



Sodium Chloride - Analytical Standard



Determination of Fluorides Potentiometric method

EuSalt/AS 017-2005

Former numbering: ESPA/CN-E-117-1999 Rev. 1

1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes electrometric methods using an ion-selective electrode for the determination of water-soluble fluorides.

The methods are applicable to products with fluoride contents greater than 10 mg per kilogram of salt.

The first method is used for products without additives or products containing anticaking agents like potassium, sodium- or calcium-ferrocyanide which do not form complexes with fluoride.

The second method may be used with salts having a total calcium and magnesium content less than 0.6 mol/kg of salt, added as calcium carbonate, tricalcium phosphate, magnesium carbonate, magnesium hydroxide or magnesium oxide.

2. PRINCIPLE

Dissolution of the sample in water (procedure I) or in diluted hydrochloric acid (procedure II).

Release of fluoride with a buffer solution containing a decomplexing agent (CDTA).

Potentiometric measurement of the fluoride content with an ion-selective electrode combined with an Ag/AgCl reference electrode.

3. REAGENTS

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

3.1. Hydrochloric acid, $c_{(\text{HCl})} = 1 \text{ mol/l}$

3.2. Sodium hydroxide solution, $c_{(\text{NaOH})} \approx 8 \text{ mol/l}$

3.3. TISAB buffer solution I

(Total Ionic Strength Adjustment Buffer solution)

Dissolve 58 g of sodium chloride in about 500 ml of water. Add 57 ml of glacial acetic acid, $\rho \approx 1.05 \text{ g/ml}$, 100 % (m/m) solution, and 5 g of CDTA [trans-1,2-diaminocyclohexane-NNN'N'-tetra-acetic acid, $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_8 \cdot \text{H}_2\text{O}$]. Add sodium hydroxide solution (3.2.) to obtain a pH of 5.5 after cooling at room temperature. Make up with water to 1000 ml in a volumetric flask and mix.

3.4. TISAB buffer solution II

(Total Ionic Strength Adjustment Buffer solution)

Dissolve 58 g of sodium chloride in about 400 ml of water. Add 114 ml of glacial acetic acid, $\rho \approx 1.05 \text{ g/ml}$, 100 % (m/m) solution, and 50 g of CDTA [trans-1,2-diaminocyclohexane-NNN'N'-tetra-acetic acid, $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_8 \cdot \text{H}_2\text{O}$]. Add sodium hydroxide solution (3.2.) ($\approx 250 \text{ ml}$) to obtain a pH of 5.5 after cooling at room temperature. Make up with water to 1000 ml in a volumetric flask and mix.

Note: Complete dissolution of CDTA only occurs after addition of sodium hydroxide.

3.5. Fluoride, stock solution, $\beta_{(\text{F})} = 1000 \text{ mg/l}$,

commercial solution or to be prepared as follows.

Dissolve 2.210 g of sodium fluoride (NaF) or 3.058 g of potassium fluoride (KF) with water in a 1000 ml polyethylene volumetric flask, make up to the mark and mix. This solution may be kept indefinitely.

3.6. Sodium chloride, fluoride-free.

4. APPARATUS

Usual laboratory equipment and:

4.1. Polyethylene (PE) or polypropylene (PP) beakers
(150 or 400 ml)

4.2. Fluoride ion-selective electrode

4.3. Ag/AgCl reference electrode

4.4. Ion-meter (or pH-meter) allowing measurements of 0.1 mV (0.001 pH units)

4.5. Magnetic stirrer

4.6. Stopwatch

5. SAMPLING AND SAMPLES

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

6. PROCEDURE I (For samples without products forming complexes with fluoride)

6.1. Test portion

Weigh, to the nearest 0.1 g, about 50.0 g of the test sample.

6.2. Calibration

6.2.1. Calibration solutions

These preparations are used for samples containing fluorides in the range 100 to 300 mg F/ kg.

Add 50.0 g of sodium chloride (3.6.) into a series of five 500 ml volumetric flasks. Dissolve with water and transfer the volumes of fluoride stock solution (3.5.) indicated in the next table. Make up to the mark and mix.

Store immediately these solutions into polyethylene flasks where they may be kept indefinitely.

Calibration solution No.	Fluoride, stock solution, ml	Corresponding concentration of fluoride, mg/kg of salt
1	5.0	100
2	7.5	150
3	10.0	200
4	12.5	250
5	15.0	300

6.2.2. Electrometric measurements

Proceed with the five solutions prepared in (6.2.1.) in the following way.

Transfer 50.0 ml of calibration solution and 50.0 ml of TISAB buffer solution I (3.3.) into a dry plastic beaker (4.1.).

Immerse the two electrodes (4.2.), (4.3.) in the solution and read the potential after exactly 3 minutes. Stir slowly with a magnetic stirrer during the determination.

Note: This solution may not be reused for a further measurement.

6.2.3. Calibration curve

Plot a graph on semi-logarithm paper showing the concentrations of fluoride (F), in milligrams F per kilogram of salt on the logarithm axis and the corresponding potential values in mV on the linear axis.

6.3. Determination

Transfer the test portion (6.1.) and water into a 500 ml volumetric flask, dissolve in water and dilute to the mark and mix. Transfer immediately 50.0 ml of this solution and 50.0 ml of the TISAB buffer solution I (3.3.) into a dry plastic beaker (4.1.).

Immerse the two electrodes (4.2.), (4.3.) in the solution and read the potential after exactly 3 minutes. Stir slowly with a magnetic stirrer during the determination.

7. PROCEDURE II [For samples with additives (not more than 0.6 mol/kg salt) forming complexes with fluoride]

7.1. Test portion

Weigh, to the nearest 0.1 g, about 50.0 g of the test sample.

7.2. Calibration

7.2.1. Calibration solutions

These preparations are used for samples containing fluorides in the range 100 to 300 mg F/ kg.

Add 50.0 g of sodium chloride (3.6.) into a series of five 500 ml volumetric flasks. Dissolve with water, add 100 ml of hydrochloric acid (3.1.) and transfer the volumes of fluoride stock solution (3.5.) indicated in the next table. Make up to the mark and mix.

Store immediately these solutions into polyethylene flasks where they may be kept indefinitely.

Calibration solution No.	Fluoride, stock solution, ml	Corresponding concentration of fluoride, mg/kg of salt
1	5.0	100
2	7.5	150
3	10.0	200
4	12.5	250
5	15.0	300

7.2.2. Electrometric measurements

Proceed with the five solutions prepared in (7.2.1.) in the following way.

Transfer 50.0 ml of calibration solution and 50.0 ml of TISAB buffer solution II (3.4.) into a dry 150 ml plastic beaker (4.1.).

Immerse the two electrodes (4.2.), (4.3.) in the solution and read the potential after exactly 3 minutes. Stir slowly with a magnetic stirrer during the determination.

Note: This solution may not be reused for a further measurement.

7.2.3. Calibration curve

Plot a graph on semi-logarithm paper showing the concentrations of fluoride (F), in milligrams F per kilogram of salt on the logarithm axis and the corresponding potential values in mV on the linear axis.

7.3. Determination

Transfer the test portion (7.1.), 200 ml of water and 100 ml of hydrochloric acid (3.1.) into a 400 ml beaker. Mix until complete dissolution, transfer into a 500 ml volumetric flask, make up to the mark and mix. Transfer immediately 50.0 ml of this solution and 50.0 ml of the TISAB buffer solution II into a dry 150 ml plastic beaker (4.1.).

Immerse the two electrodes (4.2.), (4.3.) in the solution and read the potential after exactly 3 minutes. Stir slowly with a magnetic stirrer during the determination.

8. EXPRESSION OF RESULTS

8.1. Evaluation

The fluoride content of the sample, $\omega_{(F)}$, is given directly from the calibration curve in mg F/kg of salt. Round off to the nearest mg/kg.

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 three analyses per sample:

	Vacuum salt (without additives)	Brine 100 g/l	Sea salt (with additives)
Number of laboratories	13	13	13
Results, mg Fluoride/ kg salt			
Mean	296	149	243
Standard deviation for:			
- repeatability (s_r)	4.2	1.8	4.6
- reproducibility (s_R)	6.0	3.2	10.6
Repeatability limit (r)	12	5	13
Reproducibility limit (R)	17	9	30

Reference: Akzo Nobel Final research report F99004 (May 1999): The determination of fluoride in NaCl.

9. REMARKS

- 9.1.** As stated in section 1, the method is applicable to products of fluoride contents greater than 10 mg/kg. However, the calibration solutions (6.2.1.) and (7.2.1.) cover the range from 100 mg/kg to 300 mg/kg. For fluoride contents outside this range the calibration solutions and/or the test portion must be adapted.
- 9.2.** Ion meters, allowing the direct reading of mg F/kg salt may be used instead of the graphical determination of the fluoride content, provided the ion meter can be calibrated with 5 calibration solutions.
- 9.3.** During the electrometric measurement air bubbles may interfere. To remove air bubbles, put the beaker into an ultrasonic bath prior to measurement.
- 9.4.** The acceptable concentration of additives (0.6 mol/kg salt) mentioned in the procedure II (see 7.) correspond to:
- Magnesium oxide MgO 24 g/kg of salt
 - Magnesium hydroxide Mg(OH)₂ 35 g/kg of salt
 - Magnesium carbonate MgCO₃ 51 g/kg of salt
 - Calcium carbonate Ca CO₃ 60 g/kg of salt
 - Calcium triphosphate Ca₃(PO₄)₂ 243 g/kg of salt