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Overcoming Challenging Matrices in Ion Chromatography

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Thermo Fisher Scientific – NA IC Tech Support

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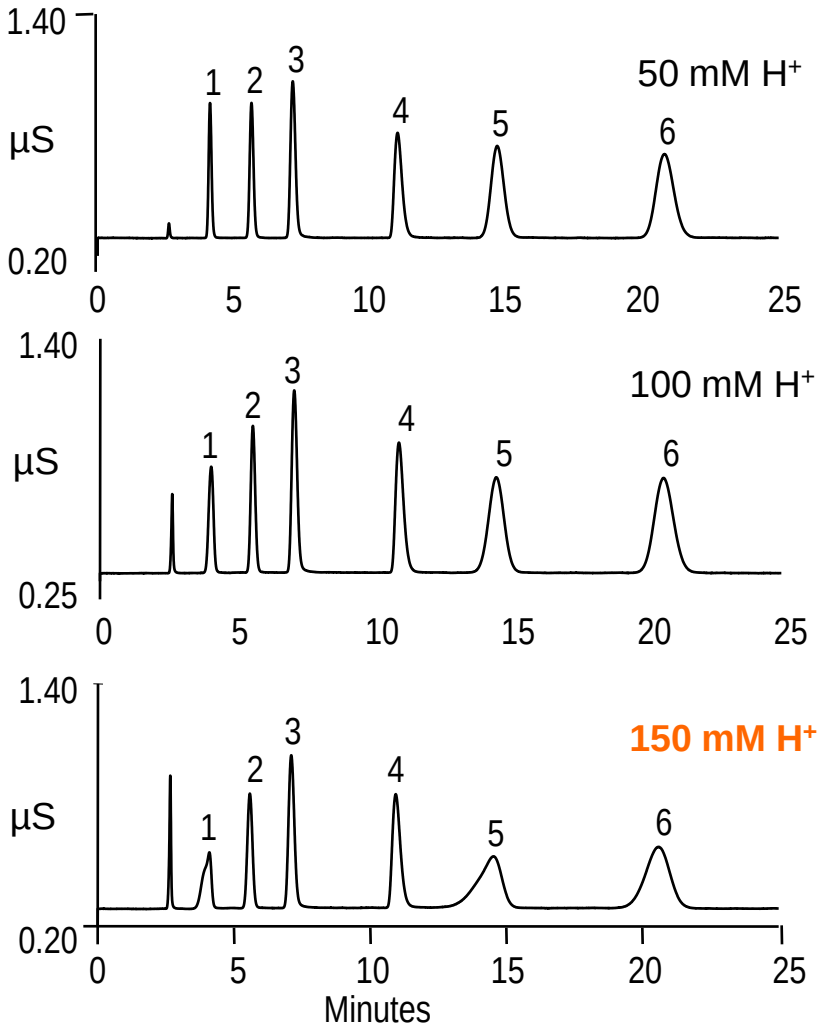
Column Selection: Dionex IonPac Columns

- Selecting the correct column for your application and sample matrix is important optimization and often critical to accurate analysis
- Virtual column: dry lab your application
  - Use virtual column to select the best column for your sample
- We have the broadest range of IC columns
- Solutions for diverse applications
- Contact us to discuss your application!

http://www.thermoscientific.com/en/search-results.html?keyword=IonPac&matchDim=Y

Problem: Fronting Peaks when Sample pH is Low
Solution 1: Higher Capacity Column

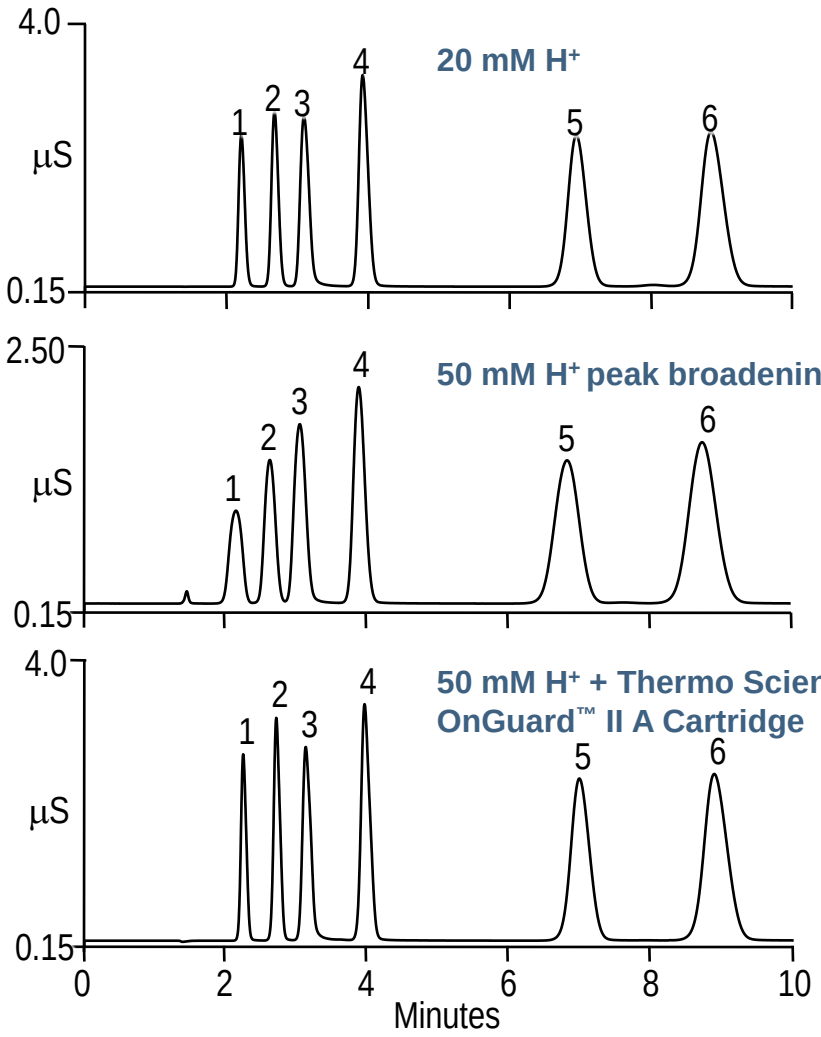


Column:	Thermo Scientific™ Dionex™ IonPac™ CS16 5 µm, 5 × 250 mm
Eluent:	30 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
Temp.:	40 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CSRS™ Cation Self-Regenerating Suppressor, 4 mm, AutoSuppression, recycle mode

Peaks:

1. Lithium	0.1	mg/L (ppm)
2. Sodium	0.4	
3. Ammonium	0.5	
4. Potassium	1.0	
5. Magnesium	0.5	
6. Calcium	1.0	

Solution 2: Neutralize Sample using Dionex OnGuard II A (Bicarbonate-Form Resin)



Column:	Dionex IonPac CS12A 5 µm, 3 ×150 mm
Eluent:	20 mM Methanesulfonic acid
Flow Rate:	0.50 mL/min
Temperature:	30 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, Dionex CSRS suppressor, 2 mm, AutoSuppression, recycle mode

Peaks:		
1.	Lithium	0.12 mg/L (ppm)
2.	Sodium	0.50
3.	Ammonium	0.62
4.	Potassium	1.25
5.	Magnesium	0.62
6.	Calcium	1.25

Why is Matrix Elimination Needed?

- Matrix elimination is sometimes necessary to achieve acceptable separation of peaks of interest from each other or adjoining peaks
  - Necessary to provide reliable and accurate results
  - Peaks of interest must be at least partially resolved from adjoining peaks
  - Minimize peak suppression from column overload

Special Case

- Disparate concentrations: Low concentration of peak of interest is hidden under an adjoining peak with high concentration

Possible Effects from Samples Matrixes

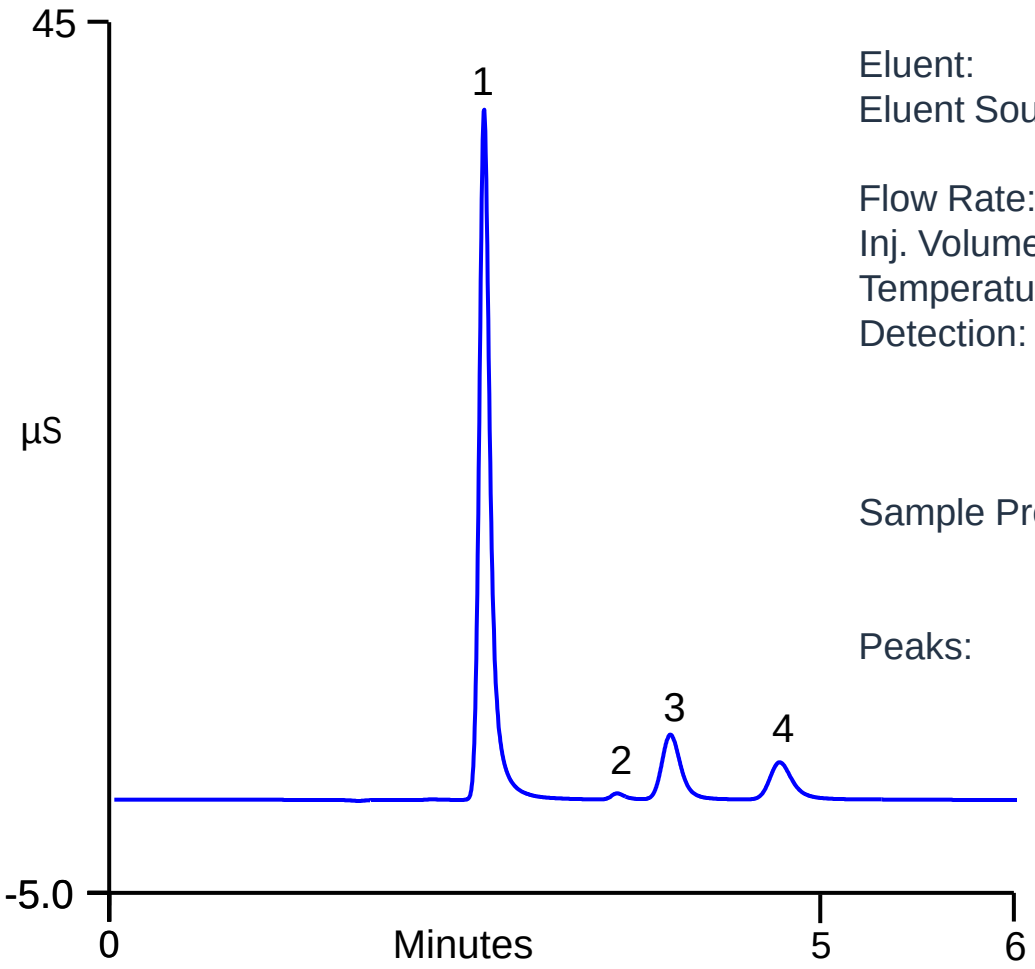
- Particulates
  - Clog columns and electrolytic devices
- High concentrations
  - Column overload, causing peak suppression & nonlinear response
- Dissolved metals
  - Bind to ion-exchange sites, fouling column
  - Precipitate in electrolytic devices
- Organic compounds
  - Foul columns
- Disparate concentrations
  - Small peak is hidden under a very large adjoining peak

First Approach: Dilute and Filter

Dilute and filter should always be the first approach to minimize matrix interferences

- Diluting reduces column overload and places the analytes of interest in the linear range
- Filtering removed particulates that can clog separation columns or electrolytic devices

Dilute and Filter: Salton Sea, Palm Springs



Column:	Dionex IonPac CG12A 5 µm/ Dionex IonPac CS12A 5 µm
Eluent:	35 mM MSA
Eluent Source:	Thermo Scientific Dionex EGC III MSA cartridge
Flow Rate:	0.50 mL/min
Inj. Volume:	25 µL
Temperature:	30 ˚C
Detection:	Suppressed Conductivity, Thermo Scientific Dionex ASRS 300 Suppressor, AutoSuppression, recycle mode
Sample Prep.:	1:1000 dilution, filter, 0.45 µm

Peaks:		Measured
	1. Sodium	17.6 mg/L
	2. Potassium	0.32
	3. Magnesium	1.9
	4. Calcium	1.6

Matrix Elimination, Interfering Matrices

- Trap columns
  - Dionex OnGuard sample preparation cartridge
    - Humic acid
    - Highly acidic sample
    - Trace metals in seawater
  - Thermo Scientific™ Dionex™ InGuard™ sample preparation cartridge
    - Nitrite, nitrate, sulfate in brine
  - Cation or anion trap columns
- Actively eliminate matrix
  - Anions in solvents
  - 2D-IC
  - Ion-exclusion columns

Pretreatment: IC Consumables Products

- Dionex OnGuard II Sample Pretreatment Cartridges (Off-Line)
- Dionex InGuard Sample Pretreatment (In-Line)

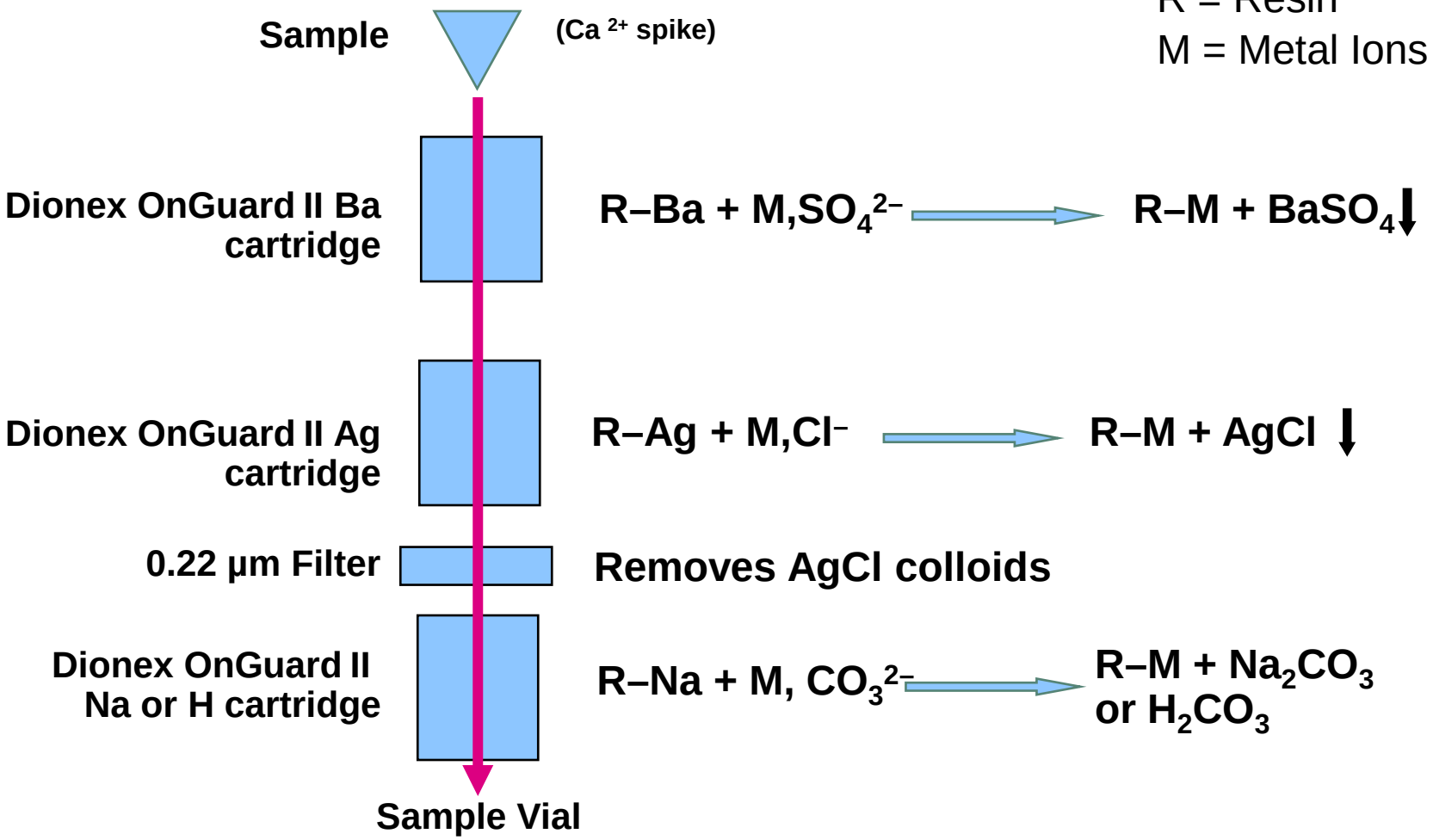
Purpose of Dionex OnGuard and Dionex InGuard Cartridges

- Isolate analytes from sample matrix
  - Eliminate matrix species that are not of interest and may interfere with the analysis
  - Reduce concentration of species that are in very large concentration ratios to analytes of interest
  - Trap species that reduce the life of consumables
- Concentrate analytes
  - Retain analyte species onto a guard followed by elution into a smaller volume

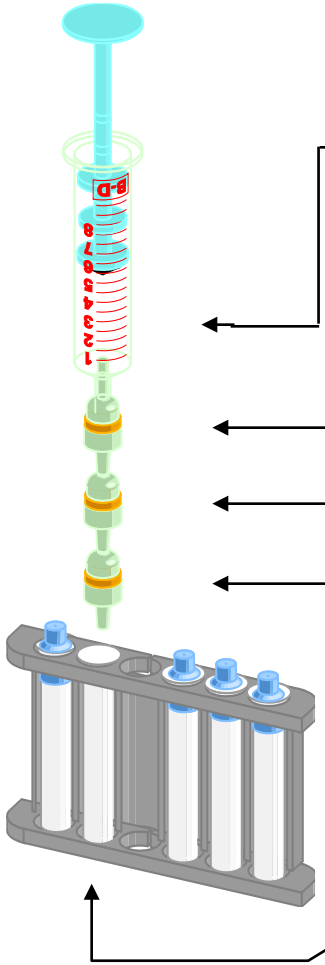
Cartridge Phase Chemistries: Multiple Phases for a Variety of Applications

Phase	Functionality	Retention Mechanism	Common Uses	Cartridge Use	Mode of Operation
Ag	Cation-exchange (Silver-form)	Precipitation Ion-exchange	Remove halides and others that precipitate with silver	Single (Dioenx OnGuard) Multiple (Dionex InGuard)	Manual Automated
A	Anion-exchange (Bicarbonate-form)	Ion-exchange	pH adjustment Remove anions	Single	Manual
Ba	Cation-exchange (Barium-form)	Precipitation Ion-exchange	Remove sulfate and others that precipitate with barium	Single	Manual
H	Cation-exchange (Hydronium-form)	Ion-exchange	Remove alkali- and alkaline earth metals, cationic transition metals; acidify sample	Single (Dionex OnGuard) Multiple (Dionex InGuard)	Manual Automated
M	Iminodiacetate (Ammonium-form)	Chelation	Concentrate and elute transition metals	Single	Manual
Na	Cation-exchange (Sodium-form)	Ion-exchange	Remove alkaline earth and cationic transition metals without a pH change	Single (Dionex OnGuard) Multiple (Dionex InGuard)	Manual Automated
P	Poly-vinylpyrrolidone	H-bonding / Complexation	Remove phenols, azo dyes, humic acids	Single	Manual
RP	Poly-divinylbenzene (DVB)	Adsorption	Remove neutral hydrophobic compounds	Single	Manual
HRP	Hydrophilic DVB	Adsorption	Remove organic material, including fats from whole milk (Not available in Dionex OnGuard cartridge format)	Multiple	Automated
Na/HRP	Combined	Combined	Contains a blend of Dionex InGuard Na and HRP cartridge resin	Multiple	Automated

Use of Dionex OnGuard Column for Off-line Matrix Elimination of Common Anions



Off-Line Matrix Elimination of Common Anions



Dionex OnGuard Cartridges

Add 1 mL of 0.5 M calcium chloride reagent and 1 mL of 0.167 M sodium carbonate reagent to 100 mL of sample

Dionex OnGuard Ba cartridge

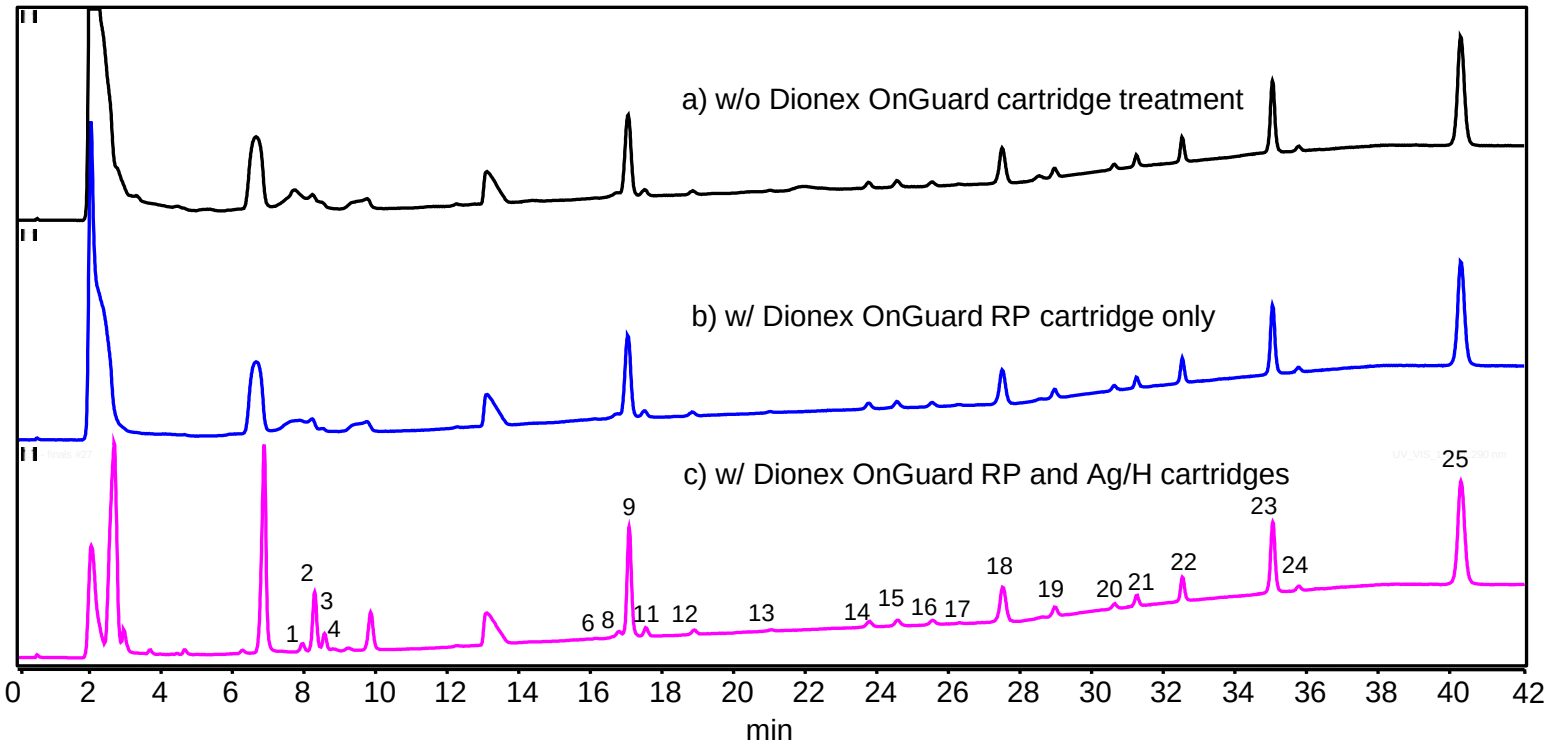
Dionex OnGuard Ag cartridge

Dionex OnGuard H cartridge

Sparge sample for 5 minutes

Used in series to remove interferences

Recovery of Inositol Phosphates

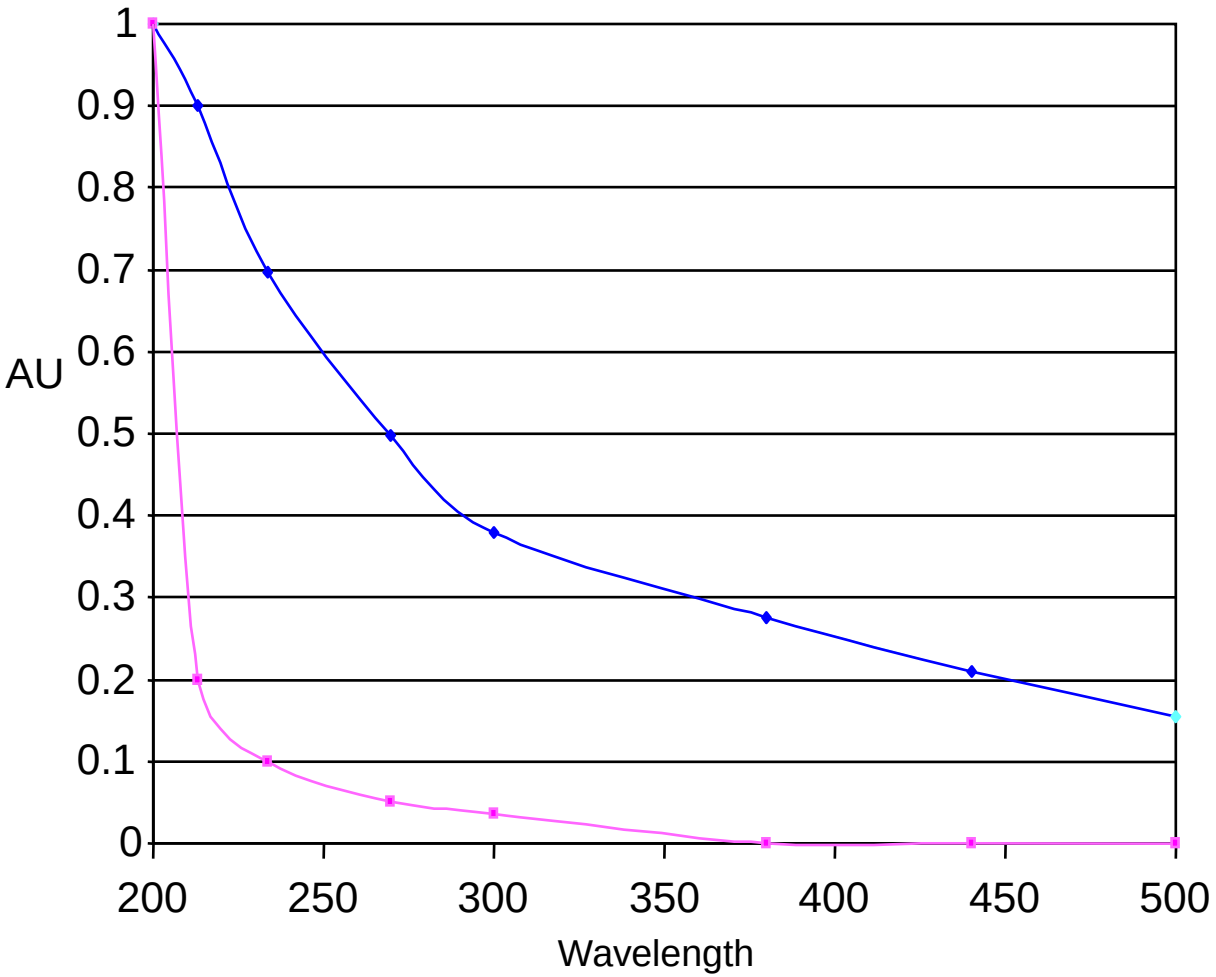


Dried distilliers grains with solubles DDGS

Problem: Anions in Inks, Dyes, High TOC (Humic acid)

- Solution: Dionex OnGuard II P cartridge, high capacity polyvinylpyrrolidone
  - Specifically traps phenols, azo dyes, cyano, via formation of a charge transfer complex
  - Preserves column capacity
  - Improves baseline

Removal of Humic Acid from Water



Sample Preparation:
Dionex OnGuard II P cartridge

Sample:
0.05% Humic acid in water, adjusted to pH 6

Before Treatment

After Treatment

15653

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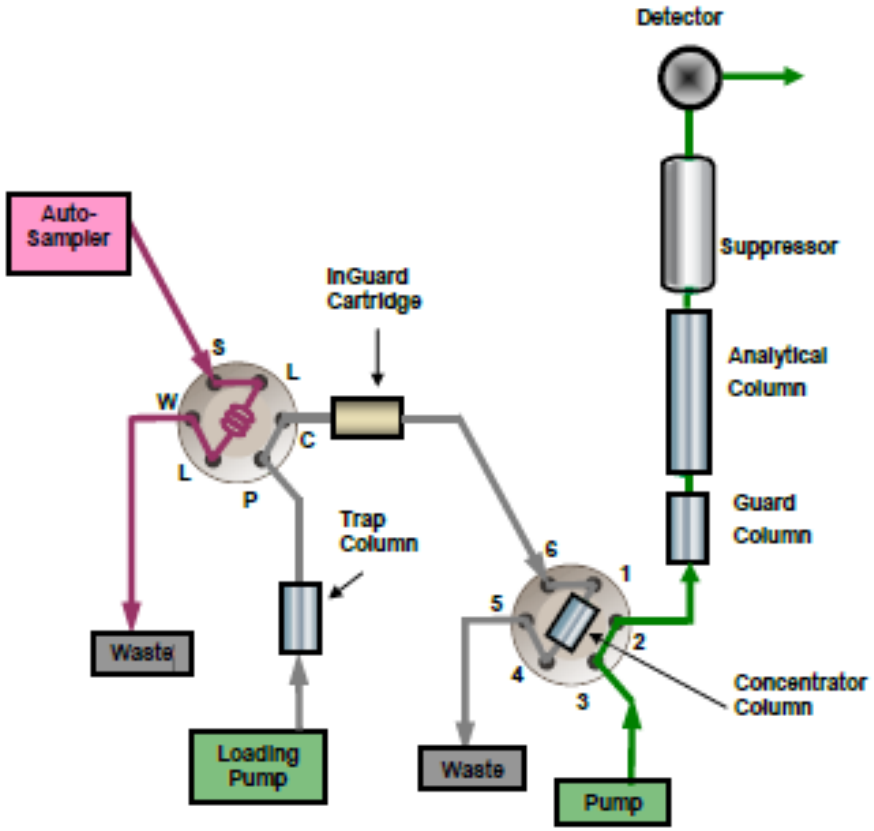
In Line Matrix Elimination

Figure 1
Preferred Configuration 1:
Two 6-port Valves and Two Pumps



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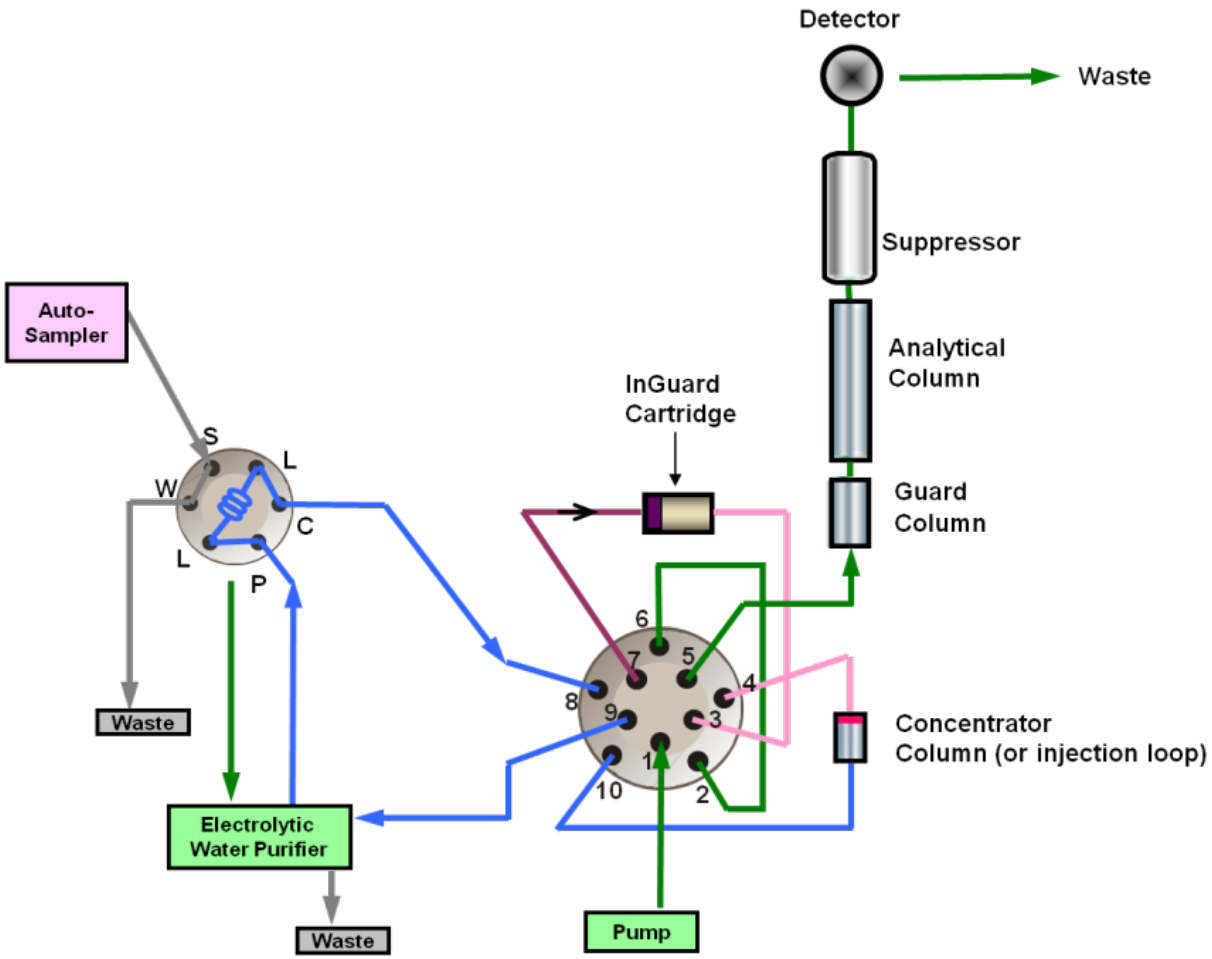
Single Pump In-Line Matrix Elimination



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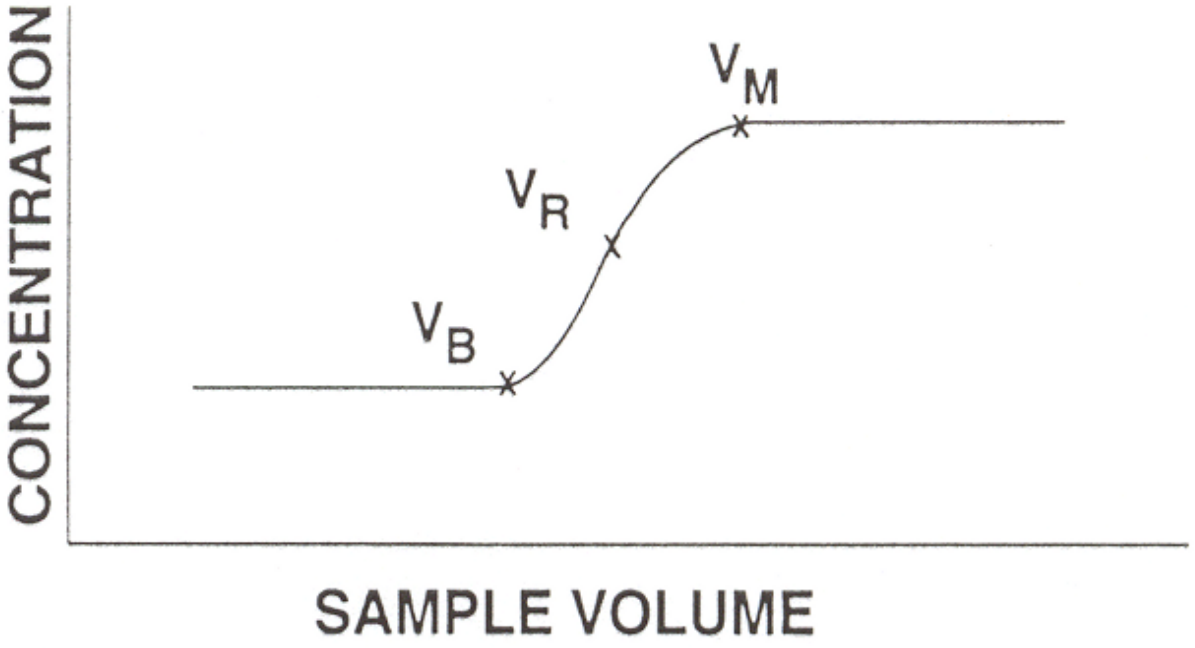
Determination of Breakthrough Volume

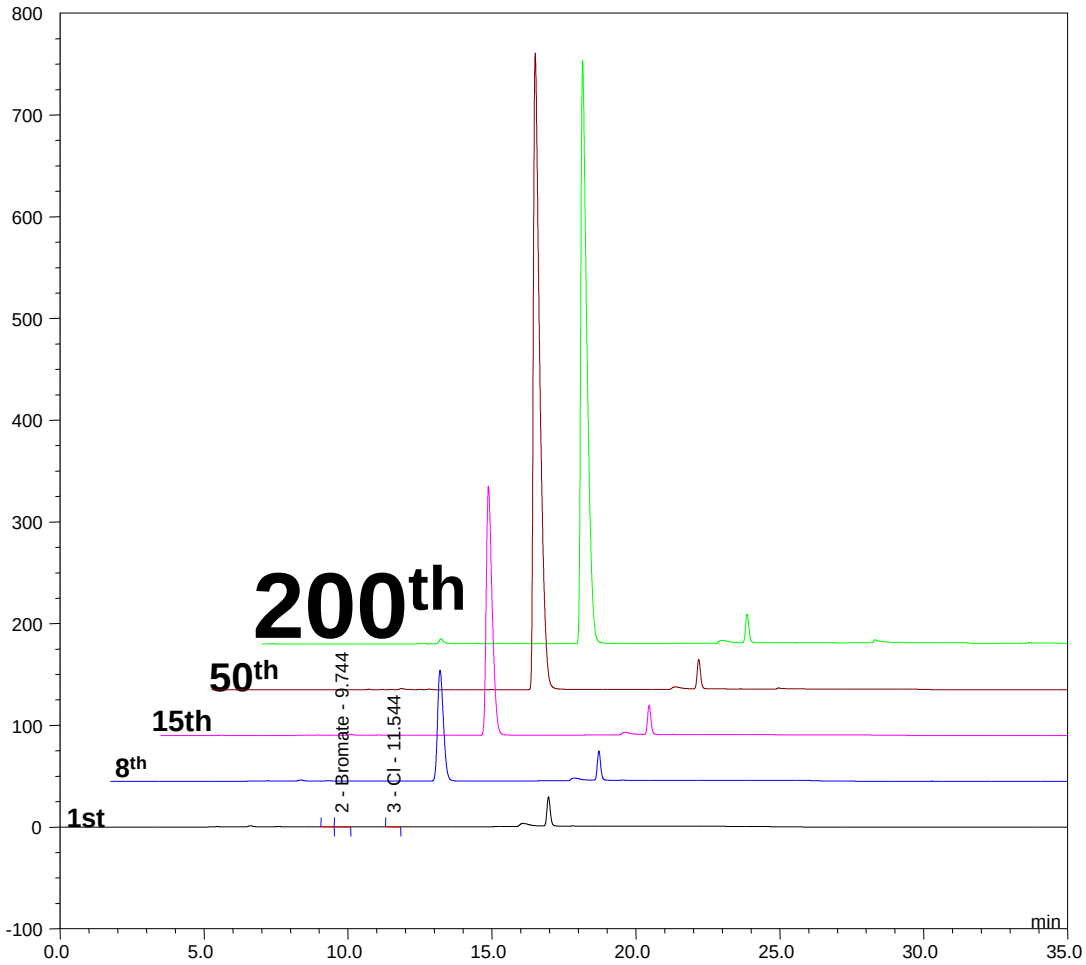


V_B = Breakthrough volume (can calculate mass); V_R = Average "Retention" volume for sample; V_M = Maximum Sampling Volume (or mass)

In-Line Matrix Removal for 200 Injections

Sample:

- 10 ppb bromate
- 300 ppm chloride
- 500 µL sample size
  bromate
  - RSD Area=0.309%

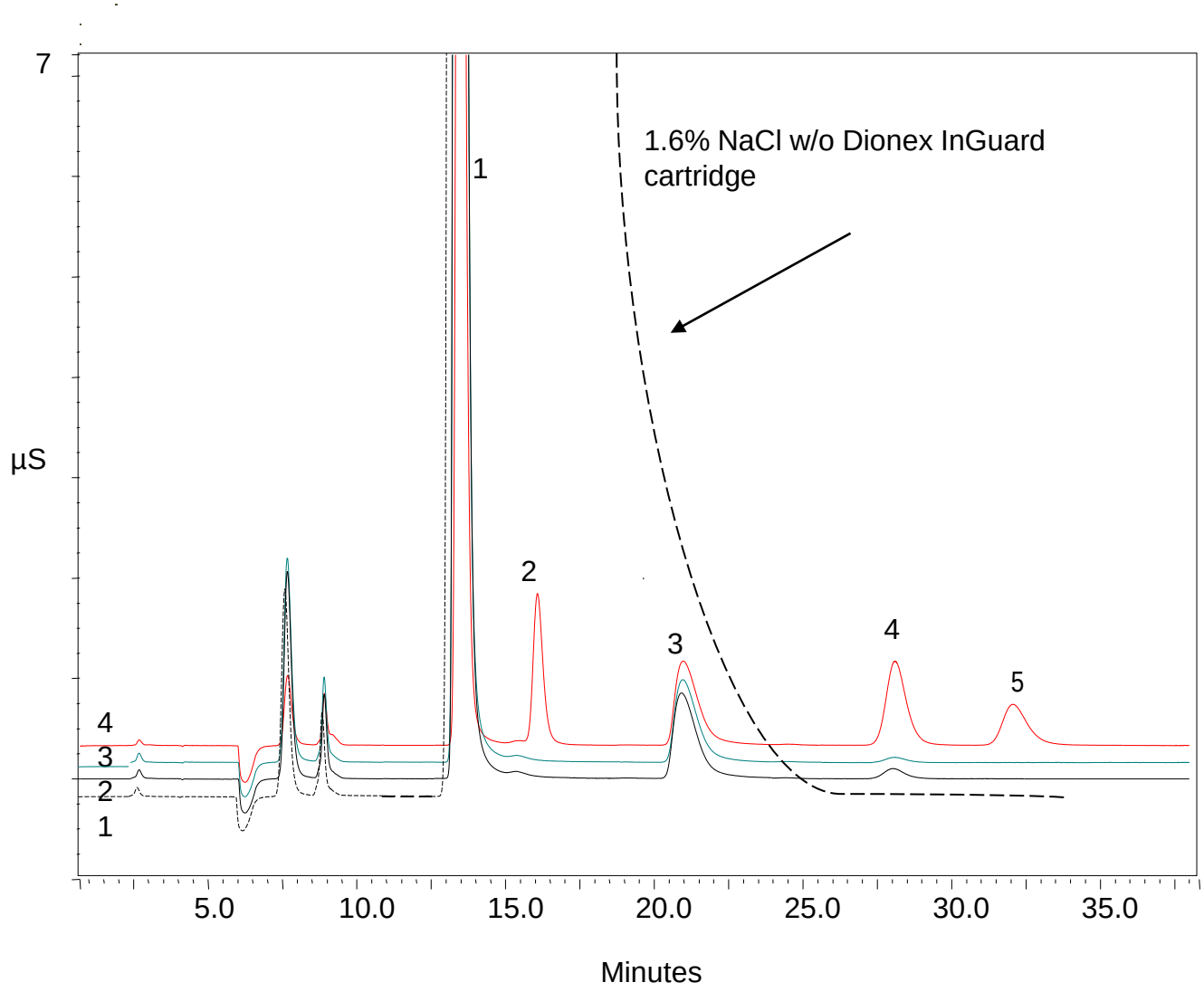


Dionex InGuard Sample Pretreatment Cartridges

- Automated sample pretreatment cartridges to remove matrix interferences
  - Uses standard 10-32 fittings for easy installation into an IC or LC system
  - Can be used multiple times
  - Some cartridges can also be regenerated
- Removes matrix interferences such as cations, transition metals, anions, or hydrophobic substances
  - Dionex InGuard Ag cartridge resin for the removal of chloride, bromide and iodide
  - Dionex InGuard H cartridge resin for the removal of alkaline earth metals, transition metals, and acidifying samples
  - Dionex InGuard Na cartridge resin for the removal of alkaline earth metals, transition metals, without acidifying samples
  - Dionex InGuard HRP cartridge resin for the removal of organic material, including fats from whole milk (Not available in Dionex OnGuard cartridge)
  - Dionex InGuard Na/HRP cartridge resin contains a blend of Dionex InGuard Na and HRP cartridge resin

Automated Inline Sample Pretreatment

Use of Dionex InGuard Ag/H Cartridge



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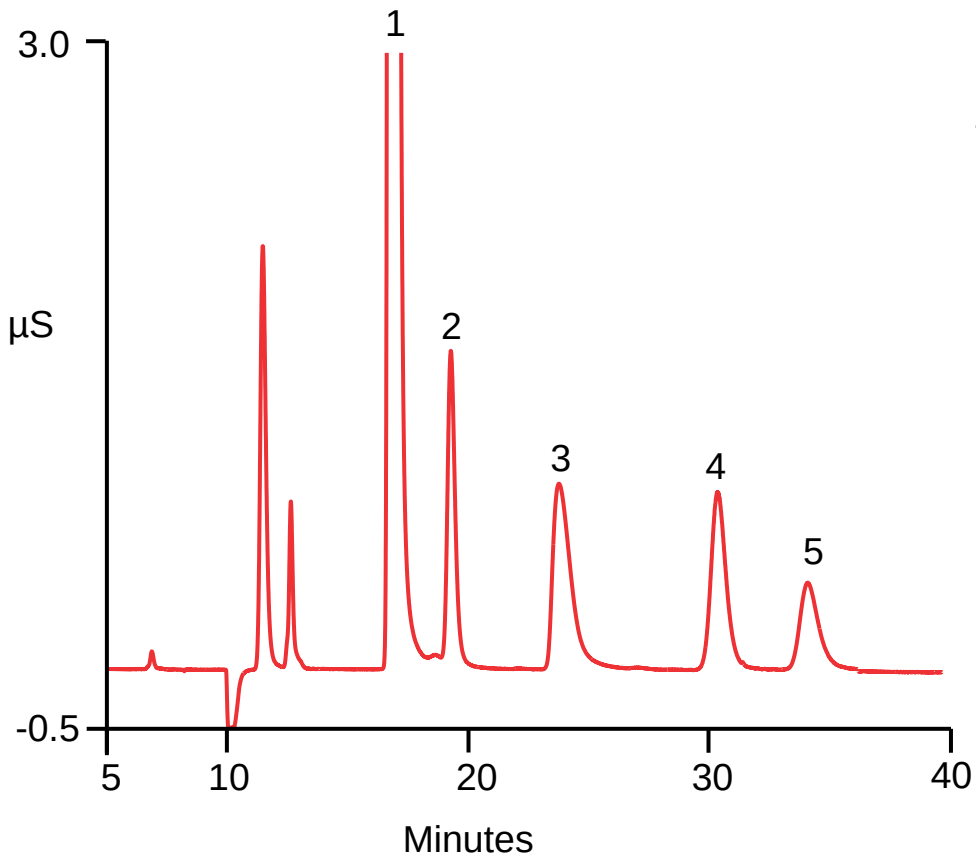
Nitrate, Nitrite, and Sulfate in NaCl Brine After In-Line Sample Pretreatment



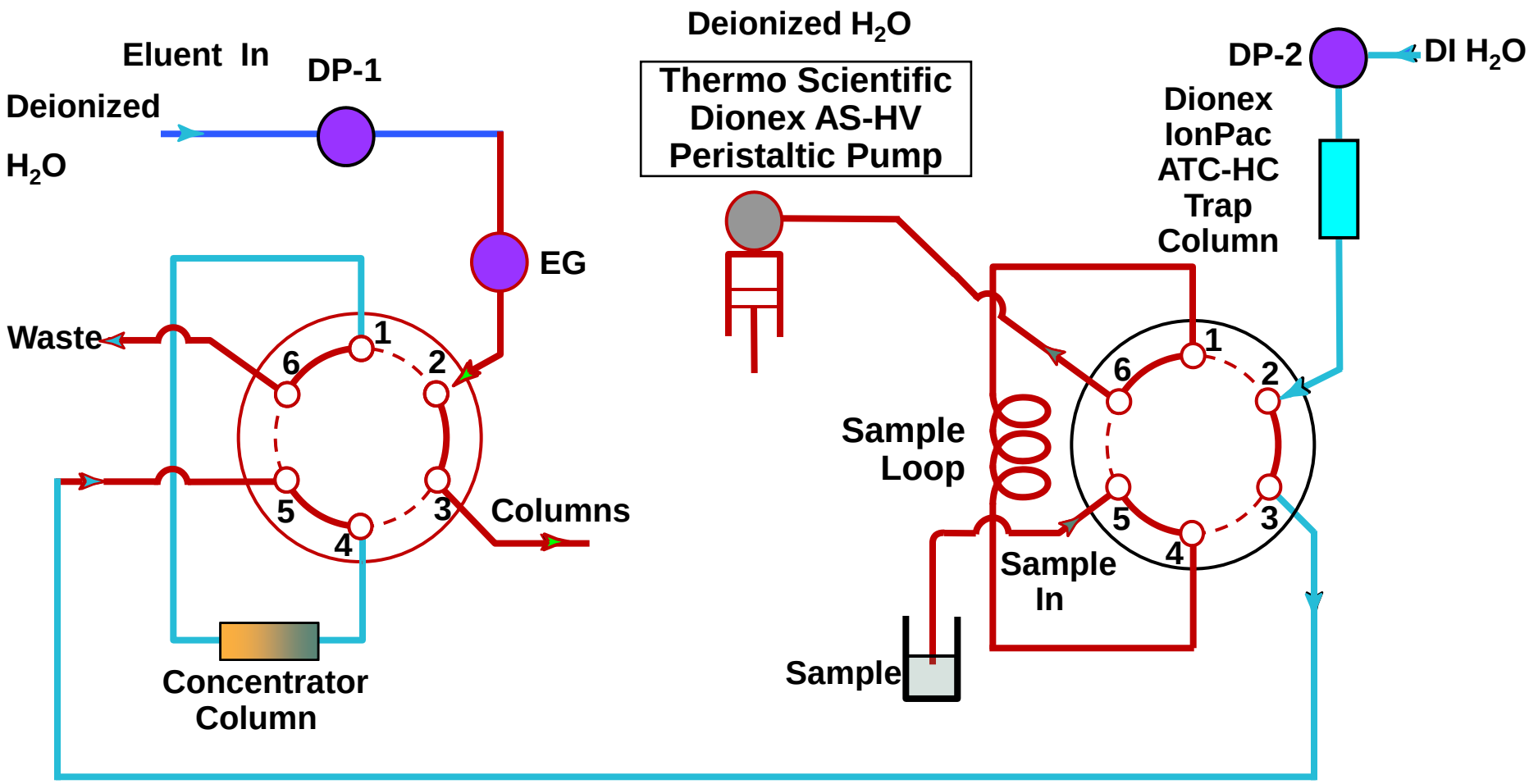
Column:	Dionex IonPac AG15, Dionex IonPac AS15 (4 mm)
Eluent (EG):	23 mM KOH
Temp.:	30 ° C
Flow Rate:	1.0 mL/min
Inj. Vol.:	100 µL
Detection:	Suppressed conductivity, Dionex ASRS suppressor
Sample:	1.6 % NaCl brine
Sample Prep.:	Dionex InGuard Ag cartridge, Dionex InGuard Na cartridge

Peaks		
1. Chloride	--	mg/L
2. Nitrite	2.0	
3. Carbonate	---	
4. Sulfate	2.0	
5. Nitrate	2.0	

Chloride removed from sample

Matrix Elimination Configuration

Thermo Scientific™ Dionex™ ICS-5000⁺ RFIC™ Dual Pump, Dual Valve System



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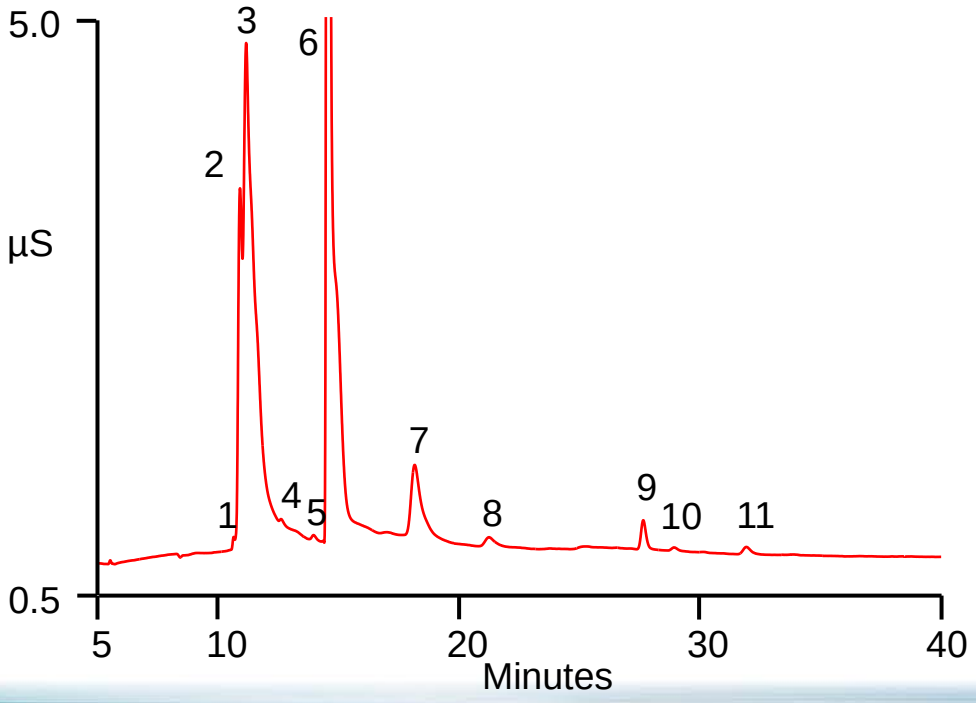
Matrix Elimination Using a Concentrator Column: Unspiked 100% Acetone

Sample Prep.

Trap Column:	Dionex IonPac ATC-HC
Carrier:	Deionized water
Matrix Eliminat.:	10 mL
Flow Rate:	2 mL/min
Inj. Vol.:	2 mL
Load Vol.:	5 mL
AS Rinse Vol.:	7 mL
AS-HV Mode:	Peristaltic Pump, Pull



Analytical

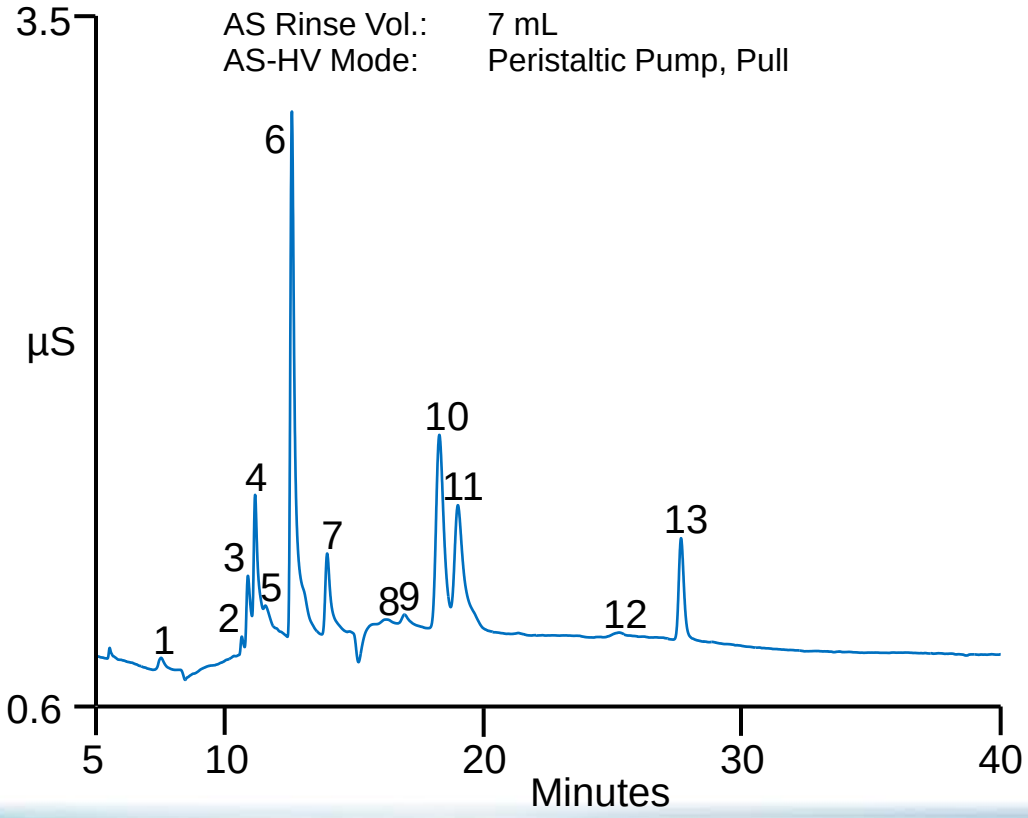
Column:	Dionex IonPac AG18, Dionex IonPac AS18 (2 mm)
Eluent (EG):	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Temp.:	30 ºC
Flow Rate:	0.25 mL/min
Concentrator:	Dionex IonPac UTAC-ULP1
Detection:	Suppressed conductivity, Dionex ASRS suppressor, recycle mode, 41 mA, Thermo Scientific Dionex CRD 200 Carbonate Removal Device

Peaks		
	1. Unknown	--- µg/L
	2. Acetate	---
	3. Formate	---
	4. Chloride	< 0.11
	5-6. Unknown	---
	7. Sulfate	5.02
	8. Unknown	---
	9. Phosphate	2.86
	10-11. Unknown	---

Matrix Elimination Using a Concentrator Column: Isopropyl Alcohol Spiked with Anions

Sample Prep.

Trap Column:	Dionex IonPac ATC-HC
Carrier:	Deionized water
Matrix Eliminat.:	10 mL
Flow Rate:	2 mL/min
Inj. Vol.:	2 mL
Load Vol.:	5 mL
AS Rinse Vol.:	7 mL
AS-HV Mode:	Peristaltic Pump, Pull



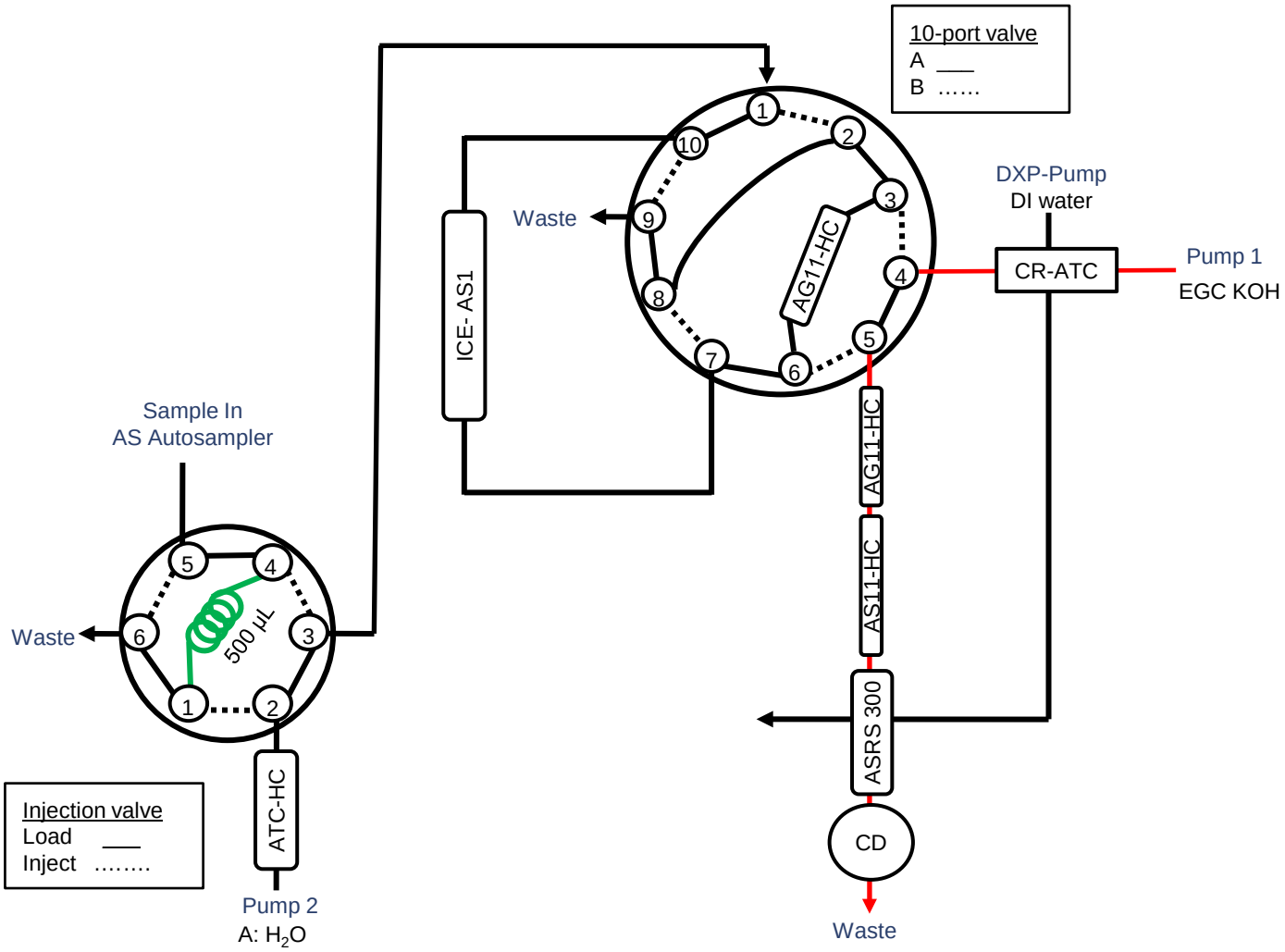
Analytical

Column:	Dionex IonPac AG18, Dionex IonPac AS18 (2 mm)
Eluent (EG):	22 mM KOH -2–15 min, 22–48 mM KOH 15–25 min, 65 mM KOH 35–40 min
Temp.:	30 ºC
Flow Rate:	0.25 mL/min
Concentrator:	Dionex IonPac UTAC-ULP1
Detection:	Suppressed conductivity, Dionex ASRS suppressor, recycle mode, 41 mA, Dionex CRD 200 device
Sample:	Isopropyl alcohol + 5 µg/L chloride, sulfate, nitrate, and phosphate

Peaks:

1. Unknown	--- µg/L
2. Acetate	---
3. Formate	---
4. Lactate	---
5. Unknown	---
6. Chloride	4.98
7. Nitrite	---
8. Carbonate	---
9. Unknown	---
10. Sulfate	5.10
11. Nitrate	5.32
12. Unknown	---
13. Phosphate	4.97

Matrix Elimination Configuration by Ion Exclusion



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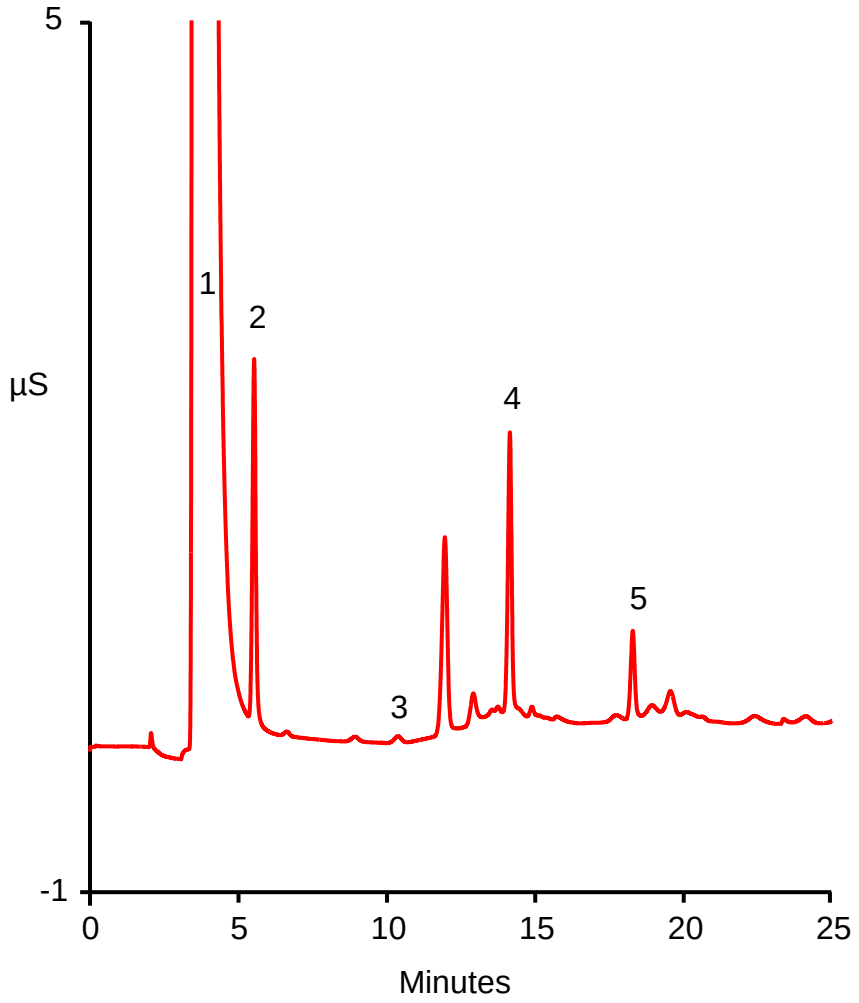
Matrix Elimination by Ion Exclusion: 12% HF

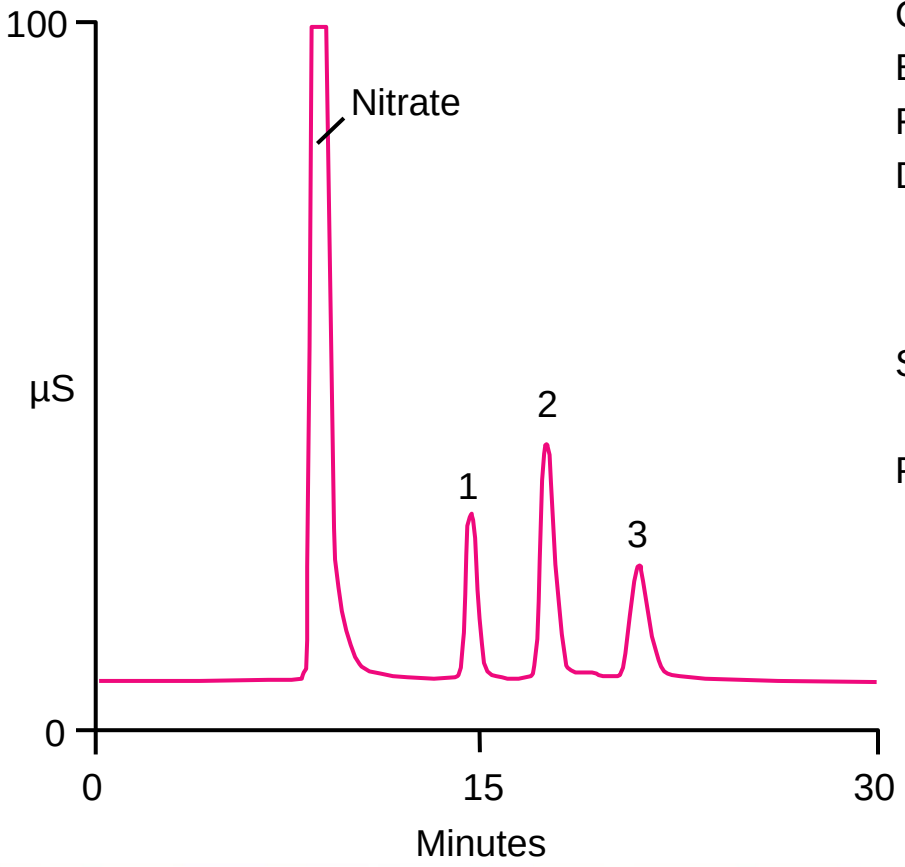


Pretreatment Column:	Dionex IonPac ICE-AS1, 9 × 250 mm
Trap Column:	Dionex IonPac ATC-HC, 9 × 75 mm
ICE Eluent:	DI Water
ICE Flow Rate:	0.5 mL/min (load), 0.8 mL/min (clean)
Inj. Volume:	500 µL
Column:	IonPac AS11-HC, 2 × 250 mm IonPac AG11-HC, 2 × 50 mm
Concentrator:	IonPac AG11-HC, 4 × 50 mm
Eluent Source:	Dionex EGC II KOH cartridge
Eluent:	8 mM KOH from 0 to 7 min, 8 to 30 mM KOH from 7 to 15 min, 30 mM to end of program
Temperature:	30 ºC
Flow Rate:	0.38 mL/min
Detection:	Suppressed conductivity, Dionex ASRS 300 suppressor, 2 mm, external water mode
Sample:	12% HF
Peaks:	1. Fluoride — 2. Chloride 17.19 µg/L 3. Nitrate 1.52 4. Sulfate 26.11 5. Phosphate 29.28

Ion Exclusion works on other weak acids

Matrix Elimination by Ion Exclusion: Organic Acids in Nitric Acid

Nitrate elutes in void volume

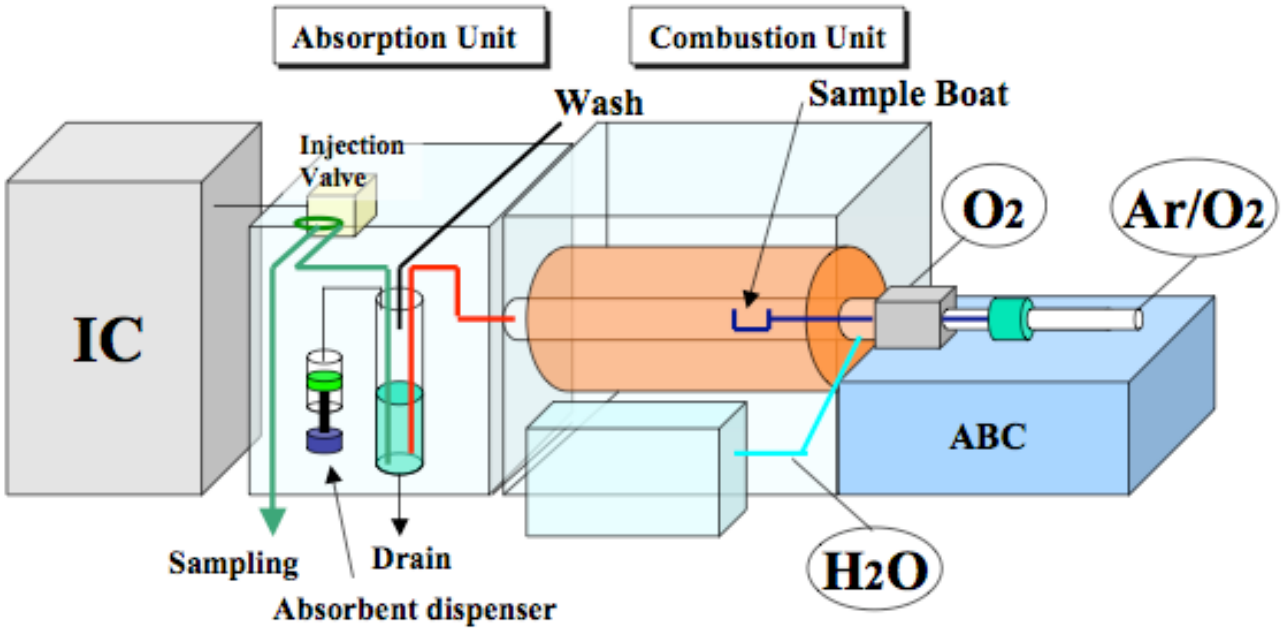


Column:	Dionex IonPac ICE-AS1 (9 × 250 mm)
Eluent:	1 mM Octanesulfonic acid
Flow Rate:	0.8 mL/min
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ AMMS-ICE™ Anion MicroMembrane Suppressor
Sample:	52% Nitric acid
Peaks:	1. Succinic acid 2. Glutaric acid 3. Adipic acid

Combustion Sample Prep for IC

Designation: D 7359 – 08

Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)[1]



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Combustion IC

Mitsubishi™ AQF2100H combustion system

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Combustion IC

PAC Antek™ MultiTek™ Furnace

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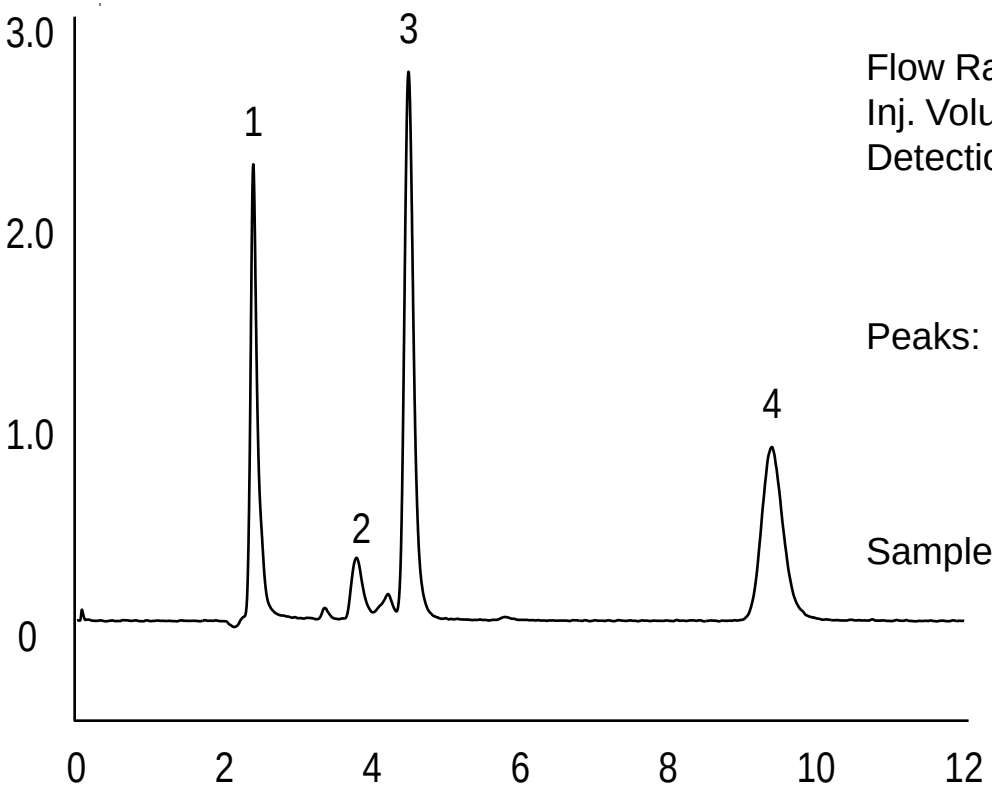
Halides and Sulfur in Liquified Petroleum Gas by On-Line CIC* with RFIC



Column:	Dionex IonPac AS11-HC
Eluent :	25 mM KOH
Eluent Source:	Dionex EGC cartridge with Thermo Scientific Dionex CR-ATC Continuously Regenerating Anion Trap Column
Flow Rate:	1.3 mL/min
Inj. Volume:	100 µL
Detection:	Suppressed conductivity, Dionex ASRS ULTRA suppressor, recycle mode

Peaks:		
1.	Fluoride	1.5 mg/L
2.	Chloride	0.019
3.	*S* as Sulfate	3.0
4.	Phosphate (int. std)	2.0

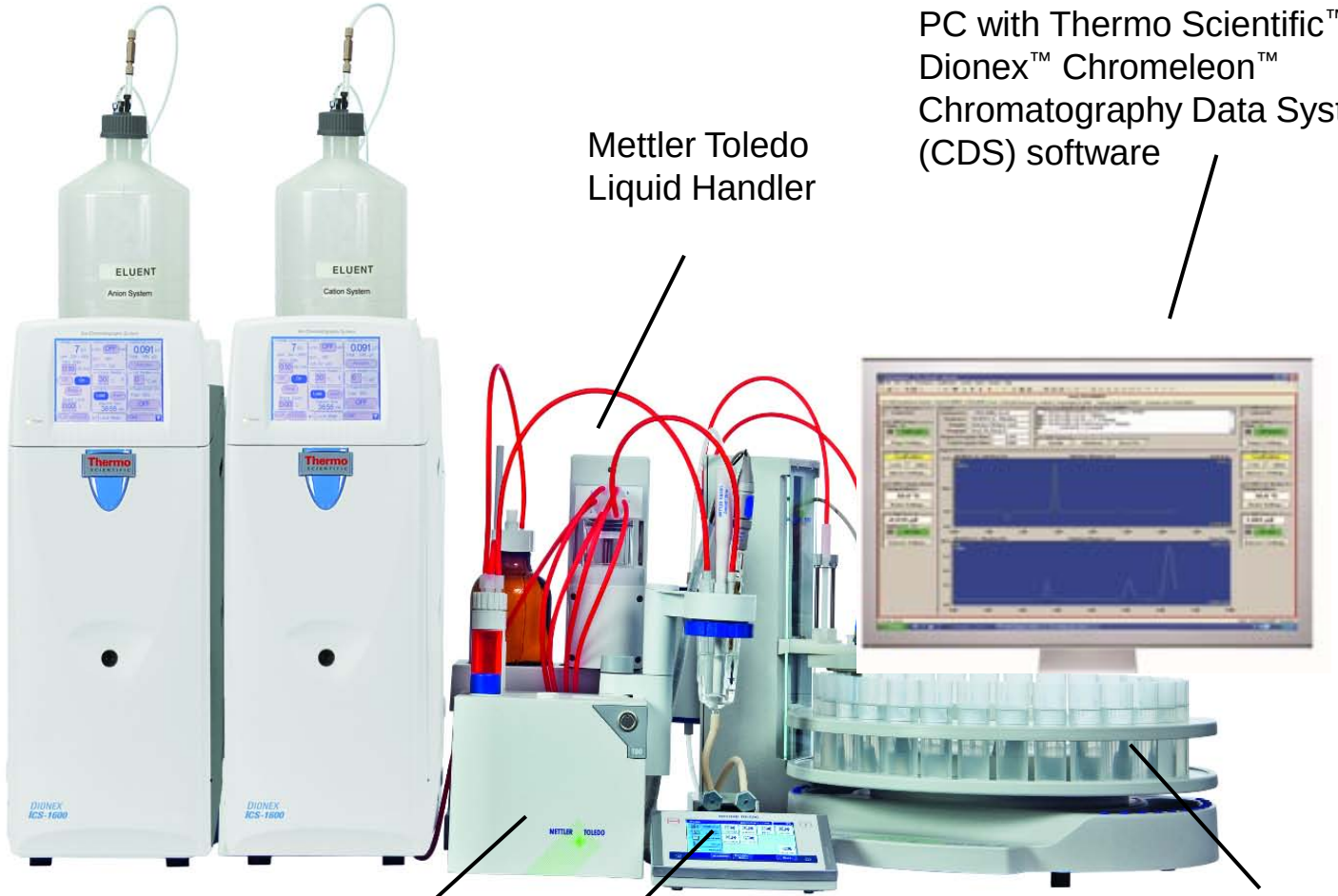
Sample Preparation: Mitsubishi AQF-100 combustion system

*CIC = Combustion Ion Chromatography

Automated Multiple Ion Analysis Ion Chromatography: Titration

The Solution: Titration/IC

Two Thermo Scientific Dionex ion chromatographs:
anion and cation



Mettler Toledo
Liquid Handler

PC with Thermo Scientific™
Dionex™ Chromeleon™
Chromatography Data System
(CDS) software

Mettler Toledo
T90 Titrator

One Click™ Terminal

Mettler Toledo Rondo 30
Sample Changer

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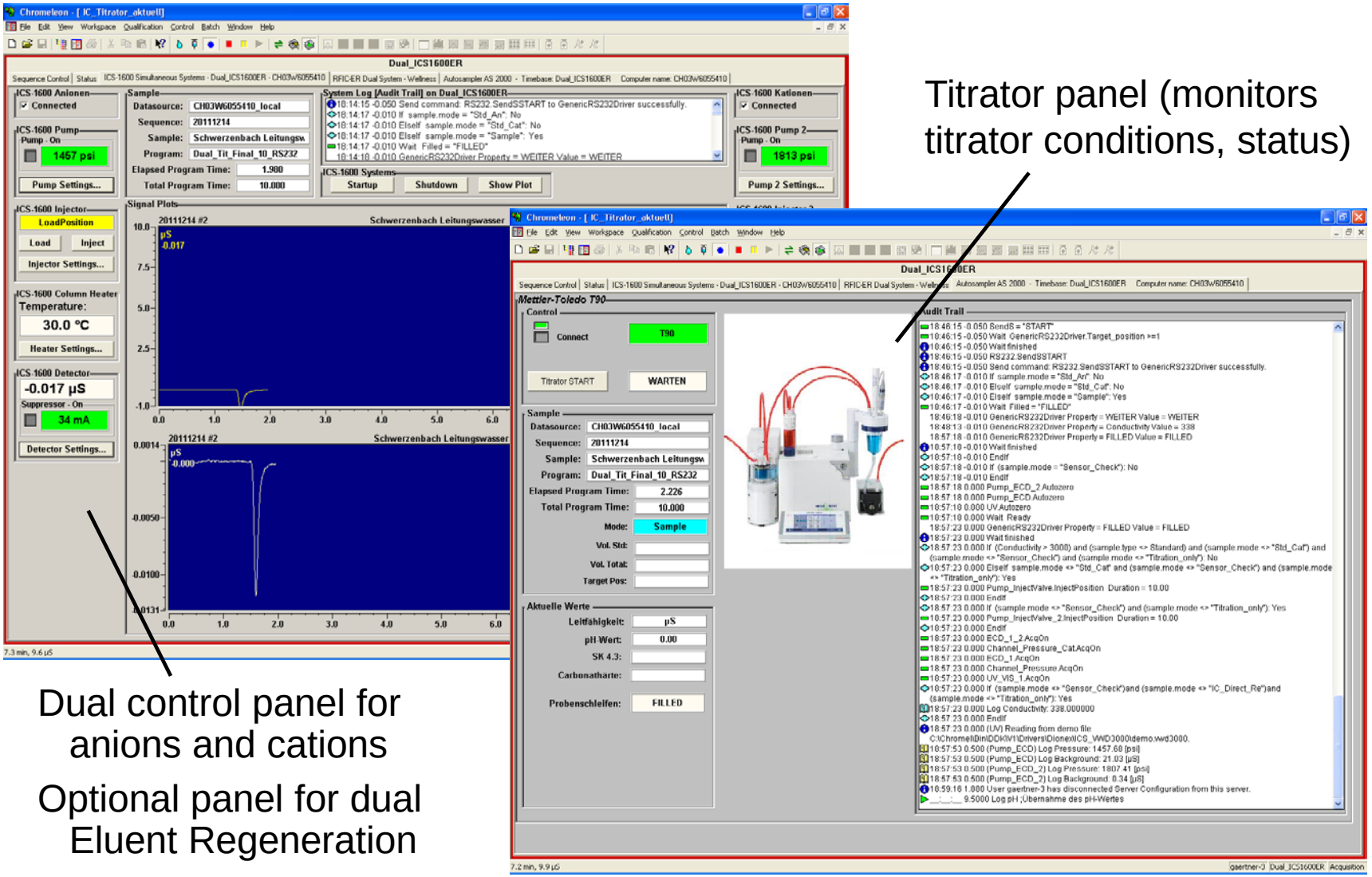
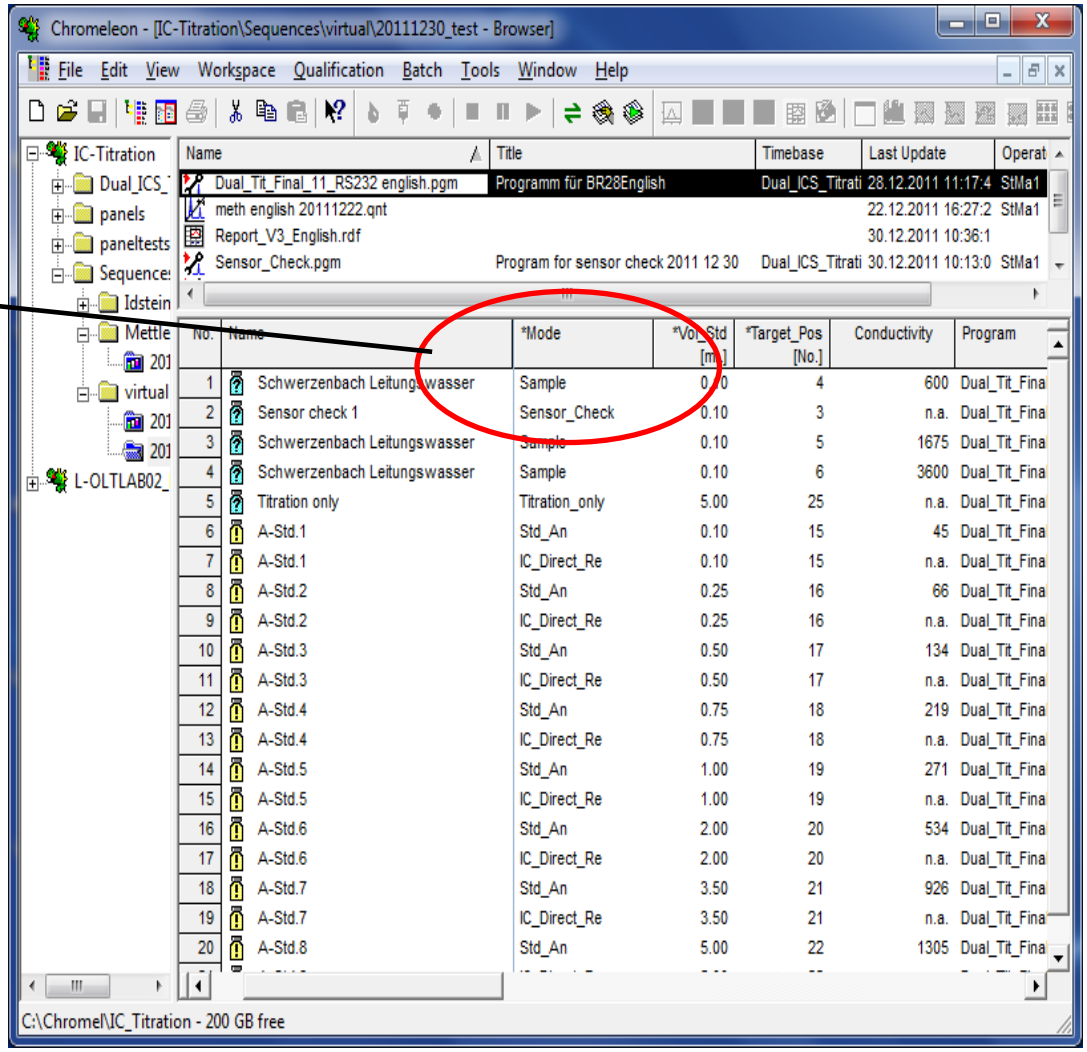
Chromeleon CDS Software Interface: Instrument Panel



Chromeleon CDS Software Interface: Sequence

- The user interacts only with the Chromeleon CDS software interface
- The different tasks are defined in a user-defined column. Choice of Mode in the sequence table:
  - Sample
  - Standard- anions
  - Standard-cations
  - Only IC
  - pH Sensor Check
  - Only titration
- One Chromeleon CDS software program controls all the different tasks



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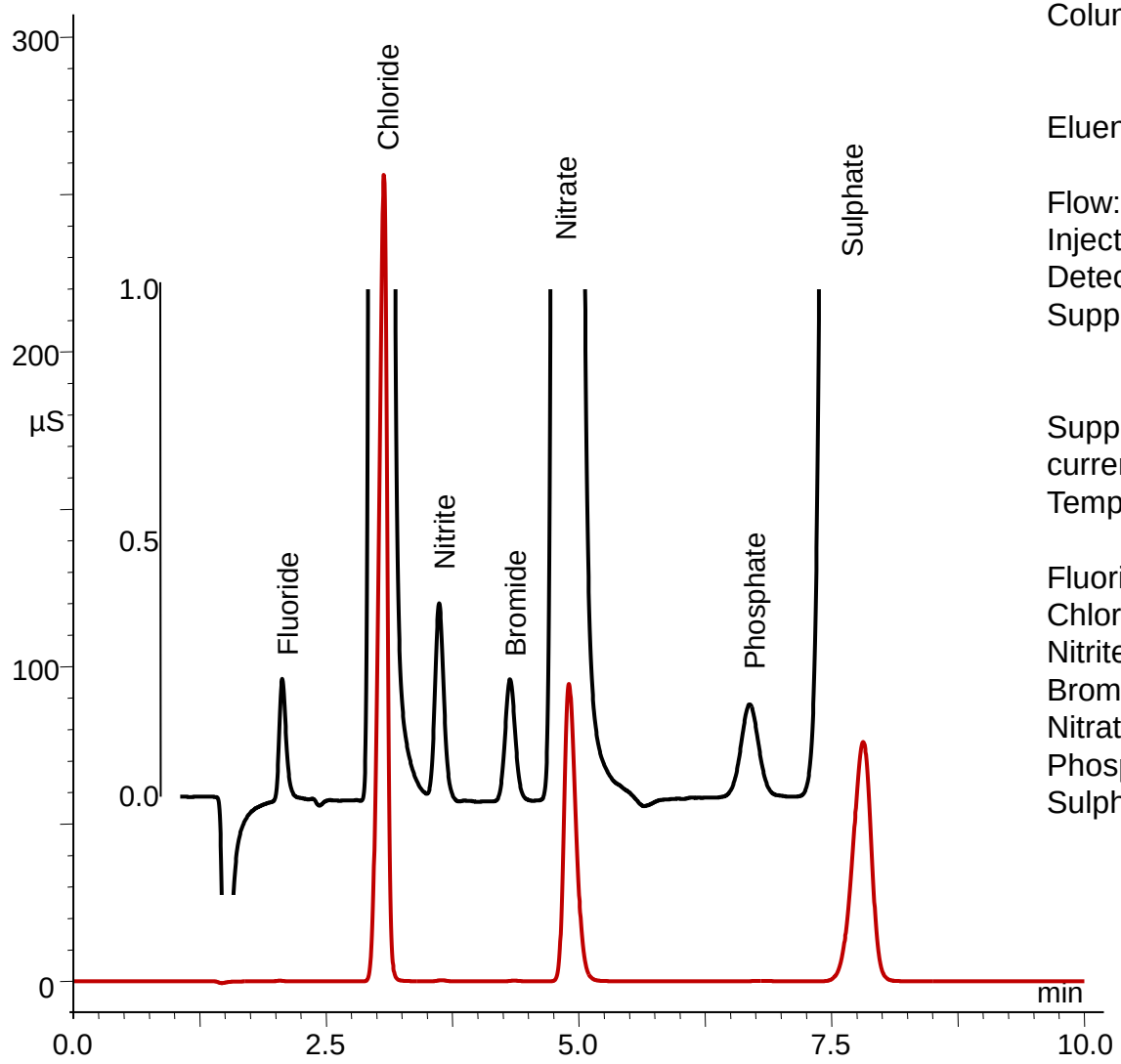
Workflow of Sample Analysis

- Start T90 Titrator via Shortcut at Terminal
- Start Chromeleon CDS software sequence
  - Rinse sample tube and conductivity sensor in the rinse beaker
  - Measure sample conductivity – transfer to Chromeleon CDS software
  - The Liquid Handler dispenses 50 mL of sample into titration beaker
  - The Liquid Handler fills the IC sample loops
  - The sample is injected and the chromatography started. Depending on the conductivity the corresponding small or large sample loop of the anion system is selected for injection.
- During Chromatography
  - pH measurement and titration of the sample is performed
  - Titration beaker is rinsed with deionized water
  - Transfer of titration results to Chromeleon CDS software (in the event that titration requires more time than the chromatography, Chromeleon CDS software waits for an end-signal before proceeding to the next sample)

Results: Anions by Conductivity Detection

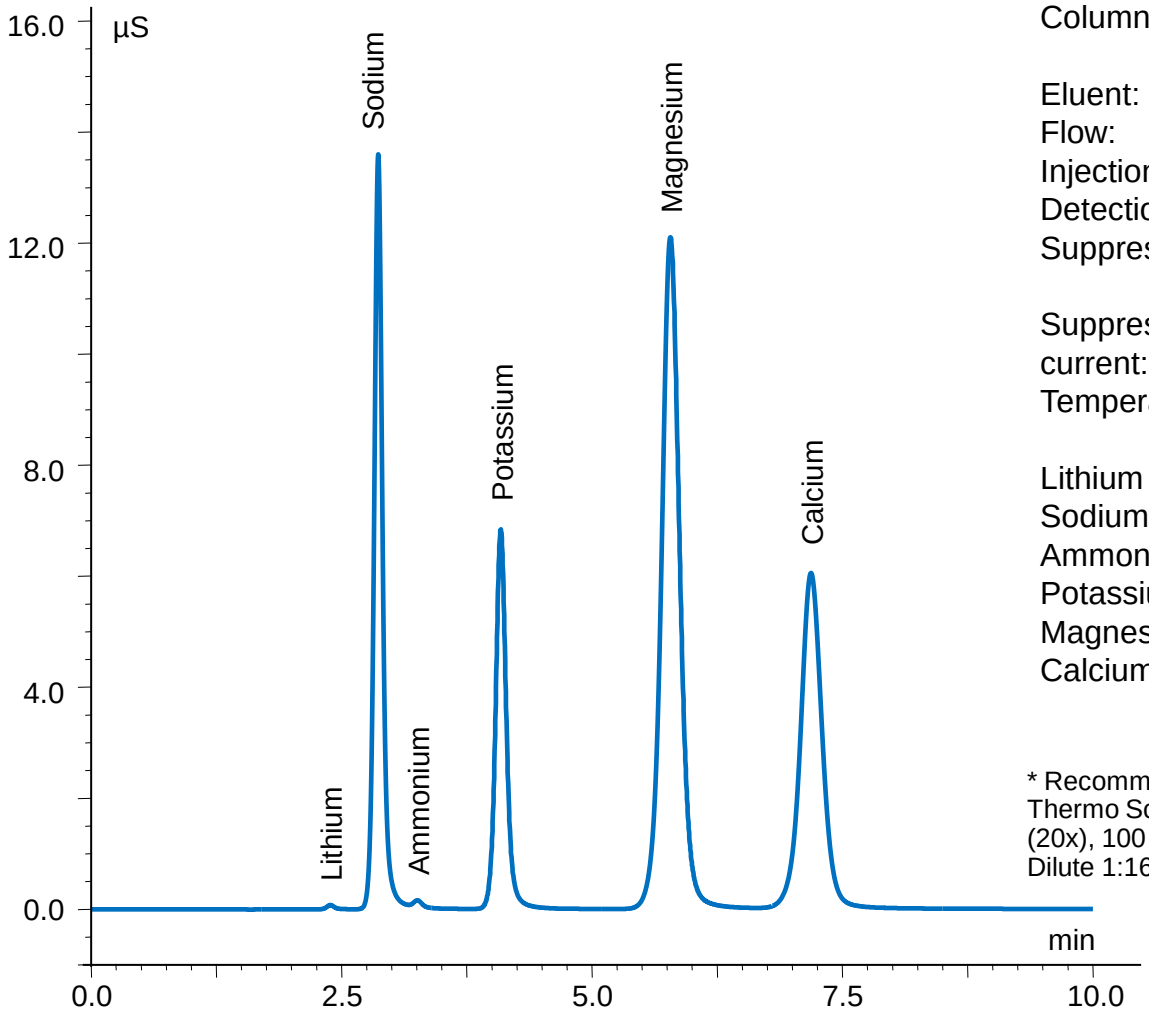


Column:	Dionex IonPac AS22-Fast (4×150 mm) with guard
Eluent:	4.5 mmol/L Na_2CO_3 1.4 mmol/L $NaHCO_3$
Flow:	1.2 mL/min
Injection vol.:	25 µL (10 µL)
Detection:	Suppressed conductivity
Suppressor:	Dionex ASRS 300 suppressor, 4 mm (Recycle mode)
Suppressor current:	31 mA
Temperature:	30 °C

Fluoride	0.088 mg/L
Chloride	106 mg/L
Nitrite	0.44 mg/L
Bromide	0.44 mg/L
Nitrate	107 mg/L
Phosphate	0.88 mg/L
Sulphate	105 mg/L

* Recommended for eluent preparation: Thermo Scientific Dionex AS22 Eluent Concentrate (100x), 250 mL, P/N 063965

Results: Cations by Conductivity Detection

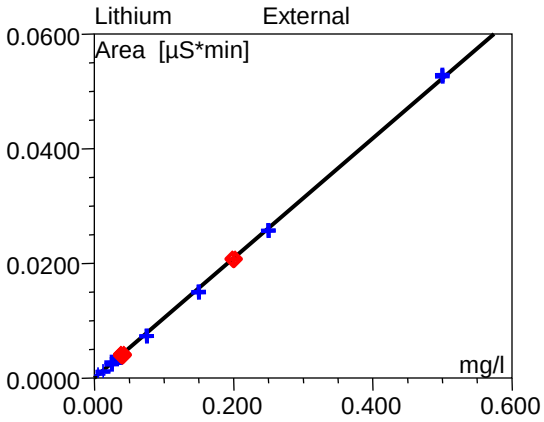


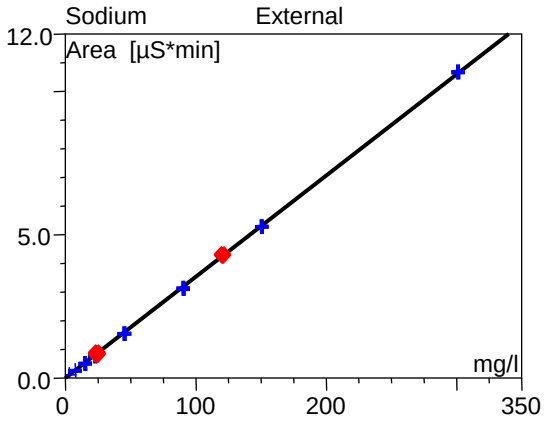
Column:	Dionex IonPac CS12A-5 µm (3×150 mm) with guard
Eluent:	25 mM MSA
Flow:	0.5 mL/min
Injection vol.:	1 µL
Detection:	Suppressed conductivity
Suppressor:	Dionex CSRS 300 suppressor, 2 mm (Recycle mode)
Suppressor current:	37 mA
Temperature	30 °C

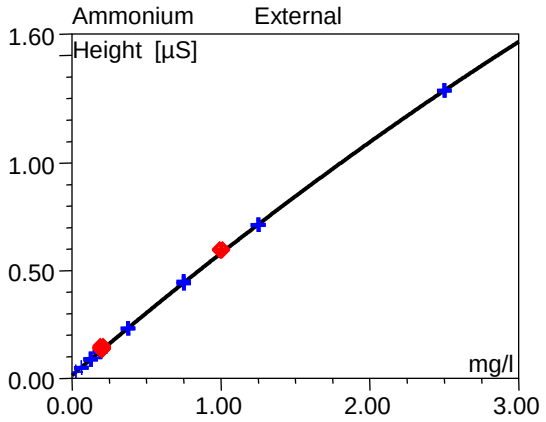
Lithium	0.075 mg/L
Sodium	45.2 mg/L
Ammonium	0.38 mg/L
Potassium	45.2 mg/L
Magnesium	45.1 mg/L
Calcium	45.2 mg/L

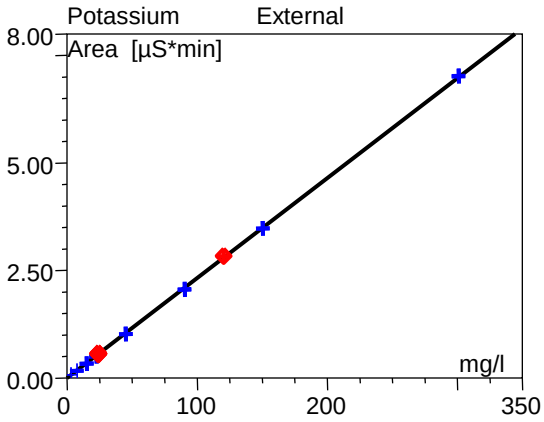
* Recommended for eluent preparation:
Thermo Scientific Dionex CS12A Eluent Concentrate (20x), 100 mL, P/N 057562
Dilute 1:16 for 25 mM

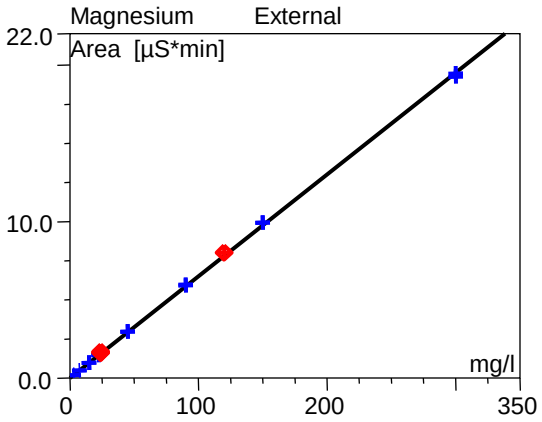
Automated IC Standards Preparation

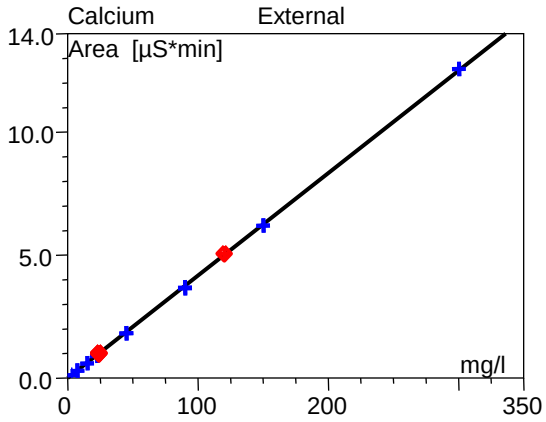








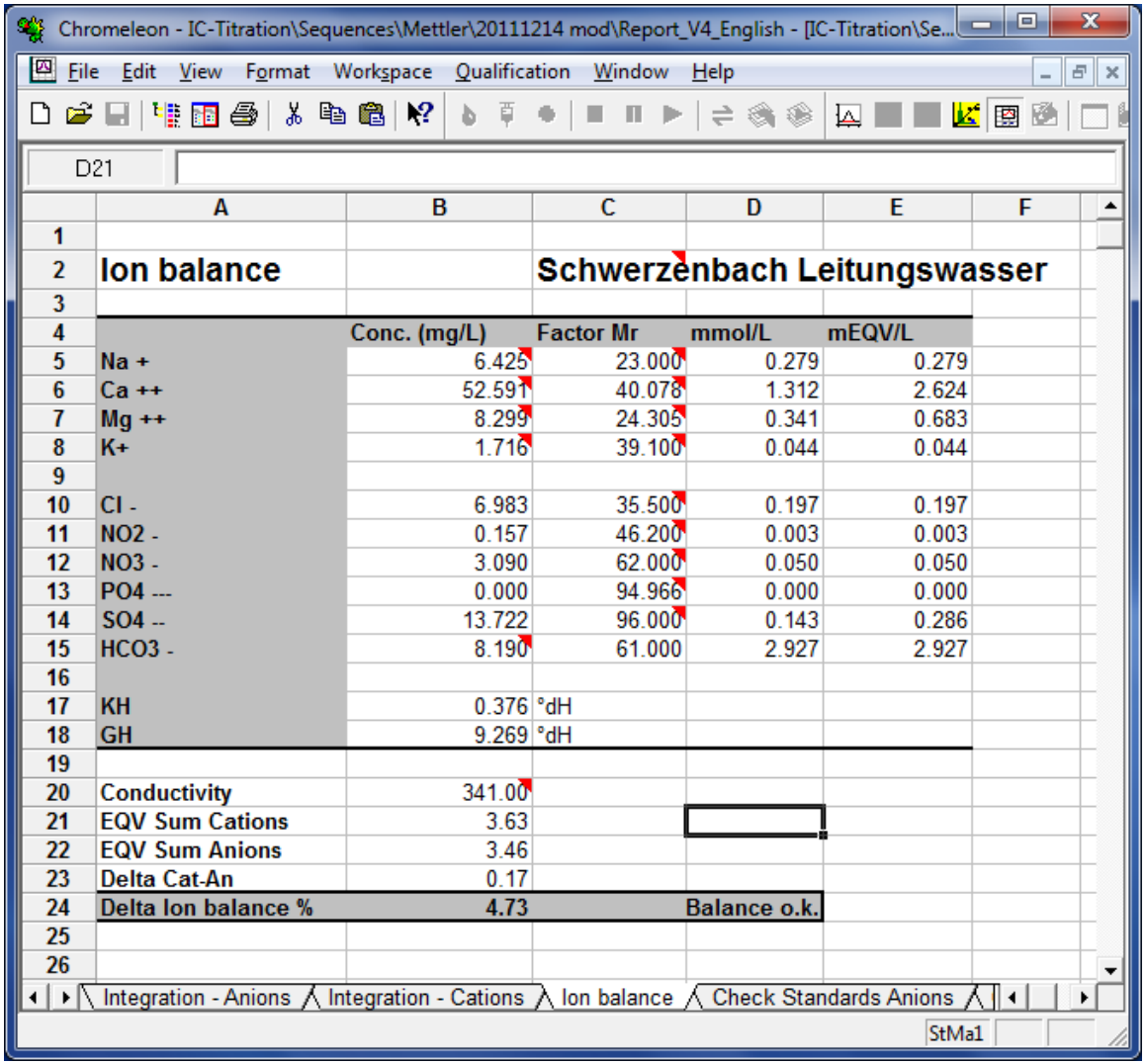




- Liquid Handler prepares standards by automated dilution
- Manually prepared check standards (red points) for validation

Reporting - Ion Balance

- One report in Chromeleon CDS software provides all results
- Ion balance calculation
- Summaries for:
  - Anions
  - Cations
  - Titration
- pH values and conductivity
- Audit trail



	Conc. (mg/L)	Factor Mr	mmol/L	mEQV/L
Na +	6.425	23.000	0.279	0.279
Ca ++	52.591	40.078	1.312	2.624
Mg ++	8.299	24.305	0.341	0.683
K+	1.716	39.100	0.044	0.044
Cl -	6.983	35.500	0.197	0.197
NO2 -	0.157	46.200	0.003	0.003
NO3 -	3.090	62.000	0.050	0.050
PO4 ---	0.000	94.966	0.000	0.000
SO4 --	13.722	96.000	0.143	0.286
HCO3 -	8.190	61.000	2.927	2.927
KH	0.376	°dH		
GH	9.269	°dH		
Conductivity	341.00			
EQV Sum Cations	3.63			
EQV Sum Anions	3.46			
Delta Cat-An	0.17			
Delta Ion balance %	4.73		Balance o.k.	

Thank You for Your Attention