eusalt
EUROPEAN SALT PRODUCERS' ASSOCIATION

Sodium Chloride – Analytical Standard

Determination of Fluorides

SFDANS Photometric Method

EUsalt/AS 010-2005
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1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a photometric method for the determination of fluorides with SPADNS [1,8-dihydroxy-2-(4-sulfophenylazo)nap hthalene-3,6-disulfonic acid trisodium salt] in sodium chloride.

The method is applicable to products of fluoride content (F) between 40 and 280 mg per kilogram of salt.

The method may be used with iodized salts and with products containing ferrocyanides, acid soluble additives like calcium carbonate, magnesium carbonate, magnesium hydroxide or magnesium oxide and non acid soluble additives like silica, calcium or magnesium silicate or sodium alumino silicate. It is not valid for salt treated with tricalcium phosphate.

2. PRINCIPLE

SPADNS reacts with zirconium ions forming a coloured complex.

In aqueous solution, zirconium ions are also complexed by fluoride ions. The intensity of the coloured complex reduces with increased fluoride concentration and this can be measured photometrically in a certain concentration range.

3. REAGENTS

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

3.1. Sodium chloride, fluoride-free

3.2. Hydrochloric acid, $\rho_{(HCl)} \approx 1.19$ g/ml, 37% (m/m)

3.3. SPADNS solution,

1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6disulfonic acid, trisodium salt, $C_{16}H_9N_2Na_3O_{11}S_3$.

Dissolve 1.049 g of SPADNS. $3H_2O$ or 0.958 g of anhydrous SPADNS in a few ml of water. Make up to 500 ml in a one-mark volumetric flask and mix.

3.4. Zirconium solution

Dissolve 0.133 g of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, in 25 ml of water, add 350 ml hydrochloric acid (3.2.) dilute with water in a 500 ml volumetric flask and mix.

3.5. Reagent solution

Mix equal volumes of SPADNS solution (3.3.) and zirconium solution (3.4.).

Prepare this solution on the day of use.

3.6. Compensation solution

Dilute 10 ml of SPADNS solution (3.3.) with 100 ml of water and add 10 ml of a diluted hydrochloric acid, containing 7.0 ml of hydrochloric acid (3.2.).

Prepare this solution on the day of use.

Note: Use this solution to adjust the zero of the spectrophotometer (4.1.) or photocolorimeter (4.2.).

3.7. Fluoride, stock solution I, $\beta_{(F)}$ = 1000 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 with water in a 1000 ml polyethylene volumetric flask, make up to the mark and mix. This solution may be kept indefinitely.

3.8. Fluoride stock solution II, $\beta_{(F)}$ = 200 mg/l

Transfer 200 ml of fluoride stock solution I (3.7.) into a 1000 ml polyethylene volumetric flask, make up to the mark and mix. This solution may be kept indefinitely.

4. APPARATUS

Usual laboratory equipment and:

4.1. Spectrophotometer or

4.2. Photocolorimeter fitted with a filter ensuring maximum transmission between 550 and 580 nm.

Note: Specify the type of apparatus used (spectrophotometer or photocolorimeter), the path length and the wavelength (or type of filter).

4.3. Water-bath set at 24 ± 1 oC

4.4. 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

6.1. Test portion

Weigh, to the nearest 0.01 g, about 10.0 g of the test sample.

6.2. Test solution

Transfer the test portion (6.1.) into a 1000 ml volumetric flask and dissolve with water. Make up to volume and mix.

Note: Proceed as follows with samples containing acid insoluble additives.

Transfer the test portion (6.1.) into a 1000 ml volumetric flask containing 50 ml of hydrochloric acid 1 mol/l. Agitate for a few minutes, make up to the mark with water and mix. If any insoluble material remains in the solution, proceed with a filtration through a dry 0.45 µm membrane and collect the filtrate after elimination of the first few millilitres.

6.3. Calibration

6.3.1. Calibration solutions

These preparations are used for photometric measurement in cuvettes of 2 cm optical path length.

Transfer the volumes of fluoride stock solution II (3.8.) indicated in the next table into a series of eight 1000 ml volumetric flasks. Add 10.0 g of sodium chloride (3.1.) dissolve with water, make up to the mark and mix.

These solutions may be kept indefinitely if transferred immediately into polyethylene flasks.

Calibration solution No.	Fluoride, stock solutions II, ml	Corresponding masses of fluoride, mg
1(*)	0	0
2	2.0	0.4
3	4.0	0.8
4	6.0	1.2
5	8.0	1.6
6	10.0	2.0
7	12.0	2.4
8	14.0	2.8
(*) zero calibation solution		

6.3.2. Colour development

Proceed with the eight solutions prepared in (6.3.1.) in the following way.

Transfer 25.0 ml of calibration solution and 25.0 ml of water in a dry 100 ml conical flask.

Put the conical flask into the water-bath (4.3.) to obtain a temperature of 24 ± 1°C.

Add 10.0 ml of reagent solution (3.5.), mix and reintroduce into the water-bath for at least 5 minutes to maintain at a well defined temperature before proceeding with the photometric measurements.

6.3.3. Photometric measurements

Adjust the apparatus to zero absorbance against the compensation solution (3.6.) and carry out the photometric measurements using a spectrophotometer (4.1.) set up at the maximum of absorption (around 570 nm) or a photocolorimeter (4.3.) fitted with the appropriate filter.

Record the absorbance of each solution after exactly 6 or 7 minutes (use a stopwatch) after the addition of the reagent solution (3.5.).

Note: Be sure that the same time is used for all samples. To fullfil this point it is necessary to carry out the analysis according to a fixed time-table.

6.3.4. Calibration curve

Plot a graph showing the masses of fluoride (F), in milligrams, added to the calibration solutions on the abscissa and the corresponding absorbances on the ordinate.

6.4. Determination

6.4.1. Colour development

Transfer 25.0 ml of test solution (6.2.) and 25.0 ml of water into a dry 100 ml conical flask and continue as described in paragraph (6.3.2) following exactly the time and temperature used for the calibration solutions.

6.4.2. Photometric measurements

Carry out the photometric measurement of the solution obtained in (6.4.1.) according to the instructions given in paragraph (6.3.3.).

7. EXPRESSION OF RESULTS

7.1. Evaluation

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

$$\omega_{(F)} = 1000 \times \frac{m_1}{m}$$

where

- $\omega_{(F)}$ is the fluoride content, in milligrams per kilogram of salt,
- m is the mass, in grams, of the test portion (6.1.),
- m_1 is the mass of fluoride, in milligrams analysed in the test solution (6.2.).

7.2. Repeatability and reproducibility

Analyses, carried out on four samples by 12 laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing three analyses per sample:

Sample	Origin	$\omega_{(F}$	k	p	n	s_r	s_R
1	Switzerland	96	12	12	3	3.6	11
2	Switzerland	157	12	12	3	2.5	10
3	France	254	12	11	3	9.6	26
4	Austria	247	12	12	3	7.5	32

where

- $\omega_{(F)}$ is the total fluoride content, in mg of F/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,
- s_r is the repeatability standard deviation, in mg of F/kg,
- s_R is the reproducibility standard deviation, in mg of F/kg.

Reference: W.J.M. Emaus, The determination of fluoride in sodium chloride, Akzo Report RGA-H R96.016, Task No. 1114, 13.03.1996.

7.3. Limit of quantitation

The limit of quantitation (40 mg of F/kg) has been estimated with the values obtained for sample 1 and based on the first order calibration line.

8. REMARKS

8.1. Carry out the determination without a break following exactly the times and temperature.

8.2. As the quality of SPADNS may vary, a new calibration curve has to be established for each new solution (3.3.).

8.3. For fluoride contents greater than 280 mg per kg of salt, the volume (25.0 ml) of test solution (6.2.) transferred into the 100 ml conical flask (see 6.4.1.) has to be reduced and the salt level must be corrected with sodium chloride.

The formula for calculation (7.1.) must be modified accordingly.