

Application Bulletin 82/4e

Determination of fluoride with an ion-selective electrode

Branch

General analytical chemistry; food, stimulants, beverages

Keywords

Fluoride; ISE; ion-selective electrode; standard addition; direct measurement; branch 1; branch 7; mouth rinse; tooth paste; table salt; 6.0502.150; 6.0750.100

Summary

This bulletin describes several fluoride determinations in different matrices using the fluoride ion-selective electrode (ISE). The electrode consists of a lanthanum fluoride crystal, and its electrochemical behavior follows the Nernstian equation.

In the first part of this bulletin, general hints 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 direct measurement or the standard addition technique. Fluoride was determined in several matrices: salt, toothpaste, and mouthwash rinse.

Instruments

- Ion Meter or Titrator with the modes MEAS CONC and/or STDADD
- Stirrer
- Buret 10 mL (Standard addition)

Electrodes

Fluoride ISE	6.0502.150
LL ISE Reference	6.0750.100
Temperature sensor Pt1000	6.1110.100

General hints

Handling of the electrode

To achieve optimal measurements, the following points are essential:

- The sensing part of the fluoride electrode is composed of a lanthanum fluoride crystal. To avoid fatty deposits, it should not be touched with bare hands. It is furthermore sensitive to mechanical shocks.
- If the electrode does not respond properly after being used for a longer time period (slow response times even at high fluoride contents), the sensor may be contaminated and should be cleaned with a liquid detergent or polished carefully with toothpaste. The polishing set for ISE (aluminum oxide) must absolutely not be used as 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 deion. H₂O for approx. 30 min.
- Rinse the electrode after each measurement with deion. H₂O.
- When conducting a series of measurements the electrode should be conditioned for 5 min in TISAB solution before each new measurement, otherwise a cumulative error can arise (results increase under otherwise identical conditions).
- The measured values depend upon 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 HF₂⁻ are formed. Both of these are not detected. At pH values over pH = 8 the electrode becomes cross-sensitive to OH⁻ ions.
- Cations such as Ca²⁺, Al³⁺, Fe²⁺, Fe³⁺, etc. bind 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 analyze and the concentration range of the sample.

- For measuring samples with a complex or unknown matrix, it is the best to use the standard addition. A direct measurement is recommended with an unproblematic sample matrix.
- For large sample numbers or online measurements the direct measurement is recommended.
- In case of low level measurements, it is recommended to either use direct measurement after calibration or spike the sample to a higher content. The reason for this is that the sensor is at the limit of detection and outside its linear range which leads to too high results for standard addition.

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 case of low level measurements (mg/L or µg/L range).

In case of a direct measurement the following points have to be considered:

- For concentrations <1 mg/L the standard solutions must have the same ionic background as the sample solutions. The response time of the sensor becomes distinctly longer. TISAB : water 1 : 1 should be used for such measurements.
- All measurements should be performed at constant temperature (for example at 25 °C).
- The addition of TISAB solution before the measurement keeps the pH value and the ionic strength constant. The TISAB solution has the additional effect to bind interfering cations and thereby releasing complexed fluoride.

Standard addition

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

There are three types of standard addition:

- manual
- auto dos
- auto

The quickest and recommended method is the automatic standard addition (mode: «auto»). In order to get exact results the potential difference ΔU should be at least 12 mV per standard addition and at least 3 standard additions should be performed (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 «auto dos» is recommended. There the individual standard addition volumes can be defined (see manual of the device in use or the online help of the software).

The volume of the added solution / the concentration of the standard must be chosen in such a way that the dosed volume does not exceed 25% of the sample volume and that the buret must not be refilled during addition.

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

In case of standard addition the following points have to 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 to bind 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 has to be dissolved in TISAB.

- In order to ensure an accurate evaluation of the standard addition, the standard concentrations (C_{std}) for the different buret volumes ($V_{\text{buret}}/\text{mL}$) must be chosen as a function of the sample concentration (C_{smpl}) according to the table below. Thereby any sample dilution has to be considered (e.g. dilution with TISAB)

Table 1: Ratio of the standard concentration and sample concentration in dependency of the buret volume

V_{buret} in mL	$C_{\text{std}} : C_{\text{smpl}}$
5	40 : 1
10	20 : 1
20	10 : 1
50	5 : 1

Example factor determination

sample concentration (C_{smpl}):	5 mg/L
Buret volume (V_{buret}):	10 mL
sample size:	10 mL
TISAB:	10 mL
total volume (V_{total}):	20 mL
Factor from table 1 ($C_{\text{std}} : C_{\text{smpl}}$):	20

Considering the dilution with TISAB the initial sample concentration is 2.5 mg/L. The optimal concentration of the standard is therefore:
 $2.5 \text{ mg/L} \cdot 20 = 50 \text{ mg/L}$.

Comments

- A historical analysis technique is the titration by lanthanum nitrate. But lanthanum creates complexes with buffers and ingredients of the TISAB and samples. This causes a too high consumption of titrant and a too high result. Therefore the titration of fluoride with lanthanum nitrate is not recommended.

Practical examples

Reagents

These reagents are needed to prepare the fluoride standard and TISAB IV (Total Ionic Strength Adjustment Buffer IV).

- Sodium fluoride, NaF > 99 %
- Sodium chloride, NaCl \geq 99.5 %
- Glacial acetic acid
- Sodium hydroxide, $c(\text{NaOH}) = 8 \text{ mol/L}$
- Complexon IV (1,2 di-amino cyclohexane N,N,N',N' tetraacetic acid)

Solutions

- All solutions have to be stored in plastic containers. The fluoride content of sample solutions stored in glass containers decreases with time.
- The solutions (standard, TISAB, sample solution) should not be stored longer than 3 months. A low electrode slope can be an indication of poor quality of the solutions.

Fluoride standard	$\beta(\text{F}^-) = 1 \text{ g/L}$ 2.210 g NaF is weighed into a 1 L volumetric flask and the exact weight is written down. The NaF is then dissolved in deion. H_2O before the flask is filled up to the mark with deion. H_2O .
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TISAB IV	58 g NaCl is dissolved in approx. 500 mL deion. H_2O . 5 g complexon IV is added and dissolved by drop wise addition of $c(\text{NaOH}) = 8 \text{ mol/L}$. 57 mL glacial acetic acid is added and the pH of the mixture is adjusted to 5.5 with the above mentioned NaOH solution. Finally it is made up to 1 L with deion. H_2O . This TISAB is used for the analysis of table salt, mouth rinse and tooth paste.
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further TISABs	For other applications the needed TISAB is mentioned separately.
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Fluoride in table salt by means of direct measurement

Sample

- Table salt, fluoride content of 50 mg/L

Solutions

- Fluoride standard (1 g/L)
- TISAB IV
- Sodium chloride solution, $\beta(\text{NaCl}) = 200 \text{ g/L}$

Sample preparation

20 g of table salt is weighed into a 100 mL volumetric flask and dissolved in 50 mL deion. H_2O . The flask is filled up to the mark with deion. H_2O .

Standard preparation

Standard	1	2	3	4
Concentration / (mg/L)	25	50	75	100

The calibration standards were prepared by diluting the fluoride standard (1 g/L) to the desired concentrations.

Analysis

Calibration

To 20 mL of standard solution (concentrations see *standard preparation*) 10 mL sodium chloride solution and 10 mL TISAB IV are added. The solution is stirred and after a brief pause the potential is measured. In between each measurement the electrode is conditioned in TISAB IV/deion. H_2O (1/1) for 5 min.

Sample

To 20 mL of sample solution 10 mL of TISAB IV and 10 mL deion. H_2O are added and the potential is measured after a brief pause. In between each measurement the electrode is conditioned in TISAB IV/deion. H_2O (1/1) for 5 min.

Parameters

Calibration

Mode	CAL MEAS Conc
Stirring rate	6
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Sample

Mode	MEAS Conc
Stirring rate	5
Signal drift	0.5 mV/min
Min. waiting time	10 s
Max. waiting time	215 s

Results

Calibration

Measured values

Standard	Conc. / (g/L)	U / mV
1	0.025	47.8
2	0.050	30.1
3	0.076	20.3
4	0.101	12.9

Slope: -57.40 mV

E(0): -44.2 mV

c(blank): 0.00 mg/L

Variance: 0.195

Sample

Sample	Conc. / (mg/L)
Mean (n = 3)	43.17
s(rel)	0.53%

Example determination

Calibration

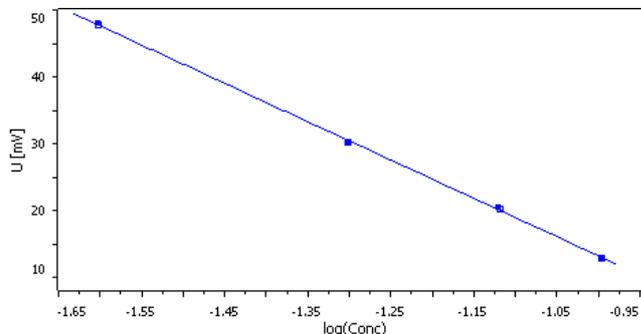


Fig. 1: Calibration curve

Comments

- The use of a sodium chloride solution for the calibration is necessary in order to obtain the same ionic background between the calibration and sample measurement.

Fluoride in table salt with automatic standard addition

Sample

- Table salt, fluoride content of 50 mg/L

Solutions

- Fluoride standard (1 g/L)
- TISAB IV

Sample preparation

20 g of table salt is weighed into a 100 mL volumetric flask and dissolved in 50 mL deion. H₂O. The flask is filled up to the mark with deion. H₂O.

Analysis

10 mL sample solution (dilution factor 10), 5 mL TISAB IV and 5 mL deion. H₂O are pipetted into the measuring vessel. The standard addition is carried out with $\beta(\text{F}^-) = 1 \text{ g/L}$. In between each measurement the electrode is conditioned in TISAB IV/deion. H₂O (1/1) for 5 min.

Parameters

Mode	STDADD auto
Stirring rate	5
Number of additions	3
Volume of aux. solution	10 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	15 mV
Signal drift	0.5 mV/min
Max. waiting time	215 s

Calculation

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

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-63.1	/
1	0.391	-78.5	-15.4
2	0.736	-93.8	-15.3
3	1.403	-108.9	-15.1

Slope: -61.46 mV

E(0): -162.53 mV

F(-1): 0.0483 g/L

Variance: 0.003

Example determination

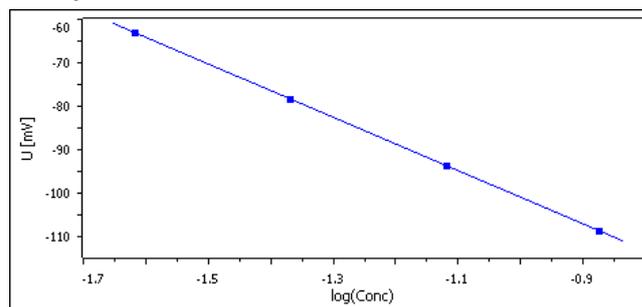


Fig. 2: Curve of the standard addition for table salt.

Fluoride in mouth rinse with automatic standard addition

Sample

- Mouth rinse, fluoride content of 220 mg/L

Solutions

- Fluoride standard (1 g/L)
- TISAB IV

Sample preparation

No sample preparation is required.

Analysis

1 mL sample, 10 mL TISAB IV and 10 mL deion. H₂O are pipetted into the measuring vessel. The standard addition is carried out with $\beta(\text{F}^-) = 1 \text{ g/L}$. In between each standard addition the electrode is conditioned in TISAB IV/deion. H₂O (1/1) for 5 min.

Parameters

Mode	STDADD auto
Stirring rate	5
Number of additions	3
Volume of aux. solution	20 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	20 mV
Signal drift	0.5 mV/min
Max. waiting time	215 s

Calculation

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

Results

Increment	dV / mL	U / mV	dU / mV
0	/	-52.7	/
1	0.285	-73.1	-20.4
2	0.652	-93.3	-20.2
3	1.541	-113.4	-20.1

Slope: -59.62 mV

E(0): -169.29 mV

F(-1): 0.2331 g/L

Variance: 0.008

Example determination

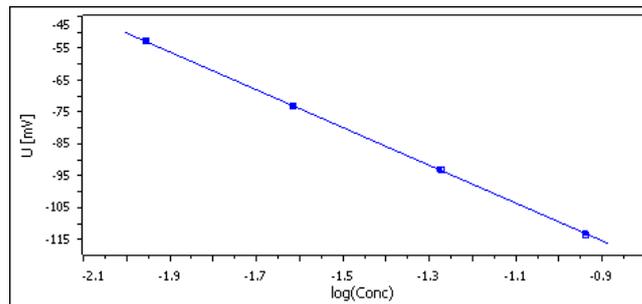


Fig. 3: Curve of the standard addition for mouth rinse.

Fluoride in toothpaste with automatic standard addition

Sample

- Toothpaste, fluoride content of 1300 g/kg

Solutions

- Fluoride standard (1 g/L)
- TISAB IV
- Hydrochloric acid, HCl, conc.

Sample preparation

5 g of sample is weighed into a 100 mL beaker. 5 mL deion. H₂O and 5 mL conc. HCl are added to the sample and homogenized by stirring for 60 s. The beaker is then placed into a water bath at 90 °C for 1 min. After cooling down to room temperature the solution is transferred to a 1000 mL volumetric flask and filled up to the mark with deion. H₂O.

Analysis

5 mL sample solution (dilution factor 200) and 20 mL TISAB IV are pipetted into a measuring vessel. The standard addition is carried out with $\beta(F^-) = 1$ g/L. In between each standard addition the electrode is conditioned in TISAB IV for 5 min.

Parameters

Mode	STDADD auto
Stirring rate	5
Number of additions	3
Volume of aux. solution	20 mL
Stop volume	10 mL
Dosing rate	Medium
Delta U	20 mV
Signal drift	0.5 mV/min
Max. waiting time	215 s

Calculation

The calculation of the result is automatically carried out by the instrument applying iteration.

Results

Increment	dV / mL	U / mV	dU / mV
0	/	3.7	/
1	0.043	-16.9	-20.7
2	0.093	-37.3	-20.4
3	0.204	-57.8	-20.5

Slope: -60.47 mV

E(0): -168.43 mV

F(-1): 1.4234 g/kg

Variance: 0.005

Example determination

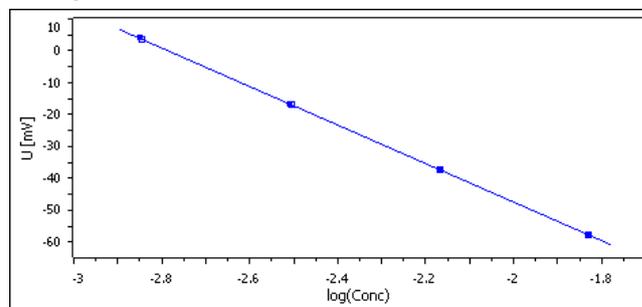


Fig. 4: Curve of the standard addition for mouth rinse.

References

- Metrohm Monograph
Electrodes in Potentiometry, 8.015.5013
- Manual Ion-selective electrodes (8.109.1476)
- AOAC method 973.10, Fluoride in hazardous substances. Potentiometric method. AOAC, 1990, 1, 232-233.
- AOAC method 975.04, Fluoride in plants. Potentiometric method. AOAC, 1990, 1, 51-52
- Jordan, D.
Determination of total fluoride and/or fluosilicic acid concentration by specific fluoride ion electrode potentiometry
J. Assoc. Off. Anal. Chem., 1970, 53, 3, 447-450.
- Singer, L.; Armstrong, W.D.
Determination of fluoride in bone with the fluoride electrode
Anal. Chem., 1968, 40, 3, 613-614.
- Abollino, O., Mentasi, E., Sarzanini, C., Modone, E., Braglia, M.,
Determination of Zr, Ba, La, Al, Na, Hf and fluoride in fluorozirconate glasses.
Fresenius J. Anal. Chem., 1992, 343, 6, 482-487.
- Langenauer, M., Krähenbühl, U., Wytttenbach, A.
Determination of fluorine and iodine in biological materials
Anal. Chim. Acta, 1993, 274, 2, 253-256.
- Edmond, C.R.
Direct determination of fluoride in phosphate rock samples using the specific ion electrode.
Anal. Chem, 1969, 41, 10, 1327-1328.
- McQuaker, N.R., Gurney, M.
Determination of total fluoride in soil and vegetation using an alkali fusion-selective ion electrode technique.
Anal. Chem, 1977, 48, 1, 53-56.

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Appendix

Sample preparations for further application examples

1. Fluoride in phosphoric acid with automatic standard addition

Sample preparation

The phosphoric acid is diluted 1/100 with deion. H₂O (sample solution).

TISAB

1 mol/L sodium nitrate 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 generating 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

Approx. 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 min in an oven at 900 °C. After the crucible has cooled down, it is placed into a 100 mL beaker. The contents are dissolved in approx. 80 mL 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 in releasing the contents. After removing the platinum crucible from the beaker, several drops of concentrated HNO₃ are added until the solution becomes clear and no more CO₂ is given off. The acid must be added very slowly drop by drop; otherwise the CO₂ is released too violently, causing the crucible contents to spill over. The solution is filtrated off and transferred to a 100 mL volumetric flask. The flask is filled to the mark with deion. H₂O (digested sample). The concentrated solution is diluted 1/25 (sample solution).

TISAB

Solution containing c(trisodium citrate) = 0.5 mol/L and c(KNO₃) = 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 given 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 with or without aluminum content.

Attention

The dilution must be big enough, in order to ensure that all aluminum is complexed.. In the example, only a 1/25 dilution resulted in correct measurements. At a 1/10 dilution the values were too low by a factor of 2. Use of the undiluted digested sample resulted in values that were too low by a factor of 5 and a too low slope.

3. Fluoride in bone by direct measurement

Sample preparation

The bone is incinerated at 550 °C (several hours). 4–6 mg of the residue is dissolved in $c(\text{HCl}) = 0.25 \text{ mol/L}$ and 1.1 mL $c(\text{NaOH}) = 0.125 \text{ mol/L}$ is added for neutralization before the pH is adjusted to 4.7 with $c(\text{NaCH}_3\text{COO}) = 0.05 \text{ mol/L}$. The total sample volume is made up to 5 mL with deion. H_2O .

Standard solution

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

Analysis

The prepared sample is measured directly after a calibration.

4. Fluoride in carbonated drinks

Sample preparation

The sample is degassed by warming to approx. 60–80 °C and introducing nitrogen for several minutes.

TISAB

Solution with $c(\text{potassium acetate}) = 1 \text{ mol/L}$ and $c(\text{KCl}) = 1 \text{ mol/L}$ 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 deion. H_2O . The melt is then mixed and dried at 180–200 °C for at least 45 min. The hot mixture is dissolved in hot deion. H_2O and after cooling down the solution is quantitatively transferred into a 250 mL volumetric flask and made up to the mark with deion. H_2O .

TISAB

230 g disodium tartrate dihydrate and 242 g tris(hydroxymethyl)-methylamine are weighed into a 1 L volumetric flask and dissolved in deion. H_2O . 84 mL conc. HCl is added and the flask is filled up to the mark, and the pH is adjusted to 8.46.

Analysis

20 mL TISAB are added to 10 mL sample solution. The mixture is diluted to 100 mL with deion. H_2O before the measurement.

6. Fluoride in animal feed

Sample preparation

The sample is weighed into a 200 mL volumetric flask, stirred for 20 min in $c(\text{HCl}) = 1 \text{ mol/L}$. After adding 50 mL $c(\text{NaCH}_3\text{COO}) = 3 \text{ mol/L}$ and 50 mL TISAB (see below) the flask is filled up to the mark with deion. H_2O .

TISAB

222 g sodium citrate dihydrate is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . 28 mL conc. HClO_4 is added and the flask is filled up to the mark with deion. H_2O .

Analysis

50 mL of the prepared sample solution is used.

7. Fluoride in fluorosilicic acidSample preparation

The 0.1–0.15 g sample is suspended in 10–20 mL deion. H₂O in a 100 mL volumetric flask. The sample is dissolved by addition of concentrated ammonia. Afterwards, 20 mL TISAB (see below) is added and the solution is diluted to the mark.

TISAB

The pH of a c(NH₄CH₃COO) = 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 mineralsSample preparation

The weighed sample is dissolved in 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 plantsSample preparation

The weighed sample is mixed with NaOH pellets and heated for 30 min at 600 °C. The residue is dissolved in deion. H₂O and the solution is adjusted to pH = 8 to 9 with concentrated HCl. The solution is filtrated and diluted 1/1 with TISAB IV.

TISAB

TISAB IV

Analysis

The prepared sample solution is analyzed.

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 deion. H₂O and the solution adjusted to pH = 8–9 with concentrated HCl. After cooling down the sample is transferred into a 100 mL volumetric flask, fill up to the mark and filtrated through a dry Whatman No. 40 filter paper.

TISAB

To 300 mL distilled water 58 mL glacial acetic acid and 12 g sodium citrate dehydrate 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 deion. H₂O.

Analysis

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

11. Fluoride in wineSample preparation

No sample preparation is necessary.

TISAB

74.5 g KCl, 98.1 g KOOCCH₃, 2.6 g KH₂PO₄ and 3.55 g Na₂HPO₄ are dissolved in dist. H₂O and made up to 1 L with dist. H₂O.

Analysis

25 mL of sample and 25 mL TISAB are used.

12. Fluoride in urineSample preparation

The sample is diluted 1/3 with deion. H₂O (sample solution).

TISAB

TISAB IV

Analysis

Equal amounts of sample solution and TISAB are used.