

Comprehensive tap water analysis inclusively oxygenated halides with TitrIC 2

Branch: water, waste water, environmental protection

Keywords

TitrIC 2 / 861 / 855 / 712 / 800 / Aquatrode plus / 6.0257.000 / Dosino / tiamo / 6.1006.630 / Metrosep SUPP 7 – 250 / 6.1010.230 / Metrosep C 2 – 250 / 2.145.0320 / 853 / MCS / branch 2

Summary

The determination of anions / cations in tap water was done on the **Metrosep SUPP 7 – 250 / Metrosep C 2 – 250** 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 the determination of oxygenated halides is shown as well. For a faster analysis of the standard anions please refer to **AB 302 e**.

Sample

Sample 1: Tap water Herisau

Sample 2: Tap water Rondelle

Reagents

Eluent: **3.6 mmol/L sodium carbonate** 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

Titration: 0.1 mol/L HCl for p-/m-value determination
1 mol/L HNO₃ for acidification

Standards [ppm] in ultra pure water

Anions:

Analyte / Level	1	2	3	4	5
fluoride	0.03	0.1	0.2	0.4	0.6
chlorite	0.005	0.01	0.02	0.05	0.1
bromate	0.005	0.01	0.02	0.05	0.1
chloride	3	6	10	20	30
nitrite	0.03	0.1	0.2	0.4	0.6
bromide	0.03	0.1	0.2	0.4	0.6
chlorate	0.005	0.01	0.02	0.05	0.1
nitrate	3	6	10	20	30
phosphate	0.06	0.2	0.4	0.8	1.2
sulfate	3	6	10	20	30

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 7 – 250	6.1006.630
Metrosep RP Guard	6.1011.020
Metrosep C 2 – 250	6.1010.230
Metrosep C 2 Guard	6.1010.200
Sample rack 59 x 120 mL	6.2041.840
Sample beaker 120 mL (x100)	6.1459.300
Column oven for 861	2.861.0500
853 MCS CO ₂ Suppressor	2.853.0010



Sample Preparation

The water samples were injected directly.

Analysis

The standards and the sample were injected 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 (with the TitrIC 2 package delivered) *tiamo* methods *TitrIC 2 – complete run* and *TitrIC 2 – IC calibration anion & cation* were used for all types of analysis mentioned.

Calculation (IC)

Automatic integration with IC Net 2.3 software using peak area.

Parameters

IC - Anions

STARTUP HARDWARE:

```

RECODER METHOD ASupp7_250-TitrIC.mtw
RECODER DATA Data acquisition [Cond]
861 Adv. Compact Unit version 4
861 Adv. Compact Polarity +
861 Adv. Compact Supp. autostep yes
861 Adv. Compact Autostep with Fill
861 Adv. Compact Peristaltic pump yes
861 Adv. Compact Flow 0.70 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
Column Thermostat Temperature 45.0 °C
    
```

IC - Cations

STARTUP HARDWARE:

```

RECODER METHOD C2_250-TitrIC.mtw
RECODER DATA Data acquisition [Cond]
861 Adv. Compact Unit version 1
861 Adv. Compact Polarity -
861 Adv. Compact Supp. autostep no
861 Adv. Compact Autostep with Fill
861 Adv. Compact Flow 1.0 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

```

0.0 Column Thermostat START
0.20 861 Adv. Compact Valve Inject
28.0 861 Adv. Compact Valve Fill
    
```

START WITH DETERMINATION

```

0.20 861 Adv. Compact Valve Inject
25.2 861 Adv. Compact Valve Fill
    
```

START WITH INJECT:

```

0.0 RECODER START
    
```

START WITH INJECT:

```

0.0 RECODER 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

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

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

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	4/11/2006
General data	
ID	Tap water Herisau
Record date	4/05/2006
Record time	14:35:14
User comment	
System comment	recalculated, within limit
Titration data	
pH	7.88
Cond. [$\mu\text{S}/\text{cm}$]	588
Temp. [°C]	22.79
m value [mmol/L]	5.59
p value [mmol/L]	0

 **Metrohm**

Anions	
F [mg/L]	0.056
ClO ₂ [mg/L]	0
BrO ₃ [mg/L]	0
Cl [mg/L]	13.11
NO ₂ [mg/L]	0
Br [mg/L]	0.004
ClO ₃ [mg/L]	0.004
NO ₃ [mg/L]	10.136
PO ₄ [mg/L]	0
SO ₄ [mg/L]	5.271
Anion balance [mEq/L]	6.07
Cations	
Na [mg/L]	6.21
K [mg/L]	0
Mg [mg/L]	17.49
Ca [mg/L]	86.502
Cation balance [mEq/L]	6.03
ionic difference [mEq/L]	-0.04
ionic difference [%]	-0.35

TitriC-Report

Print date	4/11/2006
General data	
ID	Quelle Rondelle
Record date	4/05/2006
Record time	14:36:17
User comment	
System comment	recalculated, within limit
Titration data	
pH	7.82
Cond. [$\mu\text{S}/\text{cm}$]	469
Temp. [°C]	24.01
m value [mmol/L]	4.12
p value [mmol/L]	0

 **Metrohm**

Anions	
F [mg/L]	0.054
ClO ₂ [mg/L]	0
BrO ₃ [mg/L]	0
Cl [mg/L]	14.235
NO ₂ [mg/L]	0
Br [mg/L]	0.005
ClO ₃ [mg/L]	0
NO ₃ [mg/L]	9.895
PO ₄ [mg/L]	0.009
SO ₄ [mg/L]	5.694
Anion balance [mEq/L]	4.66
Cations	
Na [mg/L]	6.559
K [mg/L]	1.292
Mg [mg/L]	13.6
Ca [mg/L]	65.188
Cation balance [mEq/L]	4.69
ionic difference [mEq/L]	0.03
ionic difference [%]	0.31

TitriC-Report: Sample 1

TitriC-Report: Sample 2

Sample 1 - Tap water Herisau:

Reproducibility: Measurement of 10 tap water samples:

IC:

anions	fluoride	chlorite	bromate	chloride	nitrite	bromide	chlorate	nitrate	phosphate	sulfate
Average (N=10)	0.060	0.000	0.000	13.066	0.000	0.005	0.009	10.149	0.005	5.285
Standard Deviation	0.003	0.000	0.000	0.054	0.000	0.000	0.001	0.050	0.001	0.041
% RSD (N=10)	4.43	-	-	0.41	-	1.11	3.87	0.49	15.31	0.78

cations	sodium	potassium	calcium	magnesium
Average (N=10)	6.228	1.729	84.911	17.424
Standard Deviation	0.104	0.098	0.896	0.260
% RSD (N=10)	1.67	5.72	1.06	1.51

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)	7.772	585.900	22.358	5.572	0.000	6.002	5.992	-0.082
Standard Deviation	0.075	2.601	0.235	0.020	0.000	0.057	0.048	-
% RSD (N=10)	0.97	0.44	1.05	0.37	-	0.95	0.80	-

Recovery: Spiked sample Tap water Herisau:

Anions [ppm]	fluoride	chlorite	bromate	chloride	nitrite	bromide	chlorate	nitrate	phosphate	sulfate
sample (av. N=10)	0.060	0.000	0.000	13.066	0.000	0.005	0.009	10.149	0.005	5.285
spiked (av. N=4)	0.084	0.006	0.005	15.917	0.023	0.029	0.014	13.044	0.050	8.088
% RSD spiked	1.39	5.64	5.08	0.29	1.02	1.73	4.85	0.11	2.66	0.12
difference	0.023	0.006	0.005	2.851	0.023	0.024	0.005	2.895	0.045	2.803
theoretical spike	0.025	0.005	0.005	3	0.025	0.025	0.005	3	0.05	3
recovery %	92.7	113.5	99.0	95.0	92.3	96.1	92.5	96.5	89.8	93.4

Cations [ppm]	sodium	potassium	calcium	magnesium
sample (av. N=10)	6.228	1.729	84.911	17.424
spiked (av. N=4)	7.229	2.242	96.101	20.740
difference	1.001	0.513	11.190	3.316
theoretical spike	1	0.5	12.5	3.75
recovery %	100.1	102.6	89.5	88.4

Sample 2 - Tap water Rondelle:

IC:

Anions [ppm]	fluoride	chlorite	bromate	chloride	nitrite	bromide	chlorate	nitrate	phosphate	sulfate
Average (N=10)	0.054	0.000	0.000	14.235	0.000	0.005	0.000	9.895	0.009	5.694

Cations [ppm]	sodium	potassium	calcium	magnesium
Average (N=10)	6.559	1.292	65.188	13.600

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)	7.82	469	24.01	4.12	0.00	4.66	4.69	0.31

Comments

This Application Bulletin is based on AW CH6-0864-042006.

Overview of the determined parameters:

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

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

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

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

The recovery as well as the reproducibility for phosphate in tap water is poor while the calibration was good. There seems to be species in the sample which lower the phosphate concentrations. This problem (probably related to the presence of humic acids in the sample) is known and also appears with direct injection.

With this setup the oxohalogenides can be determined down to 5ppb. This could be improved with implementing an Advanced Modular system.

The ionic balance 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:

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

Example: If 5 ppm sulfate is found, this corresponds to 5 mg/L \rightarrow 0.052 mmol/L ($M(SO_4) = 96 \text{ mg/mmol}$) \rightarrow -0.104 meq/L (charge SO_4^{2-} : -2).

For a more detailed information about the system setup of TitrIC 2 consult the document **AB 286 - Installation Instructions for TitrIC 2**.

For Application works of TitrIC 1 please have a look at AB 288 e.

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

Appendix

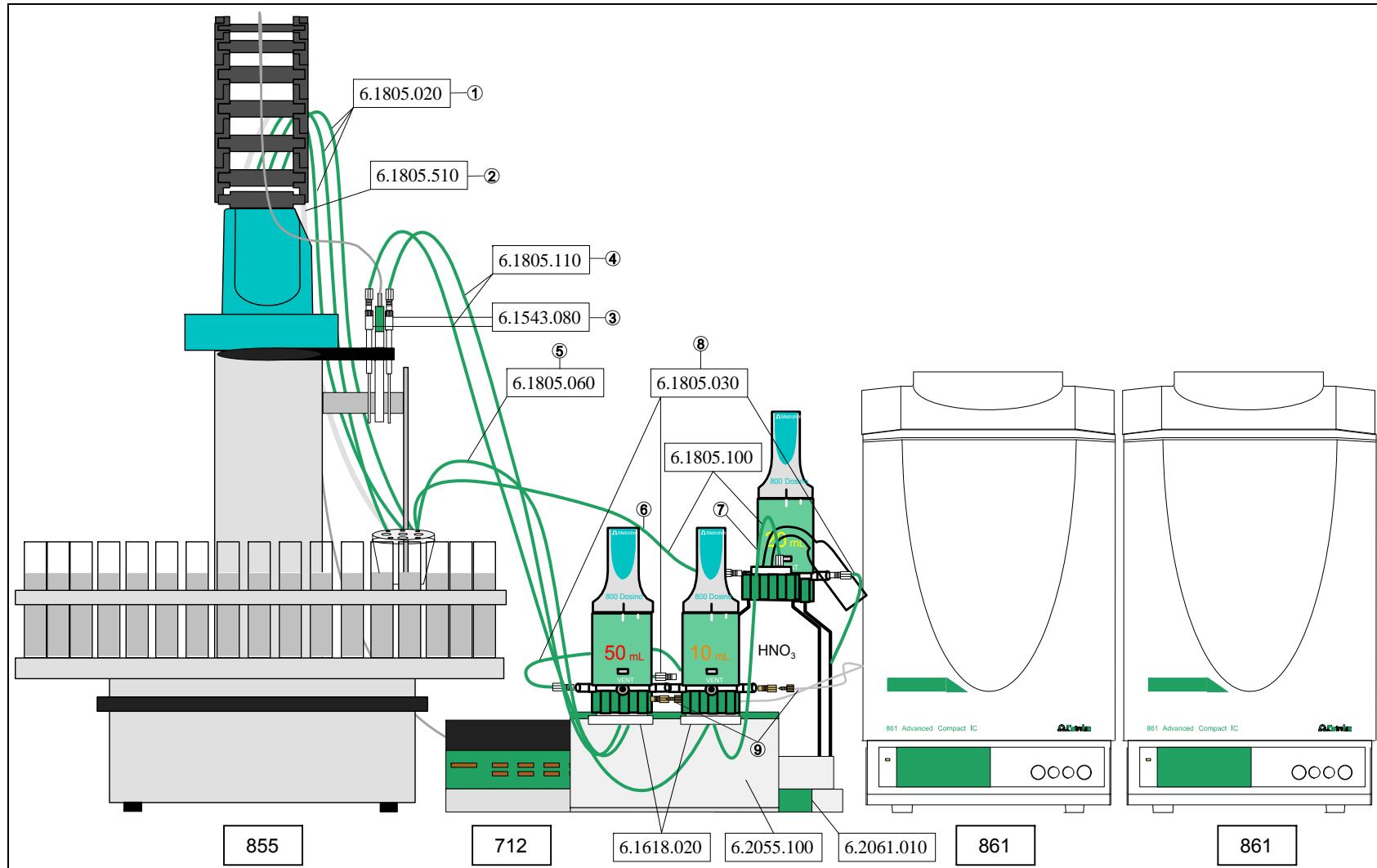
Calibration curves, reproducibility, chromatograms with peak tables and titration curves

Date

Thursday, 2006-04-05

Name

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



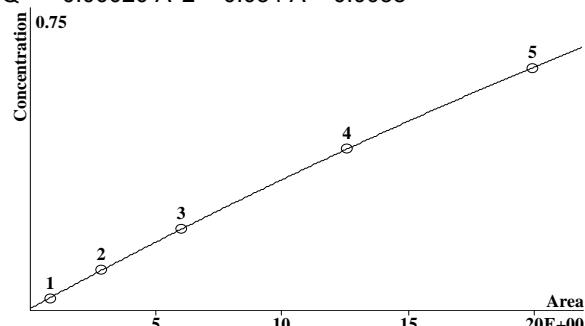
TitriC 2: System setup

Calibration

Anions:

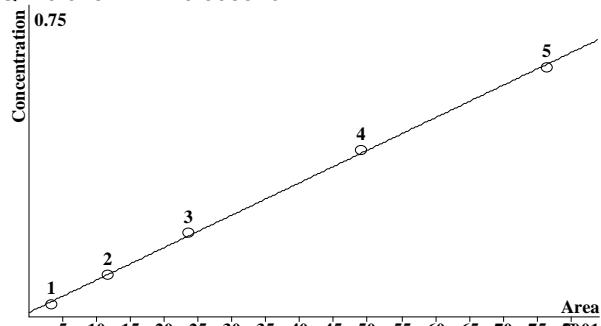
fluoride: RSD: 0.81%

$$Q = -0.00020 \cdot A^2 + 0.034 \cdot A + 0.0038$$



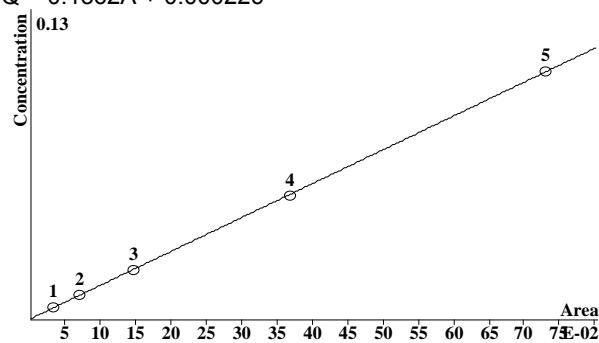
nitrite: RSD: 3.350 %, corr. coeff.: 0.99938

$$Q = 0.07824 \cdot A + 0.008926$$



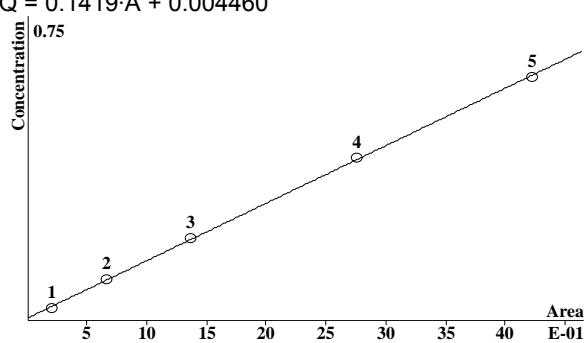
chlorite: RSD: 1.306 %, corr. coeff.: 0.999943

$$Q = 0.1362A + 0.000226$$



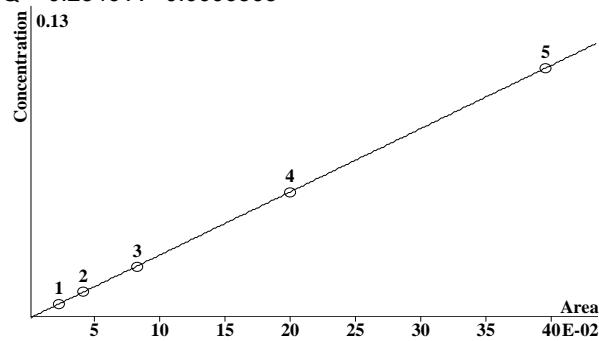
bromide: RSD: 1.804 %, corr. coeff.: 0.99984

$$Q = 0.1419 \cdot A + 0.004460$$



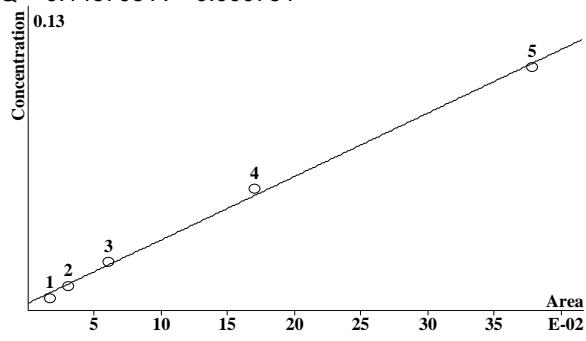
bromate: RSD: 0.496 % corr. coeff.: 0.999992

$$Q = 0.2546 \cdot A - 0.0006363$$



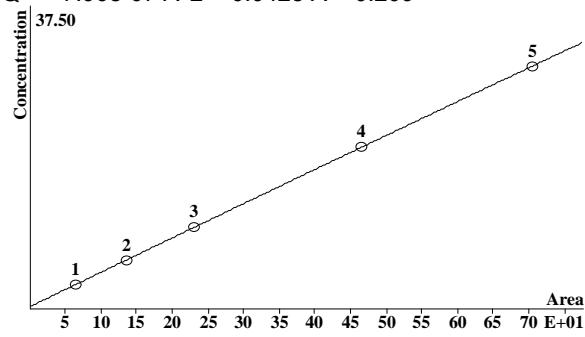
chlorate: RSD: 3.211 %, corr. coeff.: 0.99966

$$Q = 0.143708 \cdot A + 0.000734$$



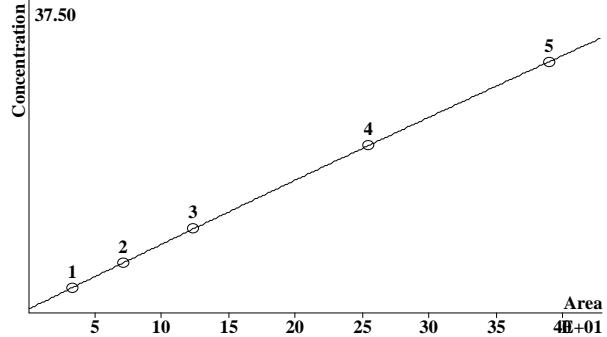
chloride: RSD: 0.05%

$$Q = -7.96e-07 \cdot A^2 + 0.0428 \cdot A + 0.209$$

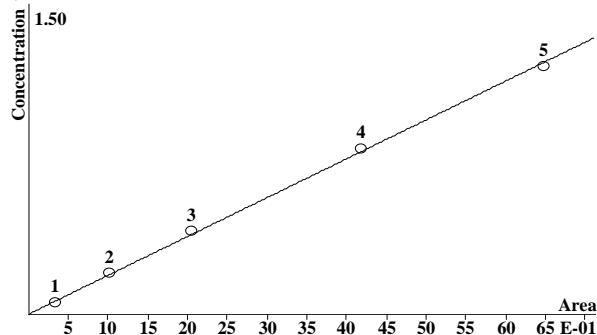


nitrate: RSD: 0.09%

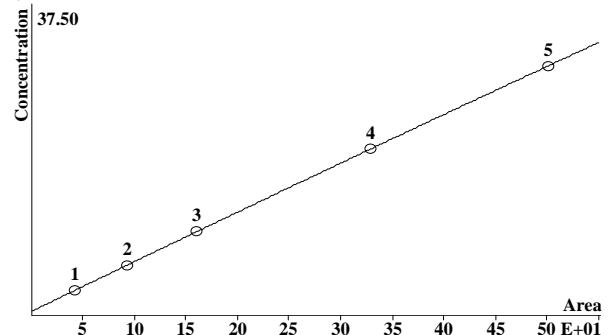
$$Q = -6.998e-06 \cdot A^2 + 0.078 \cdot A + 0.390$$



phosphate: RSD: 2.550 %, corr. coeff.: 0.99968
 $Q = 0.18538 \cdot A + 0.0105642$

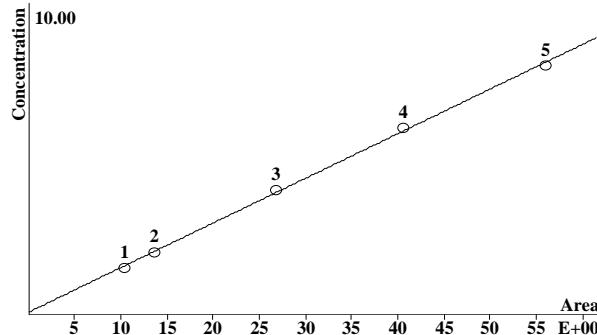


sulfate: RSD: 0.09%
 $Q = -2.759e-06 \cdot A^2 + 0.060 \cdot A + 0.392$

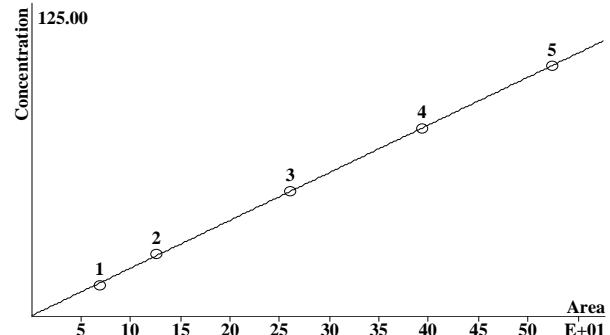


Cations:

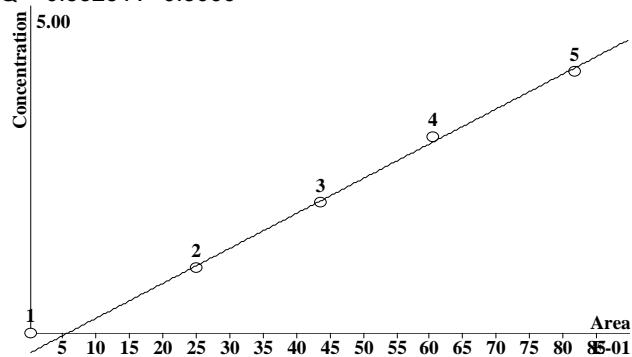
sodium: RSD: 2.38%
 $Q = 0.1434 \cdot A + 0.0674$



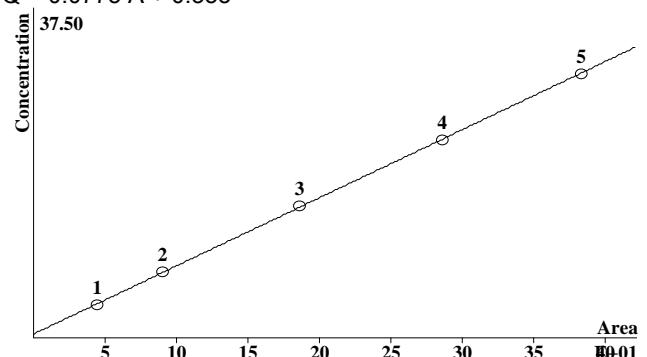
calcium: RSD: 1.30%
 $Q = 0.1903 \cdot A + 0.1929$



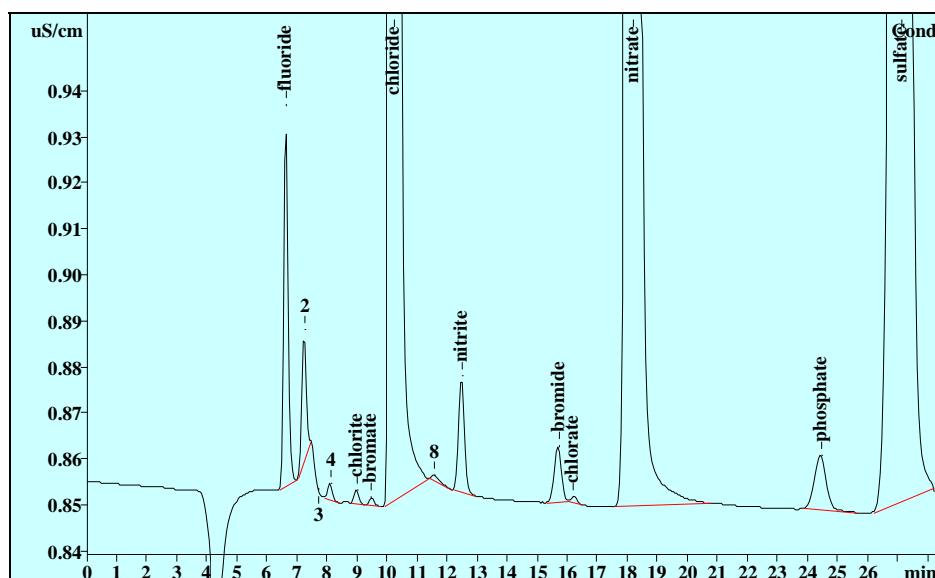
potassium: RSD: 2.77%
 $Q = 0.5325 \cdot A - 0.3066$



magnesium: RSD: 0.87%
 $Q = 0.0775 \cdot A + 0.355$



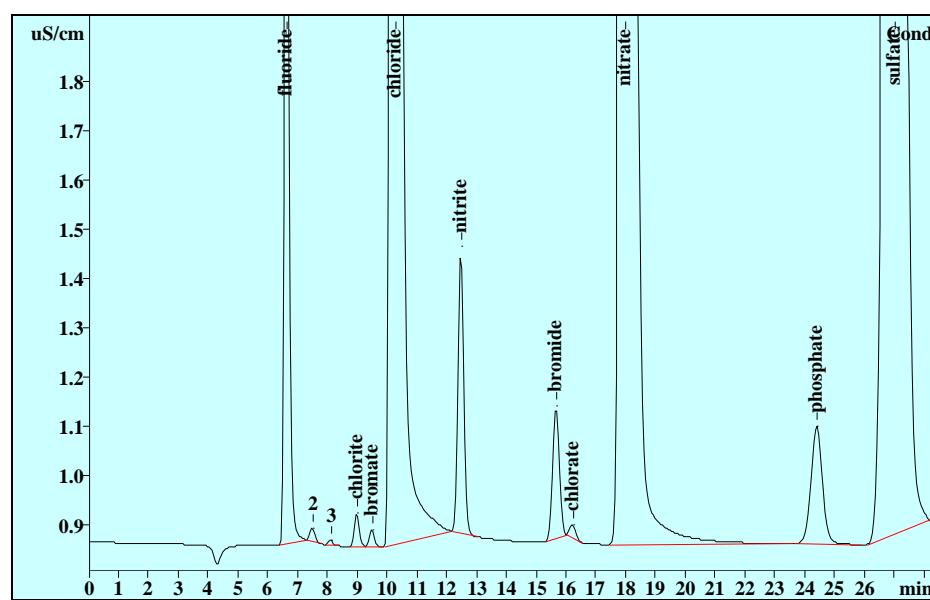
Chromatograms with peak tables - Anions



Standard 1

File q3211205
Volume: 20.0 μl
Dilution: 1.00
Amount: 1.00

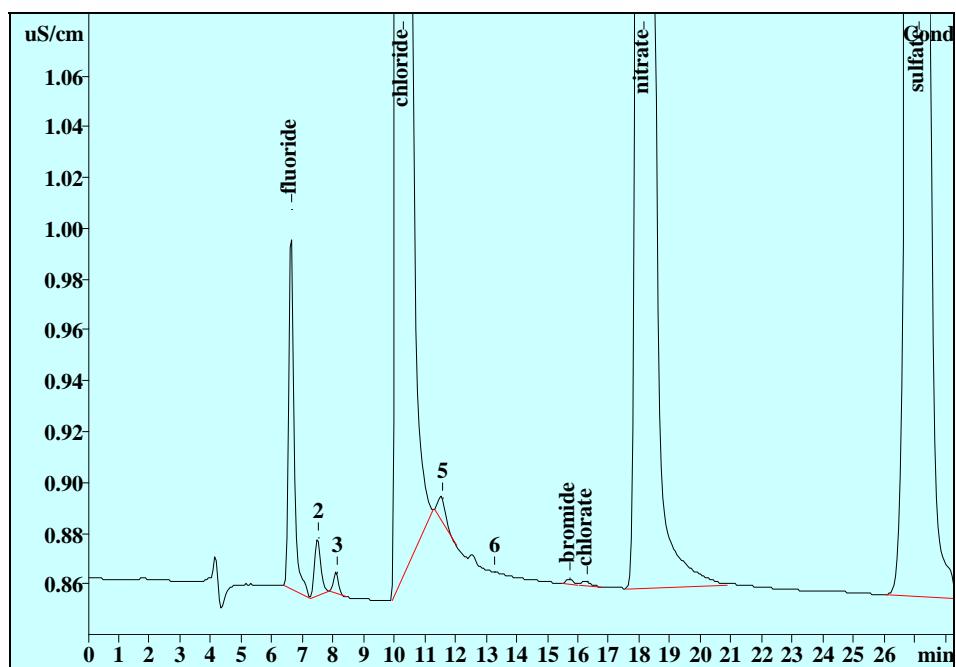
No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^2 \cdot \text{sec}$	Conc. mg/L	Name
1	6.63	0.08	0.801	0.0309	fluoride
5	8.99	0.00	0.033	0.0050	chlorite
6	9.48	0.00	0.022	0.0050	bromate
7	10.24	5.92	65.089	2.9945	chloride
9	12.48	0.03	0.341	0.0291	nitrite
10	15.69	0.01	0.199	0.0295	bromide
11	16.21	0.00	0.018	0.0057	chlorate
12	18.17	1.77	33.358	3.0096	nitrate
13	24.43	0.01	0.336	0.0669	phosphate
14	27.11	1.59	43.355	3.0100	sulfate



Standard 5

File q3211105
Volume: 20.0 μl
Dilution: 1.00
Amount: 1.00

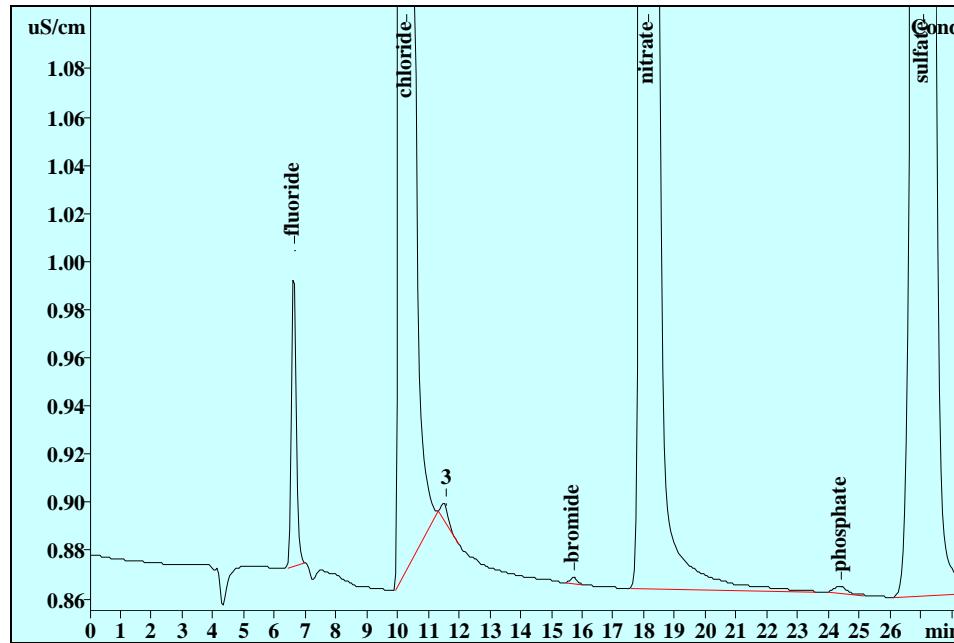
No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^2 \cdot \text{sec}$	Conc. mg/L	Name
1	6.63	2.08	19.906	0.6001	fluoride
4	8.98	0.07	0.730	0.1000	chlorite
5	9.49	0.03	0.395	0.1000	bromate
6	10.29	58.94	704.574	30.0012	chloride
7	12.48	0.58	7.637	0.6002	nitrite
8	15.67	0.27	4.221	0.6005	bromide
9	16.22	0.03	0.378	0.0999	chlorate
10	17.98	18.67	389.425	29.9971	nitrate
11	24.41	0.24	6.477	1.2010	phosphate
12	26.99	17.81	500.850	29.9971	sulfate



Sample 1

File: q3220119
Volume: 20.0 μl
Dilution: 1.00
Amount: 1.00

No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^*\text{sec}$	Conc. mg/L	Name
1	6.63	0.15	1.743	0.0625	fluoride
4	10.26	23.94	303.280	13.1299	chloride
7	15.73	0.00	0.033	0.0048	bromide
8	16.27	0.00	0.031	0.0099	chlorate
9	18.14	6.58	125.507	10.1635	nitrate
10	27.11	2.99	82.005	5.3346	sulfate

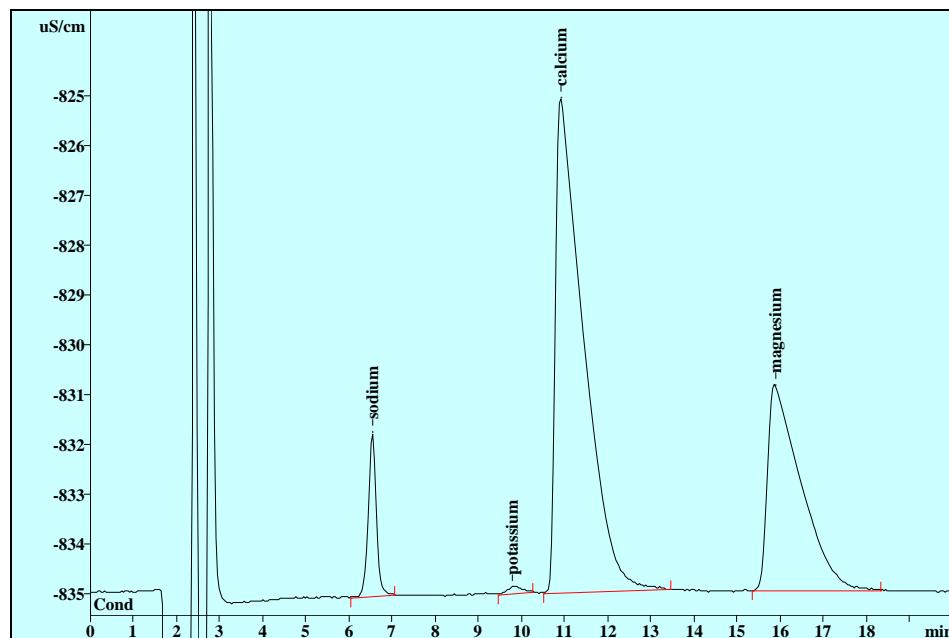


Sample 2

File: q3221750
Volume: 20.0 μl
Dilution: 1.00
Amount: 1.00

No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^*\text{sec}$	Conc. mg/L	Name
1	6.62	0.13	1.339	0.0490	fluoride
2	10.25	27.45	329.370	14.2346	chloride
3	11.76	0.01	0.089	0.0000	
4	15.72	0.00	0.042	0.0054	bromide
5	18.12	6.39	122.016	9.8952	nitrate
6	24.39	0.00	0.079	0.0092	phosphate
7	27.09	3.23	88.351	5.7155	sulfate

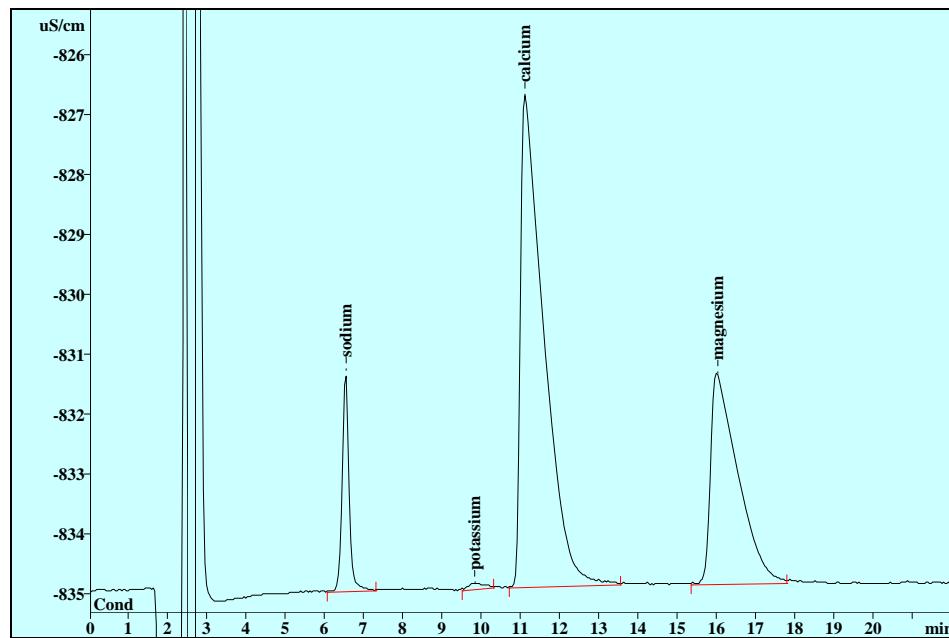
Cations:



Sample 1

File: q3220120
Volume: 10.0 μl
Dilution: 1.00
Amount: 1.00

No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^*\text{sec}$	Conc. mg/L	Name
1	6.56	3.31	42.731	6.1884	sodium
2	9.79	0.14	3.155	1.5719	potassium
3	10.92	9.97	450.169	85.2894	calcium
4	15.86	4.16	225.558	17.7705	magnesium



Sample 2

File: q3221751
Volume: 10.0 μl
Dilution: 1.00
Amount: 1.00

No	Retention min	Height $\mu\text{S}/\text{cm}$	Area $\mu\text{S}/\text{cm}^*\text{sec}$	Conc. mg/L	Name
1	6.53	3.73	45.260	6.5590	sodium
2	9.79	0.11	3.002	1.2923	potassium
3	11.10	8.24	341.400	65.1877	calcium
4	15.98	3.54	170.864	13.5999	magnesium

Titration curves – Titration of m-value (to pH 4.3)

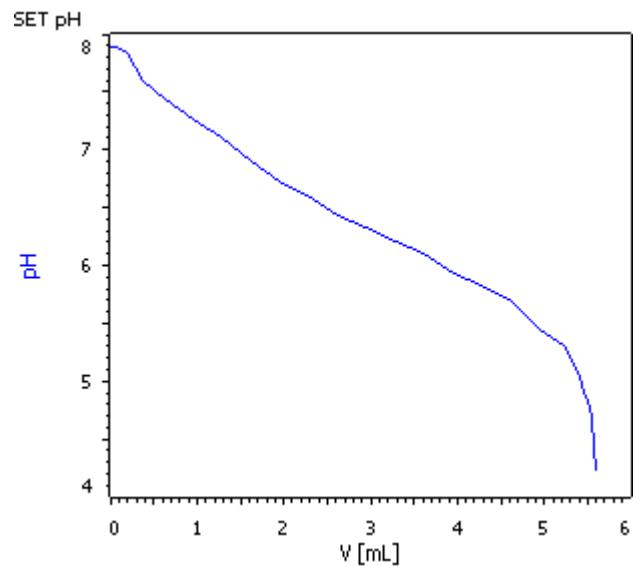


Fig. 1: SET pH of Sample 1

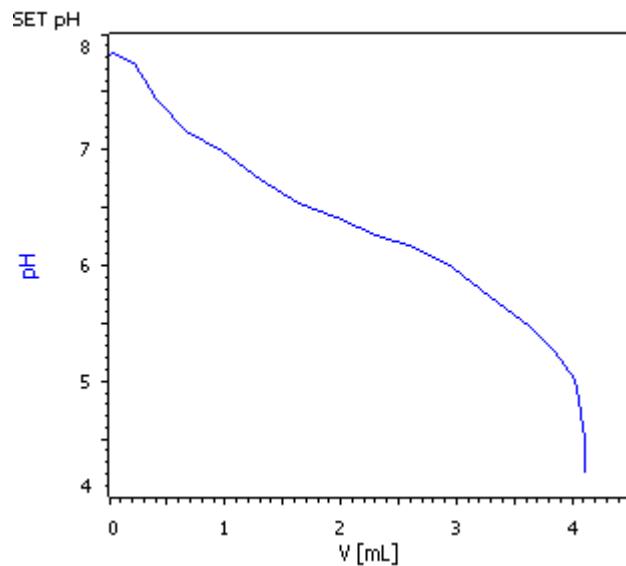


Fig. 2: SET pH of Sample 2