Robotic Fluoride Analyzer

Applications

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Metrohm
Ion analysis

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Robotic Fluoride Analyzer

Symbols used in this document:

c (X)	Molar concentration of substance X in mol/L, often written as [X]
M (X)	Molar mass of substance or atomic mass (relative mass) of substance X in g/mol
w (X)	Mass fraction of substance X, e.g. w(NaOH) = 40%
ß (X)	Mass concentration of substance X, e.g. ß(NaCl) = 20 g/L
a (X)	Activity of substance X (only corresponds to the molar concentration in very diluted solutions; as the concentration increases, dissolved particles mutually influence each other so that their activity is lower than would be expected from the concentration).
pK_p	Autoprotolysis constant of a solvent
{ }	In this document braces such as used in the formula {AgCl} indicate solid substances (precipitates) that do not consist of single molecules (in this case AgCl), but whose ionic components form an extended ionic lattice.

tiamo methods

The methods described in this document are part of the *tiamo* installation on your PC system. To use these methods you can import them into your method groups with the built-in method manager in the *tiamo* software. Please consult the *tiamo* user manual or online-help for further instructions.

The methods can be found in the following path:

C:\Program Files\Metrohm\tiamo\examples\methods\english\855 Robotic Analyzer\Fluoride

(The *tiamo* installation path of your system may be different.)

The *tiamo* user manual (in pdf file format) can be found in the following path:

C:\Program Files\Metrohm\tiamo\doc\English

Accessories of the Robotic Fluoride Analyzer

1.855.0020	855 Robotic Titrosampler
1.800.0010	Dosino 2x
1.802.0010	Rod stirrer
6.0502.150	Ion-selective electrode, F OK
6.0750.100	LL ISE Reference electrode OK
6.1236.020	Sleeve with SGJ 14/12 mm 2x
6.1458.040	Titration head insert 'Macro'
6.1459.310	Sample beakers 200 mL PP
6.1462.170	Robotic arm with sensor
6.1543.170	Aspiration tip M8
6.1546.030	Piston rod
6.1608.023	Bottle 1 L, 2x
6.1621.000	PE container 10 L 2x
6.1805.060	FEP tubing / M6 / 60 cm 3x
6.1805.120	FEP tubing / M6 / 100 cm
6.1805.510	PTFE tubing M8, 60 cm
6.1812.000	PTFE tubing 4/6 mm, 4m
6.1828.000	PVDF connection nipple 2x
6.1909.040	Stirring propeller PP, 104 mm
6.2001.120	Bottle holder base
6.2041.830	Sample rack 28 x 200 mL
6.2053.000	Cable clip 10x
6.2061.010	Bottle holder
6.2104.020	Electrode cable 1 m
6.2106.020	Strand (2x B) 1 m
6.2151.000	Cable USB A - mini-DIN 8P
6.2312.050	Electrolyte KCl 3 mol/L
6.2621.030	Hexagon key 4 mm
6.2621.070	Hexagon key 5 mm
6.2621.130	Hexagon key 2 mm
6.2621.140	Hexagon key 2.5 mm
6.2740.020	Spray nozzle 3x
6.2751.100	Safety shield
6.3032.220	Dosing Unit 20 mL
6.3032.250	Dosing Unit 50 mL
6.6056.112	tiamo 1.1 full version CD
T.2400.102	Ferrite cores 4x

Table of content

1 Application Information

1.1 Direct potentiometric measurements with ion selective electrodes (ISE)

Theoretical basis for the electrodes and measurements

As with the pH value, currentless measurements of potential differences between two electrodes (measuring electrode and reference electrode) are performed with a suitable instrument (pH meter, ion meter, titrator).

The reference electrode has a constant potential (hence its name – it is used for comparison), whereas the potential at the measuring electrode changes. The change in potential is dependent on the concentration of the ion to be determined and, like the pH value, obeys the Nernst equation. For positively charged ions with a single charge the potential at 25.0 °C increases by 59.2 mV when the concentration is increased 10-fold; for negatively charged ions with a single charge the corresponding change in potential at 25.0 °C is –59.2 mV. For positively charged ions with a double charge the theoretical slope is accordingly 59.2 : 2 = 29.6 mV per 10-fold concentration change. This also means that for positively charged ions the potential increases with the concentration, while with negatively charged ions it decreases.

The electrode slope depends on the temperature.

Theoretical electrode slope 1.00 (100%) as a function of temperature	
15.0 °C	57.2 mV
16.0 °C	57.4 mV
17.0 °C	57.6 mV
18.0 °C	57.8 mV
19.0 °C	58.0 mV
20.0 °C	**58.2 mV**
21.0 °C	58.4 mV
22.0 °C	58.6 mV
23.0 °C	58.8 mV
24.0 °C	59.0 mV
25.0 °C	**59.2 mV**

Depending on the ion that is to be determined, there are different types of ion selective electrodes:

- Glass membrane electrodes, e.g. for pH and Na^+
- Polymer membrane electrodes, e.g. for K^+, Ca^{2+}, NO_3^-
- Crystal membrane electrodes, e.g. for Cl^-, F^-, S^{2-}, Ag^+, Cu^{2+}
- Gas membrane electrodes, e.g. for NH_3 (NH_4^+), CO_2

ISEs respond «selectively» to the particular ion. But this is not quite true. They may have **cross sensitivities**, i.e. they may also respond to other ions – this causes interference, which must either be eliminated or reduced.

ISEs only measure ion activities. Ions are active when they are freely present as such in the solution. The **activity coefficient** γ can be taken from the appropriate tables. Two examples:

$$c(Na) = 10^{-1}\ mol/L;\ \gamma = 0.770 \longrightarrow a(Na) = 0.77 \times 10^{-1}\ mol/L$$

$$c(Na) = 10^{-5}\ mol/L;\ \gamma = 0.996 \longrightarrow a(Na) = 0.996 \times 10^{-5}\ mol/L$$

γ not only depends on the ionic strength of the ion to be measured, but also on the total ionic strength of the solution. In order to keep γ constant, measurements are made at a constant (high) ionic strength. This is why ISA solutions are added to the sample. **ISA** stands for **I**onic **S**trength **A**djuster. These are solutions of salts against which the ISE has no cross sensitivity at all or only a slight one.

Some of the ions to be determined are only present as free ions within a limited pH range. Outside these limits they have no activity at all or only a slight activity. Solutions for regulating the pH and ionic strength are known as TISAB solutions (**TISAB** = **T**otal **I**onic **S**trength **A**djustment **B**uffer). These TISAB solutions may also contain other compounds (e.g. complexing agents for releasing the ion to be determined or removing the interfering ions, for example Al, Ca and Fe in fluoride determination).

The pH glass electrode is the ISE par excellence. It is very selective and can be used for concentration measurements throughout a range of more than 14 decades. With other ISEs this is not the case. Their normal measuring range is 6 concentration decades at the most. This means that the lowest determination level is – depending on the electrode and sample matrix – about 50...200 μg/L.

The **determination of the content** itself can be carried out in two different ways:

a) Recording a calibration curve

mV measurements are carried out with standard solutions that have been treated with ISA or TISAB in the same way as the subsequent sample solutions. To obtain the calibration curve, U/mV is plotted on the linear scale and the concentration on the logarithmic scale. This calibration curve is used to determine the content of the sample from the measured mV value.

b) Standard addition method

The sample is treated with ISA or TISAB and its mV value is measured. A defined volume of the standard solution is added and the mV value is again measured. The content of the sample can be calculated from the difference in mV and the slope of the electrode. The advantage of this method is that it takes the sample matrix into account (this is not the case in method a). This is why we will use this method b) for the analyses. The activity coefficient γ is also temperature-dependent. This means that the measurement of the sample with and without the added standard must take place at the same temperature.

1.2 The Fluoride ISE

The only interfering ion is OH^-. However, as measurements are made at pH <7.0, this interference can be neglected. On the other hand, measurements should not be made at too low pH values as otherwise HF or H_2F_2 could be formed; these are not determined. AlF_3, FeF_3 or CaF_2 give low-bias results. For this reason a complexing agent (e.g. EDTA) can be added to the TISAB solution. This «releases» the fluoride from these compounds.

Before the first use, or if its response deteriorates, the electrode membrane should be gently polished with a fat-free concentrated dishwasher and then thoroughly rinsed with dist. H_2O. When not in use the electrode is stored dry. If small fluoride concentrations are to be determined (<1 mg/L F) then the electrode should be preconditioned overnight in dist. H_2O.

Further remarks

Do not touch electrode membranes with your fingers. Fat deposits considerably affect the response of the electrodes.

2 Calibration

2.1 Calibration of the Fluoride ISE

Recommended accessories

- 6.3032.220 Dosing Unit, 20 mL
- 6.3032.250 Dosing Unit, 50 mL
- 6.0502.150 F ISE with 6.2104.020 electrode cable
- 6.0750.100 LL-ISE reference electrode with 6.2106.020 electrode cable

Reagents

- TISAB solution: Into a 1000 mL volumetric flask, weigh out 74.5 g KCl (e.g. Merck no. 104935), 98.1 g $KOOCCH_3$ (e.g. Merck no. 104820), 2.6 g KH_2PO_4 (e.g. Merck no. 104873) and 3.55 g Na_2HPO_4 (e.g. Merck no. 106586), dissolve in dist. H_2O, make up to the mark with dist. H_2O and mix.
- Fluoride standard: $\rho(F^-) = 1000$ mg/L. Weigh out 2.210 g NaF (e.g. Merck no. 106449) into a 1000 mL volumetric flask and dissolve in 100 mL TISAB solution. Make up to the mark with dist. H_2O and mix. Store in a plastic bottle.

  1 mL corresponds to 1.00 mg F^-

General

The F ISE is a crystal membrane electrode. Its sensor material is LaF_3. It must not be polished with abrasive material (e.g. aluminum oxide powder). Its use does not normally present any problems. When not in use it is stored dry.

Determining the electrode slope

From the standard solution (1000 mg/L) a second standard solution with 10 mg/L F^- is first prepared (dilute 1:100 with dist. H_2O in a plastic volumetric flask). This solution has a limited shelf life and should be freshly prepared every week.

Add 25 mL $\rho(F^-) = 10$ mg/L, a magnetic stirrer bar and 25 mL TISAB solution to a plastic beaker. Immerse the electrode in the solution, stir, measure the mV value and record it when the potential is constant. Rinse the electrode with dist. H_2O, dab it dry with a soft paper tissue and repeat the above procedure with $\rho(F^-) = 1000$ mg/L.

Calculate the difference in mV between the two measurements and divide by 2. This gives the absolute electrode slope in mV per concentration decade. The relative electrode slope is calculated as follows:

$$\text{relative electrode slope} = \frac{\text{absolute electrode slope}}{\text{theoretical electrode slope}}$$

In practice the electrode slope seldom reaches a value of 1.00, but is normally in the range 0.92...0.98. If the slope falls significantly below this range then the electrode must be conditioned again or replaced. Be aware that incorrectly made-up standard solutions will cause apparent variations in the slope.

Remark

If the standard addition method is used for the determination the calibration of the Fluoride ISE is not necessary.

3 Typical applications for the Robotic Fluoride Analyzer

3.1 Fluoride in cooking salt

General

The fluoride content is too low for titrimetric determination. This is why direct potentiometry using an F ISE is used. However, the following points must be observed:

Selectivity
The F ISE responds not only to fluoride ions. In too strongly acidic solutions, in which HF or even H_2F_2 is present, no measurements can be made. On the other hand the F ISE has a cross-sensitivity to OH^- ions. This is why it is best to measure at pH = 5...6.5.

Ionic activity
The concentration cannot be measured directly with ion-selective electrodes. It is always the ionic activity that is measured. The activity coefficient (f) depends on the total ionic activity and the temperature of the solution. In order to avoid measuring errors the measurements are always made at a constant ionic strength and temperature.

Electrode slope
This obeys (as in pH measurement) the Nernst equation. This means that for a negatively charged fluoride ion at 25 °C a change in potential of –59.2 mV occurs when the activity (concentration) is increased by the factor 10. The table below shows the electrode slope as a function of temperature:

Theoretical electrode slope of 1.00 (100%) as a function of the temperature	
15.0 °C	57.2 mV
16.0 °C	57.4 mV
17.0 °C	57.6 mV
18.0 °C	57.8 mV
19.0 °C	58.0 mV
20.0 °C	**58.2 mV**
21.0 °C	58.4 mV
22.0 °C	58.6 mV
23.0 °C	58.8 mV
24.0 °C	59.0 mV
25.0 °C	**59.2 mV**

Interfering ions
In addition to OH^- ions, metal ions that form sparingly soluble fluoride salts also interfere. These are primarily Al, Ca and Fe and a complexing agent is added (in our case citrate) to release the fluoride ions again.

TISAB solution
TISAB = **T**otal **I**onic **S**trength **A**djustment **B**uffer. By the addition of this solution the sample solution is given a practically constant ionic strength and is buffered to an optimal pH value. As the TISAB solution also contains citrate, the Ca and Fe contained in the sample are masked.

Recommended accessories

- 6.3032.220 Dosing Unit, 20 mL
- 6.3032.250 Dosing Unit, 50 mL
- 6.0502.150 F ISE with 6.2104.020 electrode cable
- 6.0750.100 LL-ISE reference electrode with 6.2106.020 electrode cable

Reagents

- TISAB solution:
  129 g trisodium citrate and 20 g potassium nitrate are weighed out into a beaker and dissolved in approx. 600 mL dist. H_2O. The pH is adjusted to pH = 5.7 by adding c(HCl) = 2 mol/L. The solution is then made up to 1 liter with dist. H_2O and mixed.
- Fluoride standard I: ρ(fluoride) = 1000 mg/L
  2.210 g NaF is weighed out into a 1000 mL volumetric flask and dissolved in 100 mL TISAB solution. The solution is then made up to the mark with dist. H_2O and mixed. It must be stored in a plastic bottle.

Sample preparation

200 g sample are dissolved in dist. H_2O, made up to 1000 mL with dist. water and mixed.

Analysis

25 mL each of TISAB solution and sample solution are pipetted into plastic beakers and the standard addition started.

Calculations

The fluoride content is given in ppm.

3.2 *tiamo* method: Determination of fluoride in cooking salt

Application note

With this method the content of fluoride in cooking salt can be determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the determination series. The main track handles the standard addition followed by the rinsing of the electrode and the conditioning which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database 'Robotic Fluoride Analyzer' (can be modified). In the series end track the electrode is moved to a special beaker where it is stored in dist. water for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the water beaker.

Sample preparation

200 g of sodium chloride are dissolved in approximately 500 mL of dist. water and filled up to the mark. 25 mL of the sample solution are pipetted into a beaker.

Procedure

The beakers are placed on the rack and the determination series is started. 25 mL TISAB are added automatically. Then the fluoride standard c(F-) = 1000 ppm is added and the standard addition is stopped after the addition of the four increments.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for the conditioning of the ISE and for a proper electrode treatment between determination series as well as in case of an error.

Result report

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in cooking salt

Programm version tiamo 1.1

2005-10-06 14:10:21 UTC+2

Results report

Determination

Method . . . . . Fluoride in cooking salt
Method saving date . . . . . 2005-10-04 17:31:44 UTC+2
Method version 1
Method state . . . . . original
Determination ID . . . . . -57b1880c:106bbb2cba4:-7839
Determination start . . . . . 2005-10-04 18:18:37 UTC+2
Determination state . . . . . original
Determination version 1
Run number 19
User (full name) . . . . . Metrohm

Sample data

Sample Identification 1 . . . . . Cooking salt
Sample size . . . . . 25 mL

standard addition.1

STDADD auto

Slope . . . . . -60.1 mV
E (0) . . . . . 121.6 mV
F (-1) . . . . . 52.0 ppm
Variance 0.001

	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		36.5		30
Increment 1	0.638	26.4	-10.2	62
Increment 2	0.976	16.3	-10.1	102
Increment 3	1.492	6.2	-10.0	158
Increment 4	2.344	-3.9	-10.1	240

Results

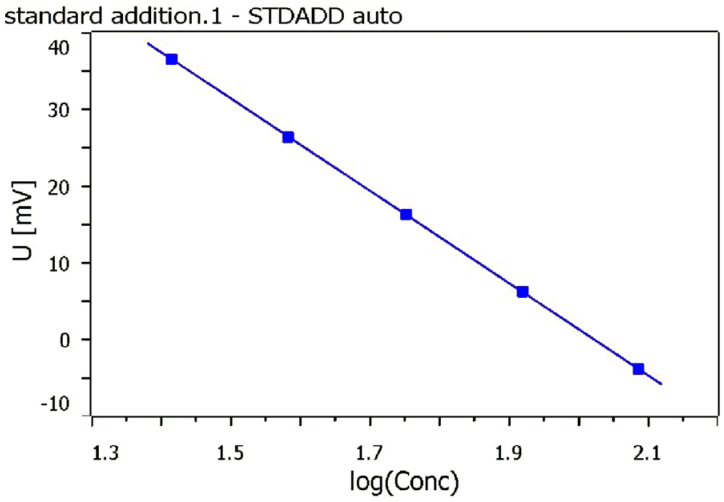
Fluoride content . . . . . 52.0 ppm

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in cooking salt

Programm version tiamo 1.1

2005-10-06 14:10:21 UTC+2



Statistical results (example)

Fluoride in cooking salt

Sample size [mL]	Fluoride content [ppm]
25.00	52.4
25.00	52.6
25.00	52.3
25.00	52.2
25.00	52.1
25.00	52.2
25.00	52.0
25.00	52.0
25.00	52.2
25.00	52.0
Mean value	52.2
abs. std. dev.	0.19
rel. std. dev. %	0.37

3.3 Fluoride in wine

General

Fluoride is only present in wine in traces. Possible sources of fluoride are:

- Aluminum, ceramic or cement works near the vineyard
- Sugar solutions made up with fluorinated drinking water.

Detailed investigations (Europe, USA) have shown that only 4...6% of the wines tested had a content >0.5 mg/L F.

Recommended accessories

- 6.3032.220 Dosing Unit, 20 mL
- 6.3032.250 Dosing Unit, 50 mL
- 6.0502.150 F ISE with 6.2104.020 electrode cable
- 6. 0750.100 LL-ISE reference electrode with 6.2106.020 electrode cable

Reagents

- TISAB solution: Into a 1000 mL volumetric flask, weigh out 74.5 g KCl (e.g. Merck no. 104935), 98.1 g $KOOCCH_3$ (e.g. Merck no. 104820), 2.6 g KH_2PO_4 (e.g. Merck no. 104873) and 3.55 g Na_2HPO_4 (e.g. Merck no. 106586), dissolve in dist. H_2O, make up to the mark with dist. H_2O and mix.
- Fluoride standard II: ρ(fluoride) = 100 mg/L
  100 mL of the fluoride standard I are pipetted in a 1 L volumetric flask and filled up to the mark and mixed. It must be stored in a plastic bottle.

Analysis

30 mL of CO_2-free sample and 5 mL TISAB solution are pipetted into a plastic beaker and the standard addition is started.

Calculations

The fluoride content of wine is given in ppm

Remarks

- Fluoride ions can also be bound on glass surfaces to form fluorosilicates; these cannot be determined. This is why beakers and storage vessels made of plastic (e.g. PE or PP) are used.
- The fluoride content of wine is normally very low at 0.05...0.5 mg/L F. A permitted maximum concentration of 0.5 mg/L (EU) or 1.0 mg/L (USA) must not be exceeded.
- In order to avoid the formation of gas bubbles on the membrane surface, measurements should always be carried out on degassed wine samples (vacuum or short boiling and cooling down).

3.4 *tiamo* method: Determination of fluoride in wine

Application note

With this method the content of fluoride in wine can be determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the determination series. The main track handles the standard addition followed by the rinsing and the conditioning of the electrode which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database 'Robotic Fluoride Analyzer' (can be modified). In the series end track the electrode is moved to a special beaker where it is stored in dist. water for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the water beaker.

Sample preparation

30 mL of the sample are pipetted into a sample beaker.

Procedure

The beakers are placed on the rack and the determination series is started. 5 mL TISAB are added automatically. Then the fluoride standard c(F-) = 100 ppm is added and the standard addition is stopped after the addition of the four increments.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for the conditioning of the ISE and for a proper electrode treatment between determination series as well as in case of an error.

Result report

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in wine

Programm version tiamo 1.1

2005-10-06 14:13:13 UTC+2

Results report

Determination

Method . . . . . Fluoride in wine
Method saving date . . . . . 2005-10-04 17:22:02 UTC+2
Method version 1
Method state . . . . . original
Determination ID . . . . . -57b1880c:106bbb2cba4:-78dd
Determination start . . . . . 2005-10-04 14:19:33 UTC+2
Determination state . . . . . original
Determination version 1
Run number 12
User (full name) . . . . . Metrohm

Sample data

Sample Identification 1 . . . . . Red wine
Sample size . . . . . 30 mL

standard addition.1

STDADD auto

Slope . . . . . -60.6 mV
E (0) . . . . . 91.1 mV
F (-1) 0.2
Variance 0.118

	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		151.8		55
Increment 1	0.094	126.0	-25.8	92
Increment 2	0.232	100.7	-25.2	133
Increment 3	0.616	75.6	-25.1	205
Increment 4	1.708	50.7	-24.9	386

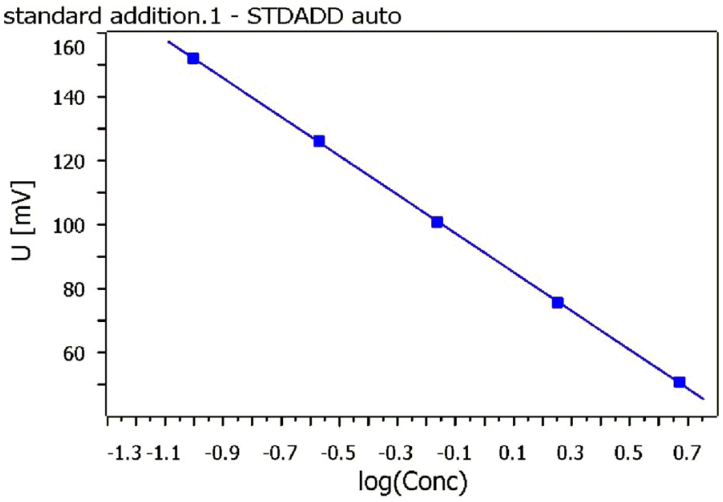
Results

Fluoride content . . . . . **0.20 ppm**

Robotic Fluoride Analyzer
Fluoride in wine

Programm version tiamo 1.1

2005-10-06 14:13:13 UTC+2



3.5 Fluoride in mouth rinse

Recommended accessories

- 6.3032.220 Dosing Unit, 20 mL
- 6.3032.250 Dosing Unit, 50 mL
- 6.0502.150 F ISE with 6.2104.020 electrode cable
- 6.0750.100 LL-ISE reference electrode with 6.2106.020 electrode cable

Reagents

TISAB solution: 58 g NACl are dissolved in approx. 500 mL dist. water. Then 5 g of Complexon IV (1,2 di-amino cyclohexane N,N,N',N' tetraacetic acid) are added and dissolved by dropwise addition of c(NaOH) = 8 mol/L. 57 mL of glacial acetic acid are 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 dist. water.

Sample preparation

No sample preparation is necessary. The mouth rinse solution can be analysed directly.

Analysis

2 mL sample and 35 mL TISAB (diluted 1:1 with dist. water) are pipetted into the measuring vessels and the standard addition is started.

Calculations

The content of fluoride in mouth rinse is calculated in ppm.

3.6 tiamo method: Determination of fluoride in mouth rinse

Application note

With this method the content of fluoride in mouth rinse can be determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the determination series. The main track handles the standard addition followed by the rinsing of the electrode and the conditioning which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database 'Robotic Fluoride Analyzer' (can be modified). In the series end track the electrode is moved to a special beaker where it is stored in dist. water for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the water beaker.

Sample preparation

2 mL of the sample are pipetted into a sample beaker.

Procedure

The beakers are placed on the rack and the determination series is started. 35 mL TISAB are added automatically. Then the fluoride standard c(F-) = 1000 ppm is added and the standard addition is stopped after the addition of the four increments.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for the conditioning of the ISE and for a proper electrode treatment between determination series as well as in case of an error.

Result report

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in mouth rinse

Programm version tiamo 1.1

2005-10-06 14:07:43 UTC+2

Results report

Determination

Method	Fluoride in mouth rinse
Method saving date	2005-10-06 08:46:13 UTC+2
Method version	1
Method state	original
Determination ID	-6edb7ef1:106c48287f7:-7dff
Determination start	2005-10-06 10:04:55 UTC+2
Determination state	original
Determination version	1
Run number	16
User (full name)	Metrohm

Sample data

Sample Identification 1	Mouth rinse
Sample size	2 mL

standard addition.1

STDADD auto

Slope	-60.8	mV
E (0)	120.9	mV
F (-1)	250.2	ppm
Variance	0.001	

	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		48.4		43
Increment 1	0.410	32.9	-15.5	72
Increment 2	0.752	17.6	-15.3	106
Increment 3	1.408	2.6	-15.0	163
Increment 4	2.798	-12.6	-15.1	243

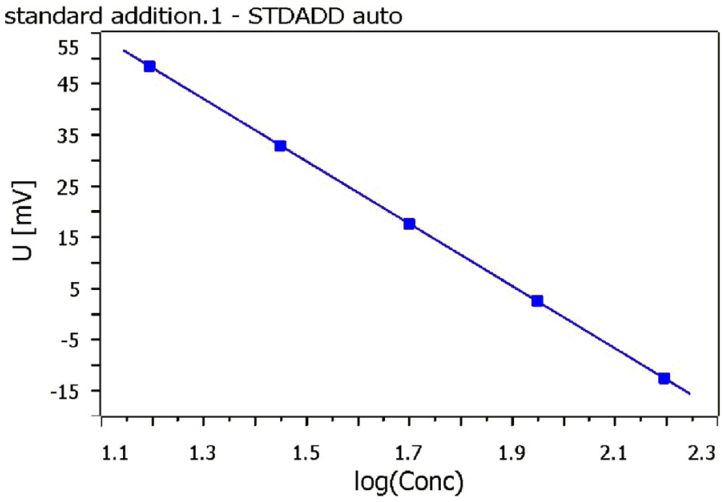
Results

Fluoride content **250.2 ppm**

Robotic Fluoride Analyzer
Fluoride in mouth rinse

Programm version tiamo 1.1

2005-10-06 14:07:43 UTC+2



Statistical results (example)

Fluoride in mouth rinse

Sample size [mL]	Fluoride content [ppm]
2.0	249.4
2.0	249.0
2.0	250.5
2.0	249.7
2.0	249.6
2.0	252.9
2.0	250.5
2.0	249.0
2.0	250.2
2.0	248.2
Mean value	249.9
abs. std. dev.	1.28
rel. std. dev. %	0.51

3.7 Fluoride in toothpaste

Recommended accessories

- 6.3032.220 Dosing Unit, 20 mL
- 6.3032.250 Dosing Unit, 50 mL
- 6.0502.150 F ISE with 6.2104.020 electrode cable
- 6.0750.100 LL-ISE reference electrode with 6.2106.020 electrode cable

Reagents

TISAB solution: Dissolve 170 g $NaNO_3$, 18 mL glacial acetic acid, 40.8 g sodium acetate and 1.5 g Na_2EDTA in 500 mL distilled water. Transfer to a 1000 mL volumetric flask, fill to the mark and mix well.

Sample preparation

Weigh 5 g of sample into a 100 mL beaker. Add 5 mL distilled water and 5 mL concentrated HCl to the sample and homogenize with a magnetic stirrer or in an ultrasonic bath. Put the beaker into a water bath at 90 °C for 1 min. Let cool and transfer to a 1000 mL volumetric flask. Fill to the mark with distilled water and mix well (= sample solution).

Analysis

5 mL of the sample solution and 30 mL TISAB are pipetted into the measuring vessels and the standard addition is started.

Calculations

The content of fluoride in toothpaste is calculated in ppm.

3.8 *tiamo* method: Determination of fluoride in toothpaste

Application note

With this method the content of fluoride in toothpaste can be determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the determination series. The main track handles the standard addition followed by the rinsing of the electrode and the conditioning which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database 'Robotic Fluoride Analyzer' (can be modified). In the series end track the electrode is moved to a special beaker where it is stored in dist. water for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the water beaker.

Sample preparation

5 g of the sample are weighed into a beaker. Then 5 mL of dist. water and 5 mL of conc. hydrochloric acid are added and the mixture homogenized with a magnetic stirrer and for about 10 minutes in the ultrasonic bath. The mixture is then heated up to 90° C for one minute and allowed to cool down. The sample is then transferred to a 1L volumetric flask and the flask filled up with dist. water to the mark. 5 mL of the sample solution are pipetted into a beaker.

Procedure

The beakers are placed on the rack and the determination series is started. 35 mL TISAB are added automatically. Then the fluoride standard c(F-) = 100 ppm is added and the standard addition is stopped after the addition of the four increments.

The factor 200 in the calculation formula is needed for the compensation of the dilution of the sample.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for the conditioning of the ISE and for a proper electrode treatment between determination series as well as in case of an error.

Result report

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in toothpaste

Programm version tiamo 1.1

2005-10-06 14:09:17 UTC+2

Results report

Determination

Method . . . . . Fluoride in toothpaste
Method saving date . . . . . 2005-10-05 16:14:41 UTC+2
Method version 1
Method state . . . . . original
Determination ID . . . . . -57b1880c:106bbb2cba4:-75fa
Determination start . . . . . 2005-10-05 17:28:10 UTC+2
Determination state . . . . . original
Determination version 1
Run number 40
User (full name) . . . . . Metrohm

Sample data

Sample Identification 1 . . . . . Toothpaste
Sample size . . . . . 5 mL

standard addition.1

STDADD auto

Slope . . . . . -61.0 mV
E (0) . . . . . 127.8 mV
F (-1) . . . . . 6.4 ppm
Variance 0.004

	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		126.0		17
Increment 1	0.254	110.8	-15.1	46
Increment 2	0.452	95.7	-15.1	79
Increment 3	0.838	80.7	-15.0	116
Increment 4	1.586	65.7	-15.0	171

Results

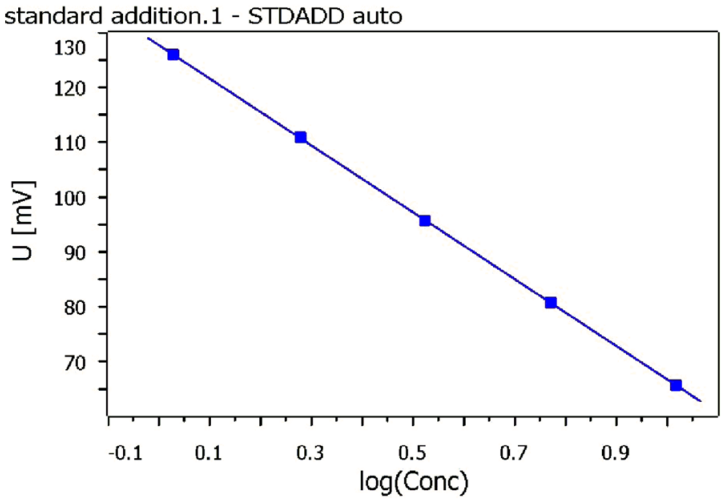
Fluoride content . . . . . 1280.0 ppm

tiamo™ titration and more

Robotic Fluoride Analyzer
Fluoride in toothpaste

Programm version tiamo 1.1

2005-10-06 14:09:17 UTC+2



Statistical results (example)

Fluoride in toothpaste

Sample size [mL]	Fluoride content [ppm]
5	1280.0
5	1280.0
5	1280.0
5	1300.0
5	1280.0
5	1300.0
5	1280.0
5	1280.0
5	1280.0
5	1280.0
Mean value	1284.0
abs. std. dev.	8.43
rel. std. dev. %	0.66

4 Troubleshooting Fluoride ISE

Cleaning: Rinse with dist. water only. Do not touch or wipe crystal membrane!

Storage: Dry, with protection cap. Condition in c(NaF) = 0.1 mol/L for 15 min., then in dist. water for 30 min before first measurement.

4.1 Troubleshooting

Electrode	Source of interference	Effects	Cleaning
Ion-selective crystal membrane	Dissolution processes, oxidation processes	Rough surface ➔ slow response, poor detection limits	Polish with polishing cloth and tooth paste
	Electrode poisons	Formation of more sparingly soluble salts on the electrode surface than with the ion to be measured ➔ zero point shift, reduced linearity range	Polish with polishing cloth and toothpaste, mask interfering ion

5 Method reports

5.1 Determination of fluoride in cooking salt

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:47 UTC+1

Method parameters

Method . . . . . Fluoride in cooking salt
Method saving date . . . . . 2005-11-08 08:29:40 UTC+1
Method version 1
Method group . . . . . Robotic Fluoride Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . off
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject	Message from tiamo - Method 'Fluoride in cooking salt 1' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on. . . . . Sample position
Value	off.
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Message from tiamo - Method 'Fluoride in cooking salt 1' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on. . . . . Sample size unit
Value	off.
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on. ID1
Value	off.

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ADD **TISAB**

General/Hardware
- Device
  - Device name . . . . . 855_1
- Dosing device
  - Dosing device 2
  - Solution . . . . . TISAB
  - Tandem dosing . . . . . off
- Stirrer
  - Stirrer . . . . . off
  - Stirring rate 9
  - Switch off automatically . . . . . on
- Dosing parameters
  - Volume . . . . . 25 mL
  - Dosing rate . . . . . maximum mL/min

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:47 UTC+1

Filling rate . . . . . maximum mL/min
Fill automatically at end . . . . . on

STDADD auto **standard addition**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . Fluoride standard
Sensor
Measuring input 1
Sensor . . . . . F-ISE
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 5
Switch off automatically . . . . . on

Standard addition

Number of additions 4
Volume auxiliary solution . . . . . 25 mL
Stop volume . . . . . 20 mL

Control parameters
Dosing rate . . . . . fast
Delta U . . . . . 10 mV

Measuring parameters

Measurement with drift control
Signal drift . . . . . 0.5 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 215 s
Measuring interval . . . . . 2.0 s
Temperature
Temperature . . . . . 25.0 °C
Switch off stirrer during . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **aspirate and rinse**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:47 UTC+1

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **empty beaker**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

MOVE **to water beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . on
Stop determination . . . . . off
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

STIR **stirrer on**
Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8
Action
Switch on . . . . . on

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:47 UTC+1

Switch off . . . . . off
Duration . . . . . off

WAIT **wait 60 sec**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 60
Unit . . . . . s

Message
Record message . . . . . off
Message by e-mail . . . . . off
Acoustic signal . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1

Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8

Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Fluoride content	= 'standard addition.RES'	ppm	1	RS01	off

Result name . . . . . **Fluoride content**
Formula . . . . . = 'standard addition.RES'
Unit . . . . . ppm
Decimal places 1
Assignment RS01

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:47 UTC+1

Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . Fluoride in cooking salt
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\fluoride in cooking salt.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Fluoride Analyzer

SERIES END **Series end track**

MOVE **to storage beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target
Tower 1

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:47 UTC+1

Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

5.2 Determination of fluoride in wine

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:31 UTC+1

Method parameters

Method . . . . . Fluoride in wine
Method saving date . . . . . 2005-11-08 08:56:05 UTC+1
Method version 1
Method group . . . . . Robotic Fluoride Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view

Current view . . . . . on

Track view for live window

Live display 1 . . . . . Main track

Live display 2 . . . . . Main track

Statistics . . . . . off

Conditioning

Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject . . . . . Message from tiamo - Method 'Fluoride in cooking salt' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample position
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'Fluoride in cooking salt' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on . . . . . Sample size unit
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text
Assignment . . . . . on ID1
Value . . . . . off . . . . .

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ADD **TISAB**

General/Hardware
- Device
  - Device name . . . . . 855_1
- Dosing device
  - Dosing device 2
  - Solution . . . . . TISAB
  - Tandem dosing . . . . . off
- Stirrer
  - Stirrer . . . . . off
  - Stirring rate 9
  - Switch off automatically . . . . . on
- Dosing parameters
  - Volume . . . . . 5 mL
  - Dosing rate . . . . . maximum mL/min

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:31 UTC+1

Filling rate . . . . . maximum mL/min
Fill automatically at end . . . . . on

STDADD auto **standard addition**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . Fluoride standard 100
Sensor
Measuring input 1
Sensor . . . . . F-ISE
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 5
Switch off automatically . . . . . on

Standard addition

Number of additions 4
Volume auxiliary solution . . . . . 5 mL
Stop volume . . . . . 20 mL

Control parameters
Dosing rate . . . . . medium
Delta U . . . . . 20 mV

Measuring parameters

Measurement with drift control
Signal drift . . . . . 0.5 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 215 s
Measuring interval . . . . . 2.0 s
Temperature
Temperature . . . . . 25.0 °C
Switch off stirrer during . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **aspirate and rinse**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:31 UTC+1

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **empty beaker**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

MOVE **to water beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . on
Stop determination . . . . . off
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

STIR **stirrer on**
Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8
Action
Switch on . . . . . on

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:31 UTC+1

Switch off . . . . . off
Duration . . . . . off

WAIT **wait 60 sec**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 60
Unit . . . . . s

Message
Record message . . . . . off
Message by e-mail . . . . . off
Acoustic signal . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1

Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8

Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Fluoride content	= 'standard addition.RES'	ppm	2	RS01	off

Result name . . . . . **Fluoride content**
Formula . . . . . = 'standard addition.RES'
Unit . . . . . ppm
Decimal places 2
Assignment RS01

Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . Fluoride in wine
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\fluoride in cooking salt.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Fluoride Analyzer

SERIES **Series end track**
END

MOVE **to storage beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target
Tower 1

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:31 UTC+1

Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

5.3 Determination of fluoride in mouth rinse

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:42 UTC+1

Method parameters

Method . . . . . Fluoride in mouth rinse
Method saving date . . . . . 2005-11-08 08:57:42 UTC+1
Method version 1
Method group . . . . . Robotic Fluoride Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . off
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject . . . . . Message from tiamo - Method 'Fluoride in toothpaste' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on. . . . . Sample position
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . . .
Upper limit . . . . . .
Message . . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . . .
Subject . . . . . Message from tiamo - Method 'Fluoride in toothpaste' - Command 'Main track'
User . . . . . .
Mail from . . . . . .
SMTP Server . . . . . .
POP3 Server . . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on. . . . . Sample size unit
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text
Assignment . . . . . on. ID1
Value . . . . . off. . . . . .

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Sample position
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ADD **TISAB**

General/Hardware
Device
Device name . . . . . 855_1
Dosing device
Dosing device 2
Solution . . . . . TISAB
Tandem dosing . . . . . off
Stirrer
Stirrer . . . . . off
Stirring rate 9
Switch off automatically . . . . . on
Dosing parameters
Volume . . . . . 35 mL
Dosing rate . . . . . maximum mL/min

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:42 UTC+1

Filling rate . . . . . maximum mL/min
Fill automatically at end . . . . . on

STDADD auto **standard addition**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . Fluoride standard
Sensor
Measuring input 1
Sensor . . . . . F-ISE
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 4
Switch off automatically . . . . . on

Standard addition

Number of additions 4
Volume auxiliary solution . . . . . 35 mL
Stop volume . . . . . 20 mL

Control parameters
Dosing rate . . . . . fast
Delta U . . . . . 15 mV

Measuring parameters

Measurement with drift control
Signal drift . . . . . 0.5 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 215 s
Measuring interval . . . . . 2.0 s
Temperature
Temperature . . . . . 25.0 °C
Switch off stirrer during . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **aspirate and rinse**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:42 UTC+1

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **empty beaker**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

MOVE **to water beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . on
Stop determination . . . . . off
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

STIR **stirrer on**
Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 6
Action
Switch on . . . . . on

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:42 UTC+1

Switch off . . . . . off
Duration . . . . . off

WAIT **wait 60 sec**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 60
Unit . . . . . s

Message
Record message . . . . . off
Message by e-mail . . . . . off
Acoustic signal . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1

Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 6

Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Fluoride content	= 'standard addition.RES'	ppm	1	RS01	off

Result name . . . . . **Fluoride content**
Formula . . . . . = 'standard addition.RES'
Unit . . . . . ppm
Decimal places 1
Assignment RS01

Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . Fluoride in mouth rinse
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\fluoride in mouth rinse.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Fluoride Analyzer

SERIES END **Series end track**

MOVE **to storage beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target
Tower 1

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:42 UTC+1

Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

5.4 Determination of fluoride in toothpaste

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:36 UTC+1

Method parameters

Method . . . . . Fluoride in toothpaste
Method saving date . . . . . 2005-11-08 08:59:57 UTC+1
Method version 1
Method group . . . . . Robotic Fluoride Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view

Current view . . . . . on

Track view for live window

Live display 1 . . . . . Main track

Live display 2 . . . . . Main track

Statistics . . . . . off

Conditioning

Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject . . . . . Message from tiamo - Method 'Fluoride in toothpaste' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample position
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'Fluoride in toothpaste' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on . . . . . Sample size unit
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text
Assignment . . . . . on ID1
Value . . . . . off . . . . .

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ADD **TISAB**

General/Hardware
- Device
  - Device name . . . . . 855_1
- Dosing device
  - Dosing device 2
  - Solution . . . . . TISAB
  - Tandem dosing . . . . . off
- Stirrer
  - Stirrer . . . . . off
  - Stirring rate 9
  - Switch off automatically . . . . . on
- Dosing parameters
  - Volume . . . . . 30 mL
  - Dosing rate . . . . . maximum mL/min

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:36 UTC+1

Filling rate . . . . . maximum mL/min
Fill automatically at end . . . . . on

STDADD auto **standard addition**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . Fluoride standard 100
Sensor
Measuring input 1
Sensor . . . . . F-ISE
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 4
Switch off automatically . . . . . on

Standard addition

Number of additions 4
Volume auxiliary solution . . . . . 30 mL
Stop volume . . . . . 20 mL

Control parameters
Dosing rate . . . . . fast
Delta U . . . . . 15 mV

Measuring parameters

Measurement with drift control
Signal drift . . . . . 0.5 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 215 s
Measuring interval . . . . . 2.0 s
Temperature
Temperature . . . . . 25.0 °C
Switch off stirrer during . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **aspirate and rinse**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **empty beaker**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

MOVE **to water beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . on
Stop determination . . . . . off
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

STIR **stirrer on**
Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 6
Action
Switch on . . . . . on

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License ID 124049905 Program version tiamo 1.1 - 36
Client name TITRATION14
User Metrohm 2005-11-08 09:57:36 UTC+1

Switch off . . . . . off
Duration . . . . . off

WAIT **wait 60 sec**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 60
Unit . . . . . s

Message
Record message . . . . . off
Message by e-mail . . . . . off
Acoustic signal . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1

Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 6

Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Fluoride content	= 'standard addition.RES' * 200	ppm	1	RS01	off

Result name . . . . . **Fluoride content**
Formula . . . . . = 'standard addition.RES' * 200
Unit . . . . . ppm
Decimal places 1
Assignment RS01

Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . Fluoride in toothpaste
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\fluoride in toothpaste.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Fluoride Analyzer

SERIES END **Series end track**

MOVE **to storage beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target
Tower 1

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 36
Client name	TITRATION14		
User	Metrohm	2005-11-08	09:57:36 UTC+1

Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s