given in the next table.

Table 2: Typical operating parameters of an ion chromatograph

Parameter	Unit	Specifications
Sample volume	µl	10-50-100
Eluent flow rate	ml/min	1
Suppressor technique		a. chemical (12.5-25 mM H_2SO_4), or b. electrochemical
Degassing	Bar	a. Helium, 1 bar minimum, or b. Degassing equipment, e.g. ultrasonic
Nitrogen pressure	Bar	6 minimum
Expected background conductivity	µS	10-30
Conductivity scale	µS	0-300

6. PROCEDURE

6.1. Test solutions, $\beta_{(NaCl)}$ = 2 g/l or $\beta_{(NaCl)}$ = 10 g/l.

Weigh, to the nearest 0.1 g, about 5 g of the laboratory sample. Use a dilutor to obtain a solution at 100 g/l exactly. Then, transfer:

a. 2 ml of this solution to a 100 ml volumetric flask, make up to the mark and mix to prepare the test solution at 2 g/l for the determination of F^-.

b. 10 ml of this solution in a 100 ml volumetric flask, make up to the mark and mix to prepare the test solution at 10 g/l for the determination of the anions Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}.

6.2. Calibration and verification solutions

Transfer the sodium chloride solution (4.1.) and the volumes of mixed stock solution II (4.3.) to a series of 100 ml volumetric PTFE- or Polycarbonate- flasks as defined in the tables below. Make up to the mark and mix.

Table 3: F- calibration solutions

Calibration solution N°	NaCl solution (4.1.) (ml)	Mixed stock solution (4.3.) (ml)	NaCl concentration (g/l)	Concentration Calibration solution (mg anion /kg NaCl)
1	2	0.4	2	20
2	2	0.8	2	40
3	2	1	2	50
4	2	1.5	2	75
5	2	2	2	100
6	2	3	2	150
7	2	4	2	200
8	2	5	2	250
9	2	6	2	300

Table 4:

Br^-, NO_3^-, PO_4^{3-} or SO_4^{2-} calibration solutions

Calibration solution N°	NaCl solution (4.1.) (ml)	Mixed solution (4.3.) (ml)	NaCl concentration (g/l)	Concentration Calibration solution (mg anion/kg NaCl)
10*)	10	2.5	10	25
11	10	5	10	50
12	10	7.5	10	75
13	10	10	10	100
14	10	15	10	150
15	10	20	10	200
16	10	25	10	250
17	10	30	10	300
*) below LOQ for PO_4^{3-} and SO_4^{2-}				

Note: Fewer calibration solutions are possible (minimum 3) provided the calibration curve is linear and the concentration range is known.

6.3. Determination

6.3.1. Preparation of the apparatus

Set all instrument parameters of the Ion Chromatograph (5.) in accordance with the operating manual of the manufacturer. Equilibrate the column (flows/pressures) with eluent before starting the analyses.

6.3.2. Chromatographic measurements

Calibrate the Ion Chromatograph with the calibration solutions (6.2.). Control and check the linearity of the calibration curve given automatically by the peak evaluation software ($r > 0.995$).

Continue the measurements in the following order:

- ultra pure water (4.).
- calibration solution in the middle of the scale.
- calibration solution in the middle of the scale.
- test solution N°1 (6.1.).
- test solution N°2 (6.1.).
- test solution N°3 (6.1.).
- test solution N°…….
- calibration solution in the middle of the scale.
- ultra pure water (4.) to rinse the instrument.

7. EXPRESSION OF RESULTS

7.1. Evaluation

Note: Samples of unknown composition should be tested for the presence of matrix effects by the analyte addition technique.

7.2. Calculation

The peak evaluation software controls the chromatographs, prepares automatically the identification of the samples, registers and reprocesses the data, and gives the analyses results directly in milligrams per kilogram of sodium chloride.

The results are expressed to the nearest 0.5 mg/kg.

7.3. Repeatability and reproducibility

Analyses carried out on three samples, containing the five anions in different concentrations, by 6 laboratories (5 laboratories retained after eliminating outliers), gave the following statistical results, each laboratory performed three replicates under repeatability conditions.

Table 5: Results of the interlaboratory study.
(For details see (2))

Blue shaded values are below the LOQ

Sample	ω	s_r	s_R	r	R
Fluoride					
1	24	1.1	3.2	3	9
2	104	1.4	3.2	4	9
3	254	2.1	3.2	6	9
Bromide					
1	10	1.1	3.9	3	11
2	50	1.4	4.6	4	13
3	254	1.8	5.7	5	16
Nitrate					
1	12	1.4	1.8	4	5
2	52	1.8	2.1	5	6
3	259	1.8	6.0	5	17
Phosphate					
1	30	3.2	5.3	9	15
2	103	3.5	4.6	10	13
3	258	4.2	4.6	12	13
Sulphate					
1	27	5.7	5.7	10	16
2	100	2.8	5.7	8	16
3	259	2.5	16.3	7	46

where

- ω is the content of anion, in mg/kg,
- s_r is the repeatability standard deviation, in mg/kg,
- s_R is the reproducibility standard deviation, in mg/kg,
- r is repeatability limit, in mg/kg,
- R is reproducibility limit, in mg/kg.

7.4 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 calculated based on the repeatability standard deviation sr of each element near the estimated LOQ and is given in Table 1.