

Comprehensive tap water analysis with TitrIC 1

Branch: water, waste water, environmental protection

Keywords

TitriC 1 / 861 / 815 / 712 / 800 / Aquatrode plus / Ca-ISE / 6.0257.000 / Dosino / tiamo / 6.1006.510 / Metrosep SUPP 5 – 100 / 2.145.0320 / 853 / MCS / branch 2

Summary

The determination of anions / cations in tap water was done on the **Metrosep SUPP 5 – 100** / using carbonate - bicarbonate eluent with chemical suppression. **TitriC 1** allows a fully automated and parallel analysis of anions by IC, titration (p- / m-value, magnesium / calcium, total hardness) and direct measurements (temperature, pH, conductivity).

Sample

Tap water Herisau

Reagents

Eluent: **3.2 mmol/L sodium carbonate**
1.0 mmol/L sodium bicarbonate in ultra pure water (resistivity >18 M Ω)

Suppressor solutions:
50 mmol/L sulfuric acid
ultra pure water

Titration: 0.1 mol/L HCl for p-/m-value determination
0.05 mol/L EDTA for Ca-/Mg-titration
0.2 mol/L TRIS, 0.1 mol/L Acetylacetone

Standards [ppm] in ultra pure water

Anions:

Analyte	1	2	3	4	5	6	7
fluoride	0.025	0.05	0.1	0.2	0.3	0.4	0.5
chloride	2.5	5	10	20	30	40	50
nitrite	0.025	0.05	0.1	0.2	0.3	0.4	0.5
bromide	0.025	0.05	0.1	0.2	0.3	0.4	0.5
nitrate	2.5	5	10	20	30	40	50
sulfate	2.5	5	10	20	30	40	50

Apparatus and Accessories

- delivered with TitriC 1 package:

861 Adv. Compact IC with seq. supp.	2.861.0020
809 Titrando (with 2 measuring inputs)	2.809.0020
815 Robotic Sample Processor	2.815.0020
712 Conductometer	2.712.0010
Cond. measuring cell Pt 1000	6.0912.110
Conductivity standard	6.2301.060
Aquatrode plus	6.0257.000
Polymer membrane electrode Ca - ISE	6.0508.110
4 Dosinos	2.800.0010
tiamo 1.1 full	6.6056.112
USB Converter Edgeport/4	2.145.0320
802 Rod Stirrer	2.802.0020

- used optional accessories for TitriC 1:

Metrosep A SUPP 5 – 100	6.1006.510
Metrosep 4/5 Guard	6.1006.500
Sample rack 59 x 120 mL	6.2041.840
Sample beaker 120 mL (x100)	6.1459.300



Sample Preparation

The water samples were injected directly.

Analysis

The standards and the sample were injected using a 800 dosino (50 mL Dosing unit). Loop volume anions: **20 μ l**. The two (with the TitriC 1 package delivered) *tiamo* methods *TitriC 1 – complete run* and *TitriC 1 – IC calibrator anion* were used for all the analysis performed.

Calculation

Automatic integration with IC Net 2.3 software using peak area.

Parameters

IC - Anions

STARTUP HARDWARE:

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RECORDER METHOD Asupp5_100-TitrIC.mtw
RECORDER DATA Data acquisition [Cond]
861 Adv. Compact Unit version 4
861 Adv. Compact Supp. autostep yes
861 Adv. Compact Autostep with Fill
861 Adv. Compact Peristaltic pump yes
861 Adv. Compact Flow 0.80 mL/min
861 Adv. Compact Pmax 15.0 MPa
861 Adv. Compact Pmin 0.0 MPa
861 Adv. Compact FullScale 50 uS/cm
861 Adv. Compact Remote 00001000
    
```

START WITH DETERMINATION

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0.0 Column Thermostat START
0.20 861 Adv. Compact Valve Inject
10.0 861 Adv. Compact Valve Fill
    
```

START WITH INJECT:

```

0.0 RECORDER START
    
```

MEAS pH

Measuring parameters:

Measurement with drift control	on
Signal drift	10.0 mV/min
Min. waiting time	15 s
Max. waiting time	52 s
Measuring interval	2.0 s
Stop measured value pH	off
Measurement without drift control	off
Temperature	25.0 °C

MEAS conductivity

Measuring parameters:

Measurement frequency	auto
Measuring time	35 s
Measuring interval	2.0 s
Stop measured value	off mS/cm
Temperature	20.0 °C

SET pH 4,3(HCl) – Titration (m-value)

Control parameters

EP1 at pH	4.3
Titration rate	user
Dynamics pH	1.00
Max. rate	10.00 mL/min
Min rate	15.00 µL/min
Stop criterion	drift
Stop drift	30 µL/min
End point 2	off

SET pH 8,2 (HCl) – Titration (p-/m-value)

Control parameters:

EP1 at pH	8.2
Titration rate	user
Dynamics pH	1.00
Max. rate	10.00 mL/min
Min rate	15.00 µL/min
Stop criterion	drift
Stop drift	30 µL/min
End point 2	on
EP2 at pH	4.3
Dynamics pH	1.00
Max. rate	10.00 mL/min
Min rate	15.00 µL/min
Stop criterion	drift
Stop drift	30 µL/min

DET Ca/Mg – Titration (Total hardness)


Start conditions

Start volume	0 mL
Start Dosing rate	5 mL/min

Titration parameters

Titration rate	user
Signal drift	50.0 mV/min
Min. waiting time	0 s
Max. waiting time	52 s
Measuring point density	1
Min. increment	10.0 µL
Max. increment	off
Dosing rate	maximum mL/min
Temperature	25°C
Stop volume	10 mL
Stop measured value	off mV
Stop EP	2
Volume after EP	off mL
Stop time	300 s
Filling rate	maximum mL/min

Results

TitrIC-Report			
Print date	6/08/2006		
General data		Anions	
ID	Tap water Herisau	Fluoride [mg/L]	0.049
Record date	6/07/2006	Chloride [mg/L]	8.824
Record time	14:00:06	Nitrate [mg/L]	10.62
User comment		Sulfate [mg/L]	5.435
System comment			
Titration data			
pH	6.76		
Cond. [μ S/cm]	598		
Temp. [$^{\circ}$ C]	21.2		
m value [mmol/L]	5.64		
p value [mmol/L]	0		
Calcium [mg/L]	82.6		
Magnesium [mg/L]	17.41		
Total Hard. [mmol/L]	2.87		

Reproducibility: Measurement of 10 tap water samples:

IC:

Anions [ppm]	fluoride	chloride	nitrite	bromide	nitrate	sulfate
Average (N=10)	0.051	8.762	0.000	0.000	10.633	5.406
Standard Deviation	0.002	0.026	-	-	0.035	0.020
% RSD (N=10)	4.69	0.30	-	-	0.34	0.38

Titration / Direct measurements:

	pH	Cond. [μ S/cm]	Temp. [$^{\circ}$ C]	m value [mmol/L]	p value [mmol/L]	Calcium [ppm]	Magnesium [ppm]	Total hardness [mmol/L]
Average (N=10)	6.76	590.7	20.16	5.65	0.00	82.66	17.26	2.77
Standard Deviation	0.008	9.202	1.340	0.007	-	1.11	0.40	0.01
% RSD (N=10)	0.13	1.56	6.65	0.13	-	1.34	2.34	0.19

Recovery: Spiked sample Tap water Herisau:

Anions [ppm]	fluoride	chloride	nitrate	sulfate
sample (av. N=10)	0.051	8.762	10.633	5.406
spiked (av. N=6)	0.098	13.449	15.887	10.239
% RSD spiked	1.77	0.07	0.15	0.26
difference	0.047	4.69	5.25	4.83
theoretical spike	0.05	5	5	5
recovery %	94.3	93.7	105.1	96.6

Cations [ppm]	Calcium	Magnesium
sample (av. N=10)	82.66	17.26
spiked (av. N=6)	102.64	37.38
% RSD spiked	1.97	4.11
difference	19.97	20.12
theoretical spike	20	20
recovery %	99.9	100.6
Cations [ppm]	Calcium	Magnesium

Blank with 80/20 ppm Ca/Mg (av.N=8)		
% RSD spiked	0.86	2.59
recovery %	97.57	102.94

Comments

This Application Bulletin is based on AW CH6-0869-062006.

Overview of the determined parameters:

- direct measurement:
conductivity, pH, temperature
- titrations:
p- and m-value (= acidic capacity)
EDTA-titration of Ca / Mg
- IC:
fluoride, chloride, nitrite, bromide, nitrate,
sulfate

TitrIC is absolutely flexible and can be adapted to determine the desired variables.

No sample preparation is necessary for tap water.

The calibration results are good which means that the filling of a loop with a dosino is working with high precision.

The recovery as well as the reproducibility are good which shows that the liquid handling and titration done by dosinos is working properly.

The Ca-ISE should be prepared the following way before a measurement:

1. place the electrode for 15 min in ultra pure water
2. place the electrode for 30 min in a solution of 0.01 M (400 ppm) CaCl₂ solution

The Aquatrode should be stored in the storage solution (6.2323.000).

There's no sense in making a ionic balance like it could be done with TitrIC 2 systems as not all important cations are measured by the TitrIC 1 system.

For more detailed information about the system setup of TitrIC 1 consult the document **AB 285 - Installation Instructions for TitrIC 1**.

For TitrIC 2 Application Bulletin see AB 288 e and AB 290 e.

Appendix

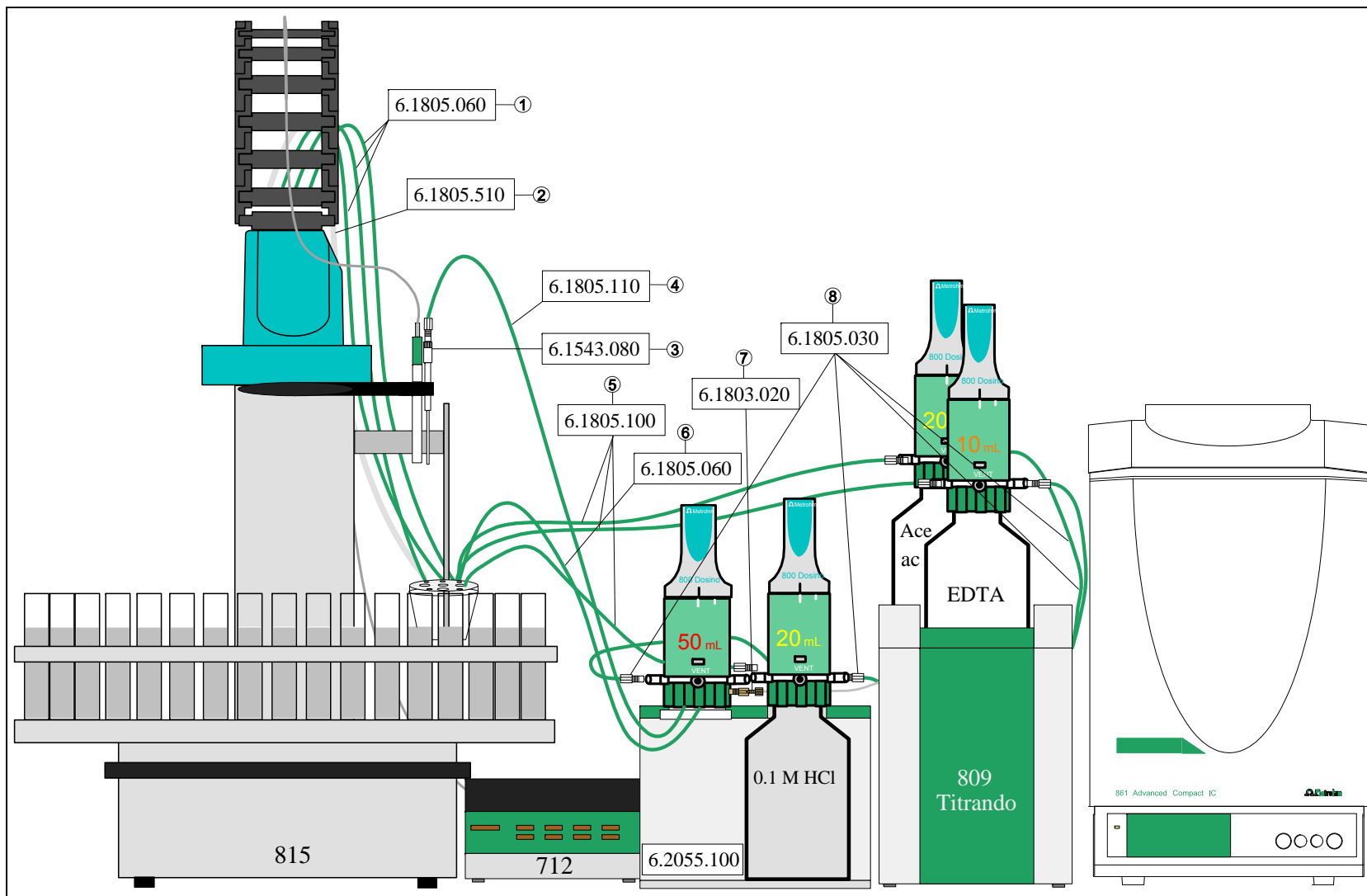
Calibration curves, reproducibility, chromatograms with peak tables and titration curves

Date

Thursday, 2006-06-06

Name

A. Rumi; IC Marketing,
Metrohm Ltd.; CH-9101 Herisau

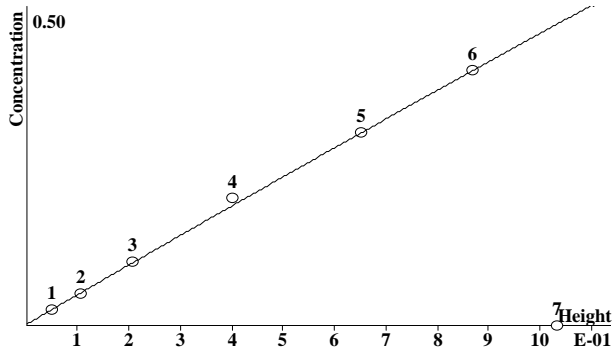


TitrIC 1: System setup

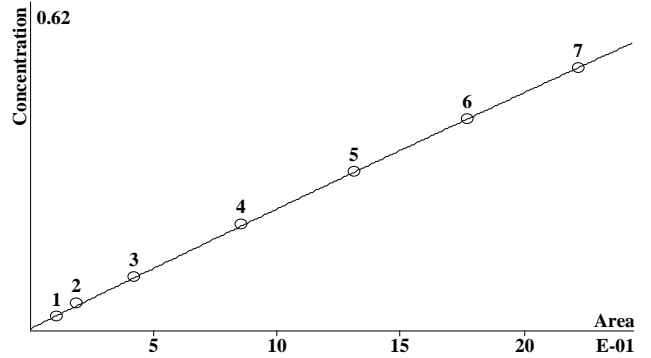
Calibration

Anions:

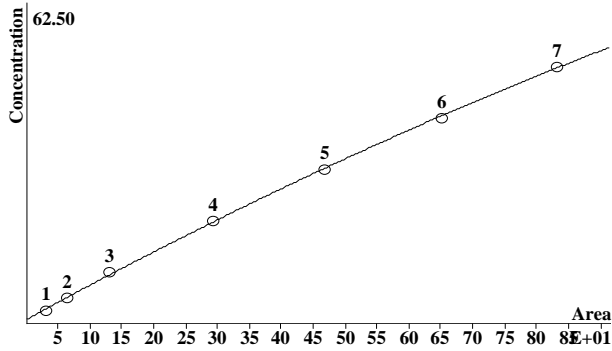
fluoride: RSD: 0.98%, corr. coeff.: 0.99996
 $Q = -0.0135 \cdot A^2 + 0.4698 \cdot A + 0.0010$, base: height



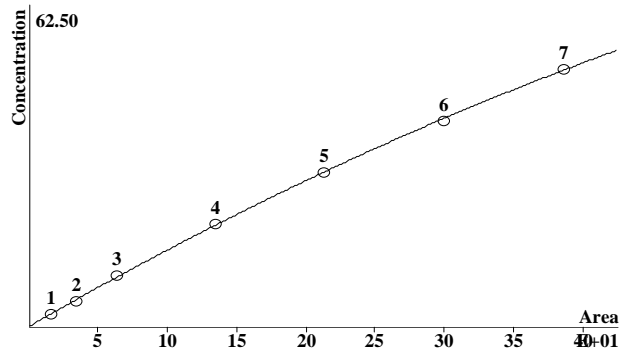
bromide: RSD: 1.10 %, corr. coeff.: 0.99989
 $Q = -0.00357 \cdot A^2 + 0.2315 \cdot A + 0.00294$, base: area



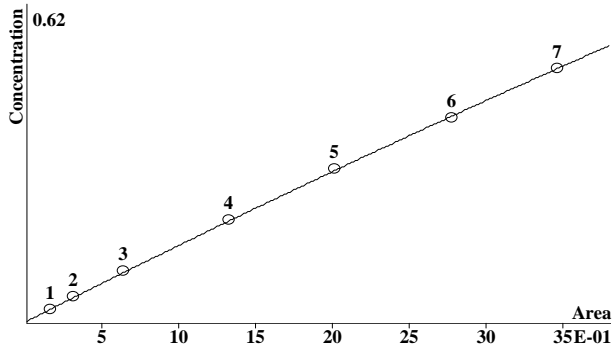
chloride: RSD: 1.78%, corr. coeff.: 0.99903
 $Q = -1.1158e-05 \cdot A^2 + 0.06826 \cdot A + 0.699$, base: area



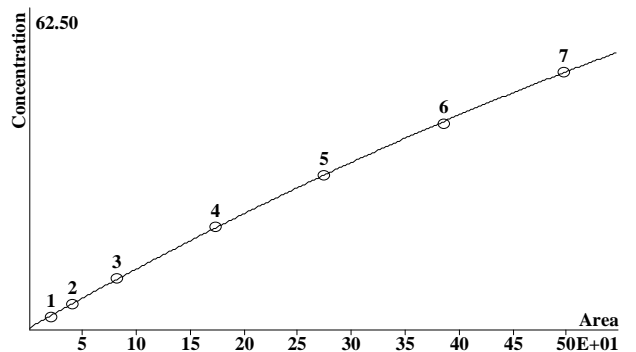
nitrate: RSD: 1.69%, corr. coeff.: 0.99843
 $Q = -6.818e-05 \cdot A^2 + 0.1549 \cdot A + 0.08382$, base: area



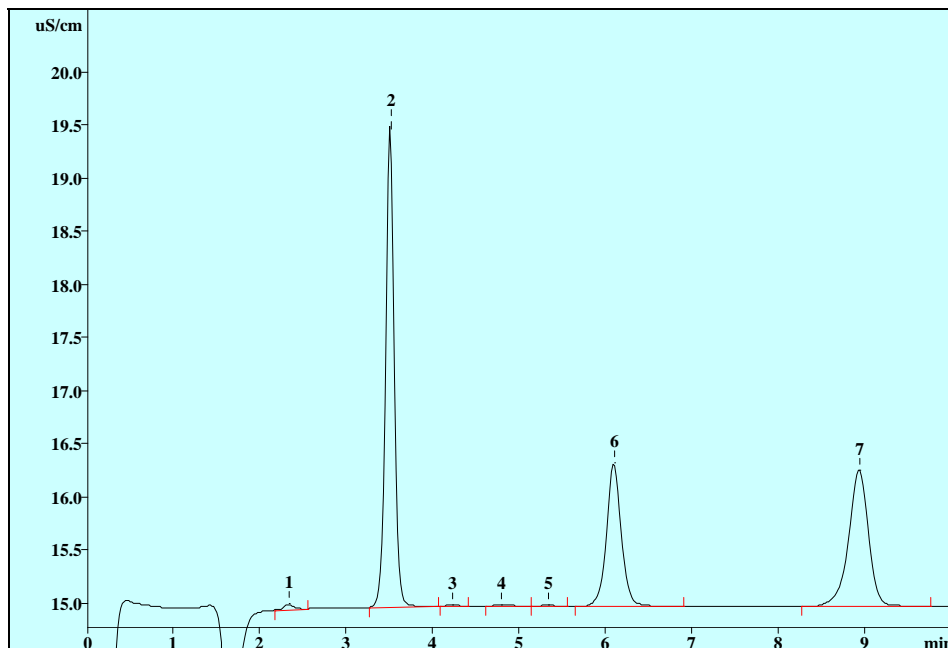
nitrite: RSD: 1.53 %, corr. coeff.: 0.99974
 $Q = -0.002735 \cdot A^2 + 0.1525 \cdot A + 0.00272$, base: area



sulfate: RSD: 1.21%, corr. coeff.: 0.998715
 $Q = -3.8386e-05 \cdot A^2 + 0.1187 \cdot A + 0.3024$, base: area



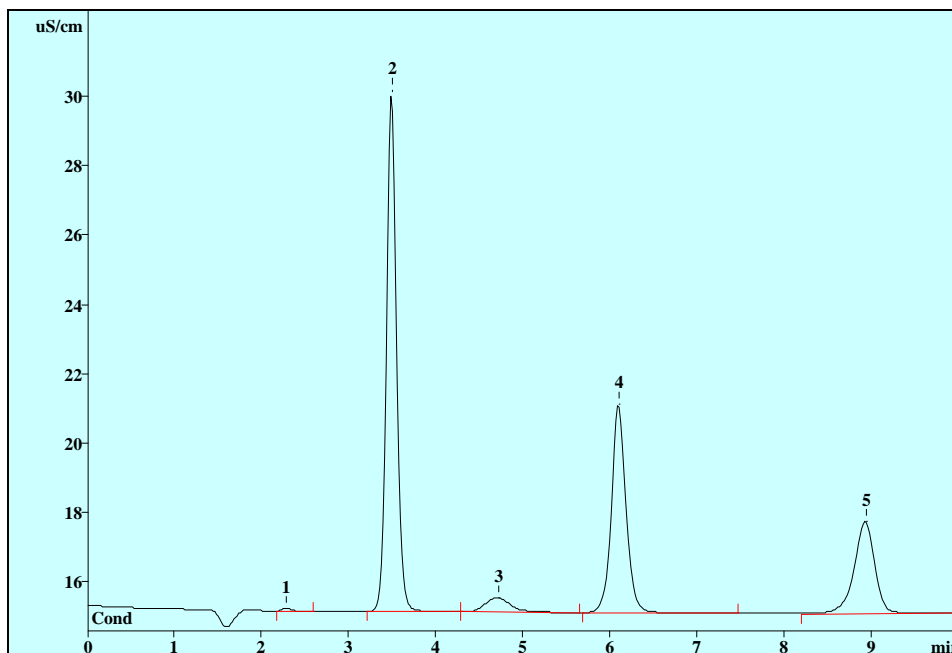
Chromatograms with peak tables - Anions



Standard 2

File: q6071108
 Volume: 20.0 µl
 Dilution: 1.00
 Amount: 1.00

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	2.32	0.05	0.369	0.0277	fluoride
2	3.50	4.57	31.153	2.8154	chloride
3	4.22	0.02	0.161	0.0272	nitrite
4	4.79	0.01	0.180	0.0000	system peak
5	5.32	0.01	0.108	0.0279	bromide
6	6.09	1.35	16.103	2.5618	nitrate
7	8.93	1.29	20.808	2.7550	sulfate



Tap water Herisau

File: q6071419
 Volume: 20.0 µl
 Dilution: 1.00
 Amount: 1.00

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	2.27	0.10	0.771	0.0515	fluoride
2	3.49	15.06	120.684	8.7757	chloride
3	4.70	0.43	8.963	0.0000	system peak
4	6.09	6.03	70.301	10.6420	nitrate
5	8.92	2.67	44.088	5.4597	sulfate

Titration curves of tap water Herisau

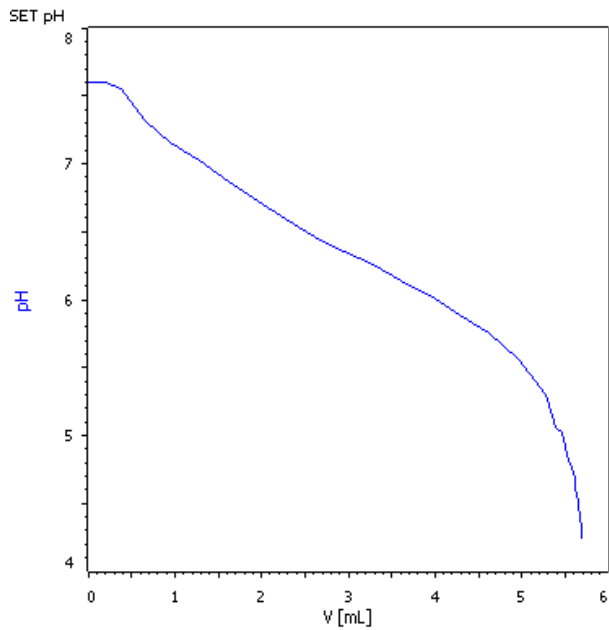


Fig. 1: Titration of *m*-value (to pH 4.3)

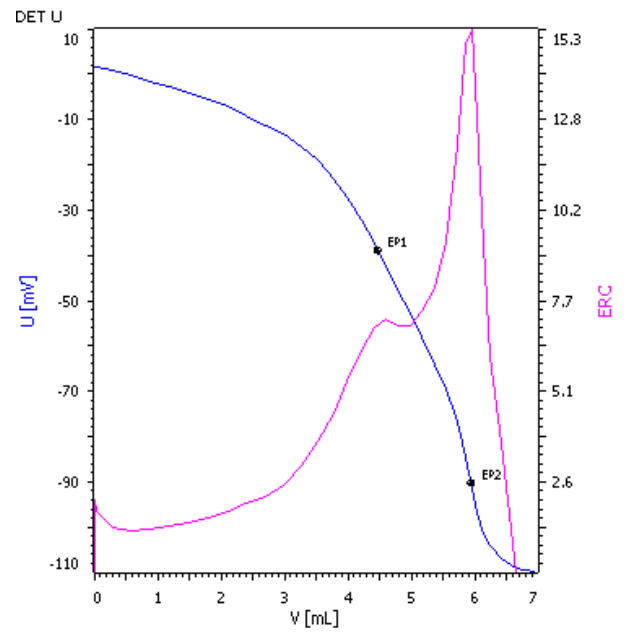


Fig. 2: Titration of Ca/Mg with EDTA