Ion Chromatography Applications in the Power Industry

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Sunnyvale, CA

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Content

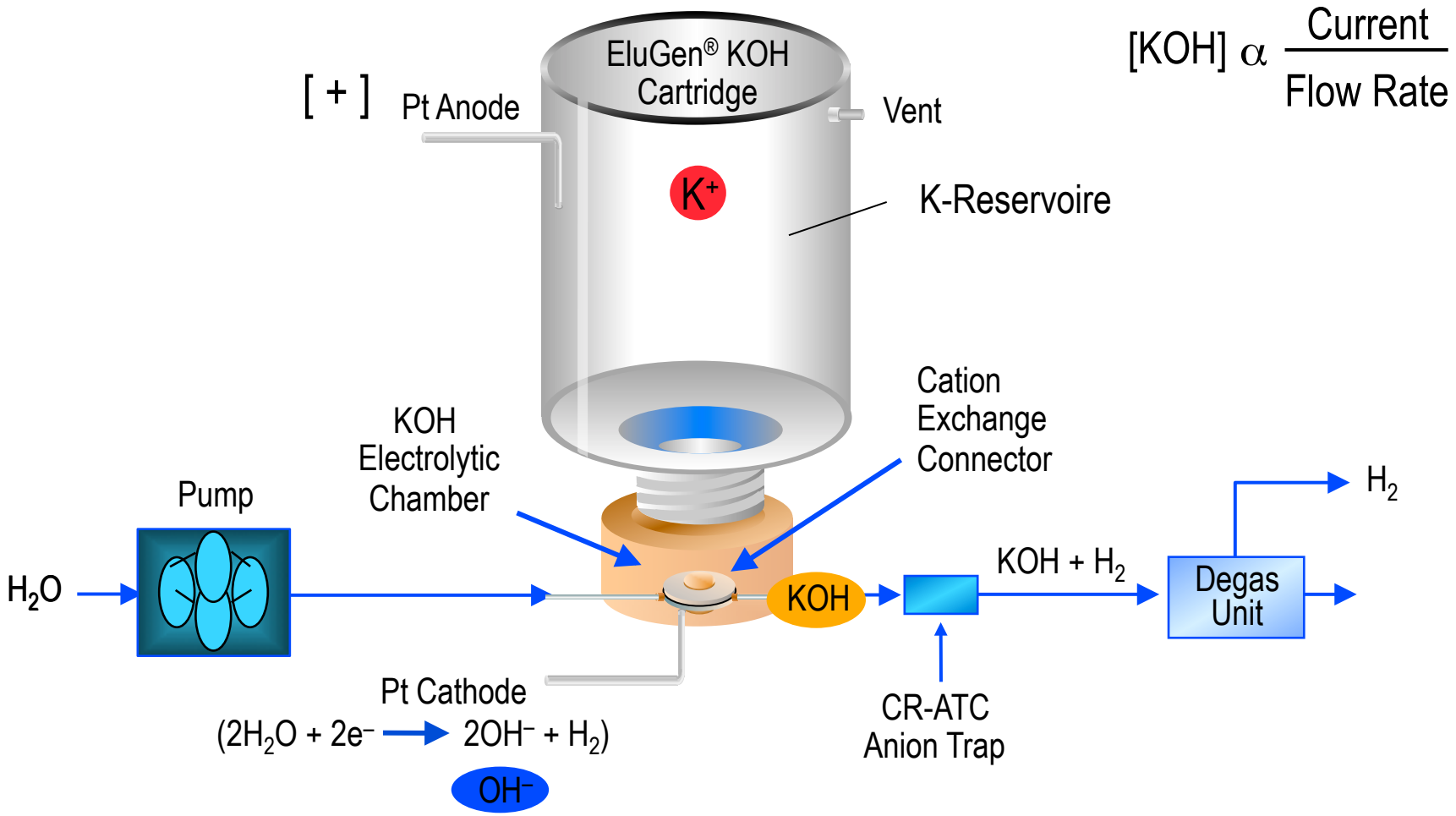
- Introduction
  - Eluent Generation and Purification
  - Suppression
- Applications
  - On-line Sample Preparation
  - Borated Waters
  - Amines – Matrices and Analytes
- Conclusions

Automation Challenges - IC for Trace Analytics

- Eluent Preparation
- Separation
- Calibration
- Sample Preparation
- Quantification

Reagent-Free Ion Chromatography (RFIC)
Eluent Generation and Purification

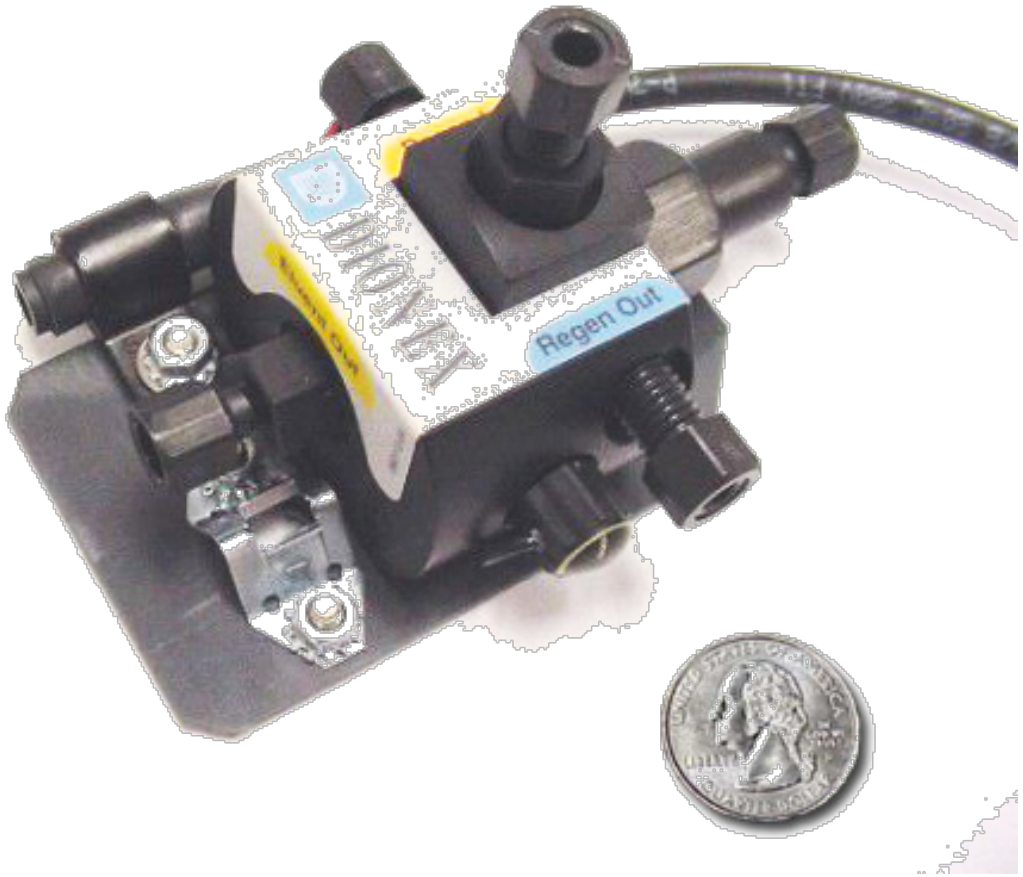
Principles of RFIC - Eluent Generation



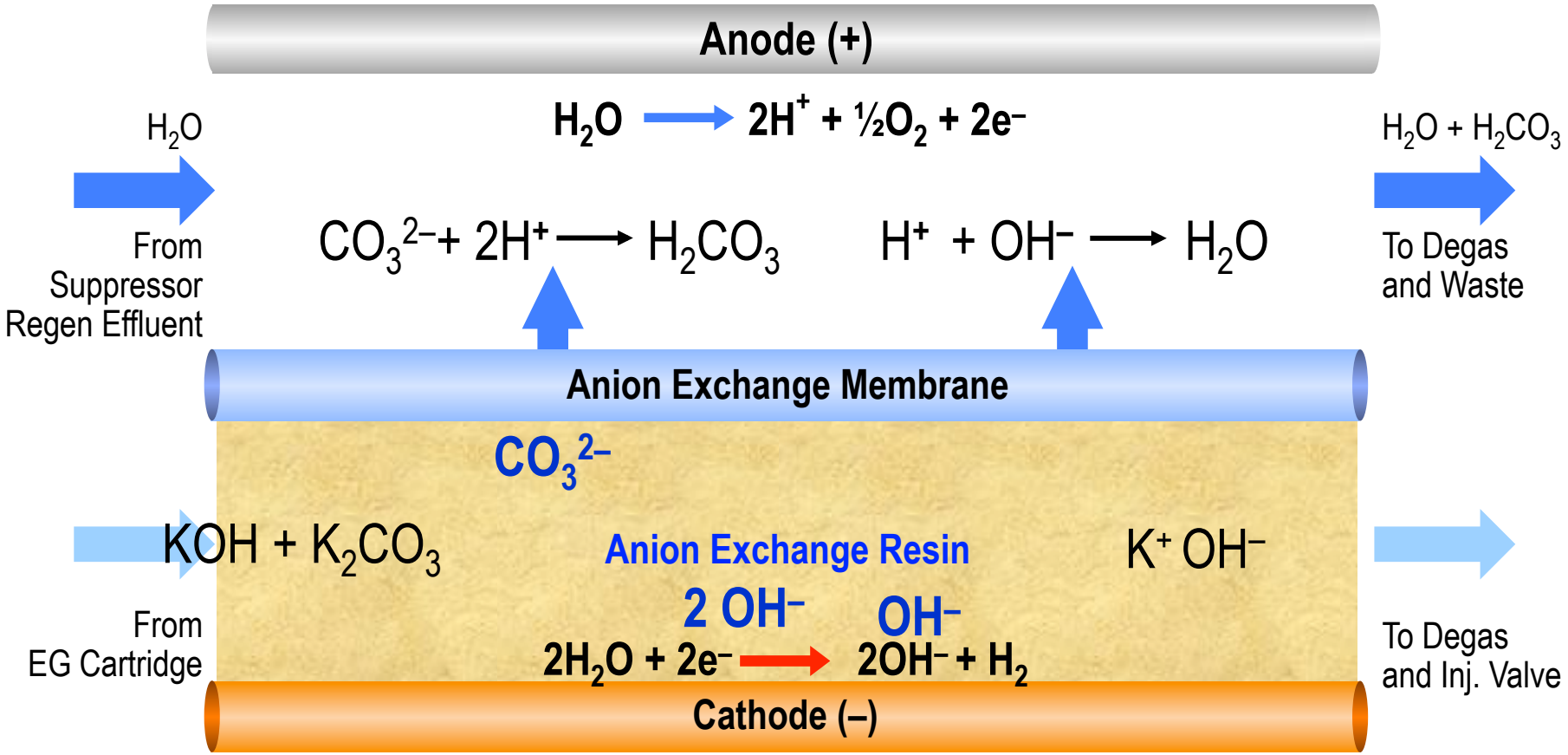
RFIC-EG Chemistries

- RFIC – KOH
- RFIC – NaOH
- RFIC – LiOH
- RFIC – MSA
- RFIC – Carbonate
- RFIC – Carbonate / Bicarbonate

Continuously Regenerated Trap Column (CR-TC)



Continuously Regenerated Anion Trap Column (CR-ATC)



Purpose: Residual Carbonate Removal from Supply Water

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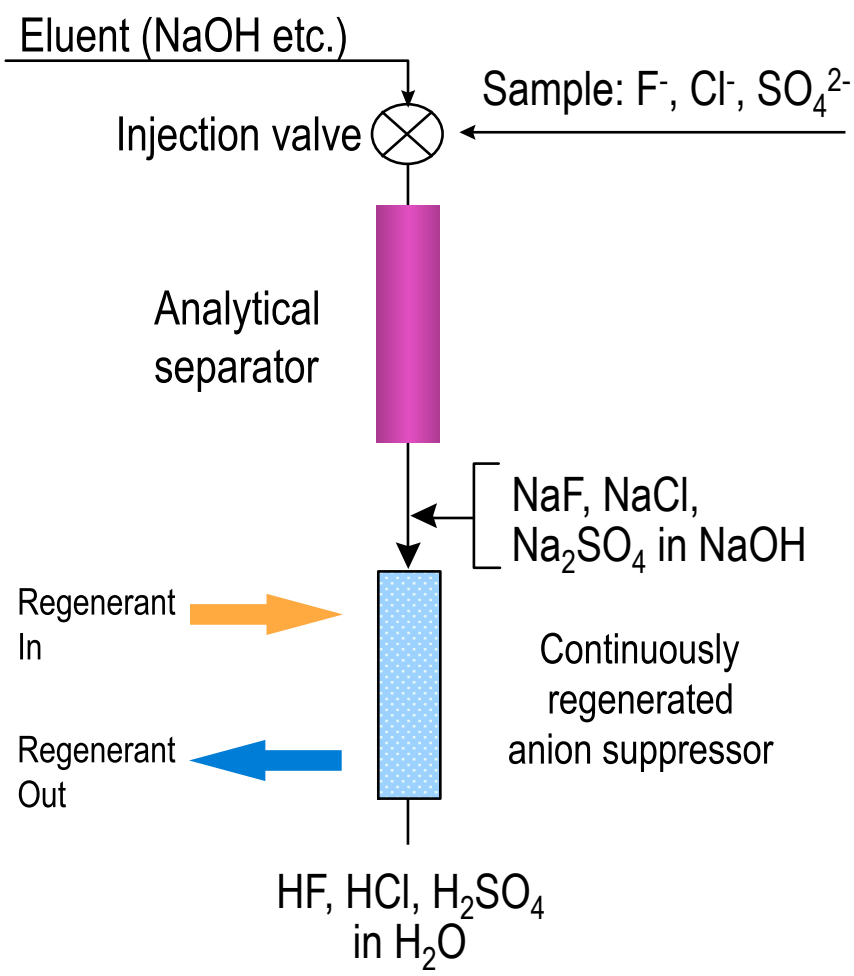
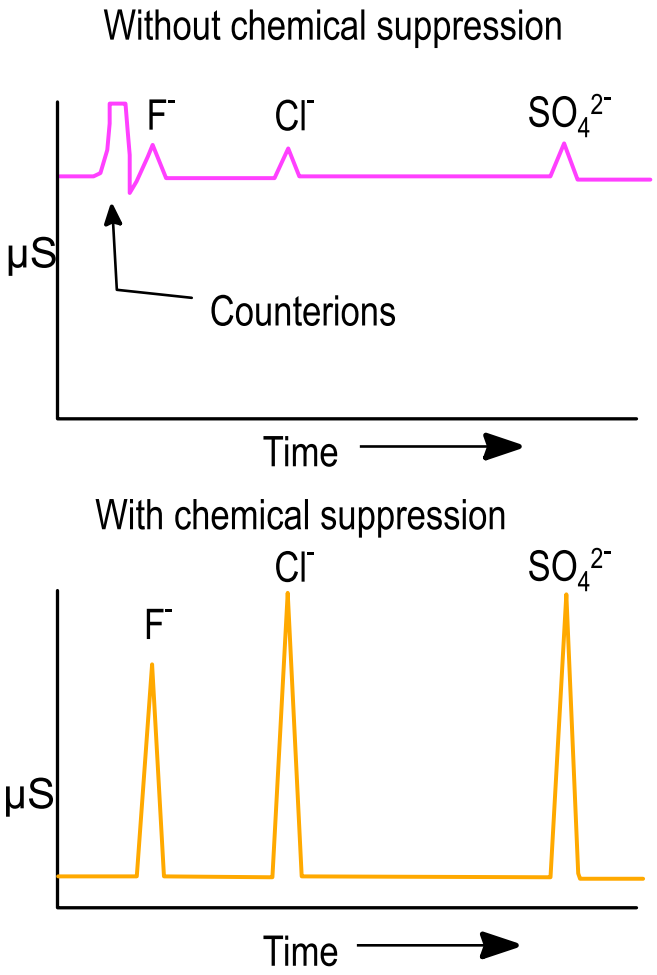
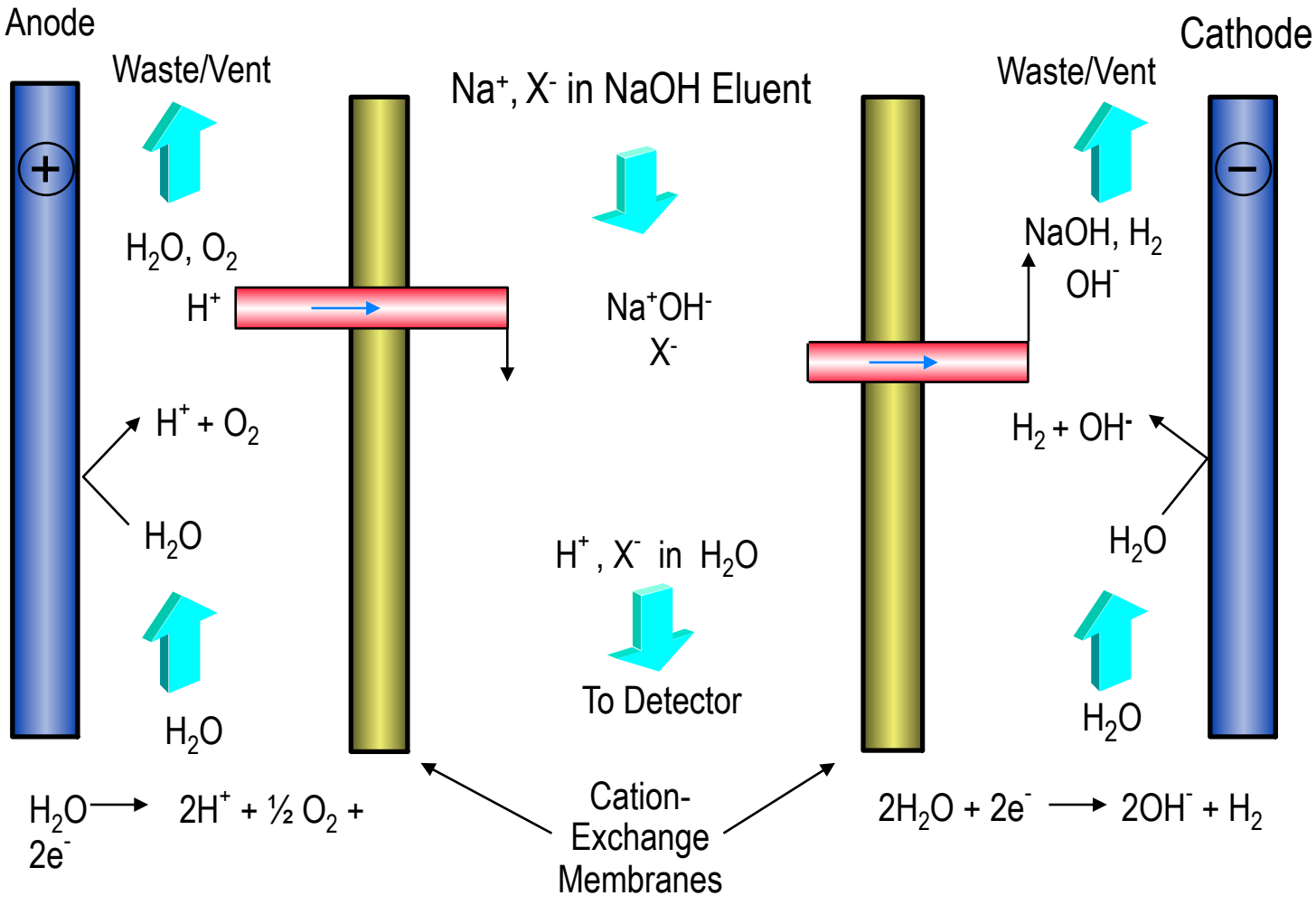
Chemical Suppression





Chemistry and Ion Movement in an Anion
Self Regenerating Suppressor (SRS®)



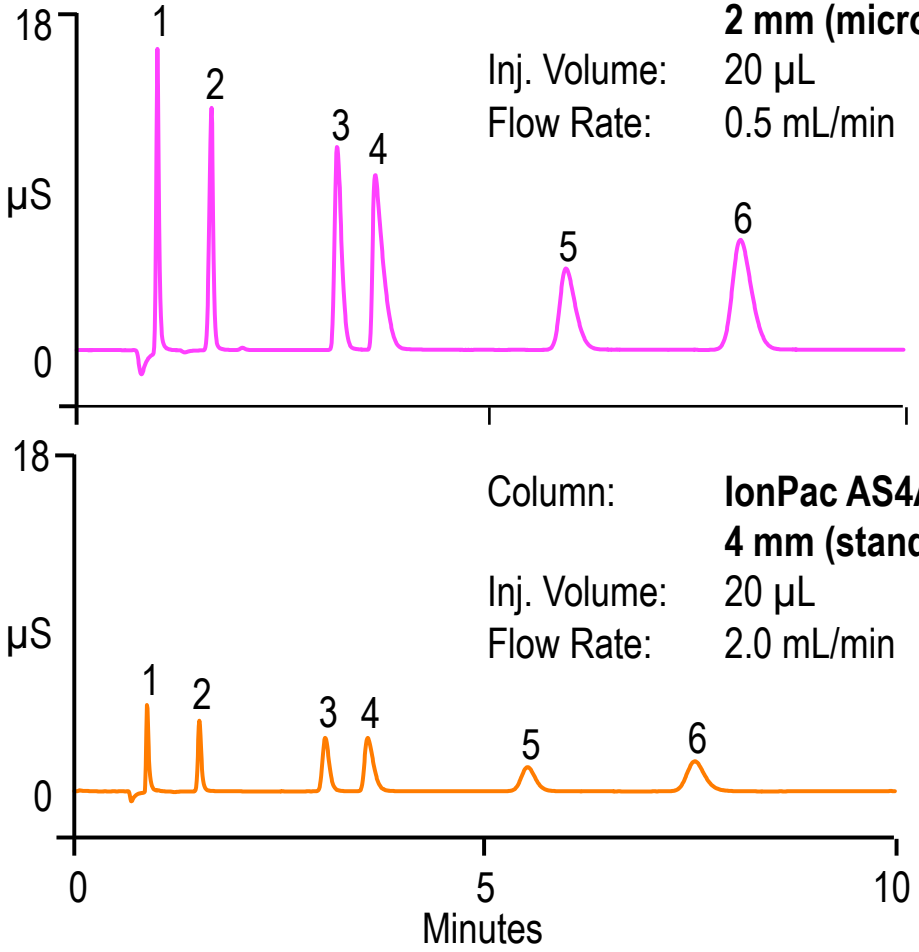
Ultrapure Water (UPW) Analysis

IC for Trace Ionic Impurities in UPW

Analytes	Detection
Anions (e.g., F^-, Cl^-, SO_4^{2-})	Suppressed conductivity
Cations (e.g., Li^+, Na^+, K^+, Mg^{2+})	Suppressed conductivity
Silica (as dissolved SiO_2^-)	Post-column derivatization with Vis detection
Transition metals (e.g., Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})	Post-column derivatization with Vis detection
Boron (as $B(OH)_4^-$)	Suppressed conductivity

Large Volume Injections

Increased Mass Sensitivity: 2 mm Technology

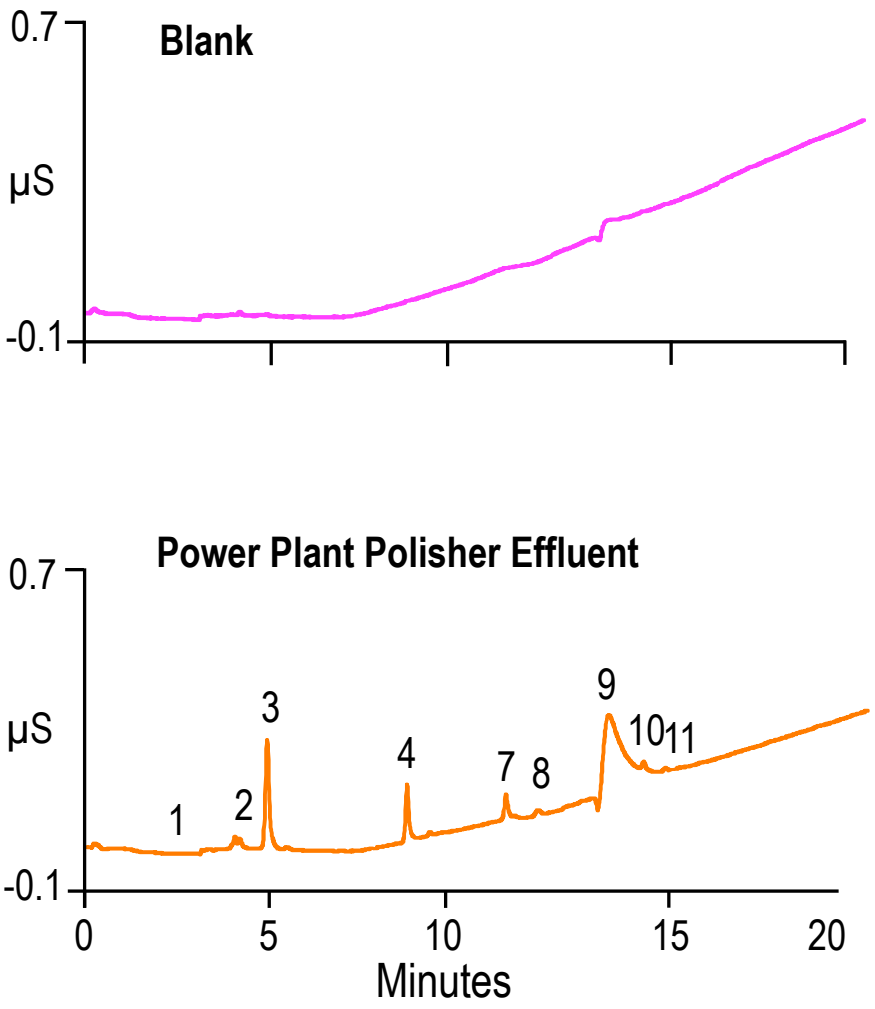


Eluent: 1.8 mmol/L Sodium carbonate
1.7 mmol/L Sodium bicarbonate

Peaks:

1.	Fluoride	2 mg/L
2.	Chloride	3
3.	Bromide	10
4.	Nitrate	10
5.	Phosphate	15
6.	Sulfate	15

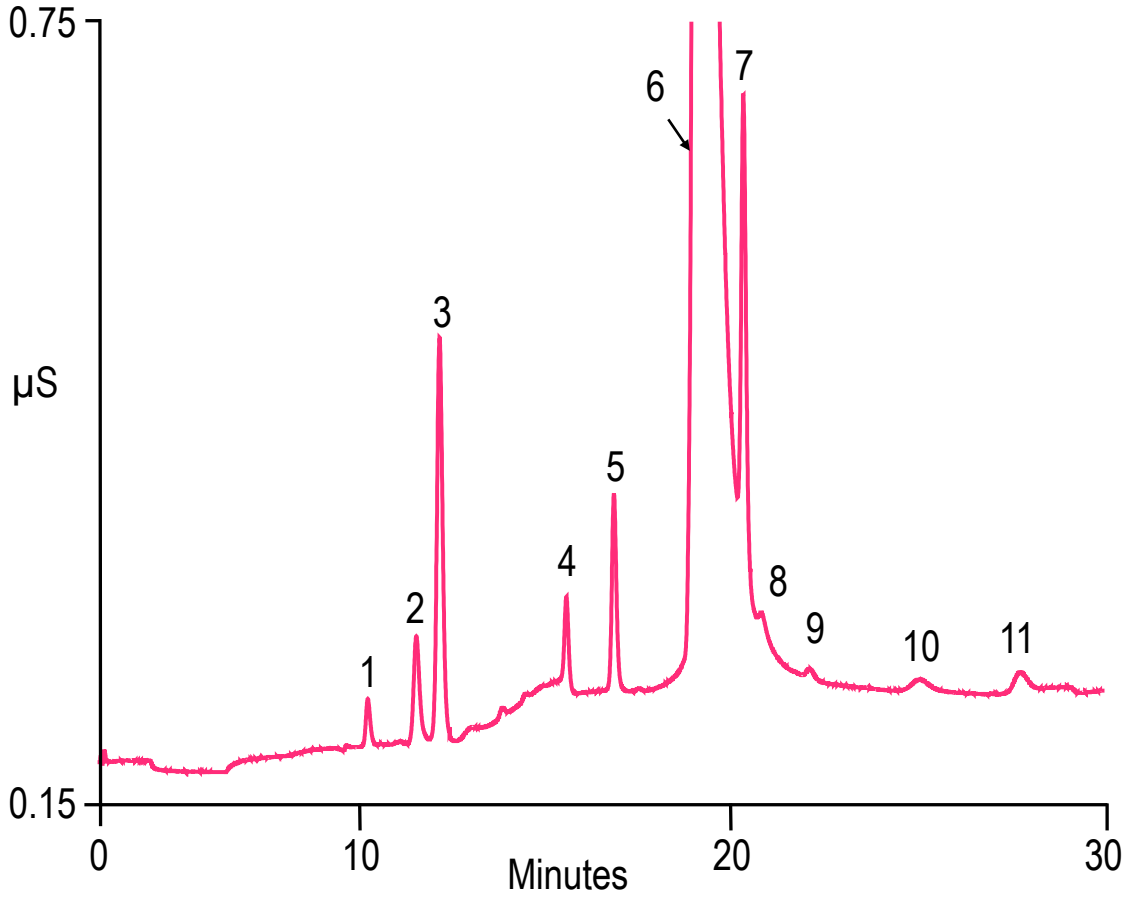
Direct Injection Analysis of Power Plant Condensate Polisher Effluent



Column:	IonPac® AS11, 2 mm
Gradient:	NaOH from 0.5 to 26 mmol/L
Inj. volume:	750 µL
Detection:	Suppressed conductivity, external water mode

Peaks:	Blank (µg/L)	Polisher Effluent (µg/L)
1. Fluoride	<0.01	0.09
2. Acetate	<0.01	0.05
3. Formate	<0.01	0.46
4. Chloride	<0.02	0.34
5. Nitrite	<0.02	<0.02
6. Bromide	<0.03	<0.03
7. Nitrate	<0.02	0.40
8. Unidentified	_	_
9. Carbonate	_	_
10. Sulfate	<0.02	0.10
11. Oxalate	<0.02	0.07
12. Phosphate	<0.1	<0.1

Fossil Fuel Power Plant - Condensate Discharge Water

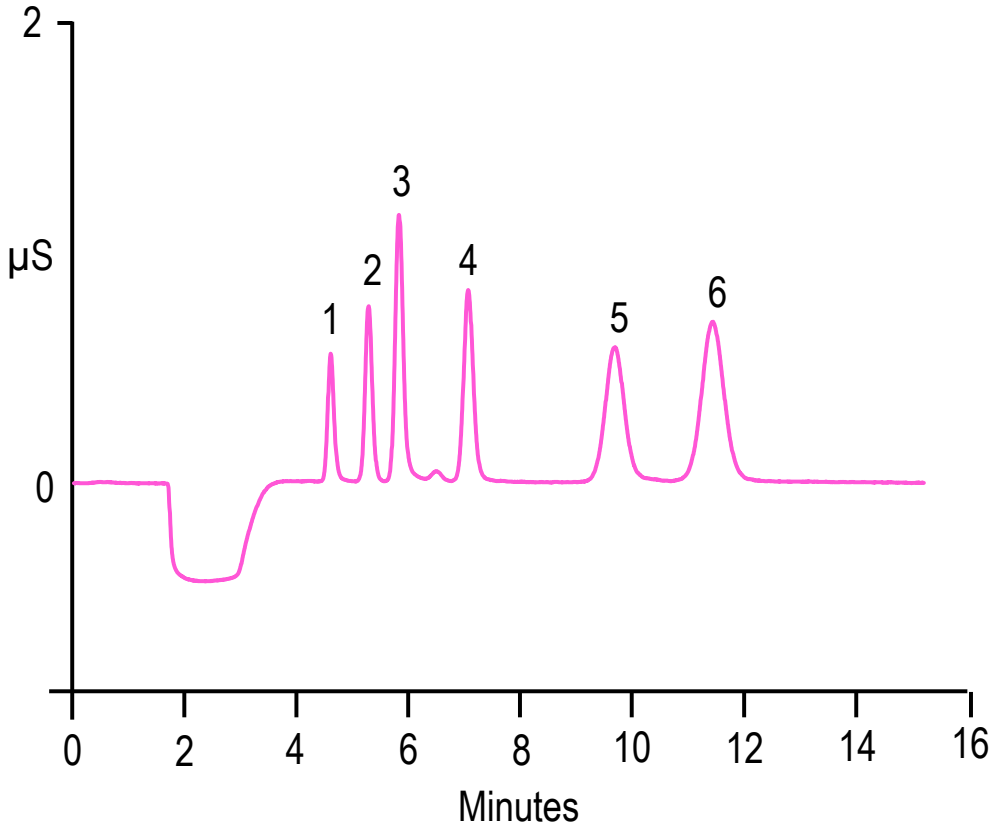


Column:	IonPac® AG15-5 µm, 3 mm AS15-5 µm, 3 mm
Eluent:	7 to 40 mmol/L KOH (EG)
Flow rate:	0.5 mL/min
Detection:	Suppressed conductivity
Inj. volume:	1000 µL

Peaks:

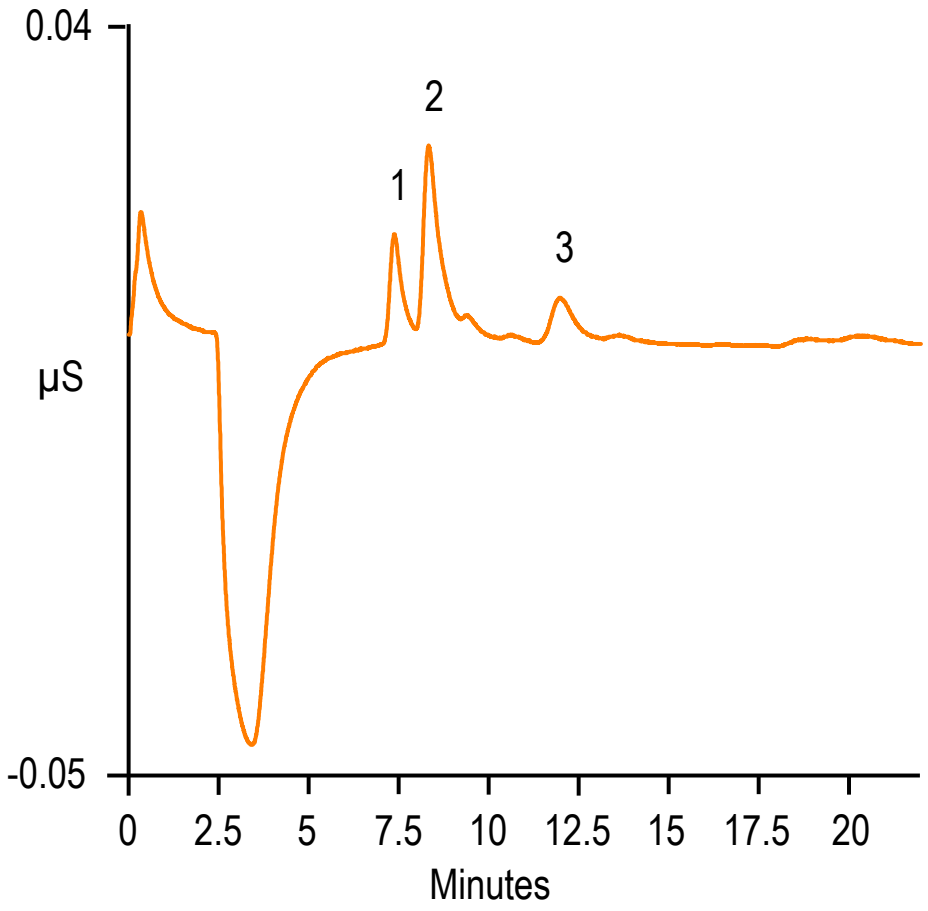
1. Fluoride	0.16 µg/L
2. Acetate	1.2
3. Formate	3.9
4. Chloride	0.44
5. Nitrite	1.3
6. Carbonate	–
7. Sulfate	3.6
8. Unknown	–
9. Nitrate	0.15
10. Unknown	–
11. Phosphate	0.86

Trace Cations by Direct Injection



Column:	IonPac® CS12A (2 mm)
Eluent:	11 mmol/L sulfuric acid
Flow rate:	0.25 mL/min
Inj. volume:	500 µL
Peaks: µg/L	1. Lithium 0.25
	2. Sodium 1.0
	3. Ammonium 1.2
	4. Potassium 2.5
	5. Magnesium 1.2
	6. Calcium 2.5

Cations in Ultrapure Water



Column:	IonPac® CS12A, 2 mm	
Eluant:	10 mmol/L sulfuric acid	
Flow rate:	0.25 mL/min	
Inj. volume:	40 mL, concentrated	
Detection:	Suppressed conductivity, External water mode	
Peaks:	1. Sodium	< 10 ng/L
	2. Ammonium	< 10
	3. Trimethylamine	-

AutoPrep – Simplifying IC Trace Determinations

AutoPrep IC System

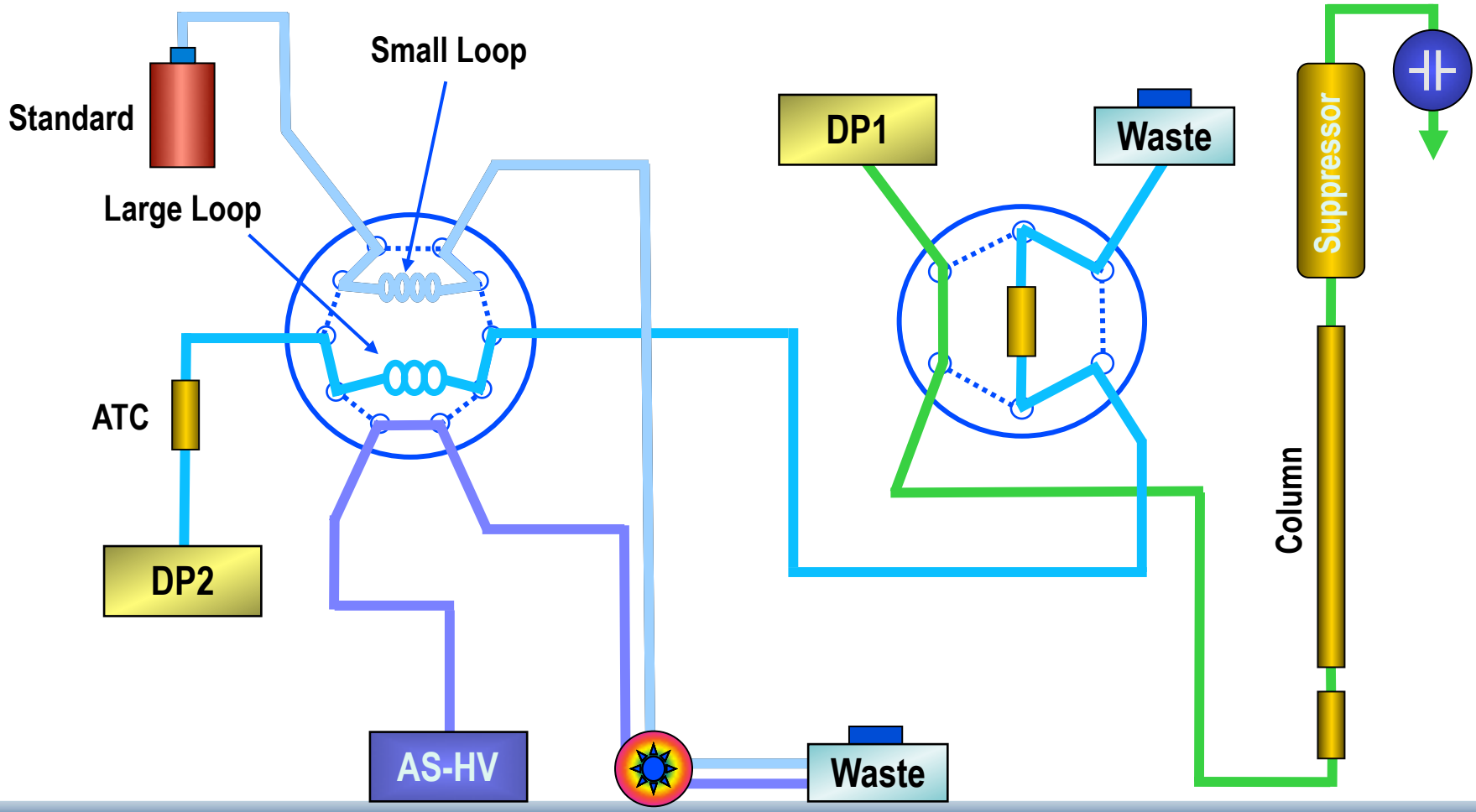
System calibration

- A small loop of known volume is loaded with standard
- Multiple valve toggles (or flips) determine the “level” of the calibration
- Contents of small loop are pushed to a concentrator column
- Contents of concentrator eluted for analysis
- Chromeleon establishes a multi-point calibration

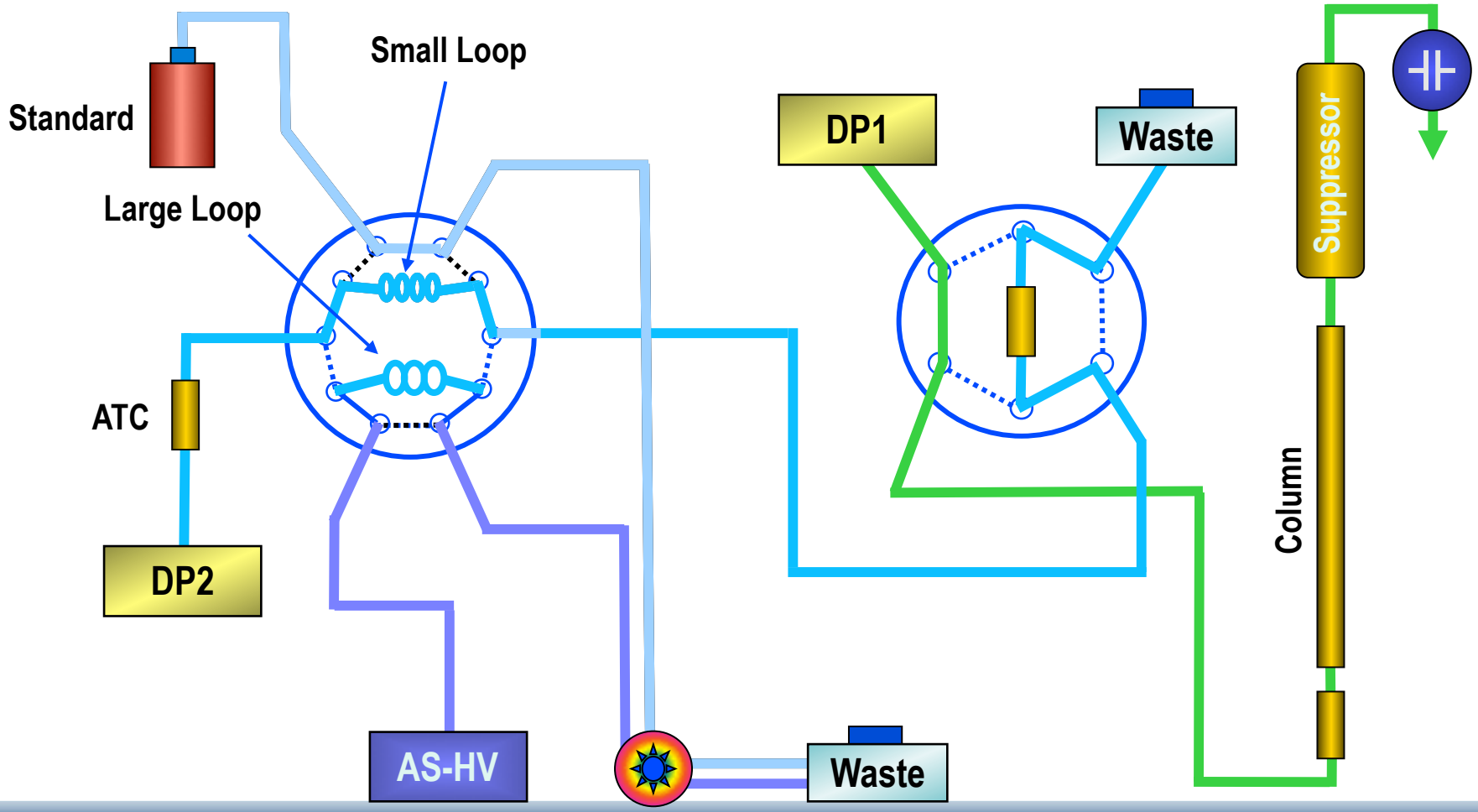
Sample analysis

- Sample is loaded onto a large volume loop (10 mL)
- The large loop contents are pushed onto the concentrator
- Contents of concentrator eluted for analysis

AutoPrep IC System



AutoPrep IC System



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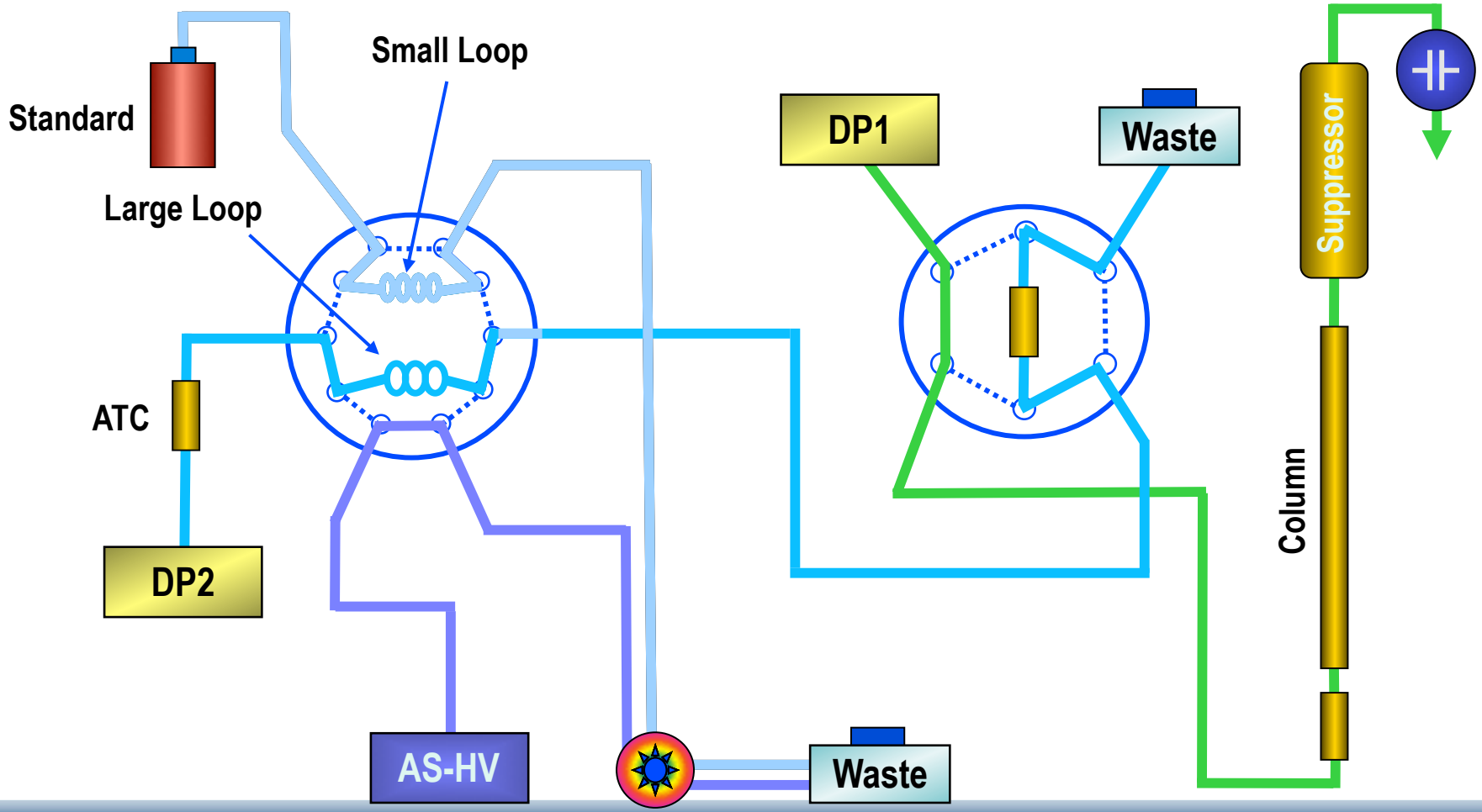

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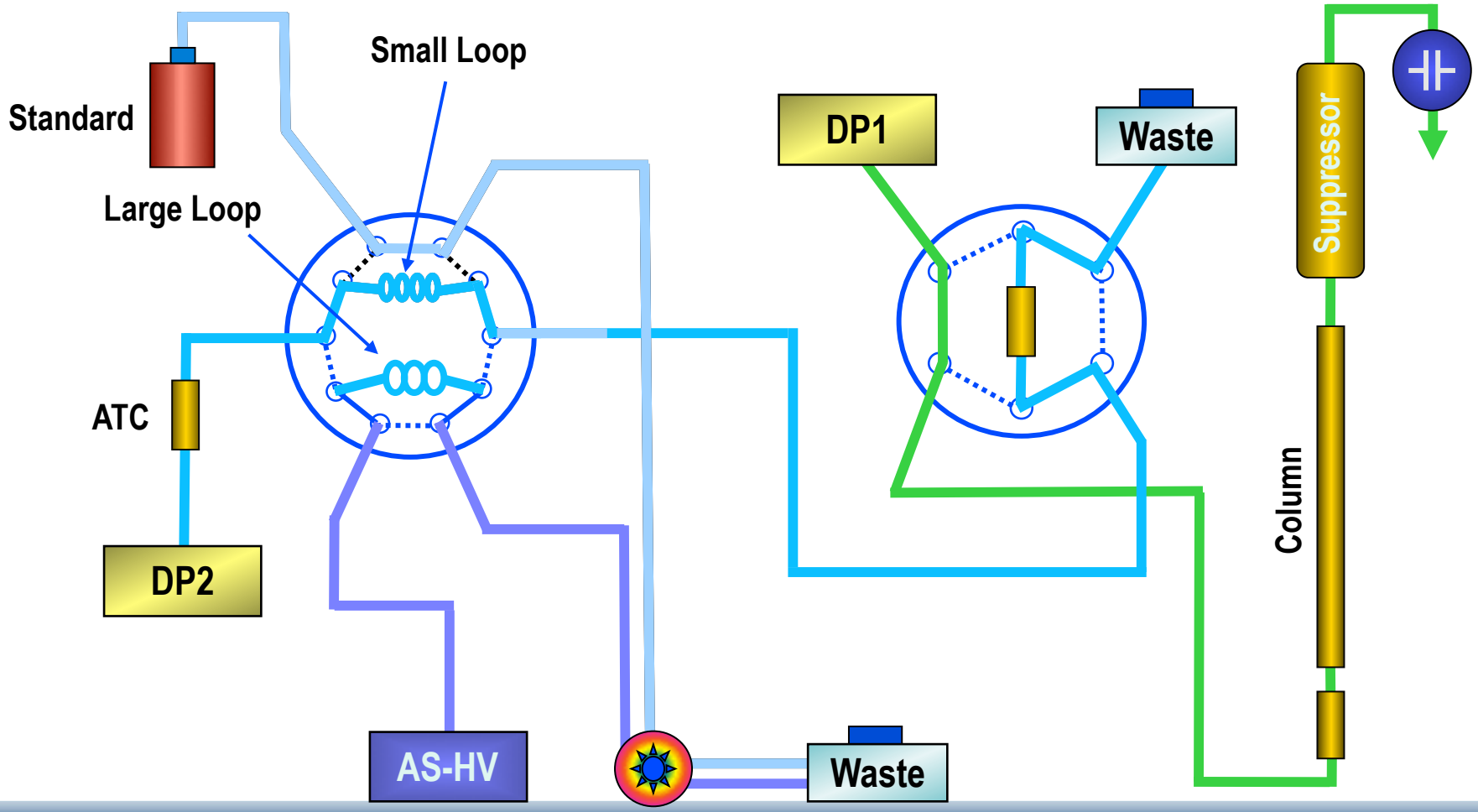

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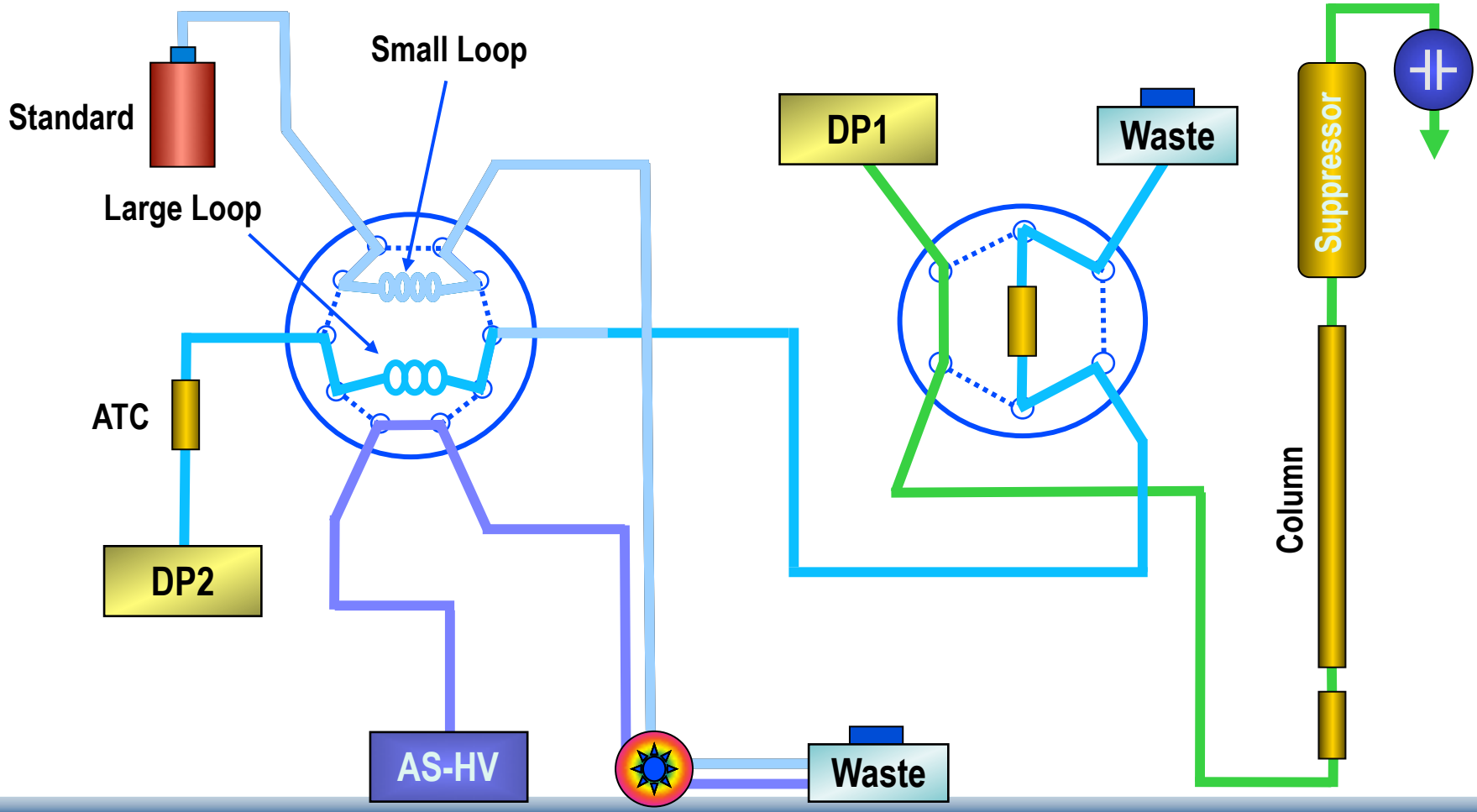

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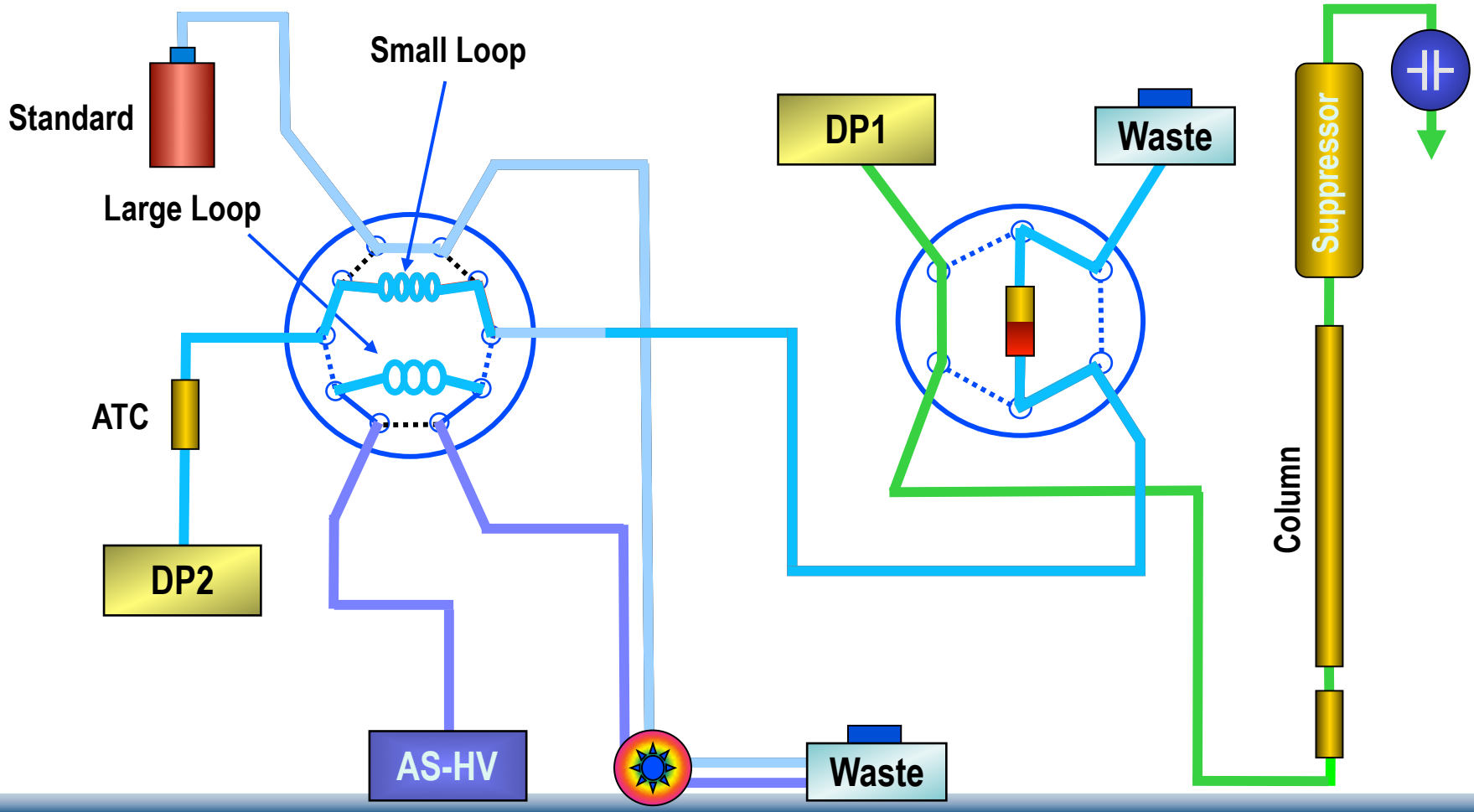

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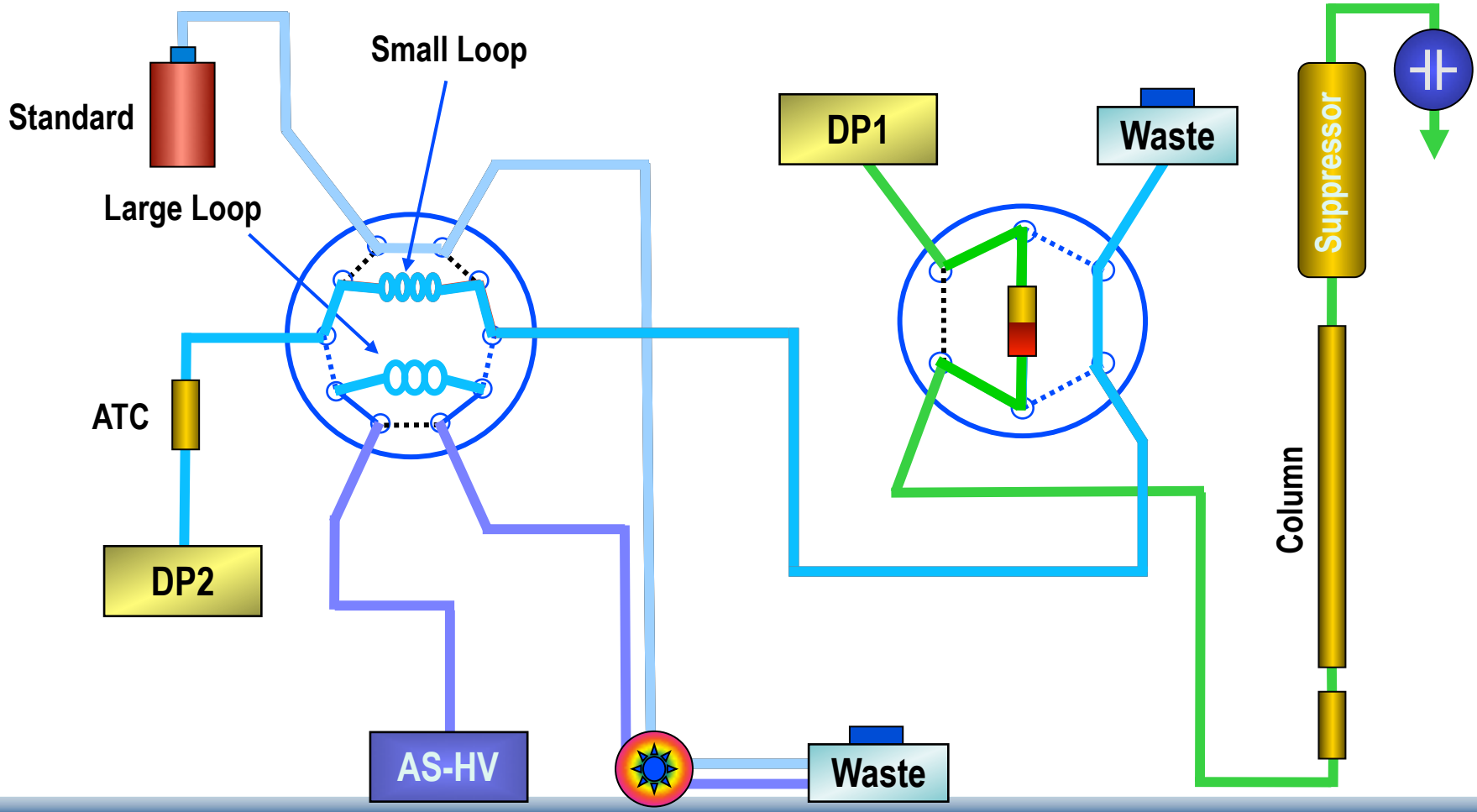

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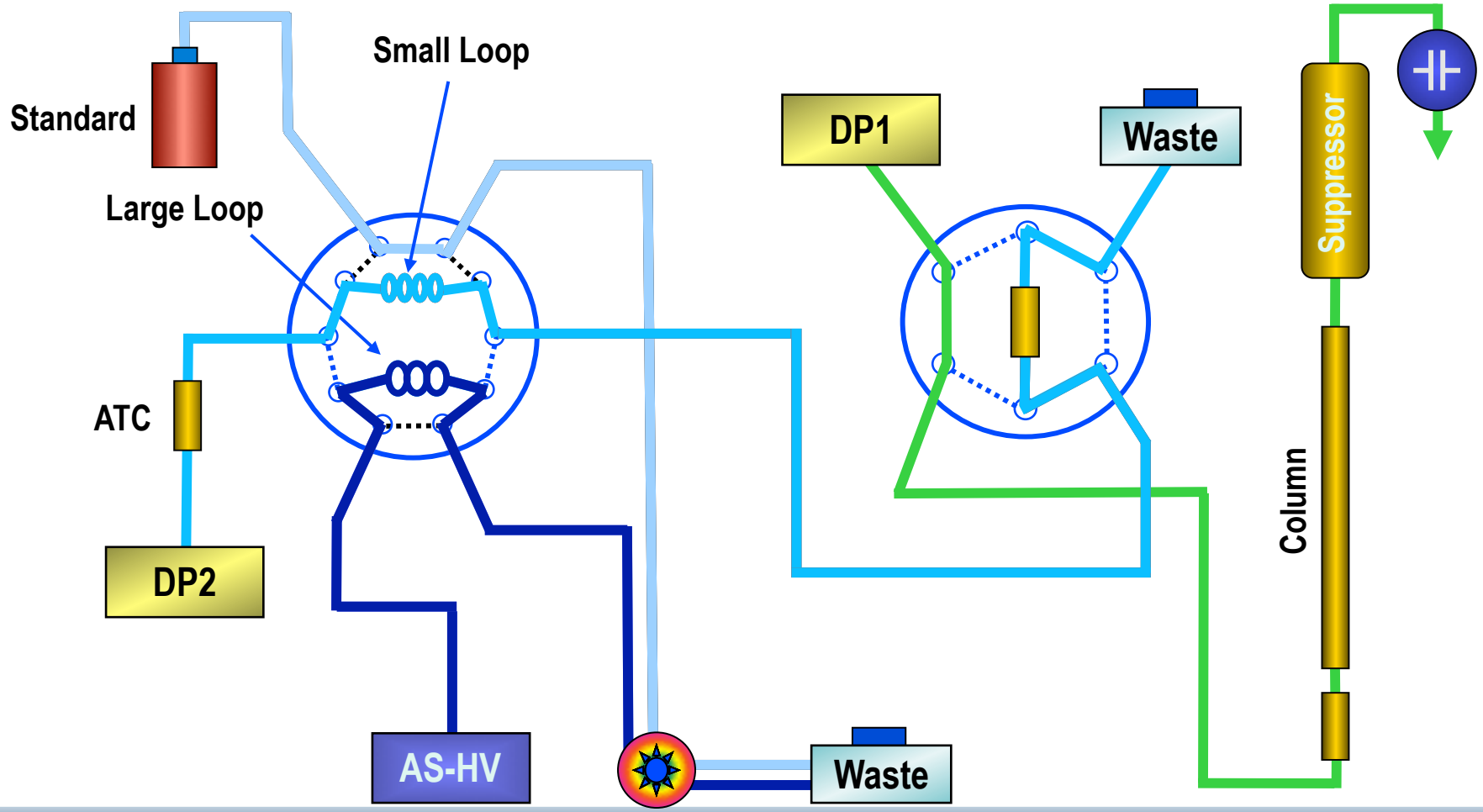

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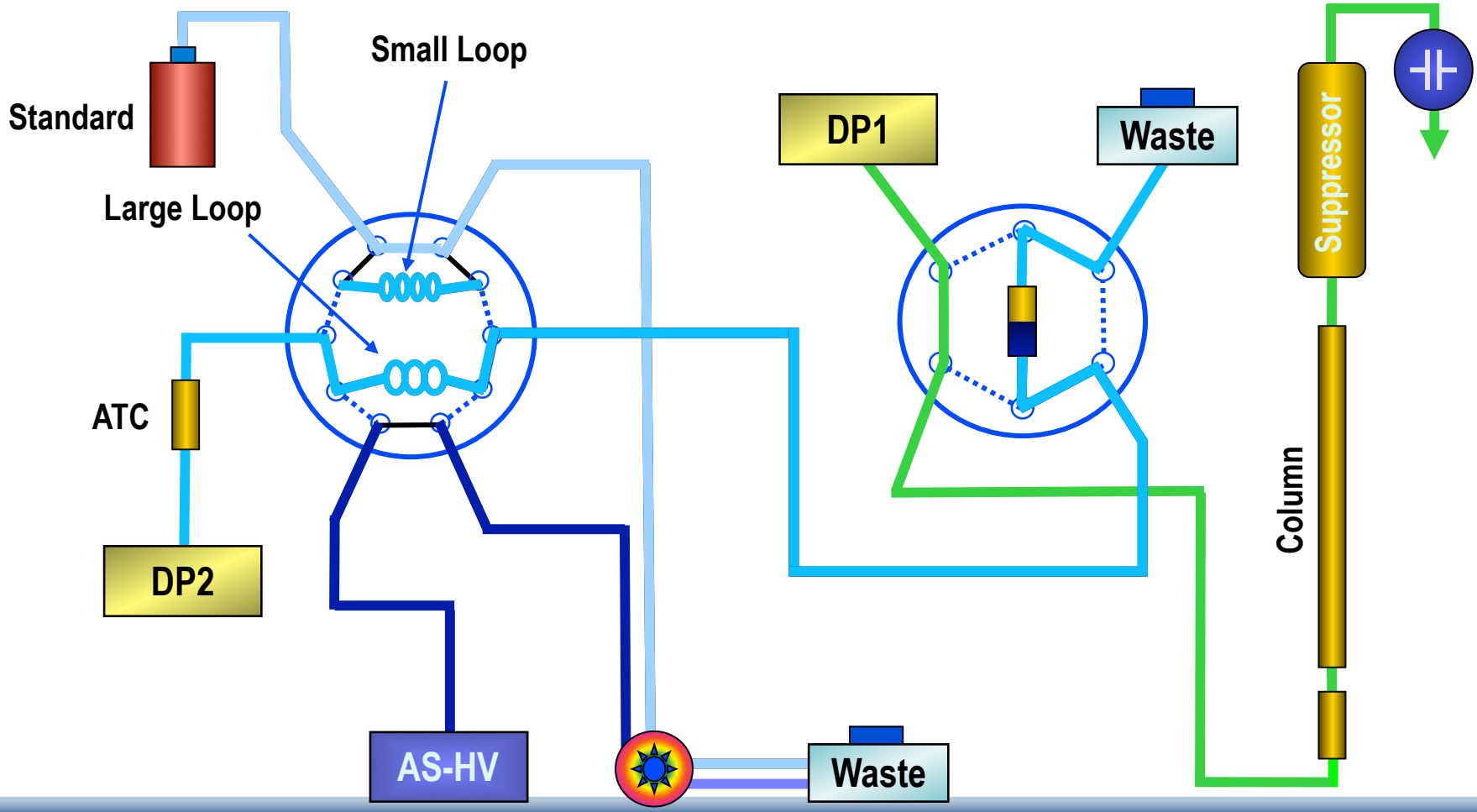
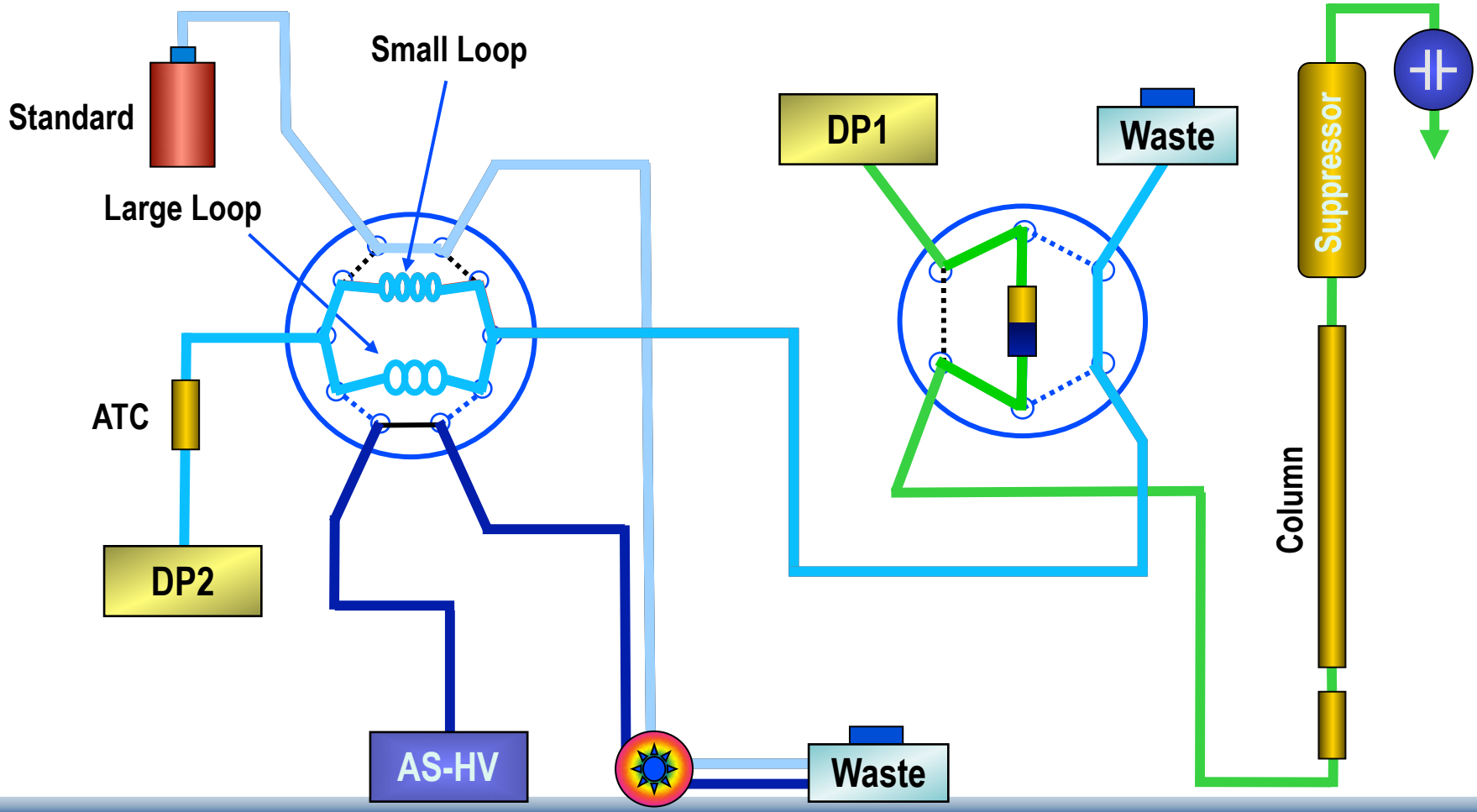
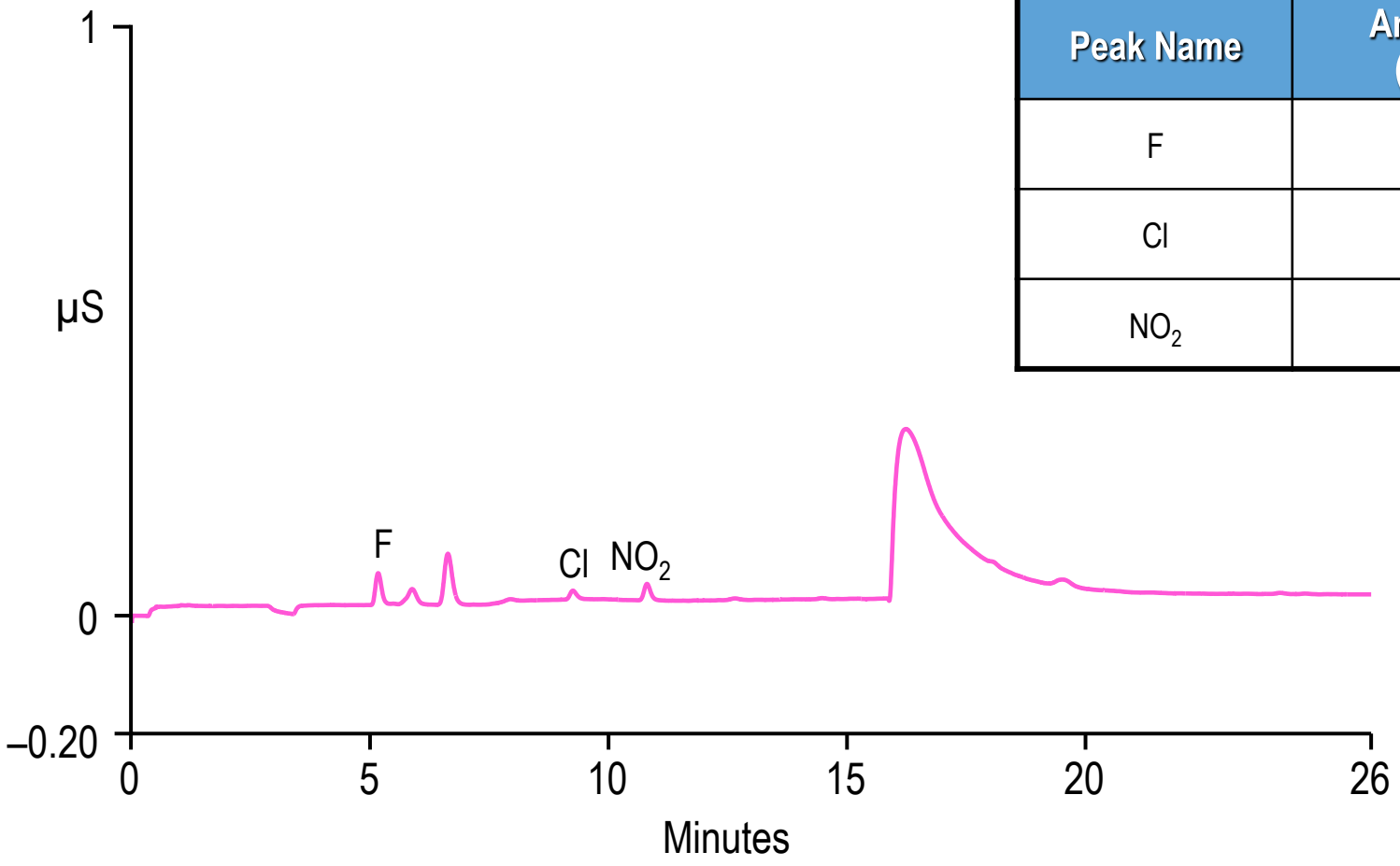


AutoPrep IC System

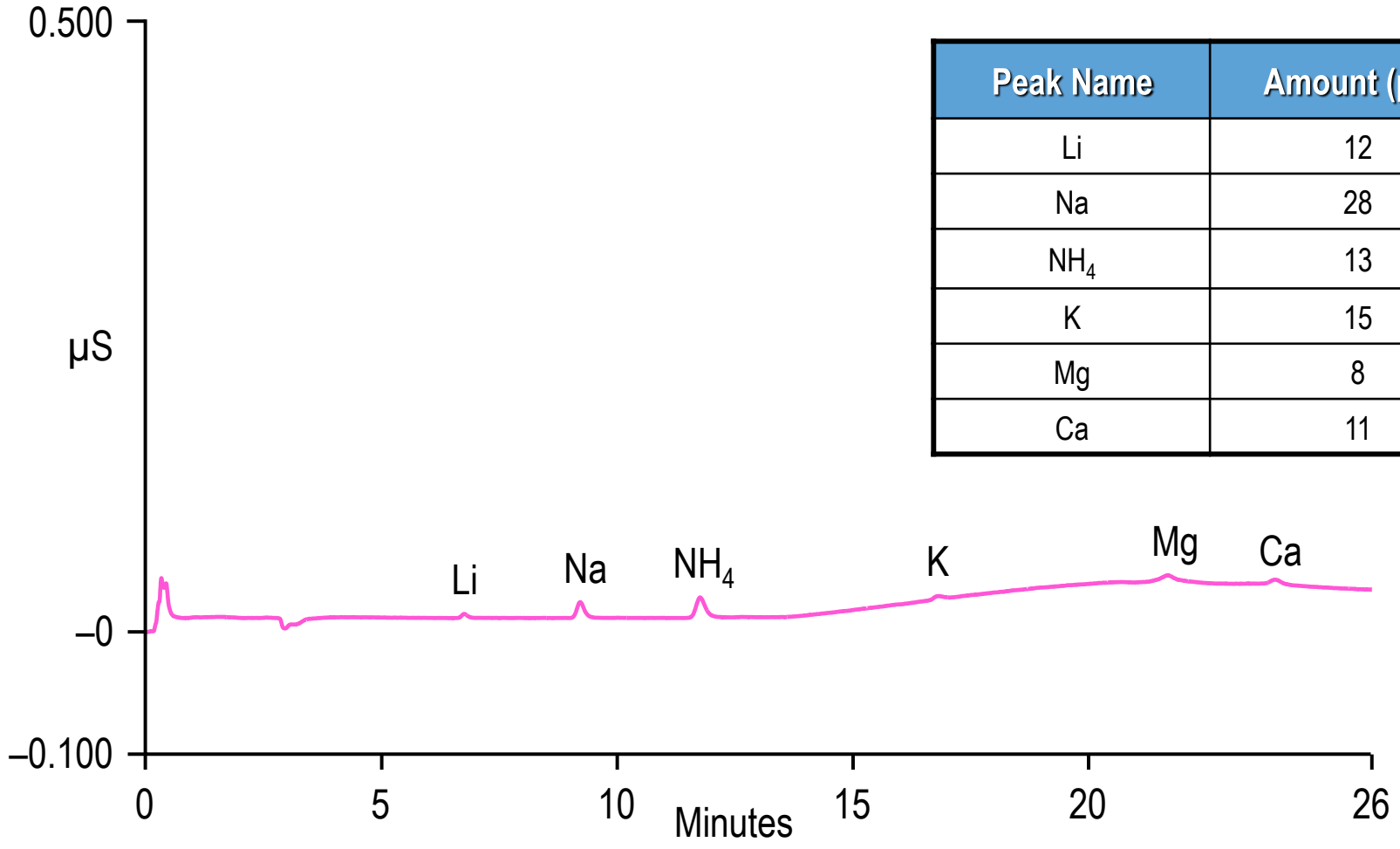


AutoPrep IC System – Ultrapure Water Analysis



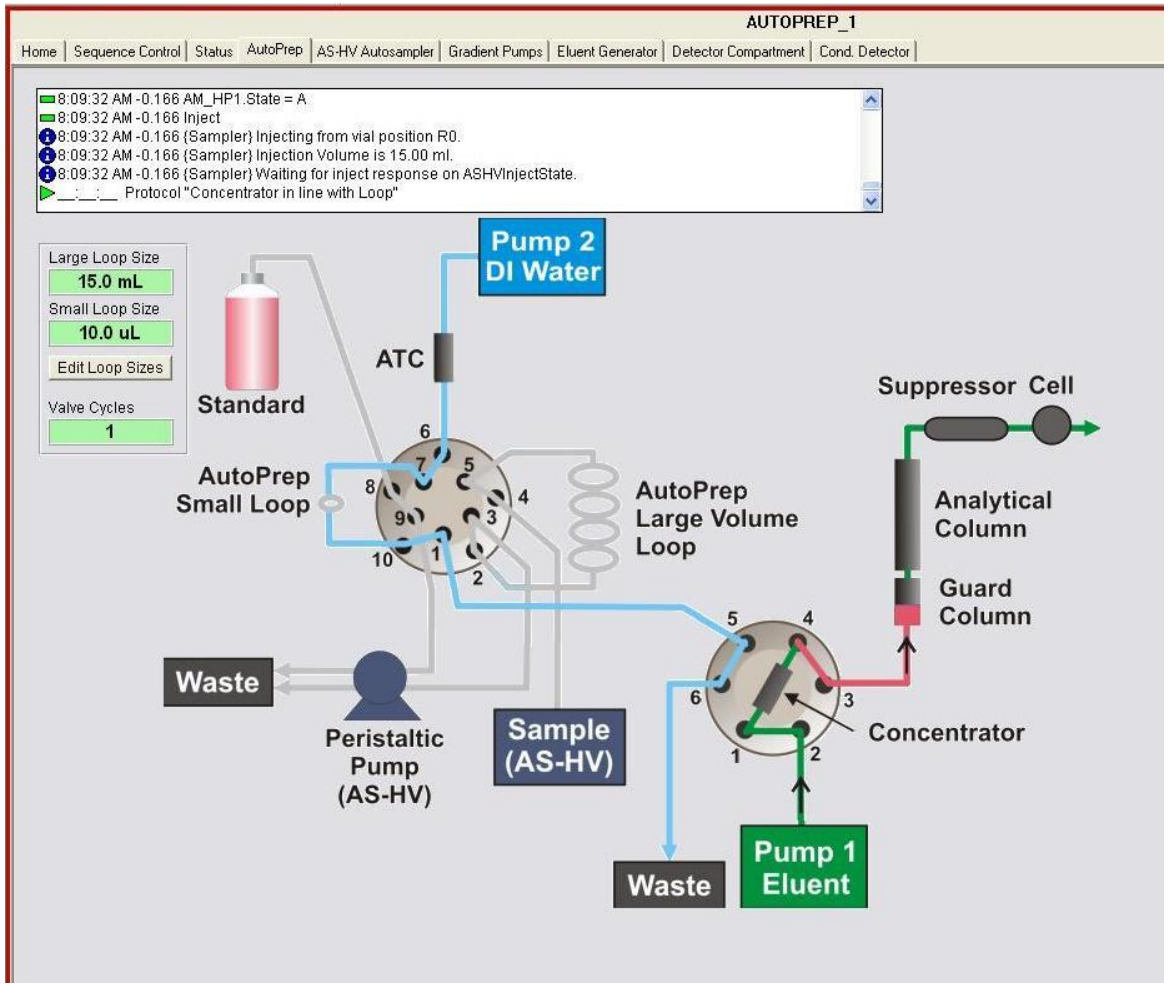
Peak Name	Amount (ppt)
F	24
Cl	22
NO_2	42

AutoPrep IC System – Ultrapure Water Analysis



Peak Name	Amount (ppt)
Li	12
Na	28
NH_4	13
K	15
Mg	8
Ca	11

AutoPrep IC System – Chromeleon® Panel



Chromeleon panel with valve switching and sampling pump cycles

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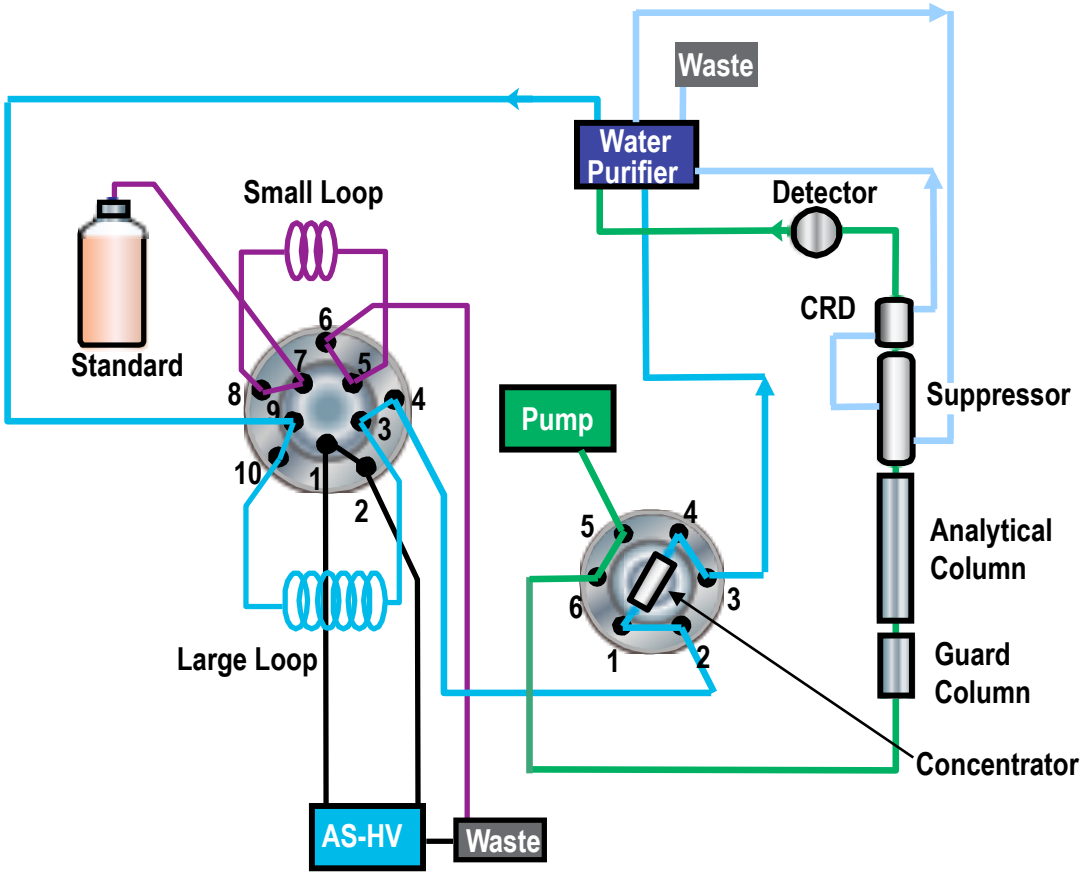
AutoPrep IC System

AutoPrep: A series of *auto*mated steps to *prep*are samples on-line.

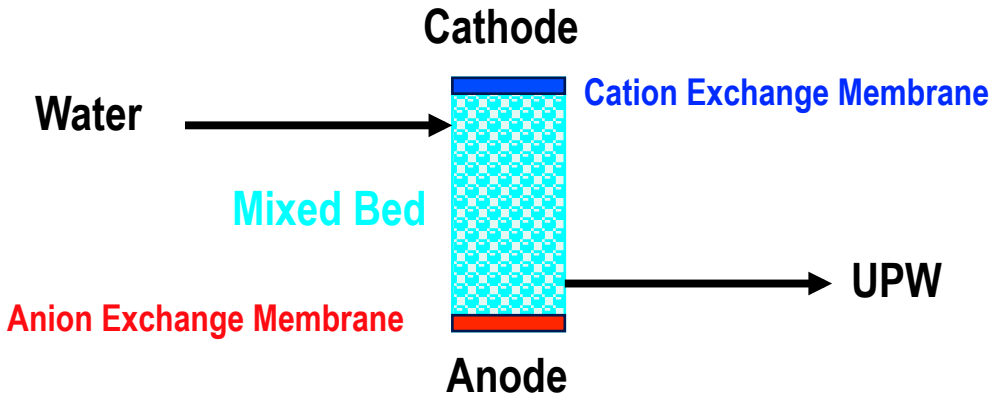
- Simplifies trace analysis
- Contamination-free
  - On-line and automated calibration
  - On-line and automated sample preparation.
- Lower detection limits
  - Less than 5 ng/L (ppt)
- Less manual errors
  - Improved reliability
- Lower labor costs

RFIC-ESP – Electrolytic Sample Preparation

RFIC-ESP on the ICS-2100

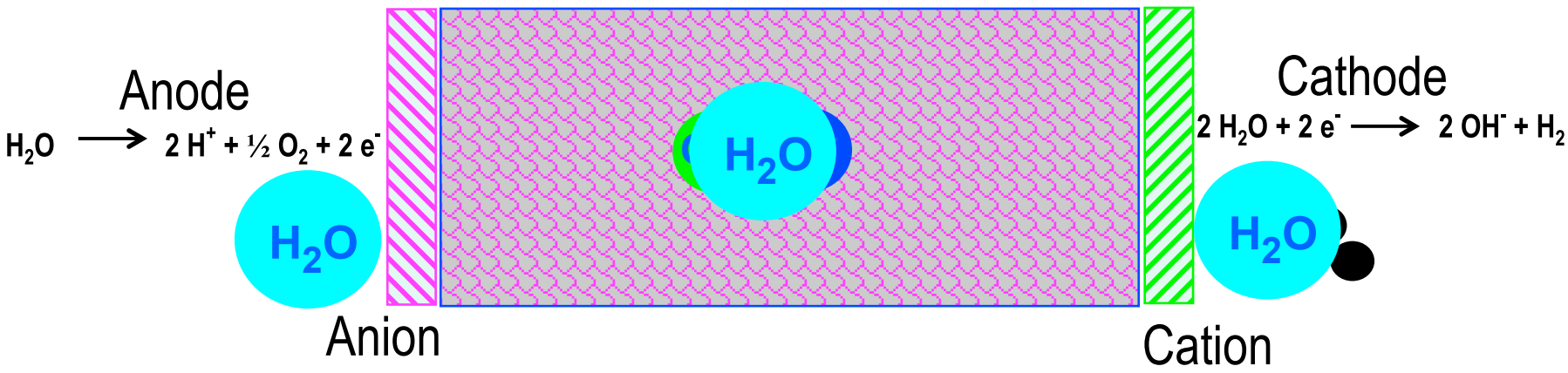


RFIC-ESP: How Does the Water Purifier Work?

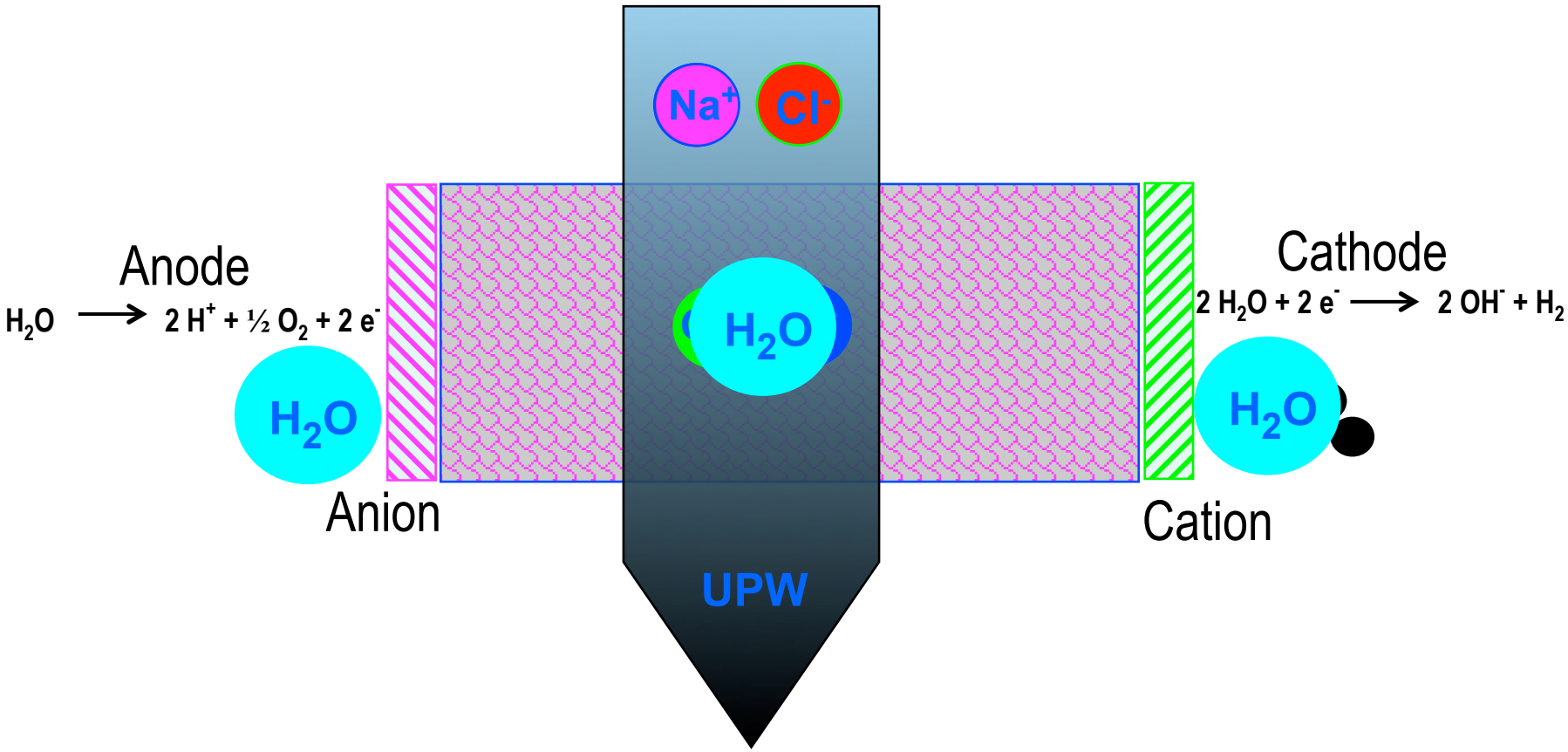


- Continuous Electrolytic Purification of aqueous input
- Point-of-use operation for automated preparation of standards and samples
- Single-digit parts-per-trillion or better quality output water
- Cleaner input water to IC produces better MDL's and system performance
- No contamination of samples during preconcentration
- Blank levels 10x lower than reported sample values

RFIC-ESP Device – Electrolytic Water Purifier

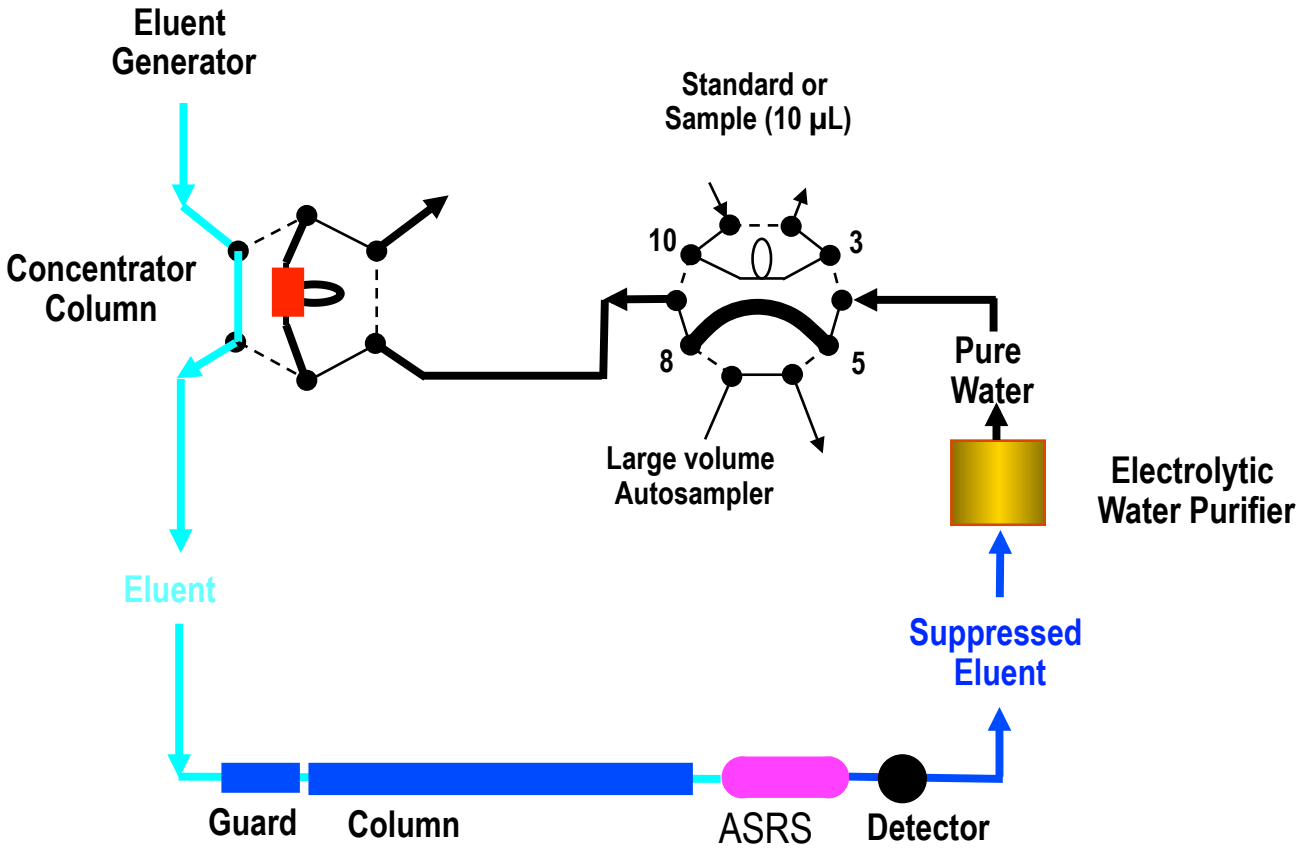


RFIC-ESP Device – Electrolytic Water Purifier



Water Purifier Simulation

New RFIC-ESP IC Technique



RFIC-ESP ICS-2100 Configuration

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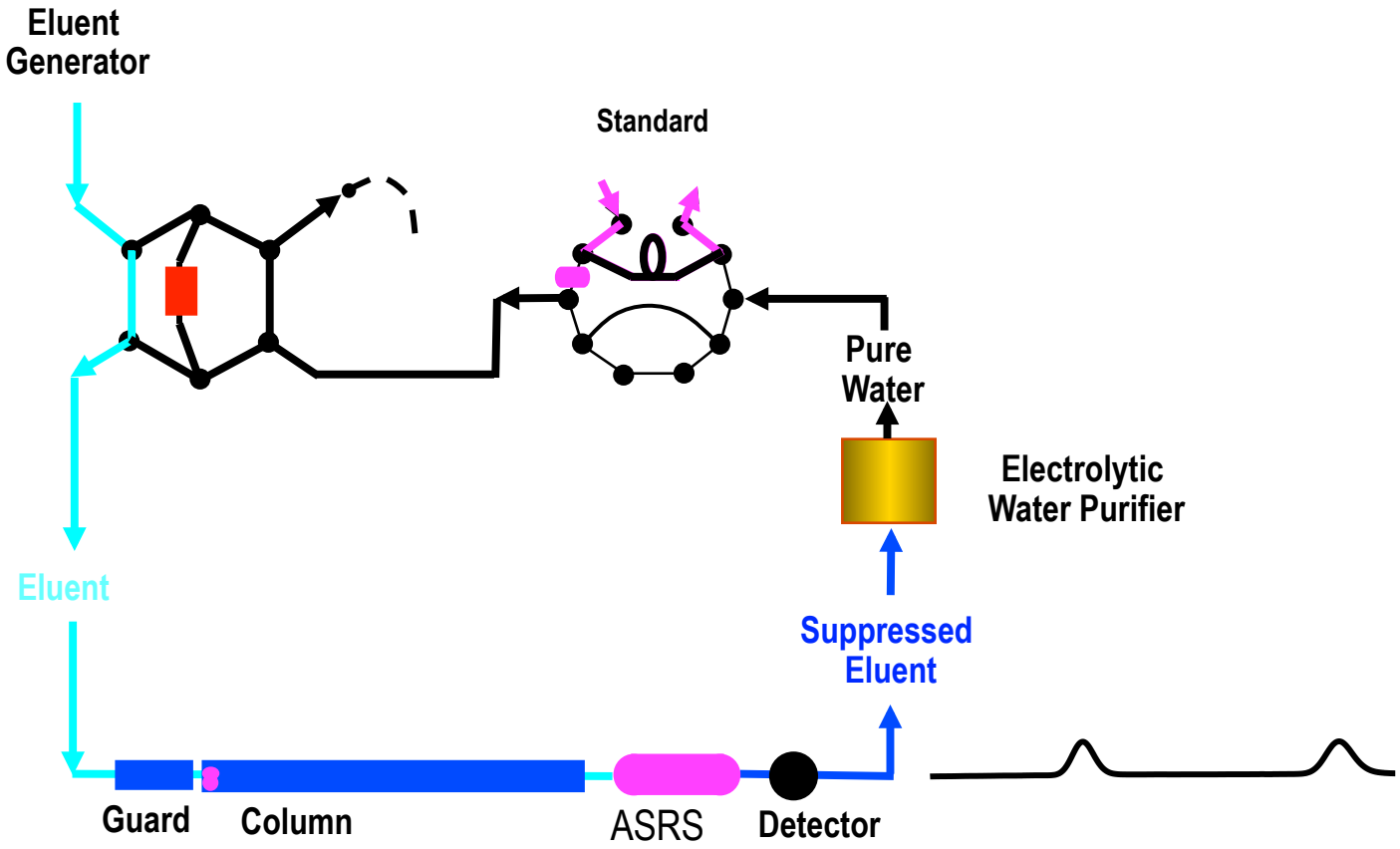
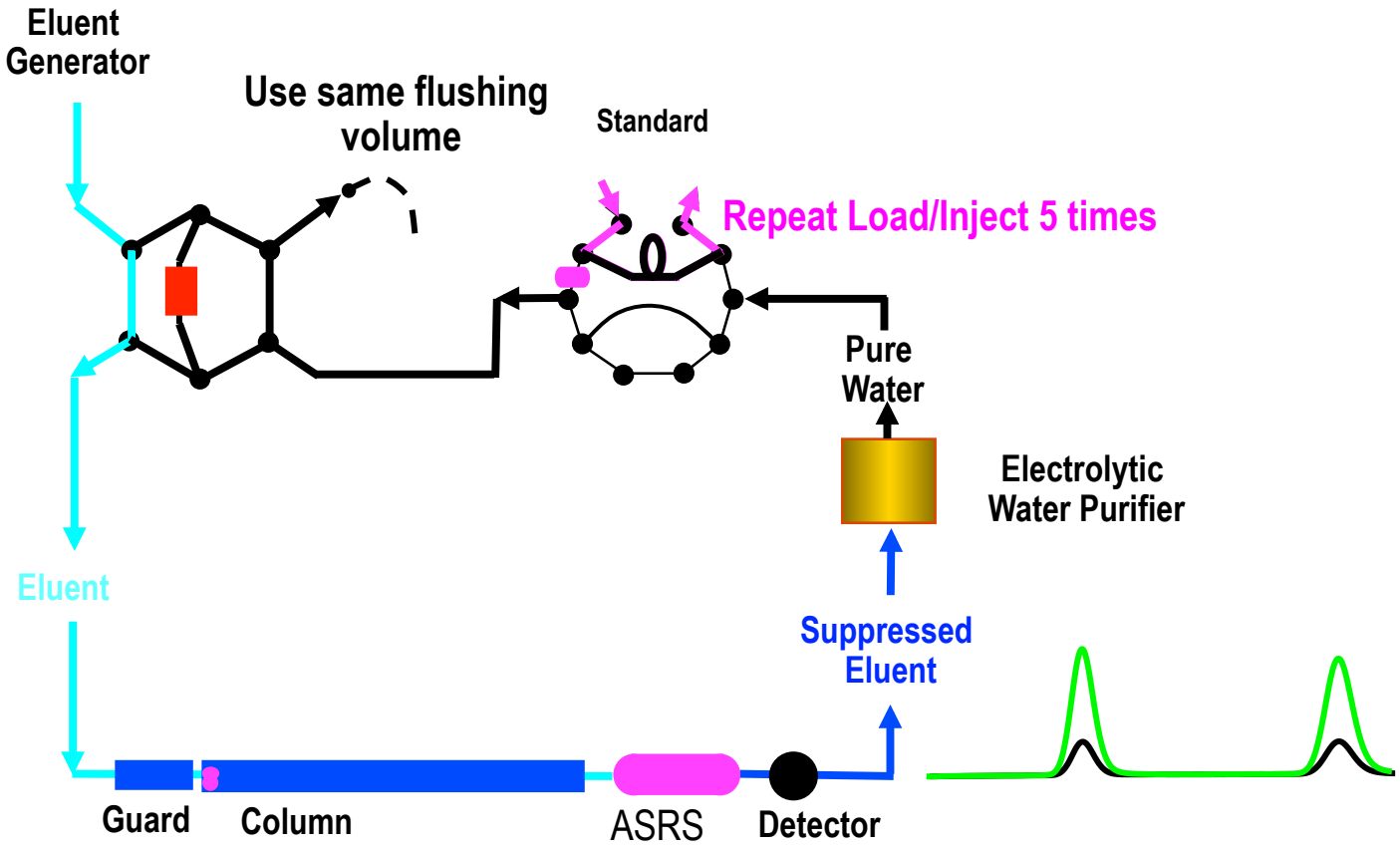
New RFIC-ESP IC Technique



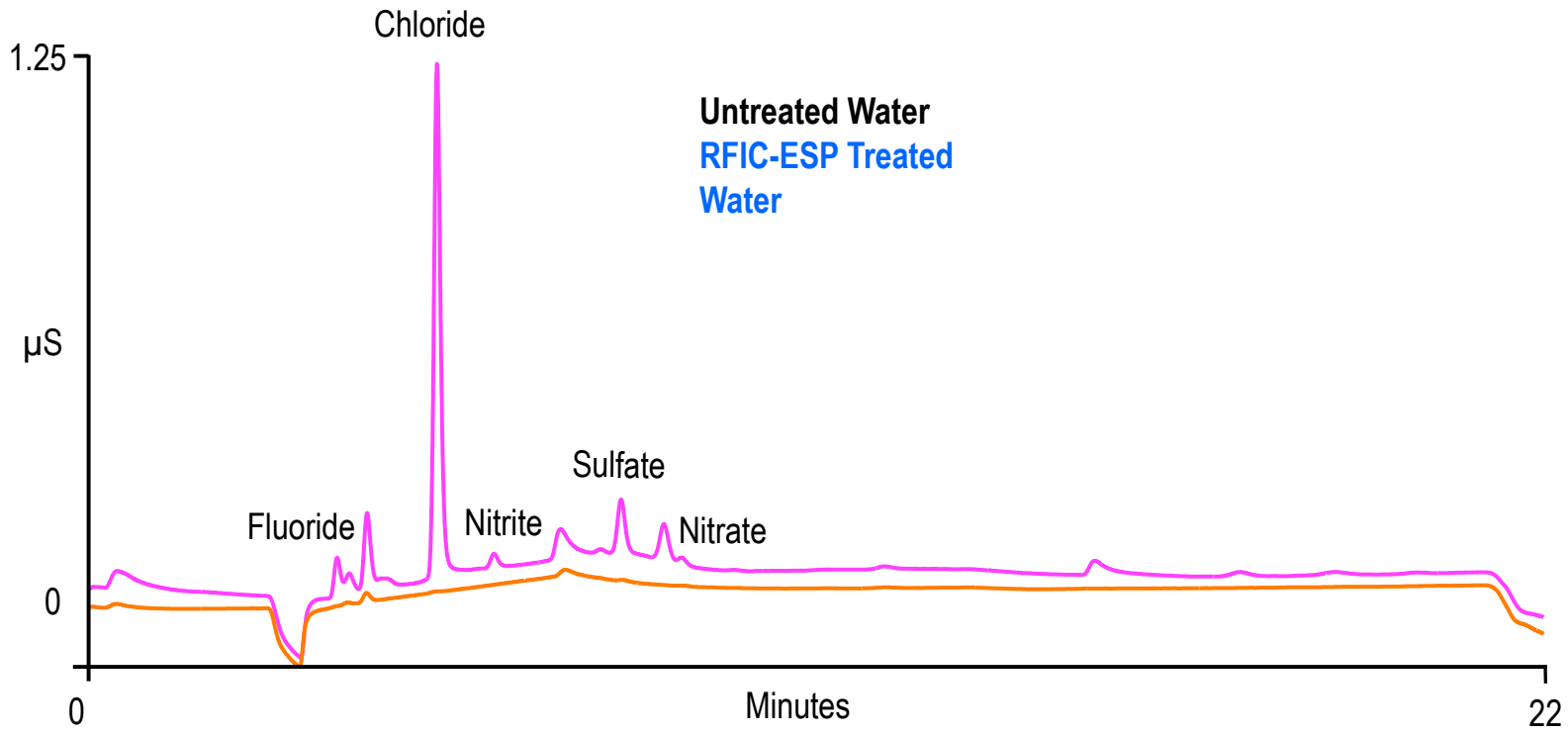
Standard Calibration (Cal 1x)

New RFIC-ESP IC Technique

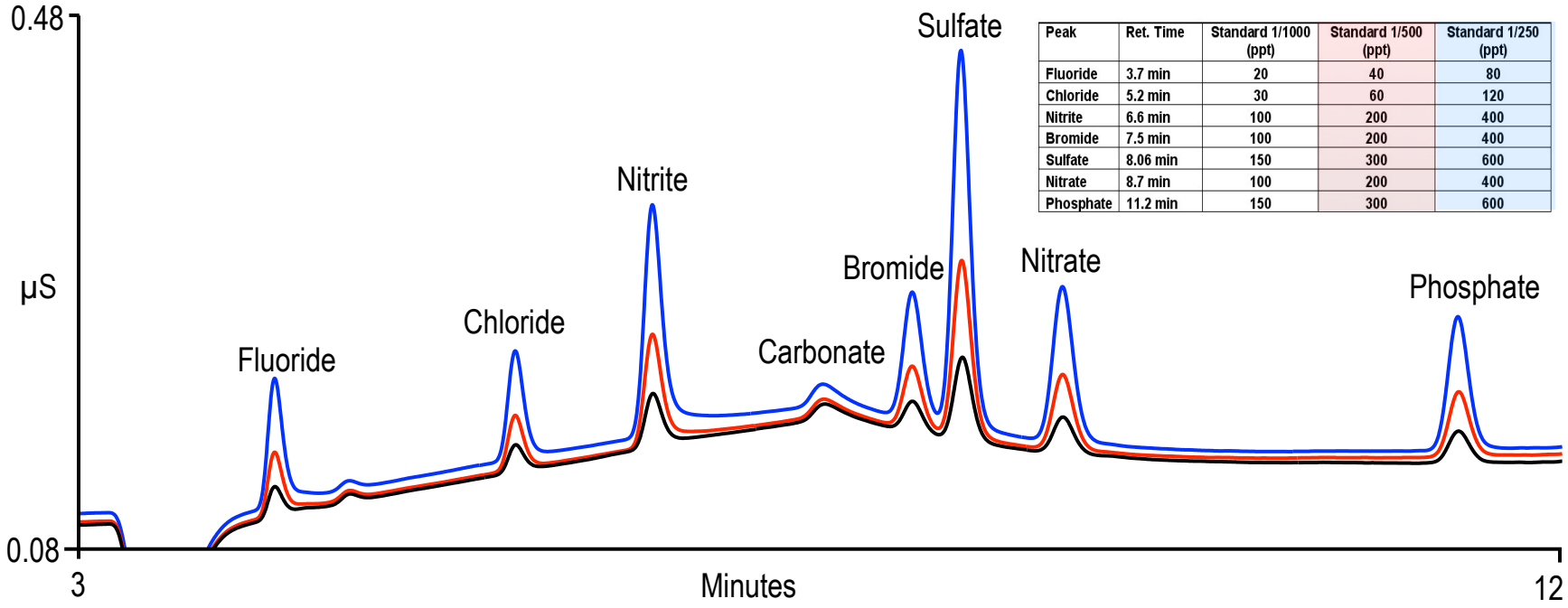


Standard Calibration (Cal 5x)

RFIC-ESP - Untreated vs. Treated Water



RFIC-ESP – Automated Calibration



Peak	Ret. Time	Standard 1/1000 (ppt)	Standard 1/500 (ppt)	Standard 1/250 (ppt)
Fluoride	3.7 min	20	40	80
Chloride	5.2 min	30	60	120
Nitrite	6.6 min	100	200	400
Bromide	7.5 min	100	200	400
Sulfate	8.06 min	150	300	600
Nitrate	8.7 min	100	200	400
Phosphate	11.2 min	150	300	600

RFIC-ESP – Automated Calibration

Standard amounts

Peak	Ret. Time	Standard 1/1000 (ppt)	Standard 1/500 (ppt)	Standard 1/250 (ppt)
Fluoride	3.7 min	20	40	80
Chloride	5.2 min	30	60	120
Nitrite	6.6 min	100	200	400
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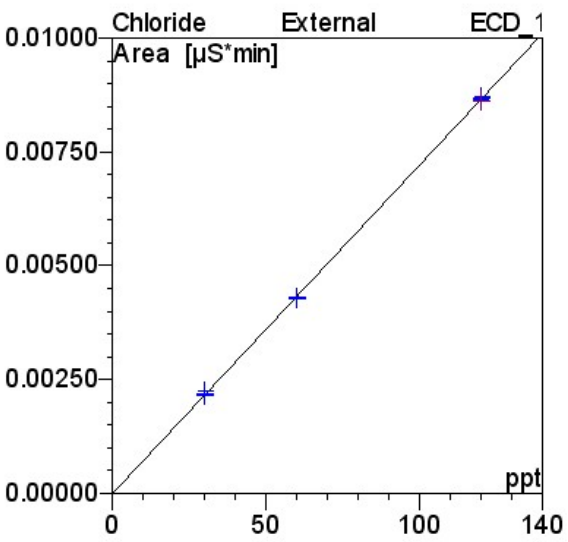
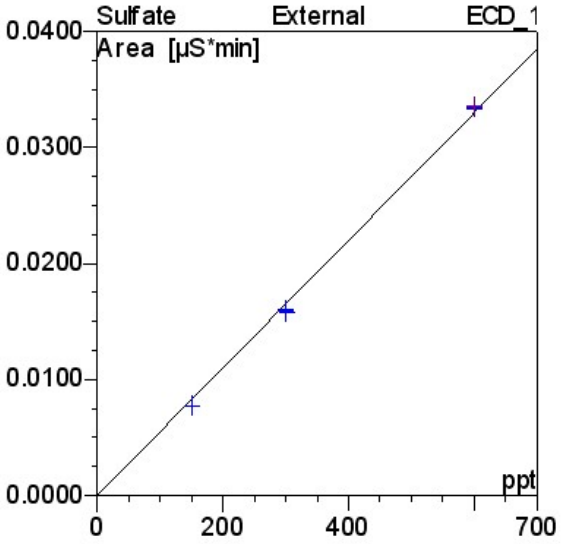
Nitrate	8.7 min	100	200	400
Phosphate	11.2 min	150	300	600





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RFIC-ESP - Summary

- Only one pump needed
- Simplifies trace analysis
- Very low backgrounds
- Very low detection limits – less than 5 ppt
- Sample calibration and concentration is automated
- High degree of automation
  - Fewer errors, improved reliability, lower labor costs

Anion Determination in Borated Water

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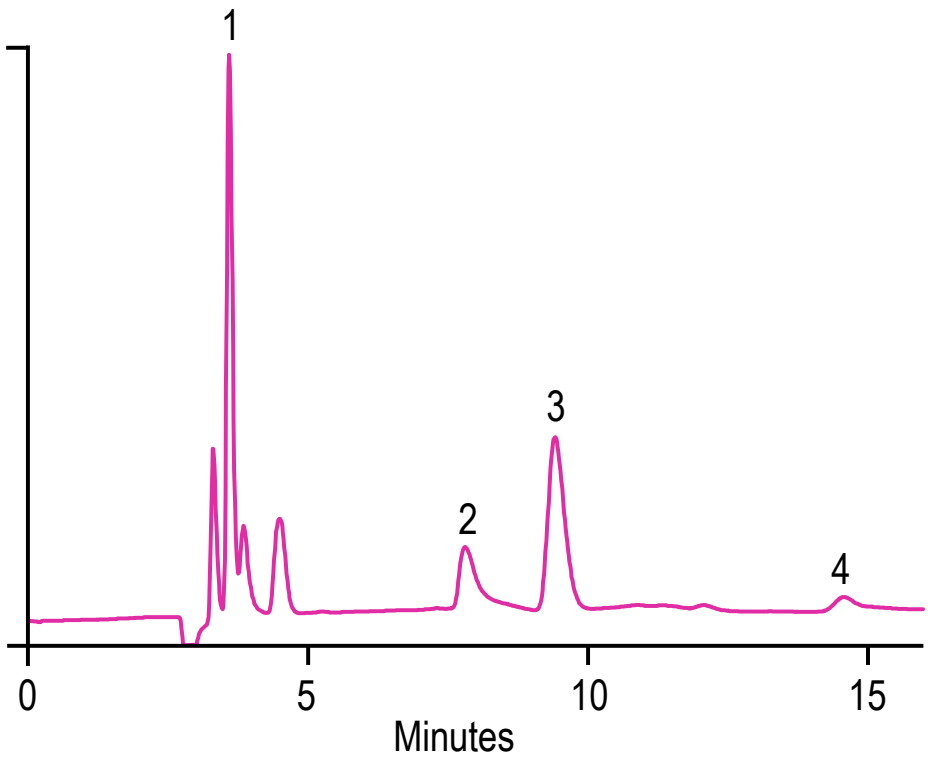
Anions in Borated Water – PWR Primary Water Circuit



Column:	IonPac® AG10, AS10
Eluent:	85 mmol/L NaOH
Flow rate:	1 mL/min
Detection:	Suppressed conductivity,
Injection:	12 mL
Concentrator:	AC10
Peaks:	1. Fluoride
	2. Borate
	3. Chloride 5 µg/L
	4. Sulfate

Manual cation exchange sample preparation to remove Lithium

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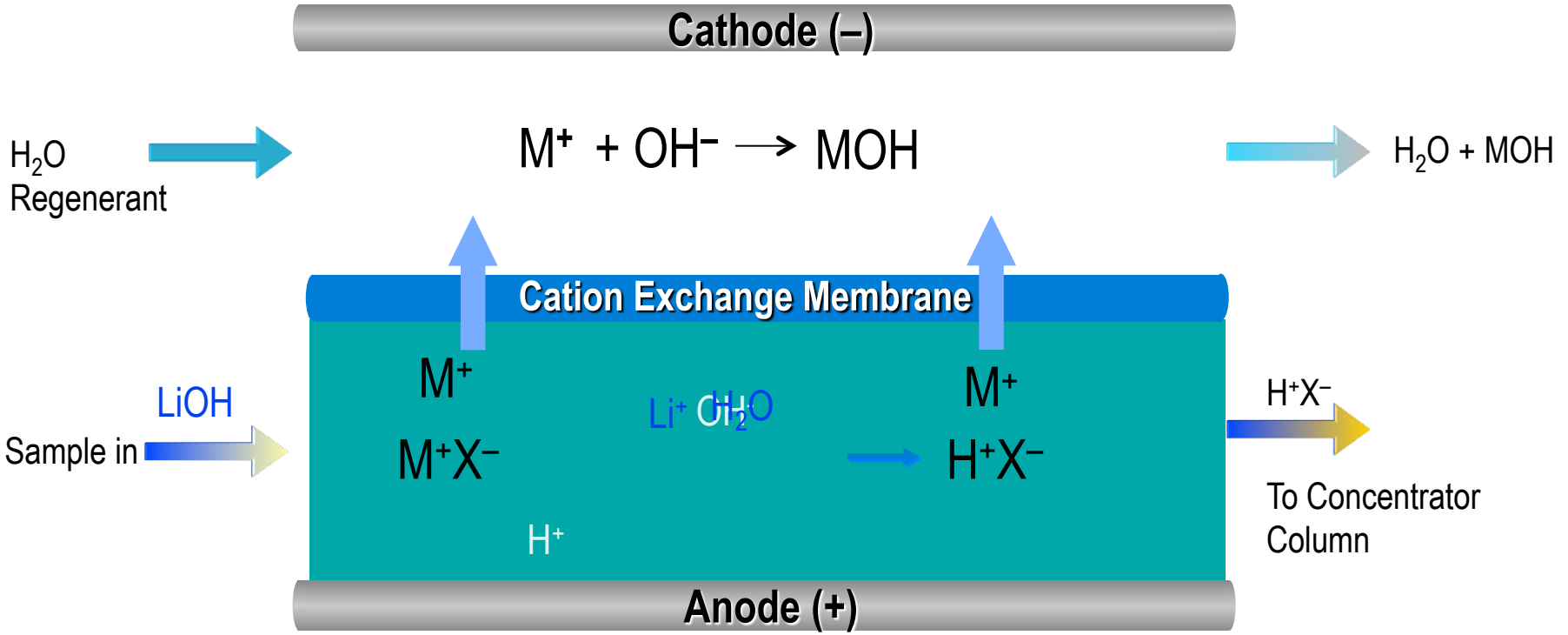
Combination of AutoPrep with On-line Matrix Elimination

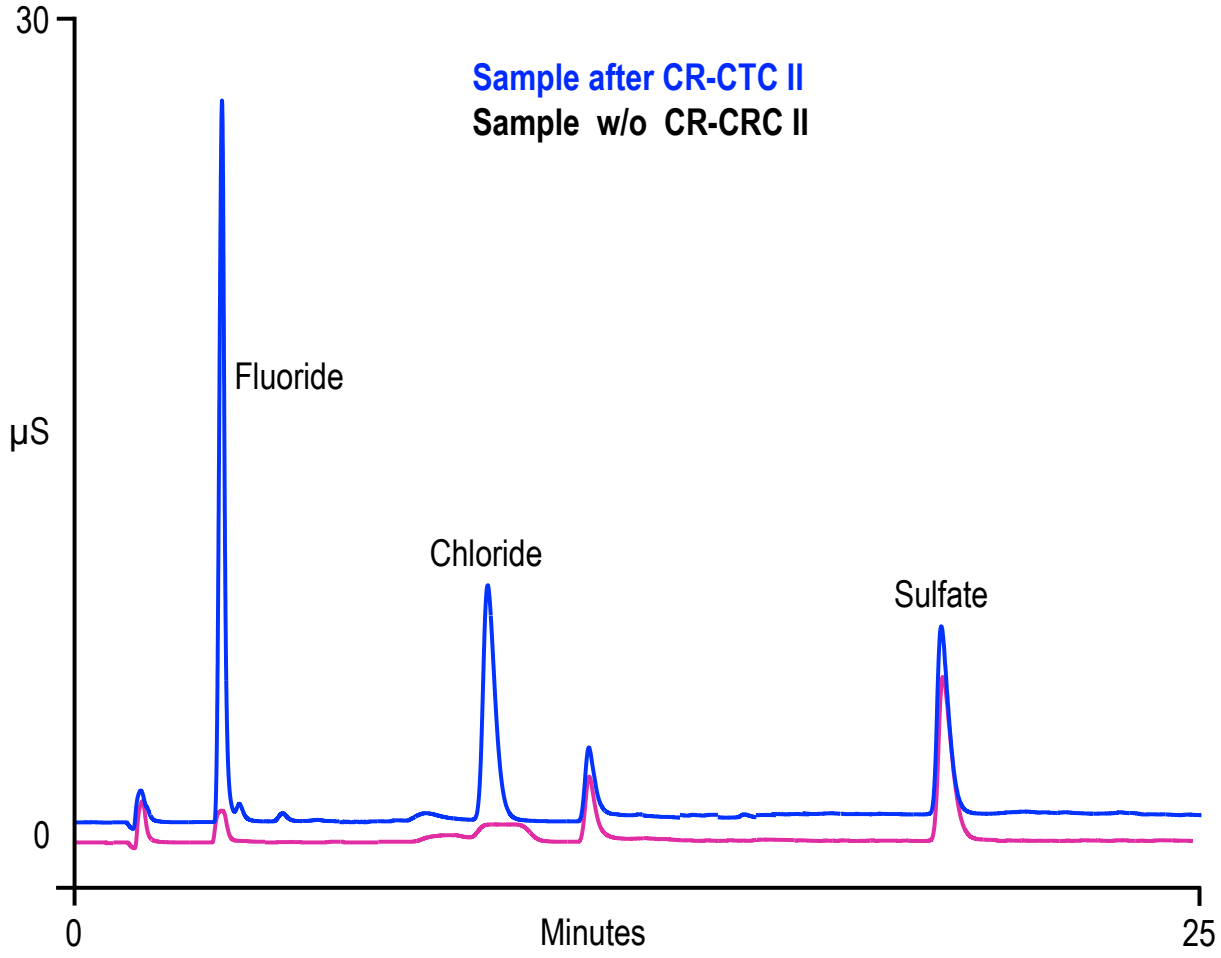
On-line Sample Preparation – CR-CTC II



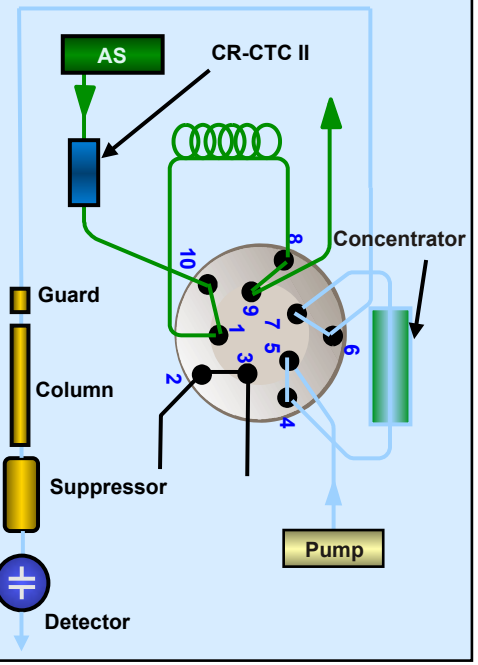
Continuously Regenerated-Cation Tray Column (CR-CTC II) for on-line RFIC sample pretreatment – Removal of cations including Lithium

Note: Power to the CR-CTC II should be turned on only when sample is flowing through the unit.

RFIC-ESP™: CR-CTC II Sample Prep when Concentrating a Large Volume (40 mL) of Sample



Instrument: ICS-3000 and AS
RFIC-ESP: CR-CTC II and AG4A concentrator
Column: IonPac® AG4A (4 mm)/ AS4A (4 mm)
RFIC-EG: KOH Gradient, 100 mM borate
Flow Rate: 1.5 mL/min
Inj. Vol.: 40 mL sample
Detection: Suppressed conductivity
Sample: Simulated reactor water, 3.5 ppm Lithium hydroxide



LiOH Interference Removed – Chromatography Conditions see Dionex Application Note 166

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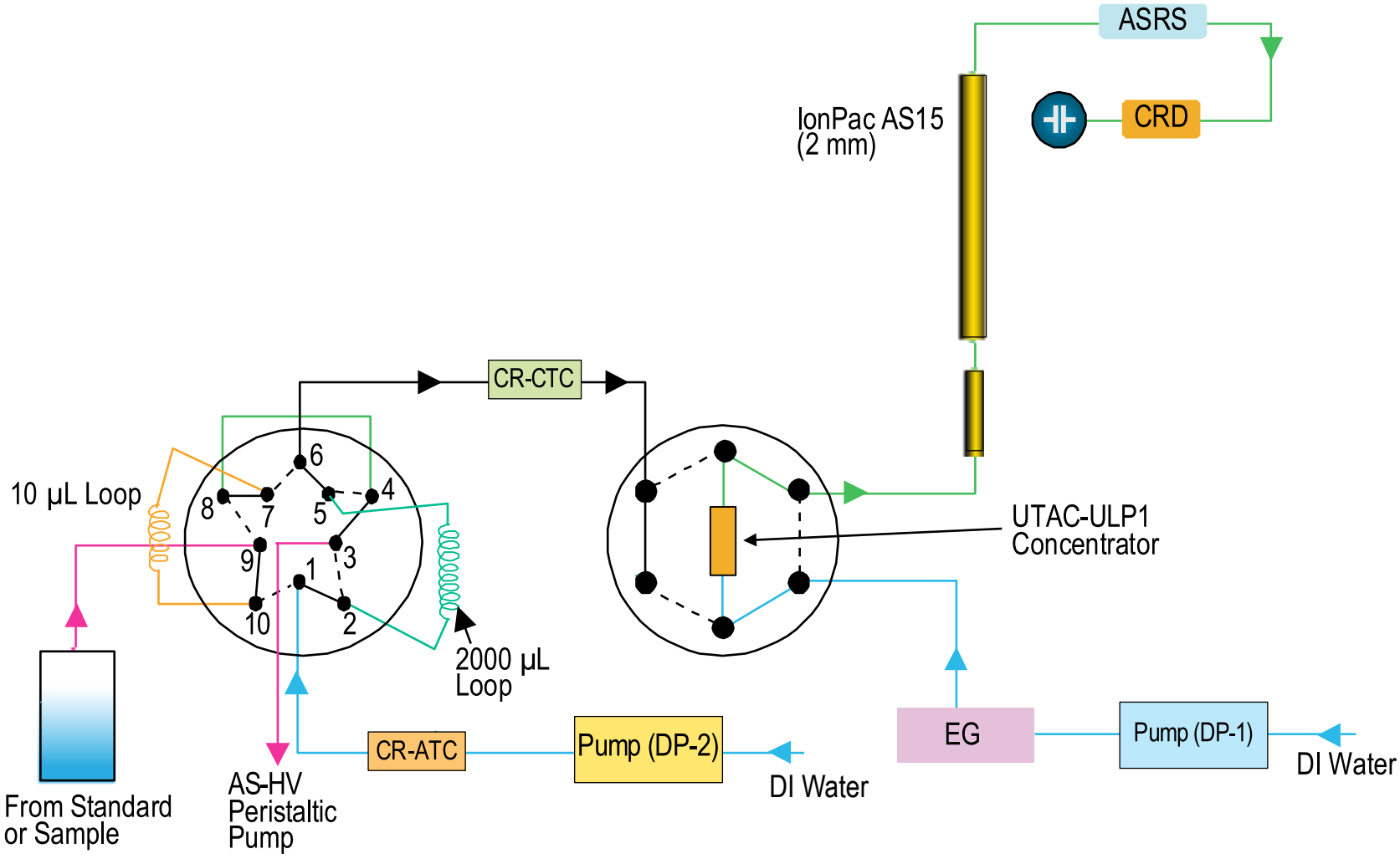
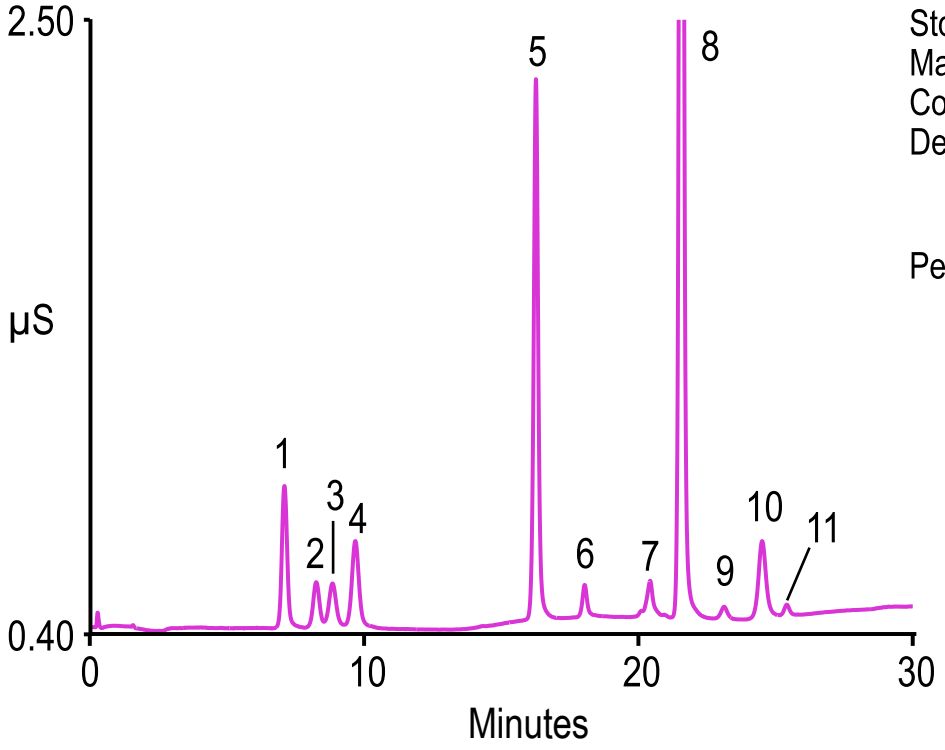
Determining Trace Anions in Borated Water



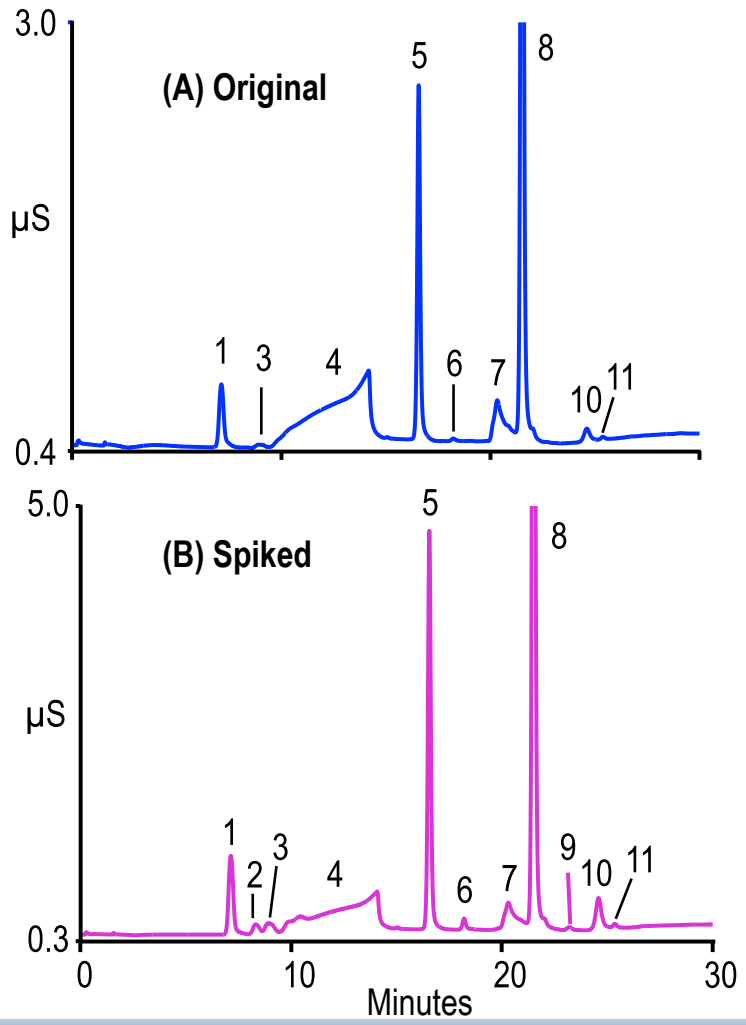
Small Organic and Common Inorganic Anions



Column:	IonPac® AG15, AS15, 2 mm
Eluent:	7 mM KOH 0-10 min, 7-40 mM 10-16 min, 40-60 mM 16-22 min, 60 mM 22-30 min
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30 ˚C
Std. Volume:	10 µL
Matrix Elim. Vol.:	10 mL
Concentrator:	UTAC-ULP1 (5 x 23 mm)
Detection:	ASRS® ULTRA II, 2 mm, recycle mode, 65 mA

Peaks:		
	1. Formate	1.0 µg/L
	2. Glycolate	1.5
	3. Acetate	1.4
	4. Formate	1.4
	5. Chloride	5.0
	6. Nitrite	0.5
	7. Carbonate	—
	8. Sulfate	25.1
	9. Bromide	0.5
	10.Nitrate	2.5
	11.Phosphate	0.5

Trace Anions in Borated Water

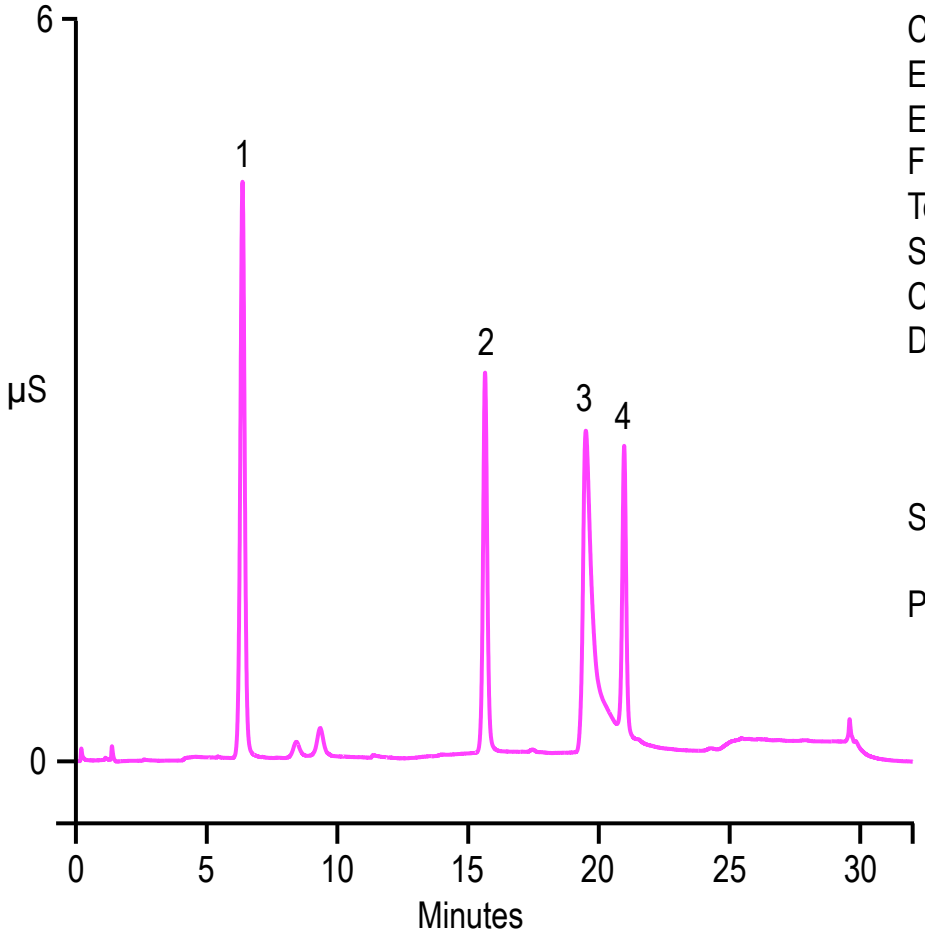


Column:	IonPac® AG15, AS15, 2 mm
Eluent:	KOH-Gradient
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30 ˚C
Sample. Volume:	2 mL
Matrix Elim. Vol.:	10 mL
Concentrator:	UTAC-ULP1 (5 x 23 mm)
Detection:	ASRS® ULTRA II, 2 mm, recycle mode, 65 mA
Chromatogram:	A) Unspiked 2000 mg/L boron + 3.8 mg/L Li B) Spiked 2000 mg/L boron + 3.8 mg/L Li

Peaks:		A	B	µg/L
	1. Fluoride	0.93	1.98	
	2. Glycolate	—	1.40	
	3. Acetate	0.30	1.86	
	4. Borate	—	—	
	5. Chloride	5.19	10.5	
	6. Nitrite	0.07	0.56	
	7. Carbonate	—	—	
	8. Sulfate	20.8	45.8	
	9. Bromide	—	0.48	
	10.Nitrate	0.77	3.2	
	11.Phosphate	0.14	0.65	

Ammonium and Hydrazine in PWR Secondary Water

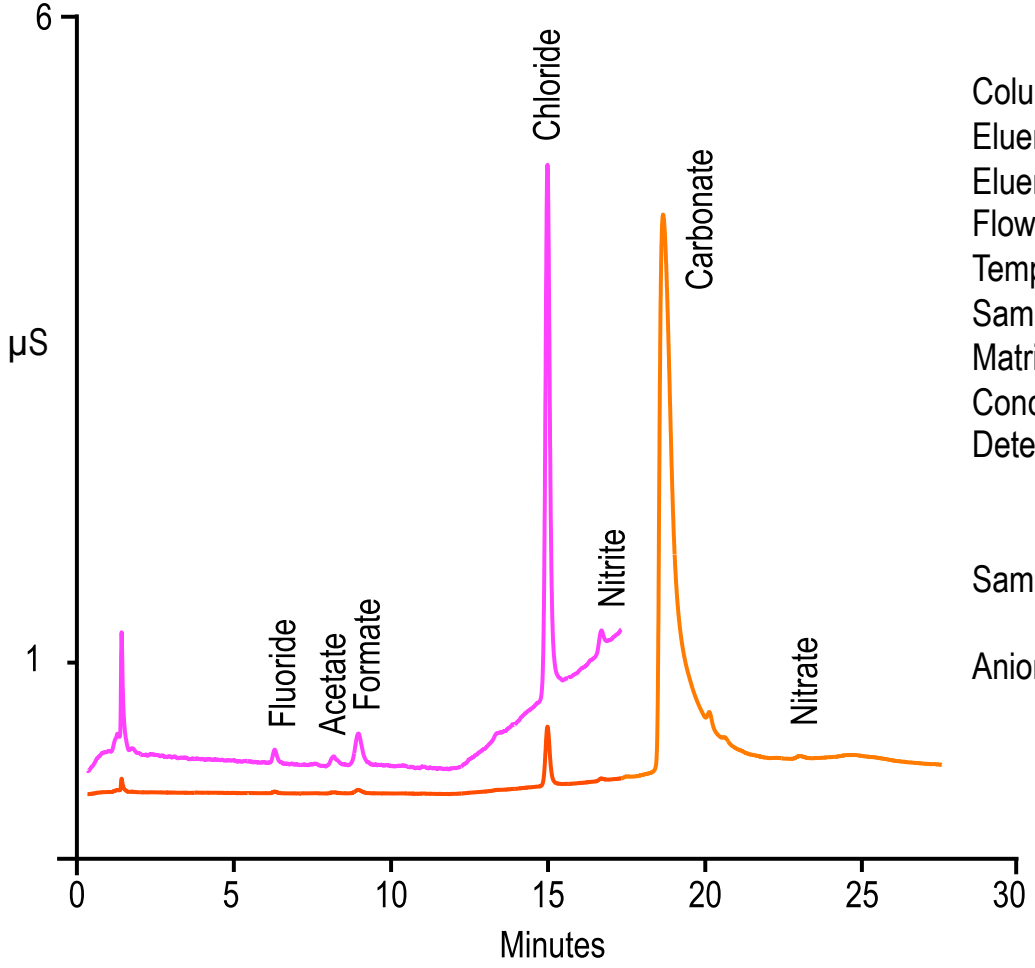
Trace Anions in Ammoniated Water



Column:	IonPac® AG15, AS15, 2 mm
Eluent:	KOH-Gradient
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30˚C
Sample. Volume:	2 mL
Concentrator:	AC10
Detection:	ASRS® ULTRA II, 2 mm, recycle mode, 65 mA Carbonate Removal Device CRD-200
Sample:	10 ppm Ammonium

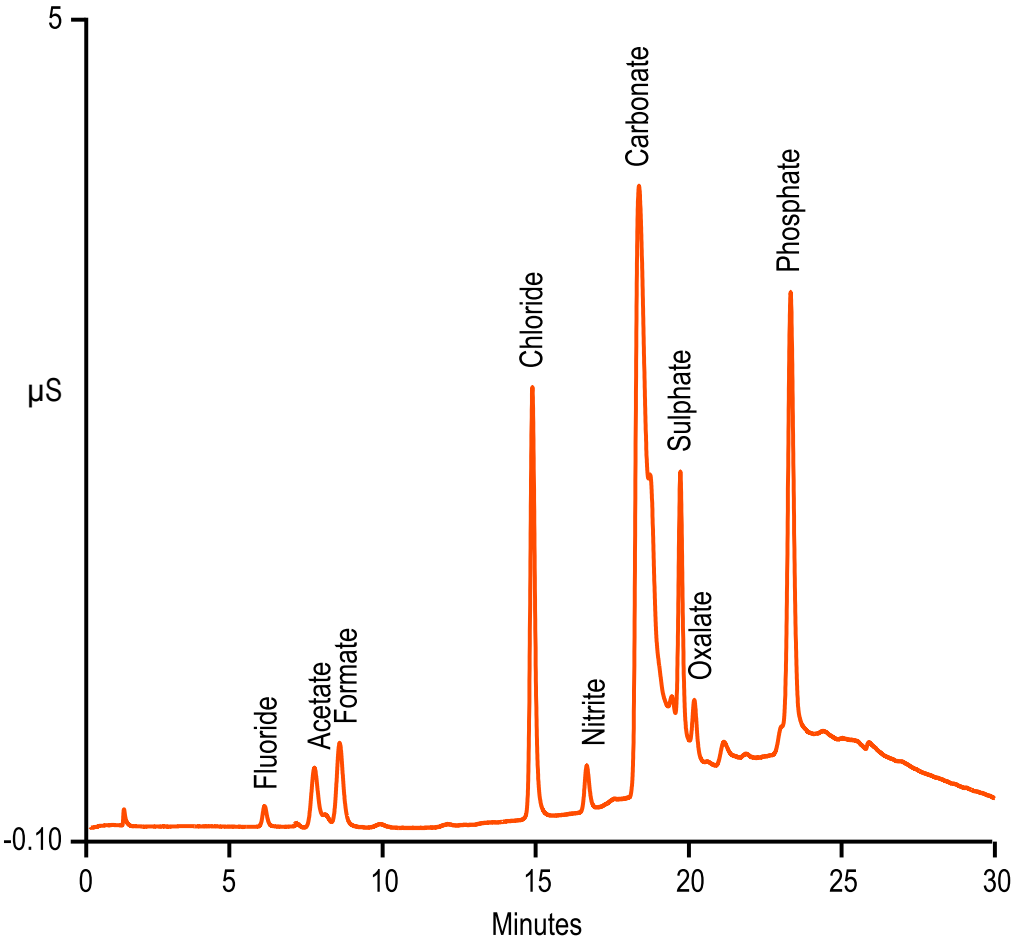
Peaks:			
	1. Fluoride	10	µg/L
	2. Chloride	10	
	3. Carbonate	–	
	3. Sulfate	10	

Hydrazinated Water – PWR Secondary Circuit



Column:	IonPac® AG15, AS15, 2 mm
Eluent:	KOH-Gradient
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30 ˚C
Sample. Volume:	10 mL
Matrix Elim. Vol.:	12 mL
Concentrator:	AC15 (2 mm)
Detection:	ASRS® ULTRA II, 2 mm, recycle mode No CRD-200 used
Sample:	Hydrazine (200 ppb) in UPW
Anions:	s. Chromatogram Concentrations single digit ppb

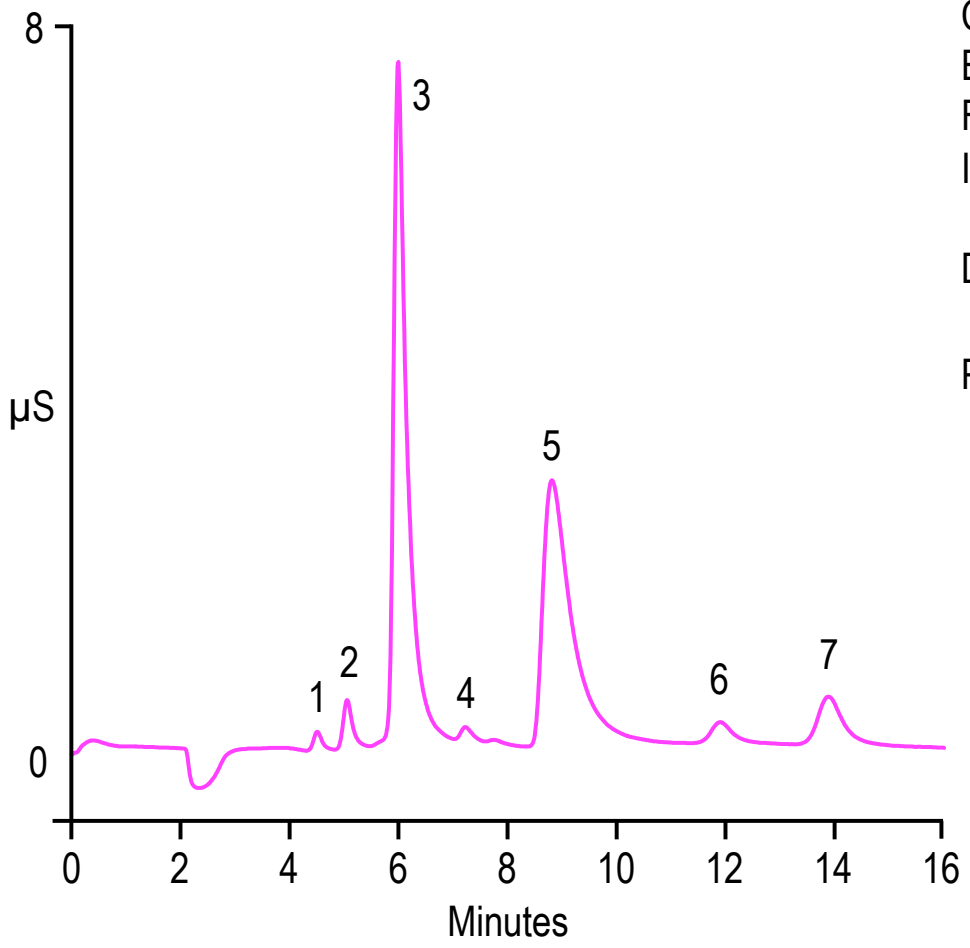
Real World Sample – PWR Secondary Cooling Water



Column:	IonPac® AG15, AS15, 2 mm
Eluent:	KOH-Gradient
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30 ˚C
Sample. Volume:	10 mL
Matrix Elim. Vol.:	12 mL
Concentrator:	AC15 (2 mm)
Detection:	ASRS® ULTRA II, 2 mm, recycle mode No CRD-200
Sample:	Cooling water
Concentrations:	single digit µg/L

Amines – Matrices and Analytes

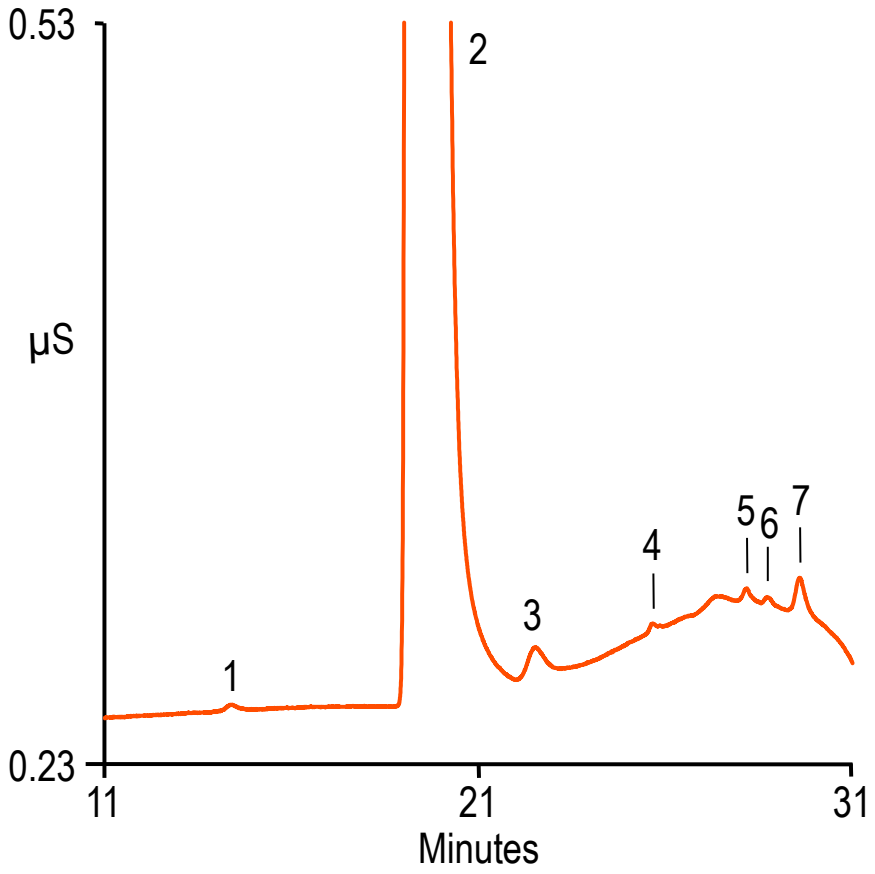
Trace Cations in Morpholine Treated Water



Column:	IonPac® CS14, CG14 (2 mm)
Eluent:	8 mmol/L MSA in 5 % CH_3CN
Flow rate:	0.25 mL/min
Inj. volume:	1.0 mL concentrated on IonPac CG14 (2 mm)
Detection:	Suppressed conductivity

Peaks:		
1.	Lithium	0.5 (µg/L)
2.	Sodium	2.0
3.	Ammonium	150
4.	Potassium	2.0
5.	Morpholine	2000
6.	Magnesium	2.0
7.	Calcium	10

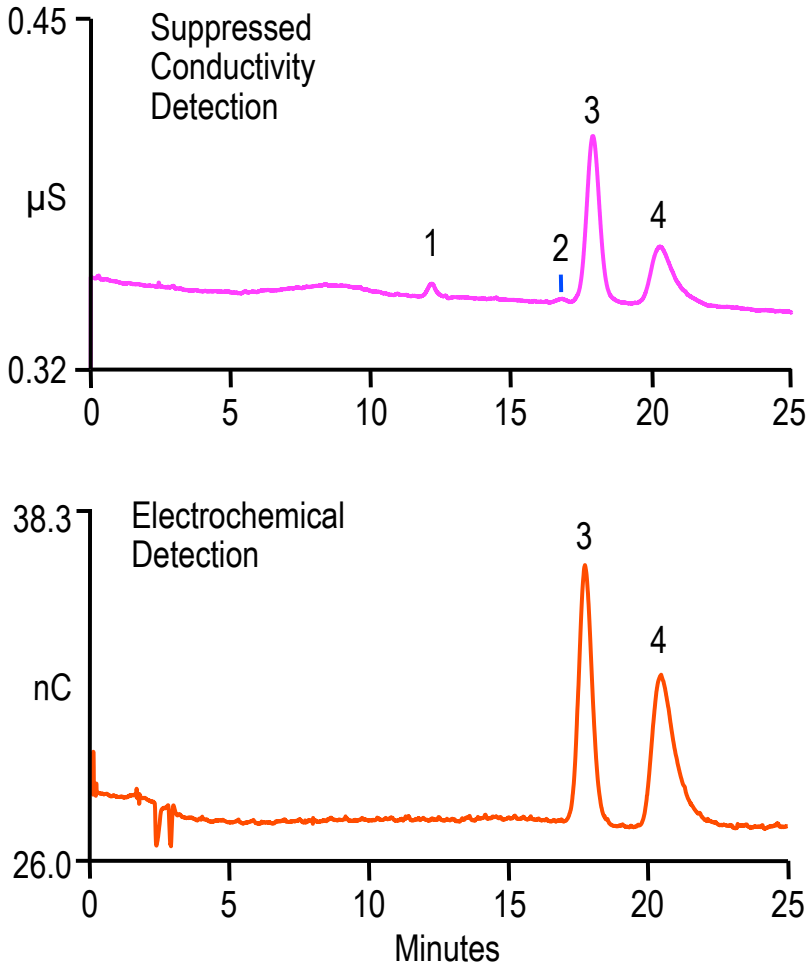
High-to-Low Ratio of Ammonium to Hydrazine



Column:	IonPac® CS16
Eluant:	7 mmol/L MSA (EG), gradient to 52 mmol/
L	MSA from 20 to 25 min, step to 7 mmol/L
	MSA at 30 min
Flow rate:	1.2 mL/min
Inj. volume:	25 µL
Temperature:	40 °C
Detection:	Suppressed conductivity
	AutoSuppression, Recycle Mode

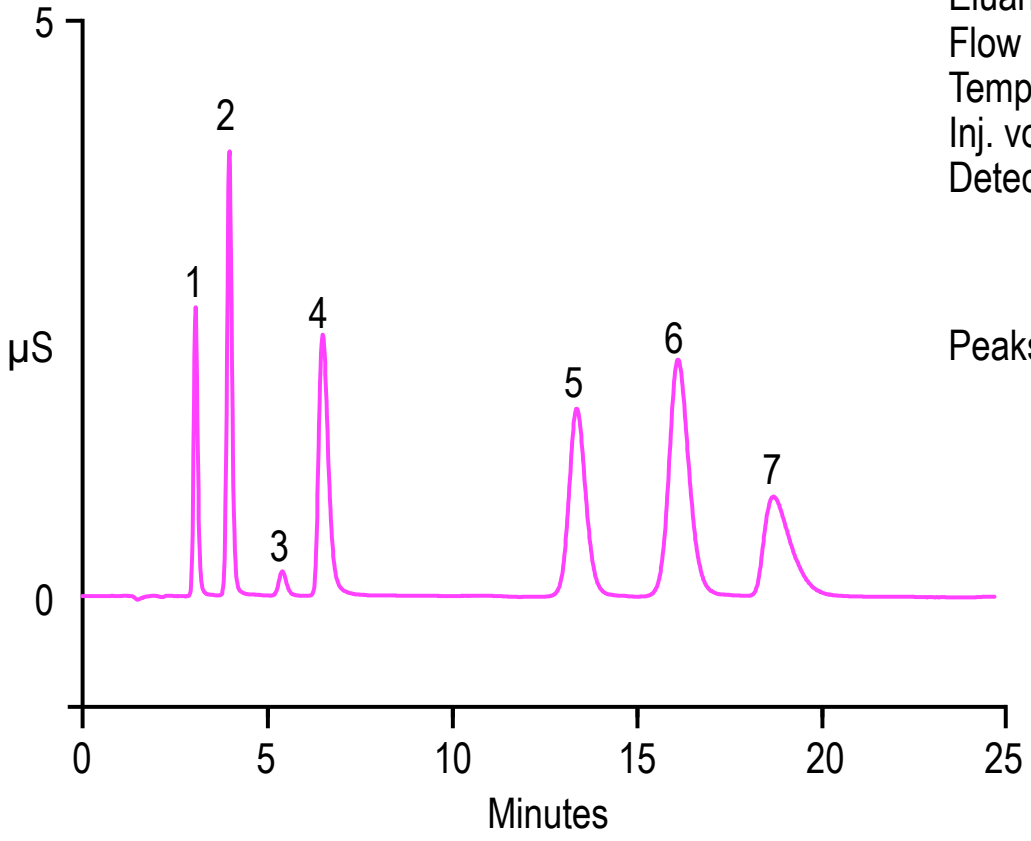
Peaks:		
1. Sodium	2	µg/L
2. Ammonium	20,000	
3. Hydrazine	200	
4. Potassium	2	
5. Magnesium		2
6. Unknown	–	
7. Calcium	14	

Elution of Ethanolamine and Hydrazine



Column:	IonPac® CS16, 3 x 250 mm		
Eluent:	EG40, 12 mM, MSA		
Temperature:	23 °C		
Flow Rate:	0.36 mL/min		
Inj. Volume:	25 µL		
Peaks:	1. Sodium	–	µg/L
	2. Ammonium	–	
	3. Ethanolamine	50	
	4. Hydrazine	200	

Isocratic Separation of Ethanolamine

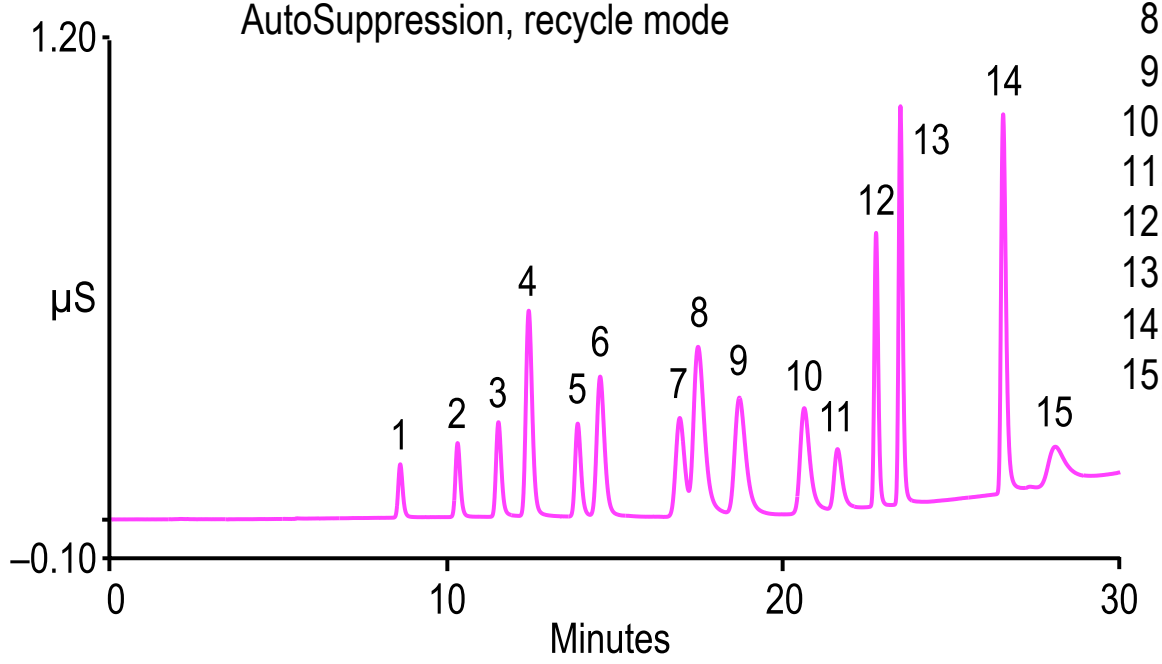


Column:	IonPac® CG15/CS15
Eluant:	5 mmol/L sulfuric acid / 9 % CH_3CN
Flow rate:	1.2 mL/min
Temperature:	40°C
Inj. volume:	25 µL
Detection:	Suppressed conductivity, AutoSuppression, external water mode

Peaks:		
1.	Lithium	1 mg/L
2.	Sodium	4
3.	Ethanolamine	3
4.	Ammonium	5
5.	Magnesium	5
6.	Calcium	10
7.	Potassium	10

Power Plant Relevant Amines

Column:	IonPac® CS18, 2 mm
Eluant:	0.5 mmol/L MSA (EG), gradient to 3 mmol/L at 16 min, gradient to 25 mmol/L at 30 min
Flow rate:	0.30 mL/min
Temperature:	40°C
Inj. volume:	5 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode



Peaks:		
1.	Lithium	0.05 mg/L
2.	Sodium	0.20
3.	Ammonium	0.25
4.	Ethanolamine	2.0
5.	Potassium	0.50
6.	2-(2-aminoethoxy)ethanol	3.0
7.	5-amino-1-pentanol	3.0
8.	Morpholine	3.0
9.	3-methoxypropylamine	3.0
10.	2-diethylaminoethanol	3.0
11.	3-quinuclidinol	2.0
12.	Magnesium	0.25
13.	Calcium	0.50
14.	Ethylenediamine	2.0
15.	Cyclohexylamine	3.0

Thank You