Application Bulletin 82/5 e

Determination of fluoride with an ion-selective electrode

Industry sector

Chemical; pharmaceuticals; food & beverage; personal care & cosmetics

Keywords

Fluoride; F-ISE; dF-ISE; combined ion-selective electrode; standard addition; direct measurement; STDADD; mouth rinse; toothpaste; table salt; 6.00500.300; 6.00500.600; S01; S010; S04; S040; S07; S070; S12; S122

Summary

This bulletin describes several fluoride determinations in different matrices using the combined fluoride-selective electrode with an integrated Pt1000 temperature sensor. The ion-selective crystal membrane of the electrode is made of a lanthanum fluoride. The electrode is combined, i.e., it no longer requires an additional reference electrode. The combined fluoride-selective electrode is available as either a digital (6.00500.300) or an analog (6.00500.600) version.

In the first section of this bulletin, some general tips are given for the handling of the electrode and the determination of fluoride. In the second part, practical examples are used to demonstrate how determinations can be performed using either direct measurement or the standard addition technique. Fluoride was determined in several matrices: table salt, mouthwash, and toothpaste.

Instruments and accessories

- Ion Meter or Titrator with the modes MEAS CONC and/or STDADD
- Stirrer
- Buret

Electrodes

Combined dF-ISE with Pt1000	6.00500.300
Combined F-ISE with Pt1000	6.00500.600

General tips

For optimal measurement results, the following points are essential to follow:

- The sensing part of the fluoride electrode is composed of a lanthanum fluoride crystal. Avoid any fat or oil deposition or scratching of the membrane—meaning it should neither be touched with bare hands nor cleaned with abrasive materials. It is also sensitive to mechanical shocks.
- If the electrode does not respond properly after a long period of use (e.g., slow response times even at high fluoride concentrations), the sensor may be contaminated and should be cleaned with a liquid detergent or polished carefully with non-abrasive toothpaste. The polishing set for ISE (aluminum oxide) must not be used because the aluminum interacts with the electrode crystal.
- The electrode should only be used in aqueous solutions.
- Before determining fluoride concentrations below 1 mg/L, the electrode should be preconditioned in deionized water for approximately 30 min. Please note, near the lower detection limit of an ISE, longer response times are generally observed.
- Clean the electrode using the spray rinse and/or dip rinse after each measurement with deion. water.
- When conducting a series of measurements, the electrode should be conditioned for at least two minutes in TISAB (Total Ionic Strength Adjustment Buffer) solution before each new measurement, otherwise a cumulative error can arise (increasing results at identical conditions).
- The measured values depend on the pH value and the total ionic strength of the solution. As the ionic strength decreases, the activity coefficient increases. At pH values below 5, HF and HF_2^- are formed. Both compounds are not detected. At pH values above 8, the electrode becomes cross-sensitive to OH^- ions. The addition of TISAB solution before the measurement keeps the pH value and the ionic strength constant.

- Because of the possible HF formation, it is generally recommended to work with plastic beakers.
- Cations such as Ca^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, etc. bind to fluoride, making it inaccessible for measurement by the fluoride ISE.

Choice of procedure

The choice of the procedure depends on the sample matrix, the number of samples to be analyzed, and the concentration range of the samples.

- For samples with a complex or unknown matrix composition, standard addition is the procedure of choice.
- A direct measurement is recommended for samples with an unproblematic sample matrix, and for large sample series or online measurements.
- For low-concentration measurements, it is recommended to either use direct measurement after calibration or spike the sample to a higher fluoride content. The reason for this is that the sensor may be at its limit of detection and outside of the linear range, giving results for the standard addition that are too high.

Sample preparation and parameters

The sample preparation and the parameters are mentioned in the section *Practical examples* or in the *Appendix*, respectively.

Direct measurement

The direct measurement is recommended for unproblematic samples and in the case of low-level fluoride measurements (mg/L or µg/L range).

When using direct measurement, the following points must be considered:

- In general, standard solutions must have the same ionic background as the sample solutions. TISAB/water (1:1) should be used for such measurements.
- The addition of TISAB solution before the measurement keeps the pH value and the ionic strength constant. The TISAB solution has the additional effect of binding interfering cations and thereby releasing any complexed fluoride.

Standard addition (STDADD)

The standard addition is recommended for undefined or complex sample matrices.

There are two types of standard addition in OMNIS:

- STDADD ISE dos
- STDADD ISE auto

The quickest and recommended method is the automatic standard addition (mode: « STDADD ISE auto »). For exact results, the potential difference ΔU should be at least 12 mV per standard addition and at least three standard additions should be performed (i.e., total ΔU at least 36 mV). If exactly defined volumes of the standard additions are required but maximum ease of operation is also desirable, the mode « STDADD ISE dos » is recommended. There the individual standard addition volumes can be defined (see manual of the device in use or the online help found in the software).

The calculation of the result is automatically carried out by OMNIS applying an iteration procedure.

When using standard addition, the following points must be considered:

- Stirring is necessary during additions. Additions without continuous stirring lead to false results.
- The addition of TISAB solution before the measurement keeps the pH value and the ionic strength constant. The TISAB solution has the additional effect of binding interfering cations and thereby releasing complexed fluoride.
- If the total volume added during standard addition is higher than 10% of the initial solution, the standard should be dissolved in TISAB to prevent a dilution effect of the TISAB-buffer capacity. Alternatively, try to reduce the sample size or use a stronger standard solution. If the added volume is too large, there is a risk of dilution error and the linearity can no longer be guaranteed, resulting in incorrect data.
- To ensure accurate evaluation of the standard addition, the following standard concentrations (c_{std}) for the different buret volumes (V_{buret}) as a function of the sample concentration (c_{smpl}) according to Table 1 are recommended. Thereby any sample dilution should be considered (e.g., dilution with TISAB).

Volume buret in mL	Ratio [c_{std} : c_{smpl}]
5	40 : 1
10	20 : 1
20	10 : 1
50	5 : 1

Table 1. Ratio of the standard concentration and sample concentration, dependent on the buret volume.

Example factor determination

Sample concentration, c_{smpl} :	100 mg/L
Sample size :	10 mL
Addition of TISAB :	20 mL
Addition of deionized water :	10 mL
Auxiliary solution volume :	30 mL
Total volume :	40 mL
Buret volume, V_{buret} :	10 mL
Factor from Table 1 (c_{std} : c_{smpl}) :	20

Considering the dilution with TISAB and deionized water, the initial sample concentration is 25 mg/L. Therefore, the optimal recommended concentration of the standard is: 25 mg/L × 20 = 500 mg/L.

Comments

- A historical analysis technique is the titration by lanthanum nitrate, but lanthanum forms complexes with buffers and ingredients of the TISAB and samples. This causes consumption of titrant to be too high and corresponding erroneous high results. Therefore, the titration of fluoride with lanthanum nitrate is not recommended.

Practical examples

Reagents

The following reagents and recommended concentrations are used to prepare the fluoride standard and TISAB IV solution.

- Sodium fluoride, NaF, ≥ 99.0%
- Sodium chloride, NaCl, fluoride-free!, ≥ 99.5%
- Glacial acetic acid, CH_3COOH, ≥ 99.8%
- Sodium hydroxide, c(NaOH) = 8 mol/L
- Complexon IV, trans-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid monohydrate, $C_{14}H_{22}N_2O_8 \cdot H_2O$, ≥ 98.0%

Solutions

- All solutions must be stored in plastic containers. If sample solutions are stored in glass, then the fluoride content of such containers decreases with time.
- The solutions (standard, TISAB, sample solution) should not be stored longer than three months. Poor quality solutions can result in a low electrode slope.

Fluoride standard solution	$\beta(F^-) = 1000$ mg/L 2.210 g NaF is weighed into a 1 L volumetric flask. 500 mL deionized water is added and the sodium fluoride is dissolved while swirling. Then, the flask is filled up to the mark with deionized water.
TISAB IV	58 g NaCl is dissolved in approx. 500 mL deionized water. 5 g complexon IV is added and dissolved by dropwise addition of c(NaOH) = 8 mol/L. 57 mL glacial acetic acid is added, and the pH of the mixture is adjusted to 5.5 with the abovementioned NaOH solution. Finally, it is made up to 1 L with deionized water.
Sodium chloride solution	β(NaCl) = 200 g/L 200 g fluoride-free NaCl is weighed into a 1 L volumetric flask. 750 mL deionized water is added and the sodium chloride is dissolved while swirling. Then, the flask is filled up to the mark with deionized water.
Further TISAB solutions	For other applications the required TISAB is mentioned separately.

Fluoride in table salt by means of direct measurement

Sample

- Table salt, fluoride content of 0.025% (250 mg/kg)

Solutions

- Fluoride standard solution, $\beta(F^-) = 1000$ mg/L
- TISAB IV
- Sodium chloride solution, β(NaCl) = 200 g/L

Sample preparation

20 g of table salt is weighed into a 100 mL volumetric flask and dissolved in 50 mL deionized water. Then, the flask is filled up to the mark with deionized water.

Standard preparation

It is highly recommended to prepare all standard solutions directly in-situ using Metrohm devices with the fluoride standard solution $\beta(F^-) = 1000$ mg/L. The following table shows the preparation for each 40 mL—ready to measure—standard solution.

To obtain the same ionic background as for the measurement itself, it is important to prepare all standard solutions with β(NaCl) = 200 g/L.

Standard	1	2	3	4
Addition of $\beta(F^-) = 1000$ mg/L	1 mL	2 mL	3 mL	4 mL
Addition of deionized water	9 mL	8 mL	7 mL	6 mL
Addition of β(NaCl) = 200 g/L	20 mL			
Addition of TISAB IV	10 mL			
Final volume	40 mL			
Concentration in mg/L	25	50	75	100

Analysis

Calibration

The prepared—ready to measure—standard solutions (1 to 4) are stirred, and the potential of each standard is measured. In between each measurement, the electrode is rinsed well with deionized water and then conditioned in TISAB IV/deionized water (1:1) for two minutes prior to measuring the next standard.

Sample

To 20 mL of sample solution, 10 mL of TISAB IV and 10 mL deionized water are added and the potential is measured. In between each measurement, the electrode is rinsed well with deionized water and then conditioned in TISAB IV/deionized water (1:1) for two minutes before measuring the next sample. The dilution factor of the sample must be considered for the result calculation.

Parameters

Calibration

Mode	CAL Conc
Stirring rate	8
Calibration standards	4 (25, 50, 75, and 100 mg/L)
Signal drift	0.5 mV/min
Min. waiting time	30 s
Max. waiting time	215 s

Sample

Mode	MEAS Conc
Stirring rate	8
Measuring parameters	Drift-controlled measurement
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Calculations

Fluoride calibration

The calibration is automatically calculated by OMNIS after the « CAL CONC » command is done. The calibration data can be found in the sample list under the calibration curves.

The « CAL WRITE » command offers an additional option of writing the calibration data to the electrode directly.

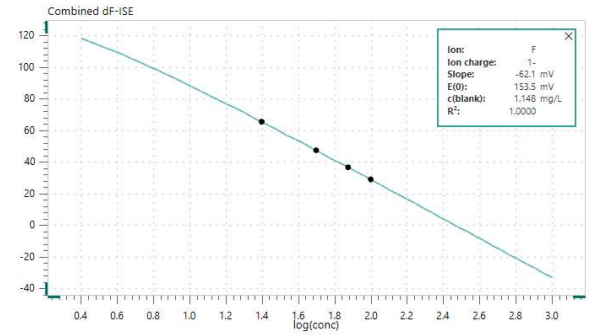
Fluoride content

$$F^- = \frac{\text{MEAS Conc}_{\text{Final}} \times d_f}{m_s \times 10}$$

F^-:	Fluoride content in %
$\text{MEAS Conc}_{\text{Final}}$:	Final measured value of the « MEAS CONC » command in mg/L
d_f:	Dilution factor of the sample
m_s:	Sample size of sample preparation in g
10:	Conversion factor for %

Example

Calibration



Subsample name	Concentration / mg/L	Potential – End value / mV	Temperature / °C
Fluoride standard solution	25.000	65.5	24.5
Fluoride standard solution	50.000	47.4	24.5
Fluoride standard solution	75.000	36.6	24.5
Fluoride standard solution	100.000	29.0	24.6

Figure 1. Calibration curve of four standard solutions with 25 mg/L, 50 mg/L, 75 mg/L, and 100 mg/L fluoride.

Slope in mV	E(0) in mV	c(blank) in mg/L	R^2	Variance
-62.1	153.5	1.148	1.000	0.000

Comments

It is necessary to use a sodium chloride solution for the calibration to obtain the same ionic background for the calibration and sample measurements. If the sample is diluted with deionized water instead of sodium chloride solution, the measured values are too low.

The conversion factor in the calculation depends on the unit selected for the sample concentration. In this case, mg/L was chosen as the unit for the concentration, resulting in a factor of 10.

Fluoride in table salt with automatic standard addition

Sample

- Table salt, fluoride content of 0.025% (250 mg/kg)

Solutions

- Fluoride standard solution, $\beta(F^-) = 1000$ mg/L
- TISAB IV

Sample preparation

20 g of table salt is weighed into a 100 mL volumetric flask and dissolved in 50 mL deionized water. Then, the flask is filled up to the mark with deionized water.

Analysis

Sample

To 20 mL of sample solution 10 mL of TISAB IV and 10 mL deionized water are added, and the standard addition is carried out with the fluoride standard solution. After measuring the concentration for the last increment, the electrode is rinsed well with deionized water and then conditioned in TISAB IV/deionized water (1:1) for two minutes before the next sample is measured.

Parameters

Sample

Mode	STDADD ISE auto
Stirring rate	8
Auxiliary solution volume	Total volume of TISAB IV and deionized water
Number of additions	3
Delta U	20 mV
Dosing rate	Fast
Stop volume	Buret volume
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Calculations

Fluoride linear regression

The linear regression is automatically done/executed by OMNIS after the « STDADD ISE auto » command is finished.

The data can be found in the sample list under calibration curves.

Fluoride content

$$F^- = \frac{\text{Sample Conc}_{\text{Result}}}{m_s \times 10}$$

F^-: Fluoride content in %

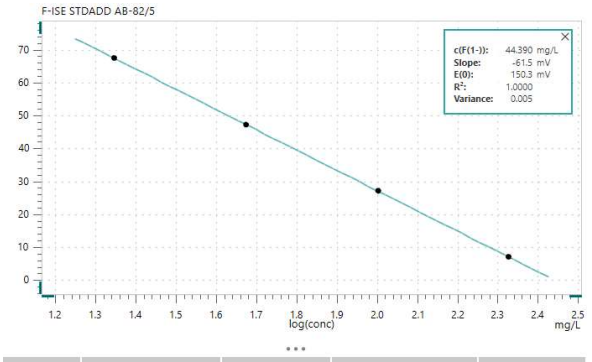
$\text{Sample Conc}_{\text{Result}}$: Command variable « SampleConcentration.Result."STDADD ISE auto" » in mg/L

m_s: Sample size of sample preparation in g

10: Conversion factor for %

Example

Sample



	Volume increment / mL	Potential / mV	Potential difference / mV	Temperature / °C
Sample		67.5		25.4
Increment 1	1.052	47.2	-20.3	25.4
Increment 2	2.440	27.1	-20.1	25.4
Increment 3	6.171	7.1	-20.1	25.6

Figure 2. Standard addition of table salt solution with three increments made with $\beta(F^-) = 1000$ mg/L.

Slope in mV	E(0) in mV	R^2	Variance
-62.5	150.3	1.000	0.005

Comments

The conversion factor in the calculation depends on the unit selected for the sample concentration. In this case, mg/L was chosen as the unit for the concentration, resulting in a factor of 10.

Fluoride in mouthwash with automatic standard addition

Sample

- Mouthwash, fluoride content of 250 mg/L

Solutions

- Fluoride standard solution, $\beta(F^-) = 1000$ mg/L
- TISAB IV

Sample preparation

No sample preparation is required.

Analysis

Sample

To 2 mL of sample solution 20 mL of TISAB IV and 20 mL deionized water are added, and the standard addition is carried out with the fluoride standard solution. In between each measurement, the electrode is rinsed well with deionized water and then conditioned in TISAB IV/deionized water (1:1) for two minutes before the next standard is measured.

Parameters

Sample

Mode	STDADD ISE auto
Stirring rate	8
Auxiliary solution volume	Total volume of TISAB IV and deionized water
Number of additions	3
Delta U	20 mV
Dosing rate	Fast
Stop volume	Buret volume
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Calculations

Fluoride linear regression

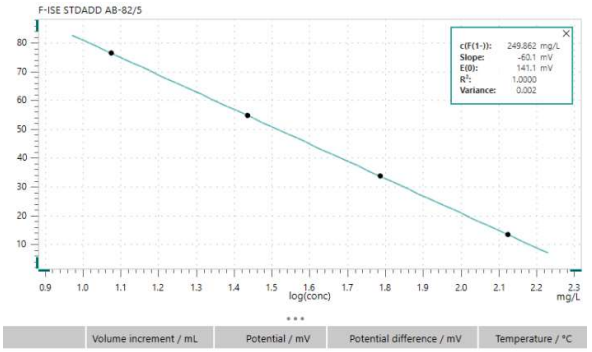
The linear regression is automatically done/executed by OMNIS after the « STDADD ISE auto » command is finished. The data can be found in the sample list under calibration curves.

Fluoride content

The fluoride content can be displayed by OMNIS with the command variable « SampleConcentration.Result."STDADD ISE auto" ».

Example

Sample



	Volume increment / mL	Potential / mV	Potential difference / mV	Temperature / °C
Sample		76.5		25.2
Increment 1	0.665	54.7	-21.7	25.2
Increment 2	1.542	33.7	-21.0	25.3
Increment 3	3.671	13.4	-20.4	25.4

Figure 3. Standard addition of mouthwash with three increments made with $\beta(F^-) = 1000$ mg/L.

Slope in mV	E(0) in mV	R^2	Variance
-60.1	141.1	1.000	0.002

Fluoride in toothpaste with automatic standard addition

Sample

- Toothpaste, fluoride content of 1450 mg/kg

Solutions

- Fluoride standard solution, $\beta(F^-)$ = 1000 mg/L
- TISAB IV
- Hydrochloric acid, HCl conc., ≥ 37%

Sample preparation

There are different fluorochemical compounds present in toothpaste depending on the manufacturer. For the sample preparation there must be a differentiation between fluoride which is ionically bound and fluoride which is covalently bound in these samples.

Examples for ionically bound fluoride:

- Sodium fluoride, NaF
- Olaflur, $C_{27}H_{60}F_2N_2O_3$

If these compounds are present in dissolved form, the fluoride is freely available and can be directly detected as F^-.

Example for covalently bound fluoride:

- Sodium monofluorophosphate, Na_2PO_3F

If this compound is present in dissolved form, the fluoride is still bound and cannot be (completely) directly detected as F^-.

Sample containing ionically bound fluoride

5 g of toothpaste is weighed into a 100 mL volumetric flask and dissolved in approximately 50 mL deionized water. Then, the flask is filled up to the mark with deionized water.

If the sample is added automatically, it is recommended to centrifuge or filter the sample beforehand.

Sample containing covalently bound fluoride (or unknown sample)

5 g of toothpaste is weighed into a 100 mL beaker and dissolved in approximately 50 mL deionized water. Then, 5 mL concentrated HCl is added and the solution is heated in a water bath at 90 °C for one minute. After cooling down to room temperature, the solution is quantitatively transferred into a 1 L volumetric flask and filled up to the mark with deionized water.

Analysis

Sample

To 10 mL of sample solution 30 mL of TISAB IV is added, and the standard addition is carried out with the fluoride standard solution. In between each measurement, the electrode is rinsed well with deionized water and then conditioned in TISAB IV/deionized water (1:1) for two minutes before measuring the next standard.

Parameters

Sample

Mode	STDADD ISE auto
Stirring rate	8
Auxiliary solution volume	Total volume of TISAB IV
Number of additions	3
Delta U	20 mV
Dosing rate	Fast
Stop volume	Buret volume
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Calculations

Fluoride linear regression

The linear regression is automatically done/executed by OMNIS after the « STDADD ISE auto » command is finished. The data can be found in the sample list under calibration curves.

Fluoride content

$$F^- = \frac{\text{Sample Conc}_{\text{Result}} \times V_F}{m_s}$$

F^-: Fluoride content in mg/kg

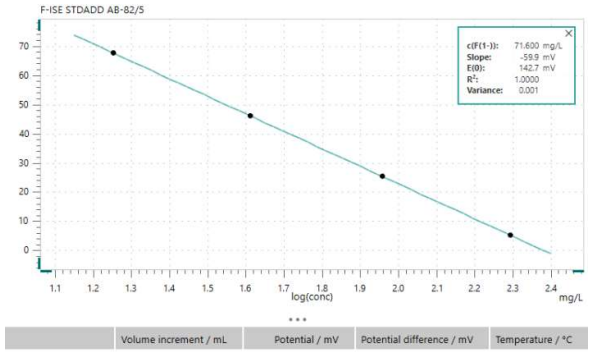
$\text{Sample Conc}_{\text{Result}}$: Command variable « SampleConcentration.Result."STDADD ISE auto" »

V_F: Final volume of sample preparation in mL

m_s: Sample size of sample preparation in g

Example

Sample



	Volume increment / mL	Potential / mV	Potential difference / mV	Temperature / °C
Sample		67.7		23.9
Increment 1	0.960	46.1	-21.5	24.0
Increment 2	2.251	25.4	-20.7	24.1
Increment 3	5.699	5.3	-20.2	24.2

Figure 4. Standard addition of toothpaste with three increments made with $\beta(F^-) = 1000$ mg/L.

Slope in mV	E(0) in mV	R^2	Variance
-59.9	142.7	1.000	0.001

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Appendix

Sample preparation suggestions for further application examples

1. Fluoride in phosphoric acid with automatic standard addition

Sample preparation

The phosphoric acid is diluted 1:100 with deionized water (sample solution).

TISAB

c(sodium nitrate) = 1 mol/L solution is adjusted to pH = 6 with c(NaOH) = 2 mol/L.

Analysis

10 mL sample solution (dilution factor 100) and 10 mL TISAB are added to the measuring vessel.

Remark

Fluoride dissolved in phosphoric acid will generate HF. Accordingly, a standard solution of fluoride in phosphoric acid cannot be produced and direct measurement is therefore not possible.

2. Fluoride in cement with automatic standard addition

Sample preparation

Approximately 250 mg of cement, 1 g sodium carbonate (dehydrated), and 0.2 g zinc oxide are weighed into a platinum crucible. The crucible is left for 30 minutes in an oven at 900 °C. After the crucible has cooled down to room temperature, it is placed into a 100 mL beaker. The mixture is dissolved in approximately 80 mL deionized water. This can take several hours. It is helpful to place a stirring rod into the crucible with its hardened contents. This allows the entire crucible to rotate in the beaker. Warming the crucible up again to 80 °C is also helpful to dissolve the contents. After removing the platinum crucible from the beaker, several drops of concentrated HNO_3 are added until the solution becomes clear and no more CO_2 produced. The acid must be added dropwise very slowly, otherwise, the CO_2 is released too violently and causes the mixture to spill. The solution is filtered and transferred to a 100 mL volumetric flask. The flask is filled to the mark with deionized water (digested sample). The concentrated solution is diluted 1:25 (sample solution).

TISAB

This solution contains c(trisodium citrate) = 0.5 mol/L and c(KNO_3) = 0.2 mol/L. The pH value is adjusted to 5.7 using c(HCl) = 2 mol/L.

Analysis

10 mL sample solution (dilution factor 25) and 10 mL TISAB are poured into the measuring vessel.

Remarks

Elements such as aluminum form complexes with fluoride. The fluoride therefore becomes partially inaccessible for measurement. The use of sodium citrate as TISAB prevents this. However, excessive concentrations of sodium citrate can cause a sluggish response of the electrode. The amount of TISAB given here results in reliable readings in cement either with or without aluminum content.

Attention

The dilution must be large enough to ensure that all aluminum is complexed. In the example, only a 1:25 dilution resulted in correct measurements. At a dilution of 1:10, the values were too low by a factor of two. Use of the undiluted digested sample resulted in values that were too low by a factor of five and a slope that was too low.

3. Fluoride in bone by direct measurement

Sample preparation

The bone sample is incinerated at 550 °C (several hours). Between 4–6 mg of the residue is dissolved in c(HCl) = 0.25 mol/L, and 1.1 mL c(NaOH) = 0.125 mol/L is added for neutralization before the pH is adjusted to 4.7 with c($NaCH_3COO$) = 0.05 mol/L. The total sample volume is made up to 5 mL with deionized water.

Standard solution

The fluoride standard solutions should contain c(NaCl) = 0.05 mol/L and c(acetate buffer, pH 4.7) = 0.005 mol/L (same ionic background).

Analysis

The prepared sample is measured directly after a calibration is performed.

4. Fluoride in carbonated drinks

Sample preparation

The sample is degassed by warming to approximately 60–80 °C and bubbling nitrogen through for several minutes.

TISAB

Solution with c(potassium acetate) = 1 mol/L and c(KCl) = 1 mol/L in a pH = 7 buffer.

Analysis

Equal amounts of sample solution and TISAB are used.

5. Fluoride in cryolite (Na_3AlF_6)

Sample preparation

5 g NaOH is added to 0.15 g sample and 1 mL deionized water. The resulting slurry is then mixed and dried at 180–200 °C for at least 45 minutes. The hot mixture is dissolved in hot deionized water, then it is cooled down the solution is quantitatively transferred into a 250 mL volumetric flask and made up to the mark with deionized water.

TISAB

230 g disodium tartrate dihydrate and 242 g tris(hydroxymethyl)-methylamine are weighed into a 1 L volumetric flask and dissolved in deionized water. 84 mL concentrated HCl is added and the flask is filled up to the mark, then the pH is adjusted to 8.46.

Analysis

20 mL TISAB is added to 10 mL sample solution. The mixture is diluted to 100 mL with deionized water before the measurement.

6. Fluoride in animal feed

Sample preparation

The sample is weighed into a 200 mL volumetric flask then stirred for 20 minutes in c(HCl) = 1 mol/L. After adding 50 mL c($NaCH_3COO$) = 3 mol/L and 50 mL TISAB (see below), the flask is filled up to the mark with deionized water.

TISAB

222 g sodium citrate dihydrate is weighed into a 1 L volumetric flask and dissolved in deionized water. 28 mL concentrated $HClO_4$ is added, and the flask is filled up to the mark with deionized water.

Analysis

50 mL of the prepared sample solution is used.

7. Fluoride in fluorosilicic acid

Sample preparation

The 0.1–0.15 g sample is suspended in 10–20 mL deionized water in a 100 mL volumetric flask. The sample is dissolved by the addition of concentrated ammonia. Afterwards, 20 mL TISAB (see below) is added and the solution is diluted to the mark with deionized water.

TISAB

The pH of a c(NH_4CH_3COO) = 3 mol/L solution is adjusted to pH = 5.7–5.8 with glacial acetic acid.

Analysis

Direct measurement is performed of the prepared sample solution.

8. Fluoride in phosphate minerals

Sample preparation

The weighed sample is dissolved in deionized water or c(HCl) = 2 mol/L.

TISAB

Citrate buffer pH = 6.0 (1 mol/L trisodium citrate is adjusted to pH = 6 with c(HCl) = 2 mol/L).

Analysis

Equal amounts of sample solution and TISAB are used.

9. Fluoride in plants

Sample preparation

The weighed sample is mixed with NaOH pellets and then heated for 30 minutes at 600 °C. The residue is dissolved in deionized water, and the solution is adjusted to pH = 8–9 with concentrated HCl. The solution is filtered and then diluted 1:1 with TISAB IV.

TISAB

TISAB IV: 58 g NaCl is dissolved in approximately 500 mL deionized water. 5 g complexon IV is added and dissolved by dropwise addition of c(NaOH) = 8 mol/L. 57 mL glacial acetic acid is added, and the pH of the mixture is adjusted to 5.5 with the abovementioned NaOH solution. Finally, it is made up to 1 L with deionized water.

Analysis

The prepared sample solution is analyzed directly.

10. Fluoride in soil samples (total fluoride)

Sample preparation

The dried and weighed sample is mixed in a nickel crucible with NaOH pellets and heated to 600 °C for 30 minutes. The residue is dissolved in deionized water and the solution adjusted to pH = 8–9 with concentrated HCl. After cooling down, the sample is transferred into a 100 mL volumetric flask, filled up to the mark and filtered through a dry Whatman No. 40 filter paper.

TISAB

To 300 mL distilled water 58 mL glacial acetic acid and 12 g sodium citrate dihydrate are added. After dissolution, the pH is adjusted to 5.2 with c(NaOH) = 6 mol/L. This solution is then diluted 1:1 with deionized water.

Analysis

25 mL of sample solution and 25 mL TISAB are used.

11. Fluoride in wine

Sample preparation

No sample preparation is necessary.

TISAB

74.5 g KCl, 98.1 g $KCOOCH_3$, 2.6 g KH_2PO_4, and 3.55 g Na_2HPO_4 are dissolved in deionized water and the resulting solution is made up to 1 L with deionized water.

Analysis

25 mL of sample and 25 mL TISAB are used.

12. Fluoride in urine

Sample preparation

The sample is diluted 1:3 with deionized water (sample solution).

TISAB

TISAB IV: 58 g NaCl is dissolved in approximately 500 mL deionized water. 5 g complexon IV is added and dissolved by dropwise addition of c(NaOH) = 8 mol/L. 57 mL glacial acetic acid is added, and the pH of the mixture is adjusted to 5.5 with the abovementioned NaOH solution. Finally, it is made up to 1 L with deionized water.

Analysis

Equal amounts of sample solution and TISAB are used.