

Comprehensive tap water analysis with TitrIC 2

Branch: water, waste water, environmental protection

Keywords

TitrIC 2 / 861 / 855 / 712 / 800 / Aquatrode plus / 6.0257.000 / Dosino / tiamo / 6.1006.430 / Metrosep SUPP 4 – 250 / 6.1010.210 / Metrosep C 2 – 100 / 2.145.0320 / branch 2

Summary

The determination of anions / cations in tap water was done on the **Metrosep SUPP 4 – 250 / Metrosep C 2 – 100** using carbonate / tartaric acid – dipicolinic acid eluent with chemical suppression. **TitrIC 2** enables a fully automated and parallel analysis of anions, cations, titration (p- and m- value), and direct measurements (temperature, pH, conductivity). In this application only the standard ions are determined. For a more complete analysis including the oxygenated halides please refer to **AB 303 e**.

Sample

Tap water Herisau

Reagents

Eluent: **2.4 mM sodium carbonate, 2.0 mM sodium bicarbonate, 5% acetone** in ultra pure water (resistivity >18 MΩ)

7 mM tartaric acid, 1.5 mM dipicolinic acid in ultra pure water

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

Standards [ppm] in ultra pure water

Anions:

Analyte / Level	1	2	3	4	5
fluoride	0.04	0.06	0.08	0.1	0.12
chloride	6	9	12	15	18
nitrate	6	9	12	15	18
sulfate	4	6	8	10	12

Cations:

Analyte / Level	1	2	3	4	5
sodium	1	2	4	6	8
potassium	0.5	1	2	3	4
calcium	12.5	25	50	75	100
magnesium	3.75	7.5	15	22.5	30

Apparatus and Accessories

- delivered with TitrIC 2 package:

861 Adv. Compact IC with seq. supp.	2.861.0020
861 Adv. Compact IC	2.861.0010
855 Robotic Titrosampler	2.855.0020
712 Conductometer	2.712.0010
Cond. measuring cell Pt 1000	6.0912.110
Conductivity standard	6.2301.060
Aquatrode plus	6.0257.000
3 Dosions	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 2:

Metrosep A SUPP 4 – 250	6.1006.430
Metrosep 4/5 Guard	6.1006.500
Metrosep C 2 – 100	6.1010.210
Metrosep C 2 Guard	6.1010.200
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 two 800 dosinos (10 and 50 mL Dosing unit) with automatic acidification for the cation run prior to injection. Loop volume anions: **20 µl**, cations **10 µl**.

The two (delivered with the TitrIC 2 package) *tiamo* methods *TitrIC 2 – complete run* and *TitrIC 2 – IC calibraton anion & cation* were used for all analysis.

Calculation (IC)

Automatic integration with IC Net 2.3 software using peak area.

Parameters

Anions

STARTUP HARDWARE:

```

RECORDER   METHOD   Asupp5.mtw
RECORDER   DATA   Data acquisition [Cond]
861 Adv. Compact Unit version      2
861 Adv. Compact Polarity          +
861 Adv. Compact Supp. autostep     yes
861 Adv. Compact Autostep with     Fill
861 Adv. Compact Flow              2.00 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

```

0.20 861 Adv. Compact Valve Inject
6.50 861 Adv. Compact Valve Fill
    
```

START WITH INJECT:

```

0.0 RECORDER START
    
```

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
    
```

Cations

STARTUP HARDWARE:

```

RECORDER   METHOD   C2_100.mtw
RECORDER   DATA   Data acquisition [Cond]
861 Adv. Compact Polarity          -
861 Adv. Compact Supp. autostep     no
861 Adv. Compact Autostep with     Fill
861 Adv. Compact Flow              1.3 mL/min
861 Adv. Compact Pmax              25.0 MPa
861 Adv. Compact Pmin              0.0 MPa
861 Adv. Compact FullScale         1000uS/cm
861 Adv. Compact Remote            00000000
    
```

START WITH DETERMINATION

```

0.20 861 Adv. Compact Valve Inject
5.70 861 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
    
```

Results

TitriC-Report



Print date	4/12/2006	Anions	
General data		F [mg/L]	0.061
ID	Tap water Herisau	Cl [mg/L]	14.088
Record date	3/09/2006	NO3 [mg/L]	10.606
Record time	19:15:16	SO4 [mg/L]	5.491
User comment		Anion balance [mEq/L]	5.6158
System comment	recalculated, within limit	Cations	
Titration data		Na [mg/L]	7.091
pH	7.72	K [mg/L]	1.736
Cond. [µS/cm]	530	Mg [mg/L]	17.537
Temp. [°C]	21.72	Ca [mg/L]	80.367
m value [mmol/L]	5.15	Cation balance [mEq/L]	5.8064
p value [mmol/L]	0	ionic difference [mEq/L]	0.1907
		ionic difference [%]	1.67

Tap water Herisau

Reproducibility: Measurement of 10 tap water Herisau samples:

IC:

anions	fluoride	chloride	nitrate	sulfate
Average (N=10)	0.062	13.795	7.463	5.809
Standard Deviation	0.002	0.284	0.230	0.163
% RSD (N=10)	2.92	2.06	3.09	2.81

cations	sodium	potassium	calcium	magnesium
Average (N=10)	7.823	1.834	86.420	18.452
Standard Deviation	0.278	0.060	3.104	0.573
% RSD (N=10)	3.55	3.26	3.59	3.11

Titration / ionic balance:

	pH	Cond. [µS/cm]	Temp. [°C]	m value [mmol/L]	p value [mmol/L]	sum anions [meq/L]	sum cations [meq/L]	ionic difference [%]
Average (N=10)	7.74	572.0	22.33	5.51	0.00	6.143	6.217	+0.74
Standard Deviation	0.039	12.1	0.268	0.167	0.00	0.064	0.059	-
% RSD (N=10)	1.21	2.12	1.20	3.03	-	1.04	0.95	-

Comments

This Application Bulletin is based on AW CH6-0865-042006.

Overview of the determined parameters:

- direct measurement:
conductivity, pH, temperature
- titrations:
p- and m-value (= acidic capacity)
- IC:
fluoride, chloride, nitrate, sulfate
sodium, potassium, calcium, magnesium

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

This Application work shows how to obtain the most important parameters for tap water analysis (conductivity, pH, m- and p-value, concentrations of F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺) in 9 minutes – thanks to the execution of the titration while the IC is already running. This parallel working enables a very high throughput of samples per day.

To obtain a fast anion analysis the A SUPP 4 – 250 mm and a special eluent was chosen with which one is able to determine all 7 standard anions in 6 minutes.

No sample preparation is necessary – even the acidification for the cation-IC-run is done automatically by a Dosino.

The calibration results are good which means that the filling of a loop with dosinos is working properly.

The ionic difference shown in the TitrIC-Report is calculated by comparison of total equivalent of anions (the carbonate concentration is calculated from the p- and m-values) and cations from the IC results:

$$\text{Ionic d. [\%]} = 100 \cdot \frac{(\text{sum cations [\text{meq/L}]}) - (\text{sum anions [\text{meq/L}]})}{(\text{sum cations [\text{meq/L}]} + \text{sum anions [\text{meq/L}]})}$$

Example: If 5 ppm sulfate is found, this corresponds to 5 mg/L → 0.052 mmol/L (M (SO₄) = 96 mg/mmol) → -0.104 meq/L (charge SO₄: -2).

For more detailed information about the system setup of TitrIC 2 please consult the document **Installation Instructions for TitrIC 2**.

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

Appendix

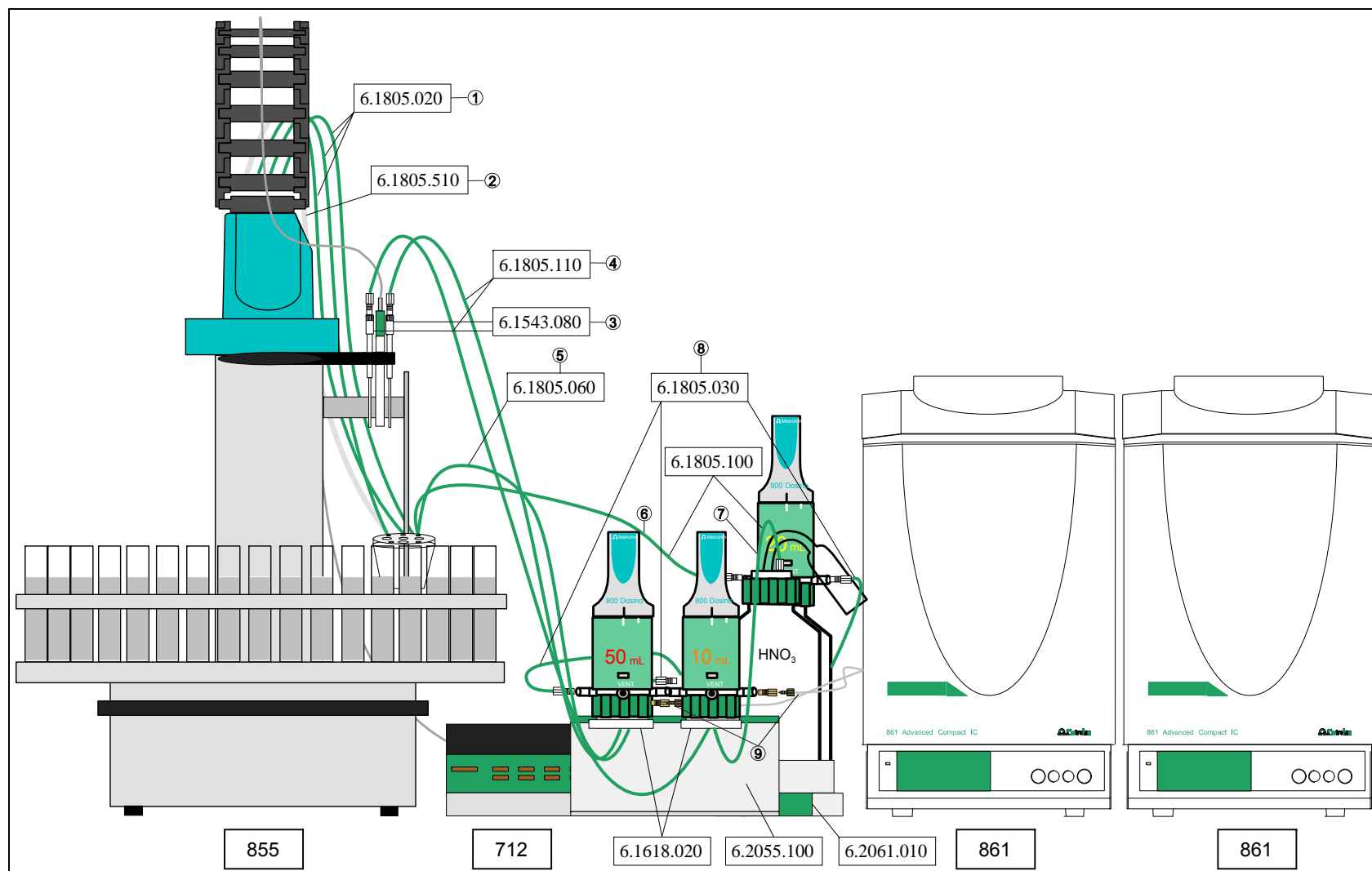
Calibration curves, reproducibility, chromatograms with peak tables and titration curves

Date

Thursday, 2006-04-12

Name

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



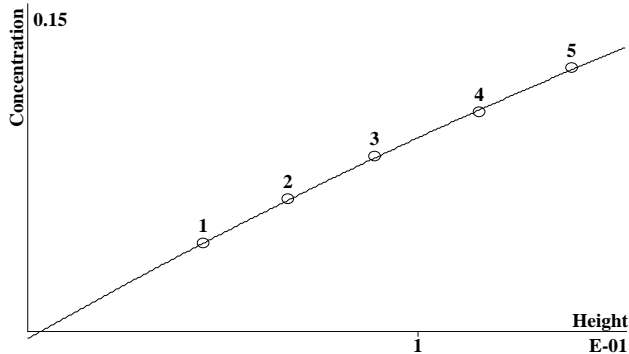
TitrC 2: System setup

Calibration

Anions:

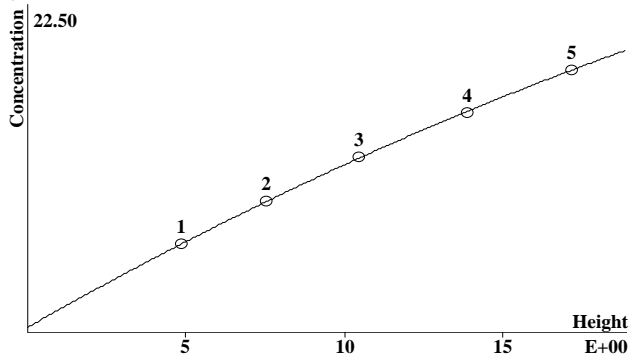
fluoride: RSD: 1.516 %

$$Q = -0.933 \cdot A^2 + 1.012 \cdot A - 0.00364$$



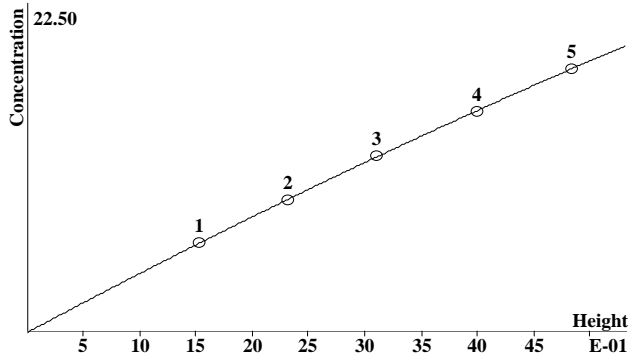
chloride: RSD: 0.845 %

$$Q = -0.0123 \cdot A^2 + 1.241 \cdot A + 0.2877$$



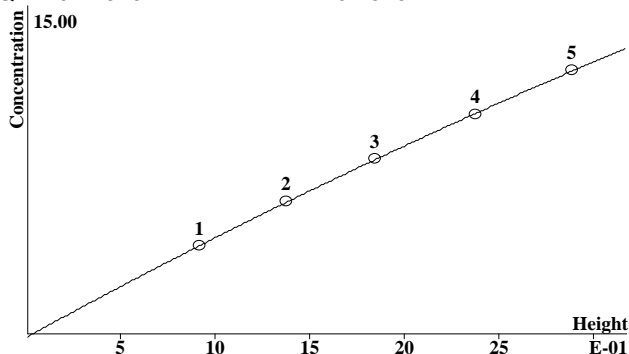
nitrate: RSD: 0.646 %

$$Q = -0.0803 \cdot A^2 + 4.1324 \cdot A - 0.1295$$



sulfate: RSD: 0.619 %:

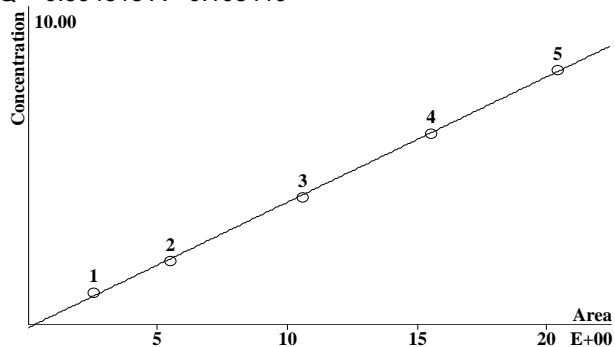
$$Q = -0.178151 \cdot A^2 + 4.727 \cdot A - 0.1549$$



Cations:

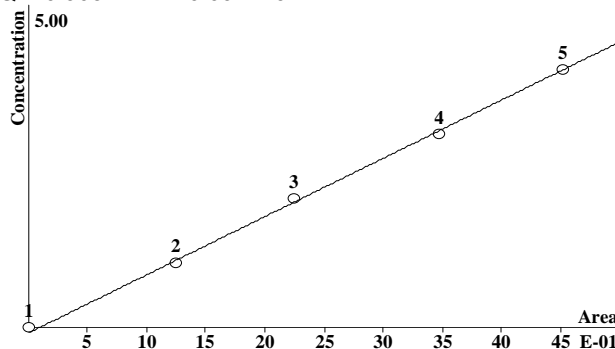
sodium: RSD: 1.94 %

$$Q = 0.394518 \cdot A - 0.108419$$



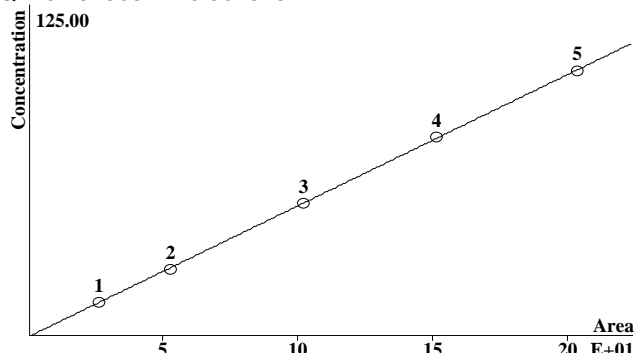
potassium: RSD: 2.45 %

$$Q = 0.905112 \cdot A - 0.0977494$$



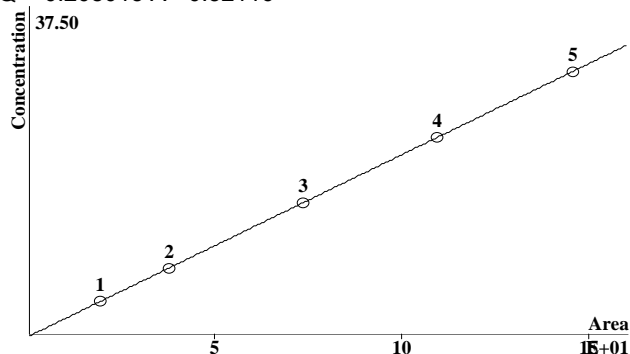
calcium: RSD: 0.83 %

$$Q = 0.494963 \cdot A - 0.564849$$

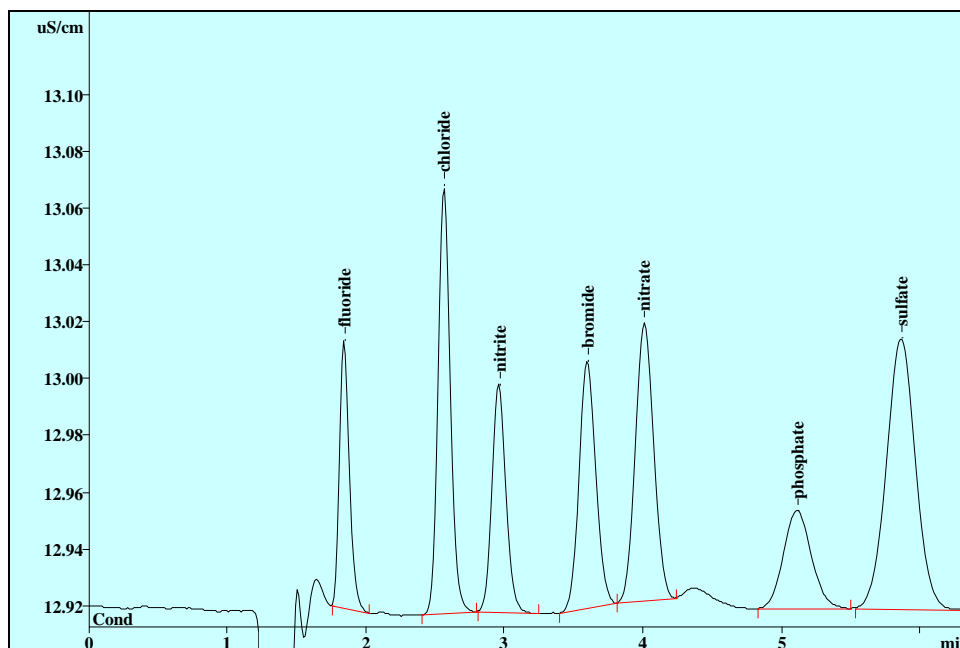


magnesium: RSD: 0.44 %

$$Q = 0.208015 \cdot A - 0.32116$$



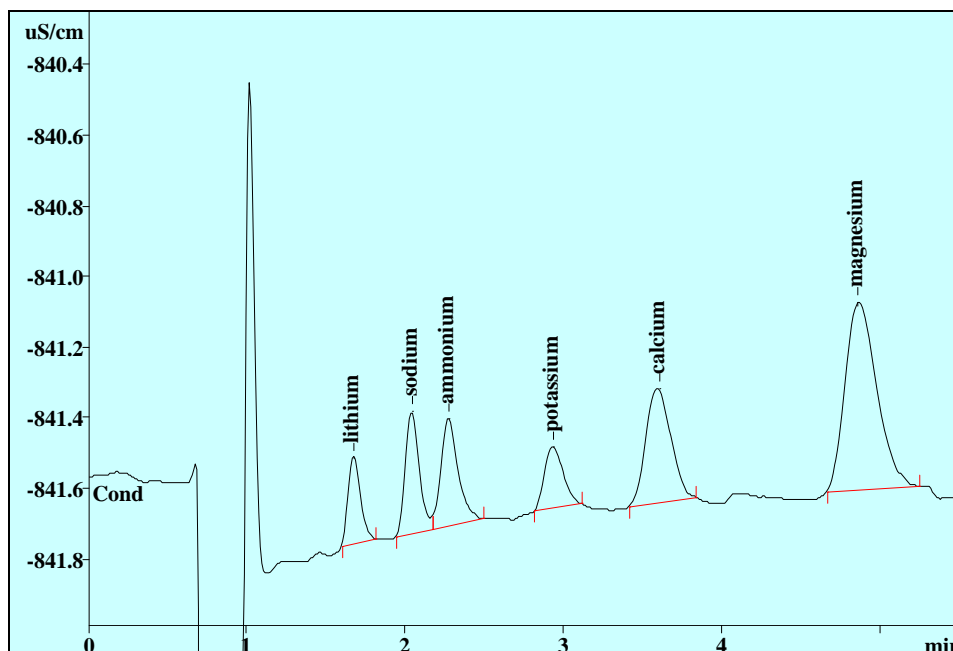
Chromatograms with peak tables



Multi-Anion Standard

File: q3091802
 Volume: 20.0 µl
 Dilution: 1.00
 Amount: 1.00

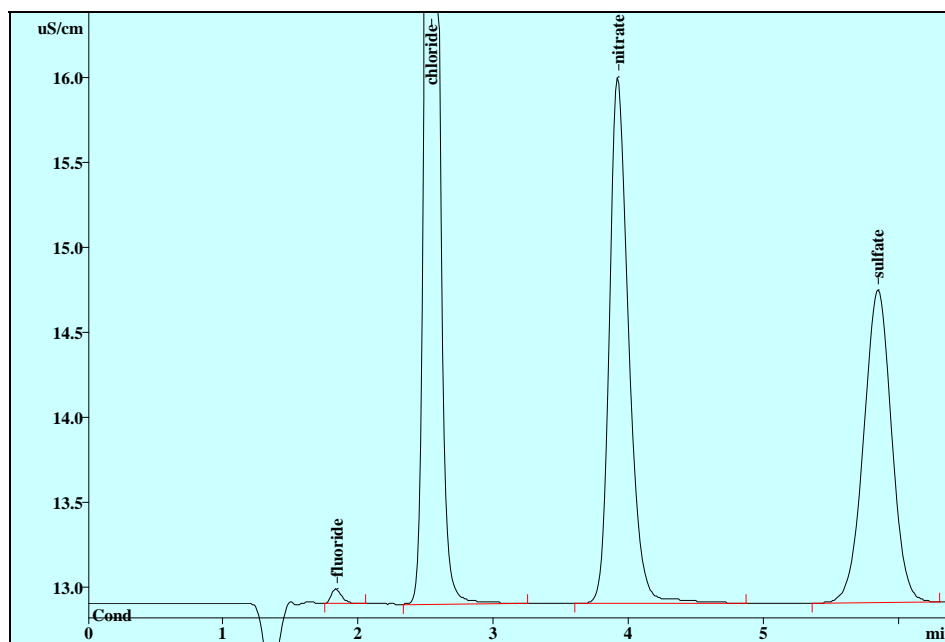
No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	1.84	0.09	0.477	0.0840	fluoride
2	2.56	0.15	0.922	0.4749	chloride
3	2.96	0.08	0.570	0.0000	nitrite
4	3.60	0.09	0.732	0.0000	bromide
5	4.01	0.10	0.906	0.2737	nitrate
6	5.11	0.03	0.493	0.0000	phosphate
7	5.86	0.10	1.382	0.2942	sulfate



Multi-Cation Standard

File: q3091821
 Volume: 10.0 µl
 Dilution: 1.00
 Amount: 1.00

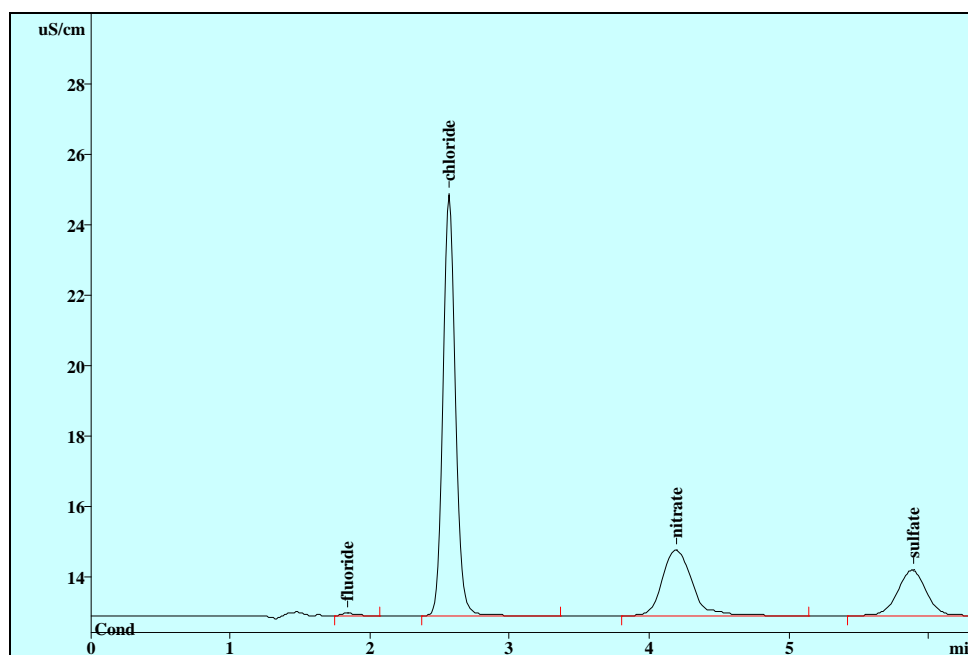
No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	1.67	0.33	1.605	0.0000	lithium
2	2.04	0.42	2.405	0.8405	sodium
3	2.27	0.36	2.762	0.0000	ammonium
4	2.93	0.20	1.624	1.3726	potassium
5	3.60	0.34	3.874	1.3526	calcium
6	4.86	0.55	7.847	1.3112	magnesium



Standard 3

File: q3091119
 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	1.83	0.09	0.482	0.0790	fluoride
2	2.54	10.47	60.282	11.9343	chloride
3	3.92	3.11	30.706	11.9327	nitrate
4	5.84	1.84	26.313	7.9521	sulfate

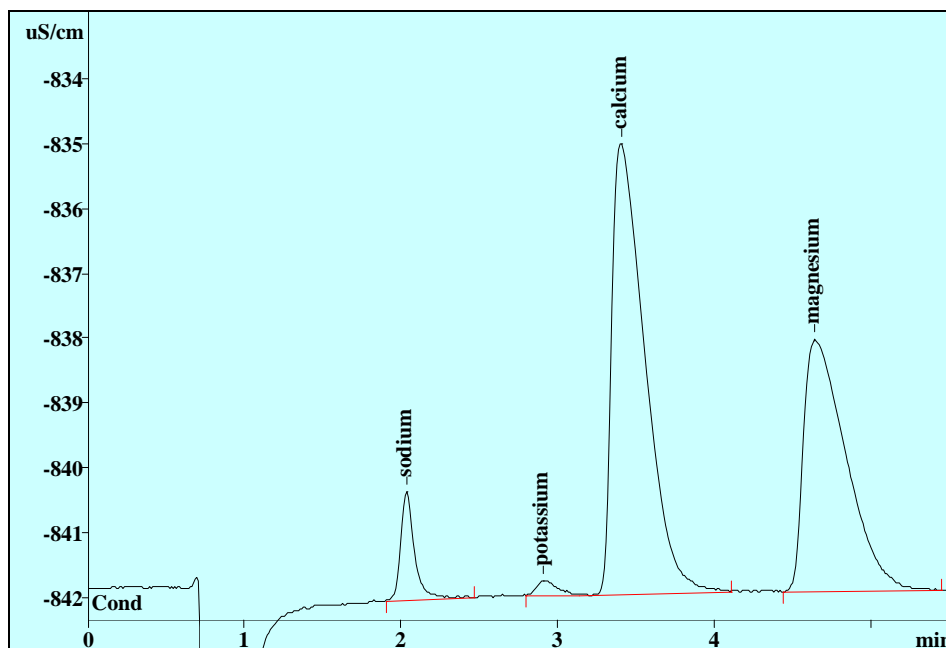


Tap water Herisau

File: q3091950
 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	1.84	0.07	0.442	0.0611	fluoride
2	2.57	12.00	73.252	13.4092	chloride
3	4.19	1.86	27.263	7.2891	nitrate
4	5.88	1.28	18.017	5.6201	sulfate

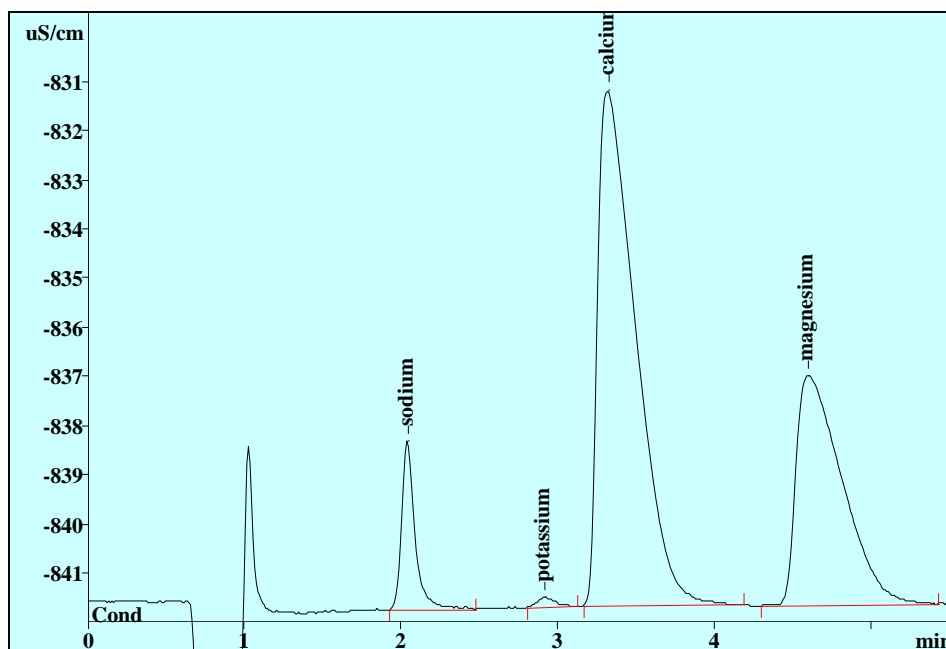
Cations:



Standard 3

File: q3091212
 Volume: 10.0 µl
 Dilution: 1.00
 Amount: 1.00

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	2.03	1.69	10.590	4.0694	sodium
2	2.90	0.24	2.245	1.9342	potassium
3	3.40	6.96	102.136	49.9889	calcium
4	4.64	3.89	73.842	15.0391	magnesium



Tap water Herisau

File: q3091857
 Volume: 10.0 µl
 Dilution: 1.00
 Amount: 1.00

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	2.04	3.44	20.854	8.1187	sodium
2	2.91	0.20	1.711	1.4505	potassium
3	3.32	10.49	176.793	86.9410	calcium
4	4.60	4.68	95.884	19.6242	magnesium

Titration curves – Titration of *m*-value with HCl

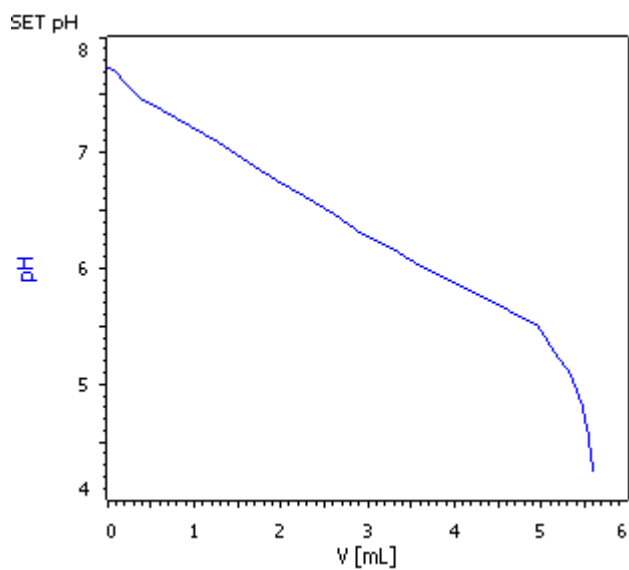


Fig. 1: SET pH of tap water Herisau