

An Improved Ion Chromatographic Method for Low Level Perchlorate Analysis

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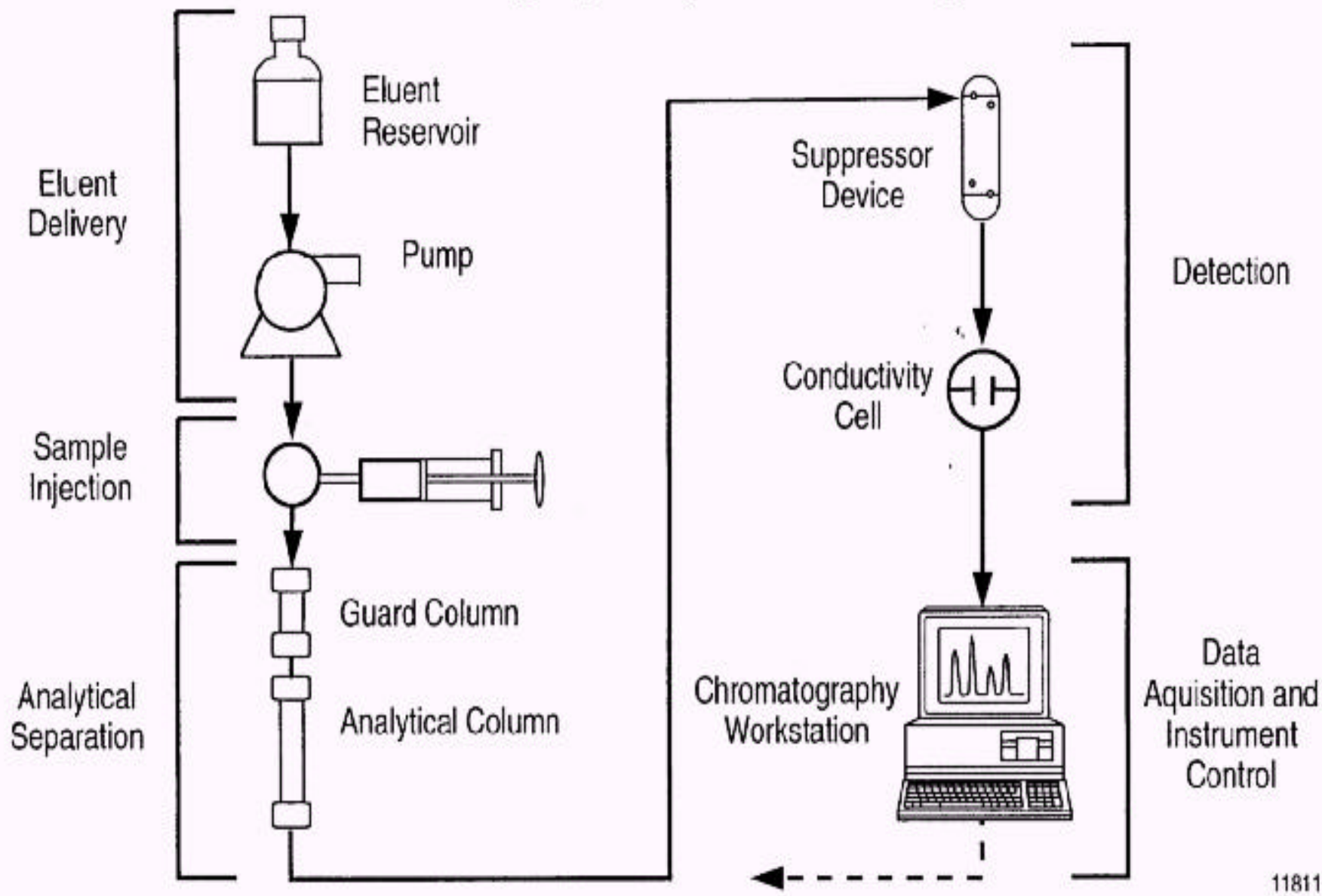
PERCHLORATE - WHAT ARE THE ISSUES

- Contamination found in CA, NV, UT & WV
- Total extent of the contamination problem across the U.S. is not known
- Is the problem localized or ubiquitous
- No federal or state regulations exist, removal treatment technologies are not available
- Are there appropriate analytical methods for perchlorate analysis

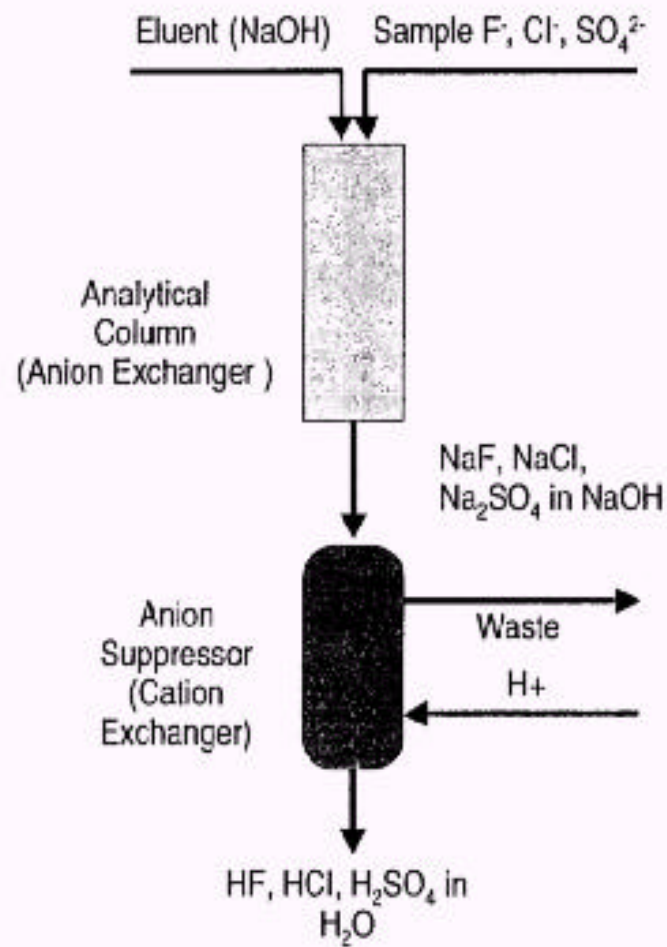
PERCHLORATE - ISSUES IN CALIFORNIA

- Perchlorate interferes with thyroid gland function
- U.S. EPA reports adequate health protection corresponding to a range of 4-18 ppb
- Urgent problem in CA, action level of 18 ppb
- >22 groundwater production wells shut down
- California Department of Health Services (CDHS) has developed an ion chromatography (IC) method for the trace analysis of perchlorate

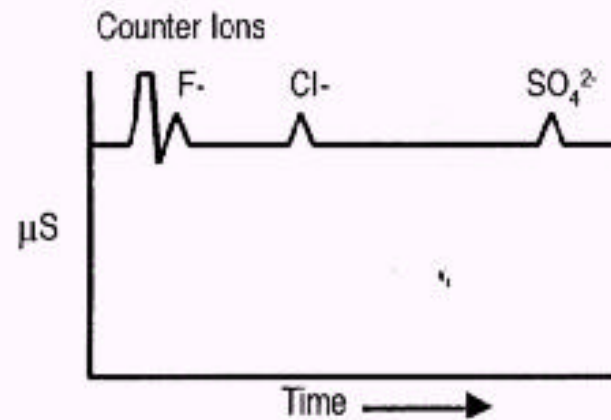
Ion Chromatograph System Configuration



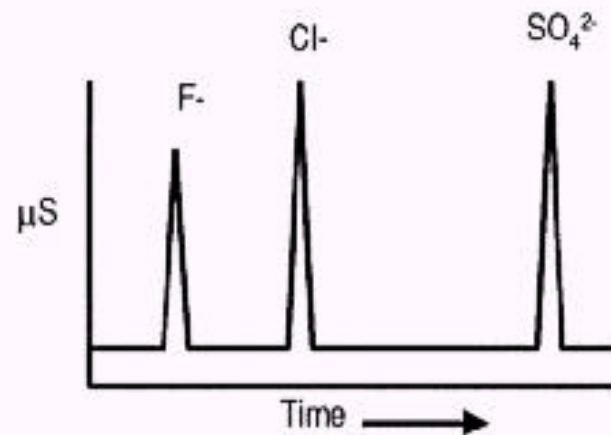
The Role of Chemical Suppression



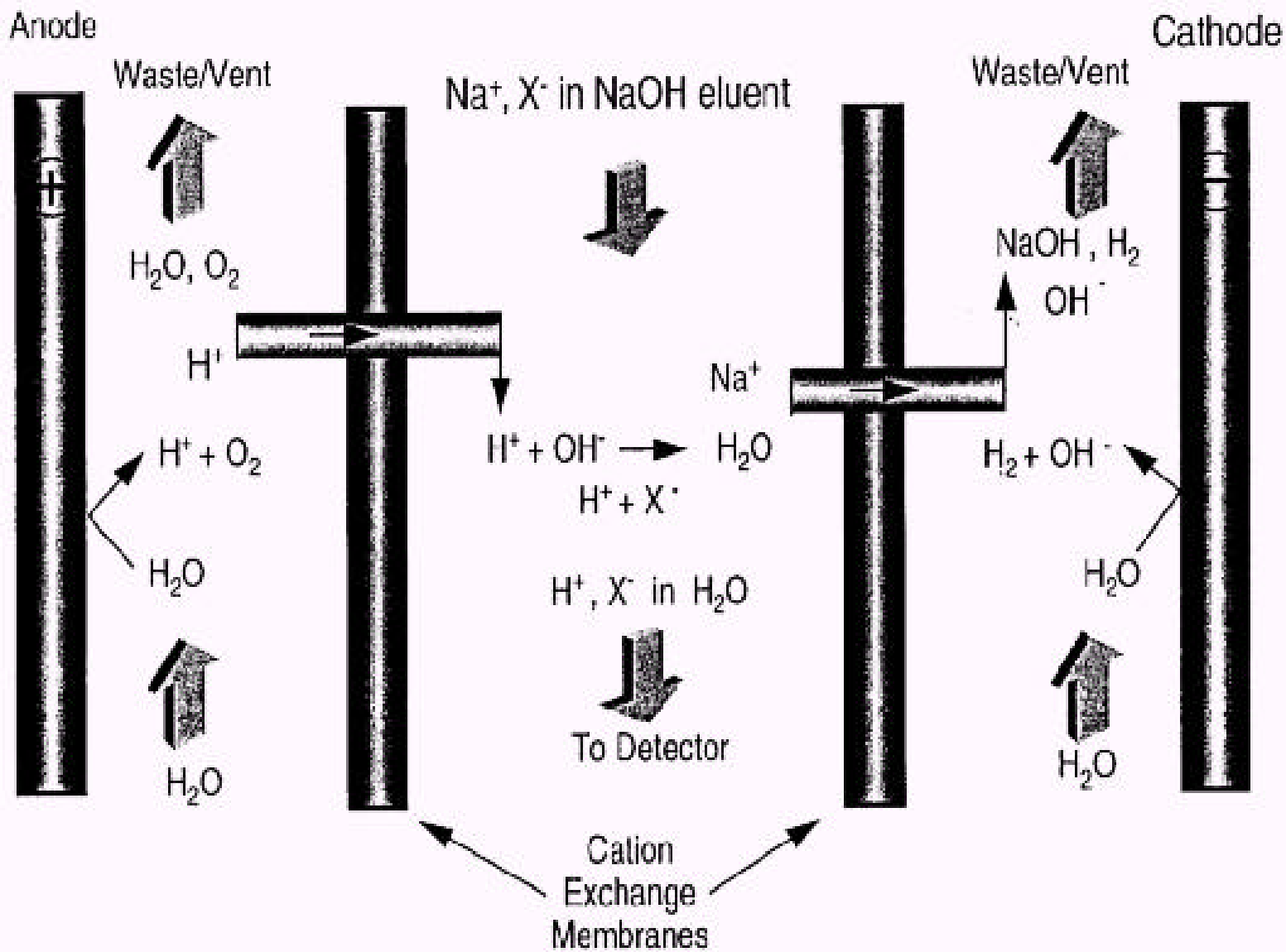
Without Suppression



With Chemical Suppression



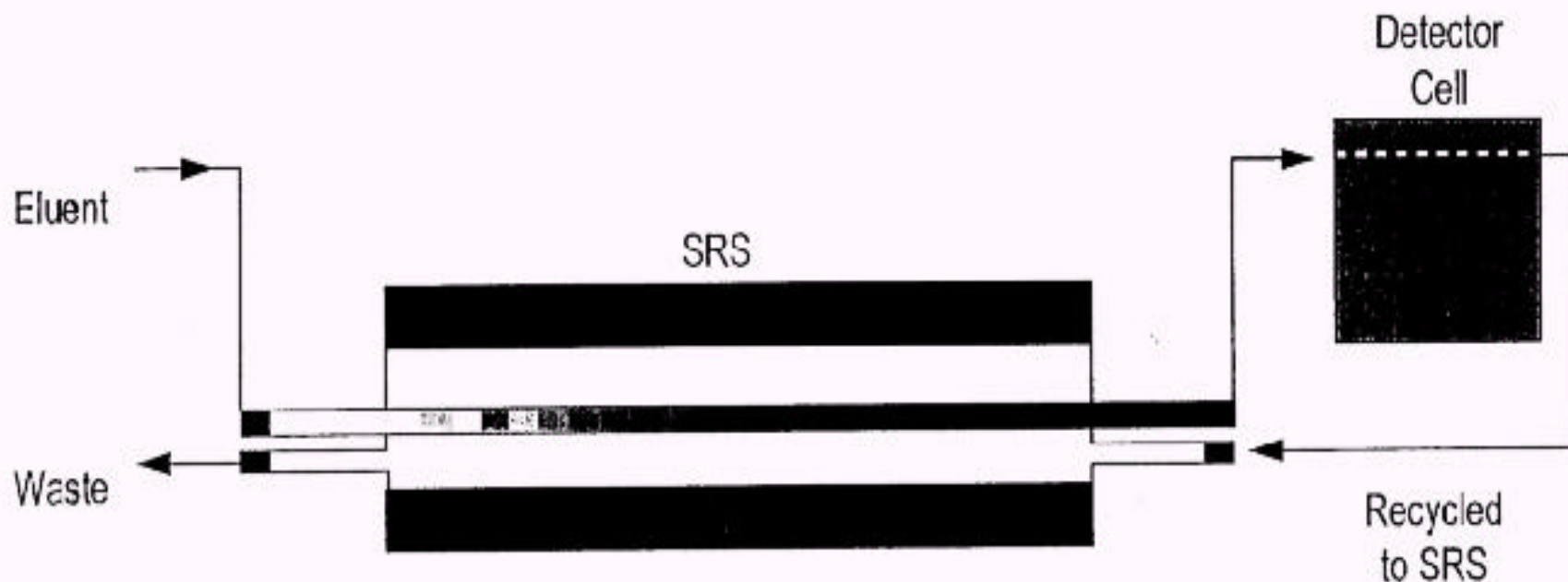
Chemistry and Ion Movement in an Anion SRS[®]



SRS[®] Suppression Modes

- ◆ Electrolytic regeneration (AutoSuppression[®])
 - Eluent recycle
 - External water
- ◆ Chemical regeneration
 - Sulfuric acid for ASRS[®]
 - Tetrabutylammonium hydroxide for CSRS[®]

SRS™ AutoSuppression™ Mode

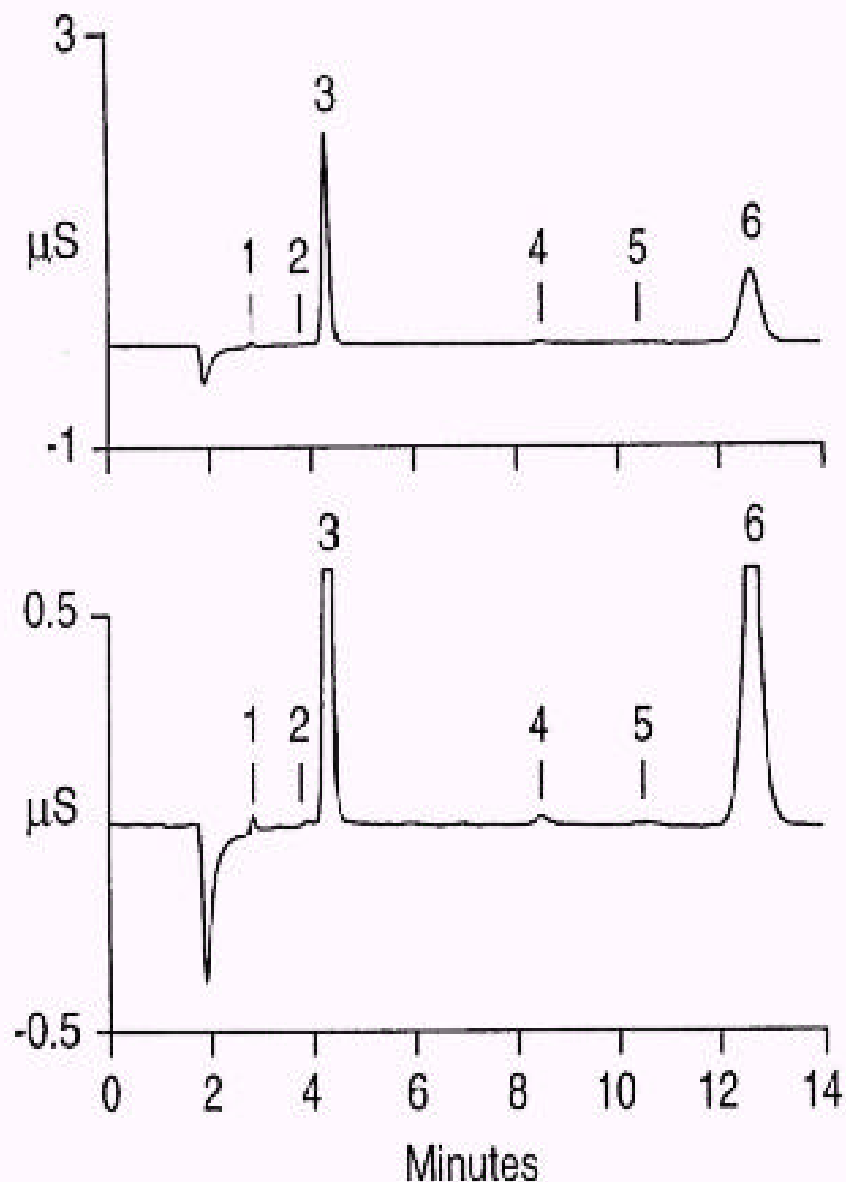


Eluents: ASRS™ — Hydroxide, carbonate/bicarbonate, boric acid/tetraborate

CSRS™ — Methanesulfonic acid (MSA), sulfuric acid

Note: Eluents containing Cl^- or NO_3^- cannot be used in this mode

Analysis of Drinking Water on the IonPac® AS14



Column: IonPac AG14, AS14

Eluent: 3.5 mM Sodium carbonate

1.0 mM Sodium bicarbonate

Flow Rate: 1.2 mL/min

Inj. Volume: 10 µL

Detection: Suppressed conductivity, ASRS™,
AutoSuppression™ recycle mode

Sample: Drinking water from Milpitas, CA

Peaks:	1. Fluoride	0.03 mg/L
	2. Bicarbonate	—
	3. Chloride	3.12
	4. Nitrate	0.15
	5. Phosphate	0.04
	6. Sulfate	4.45

United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Cincinnati, OH 45268

Office of Research and Development

Revised August 1993



Method 300.0

Determination of Inorganic Anions by Ion Chromatography

Revision 2.1

John D. Pfaff

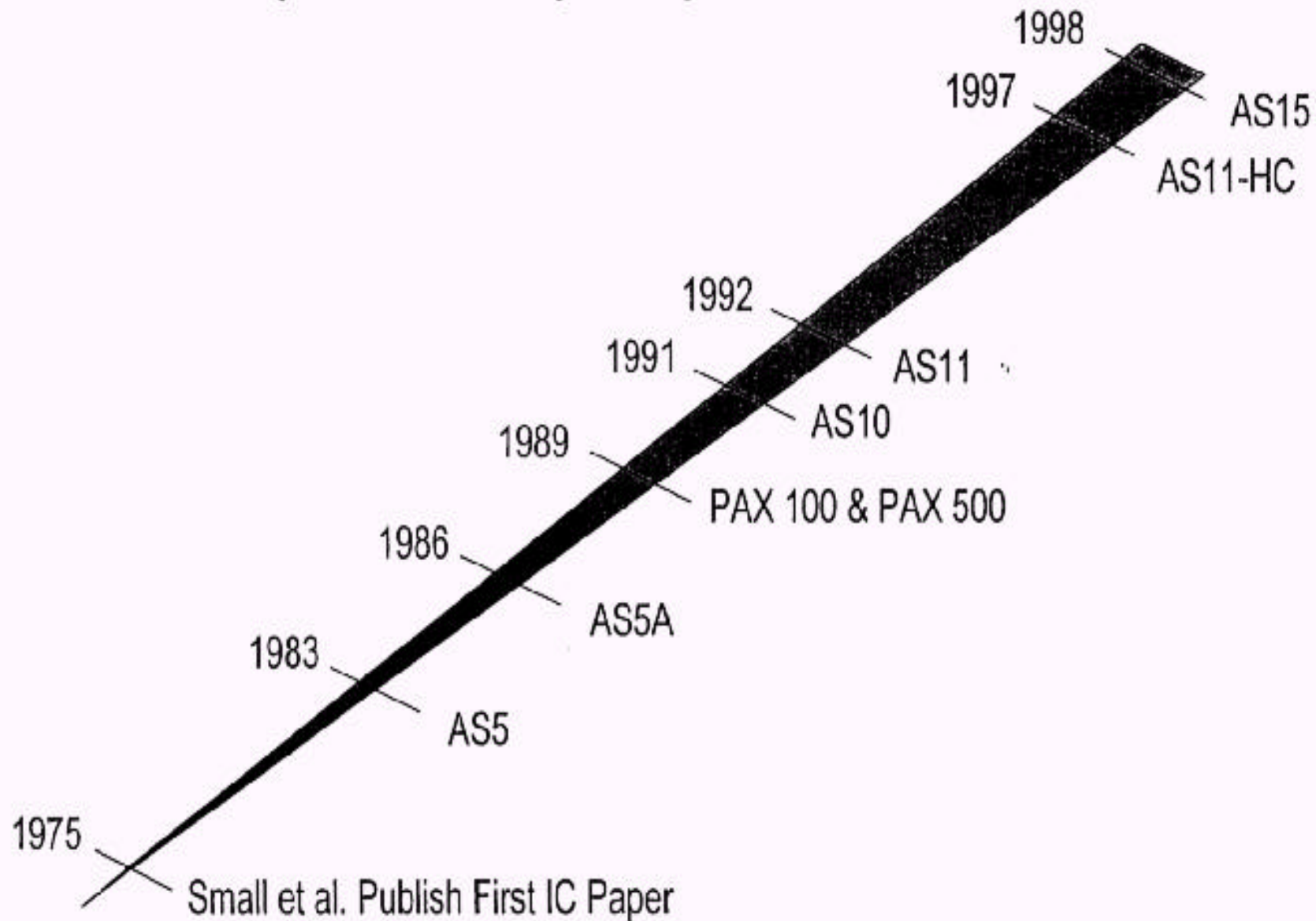
WHAT IS A POLARIZABLE ANION?

- An anion with an “easily” deformable electron cloud
- The anionic form of a “soft” acid
- A “hydrophobic” anion

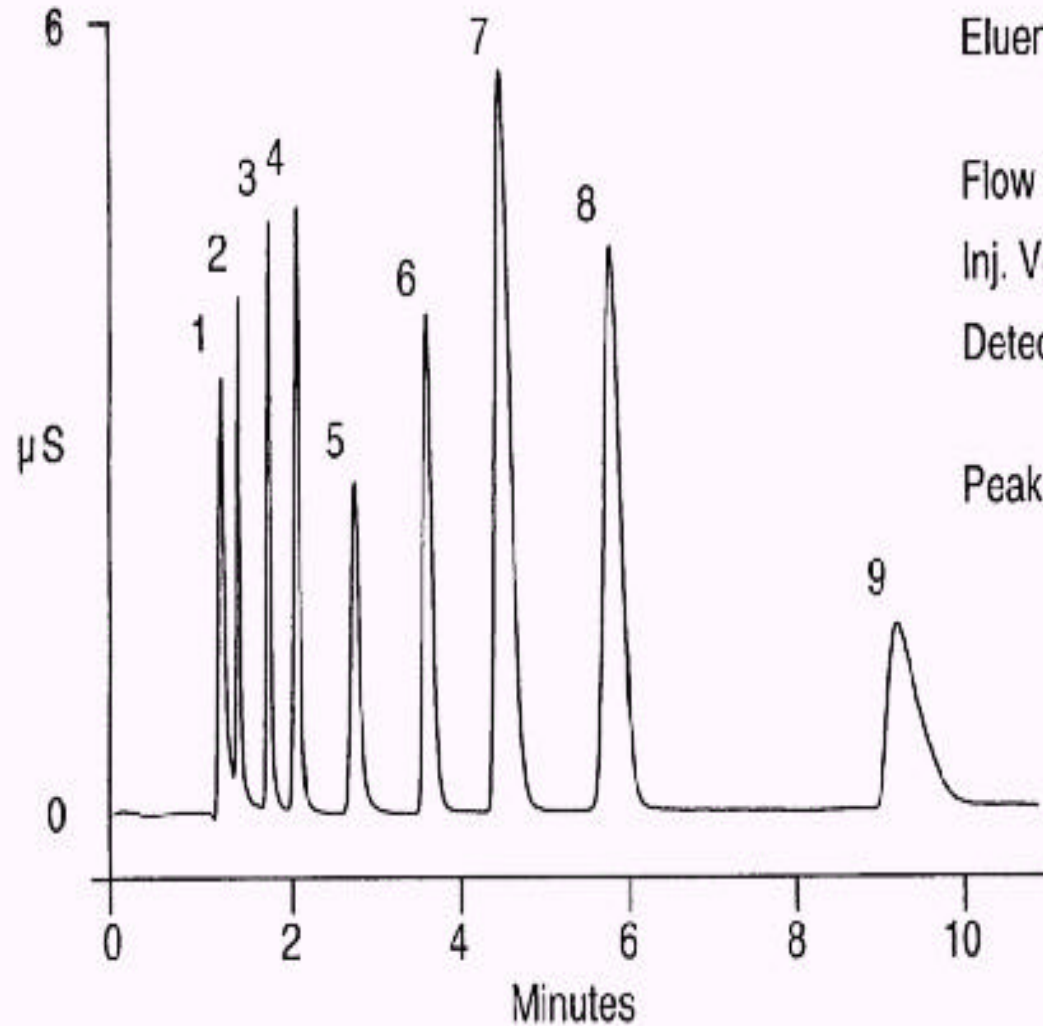
CHARACTERISTICS OF POLARIZABLE ANIONS

- Low hydration energy
- Small hydrated radius (usually)
- Disruptive of water structure (hydrophobic)
- Strong interactions with π electrons
- High refractive index

Development History of Hydroxide Selective Columns



Separation of Polarizable Anions



Column : IonPac® AS11, 4-mm

Eluent: 45 mM Sodium hydroxide
in 40% Methanol

Flow Rate: 1 mL/min

Inj. Volume: 25 μL

Detection: Suppressed conductivity,
AutoSuppression external water mode

Peaks:

1. Fluoride	2 mg/L
2. Chloride	2
3. Nitrate	5
4. Sulfate	5
5. Phosphate	10
6. Iodide	20
7. Thiocyanate	20
8. Thiosulfate	20
9. Perchlorate	20

Perchlorate on the AS11 Column w/ p-Cyanophenol

As11, 25uL, 20ppm ClO₄⁻

Column:

AS11 Column

Eluent:

50 mM Sodium hydroxide

5mM p-Cyanophenol

Flow rate:

1 mL/min

Inj. Volume:

25 μL

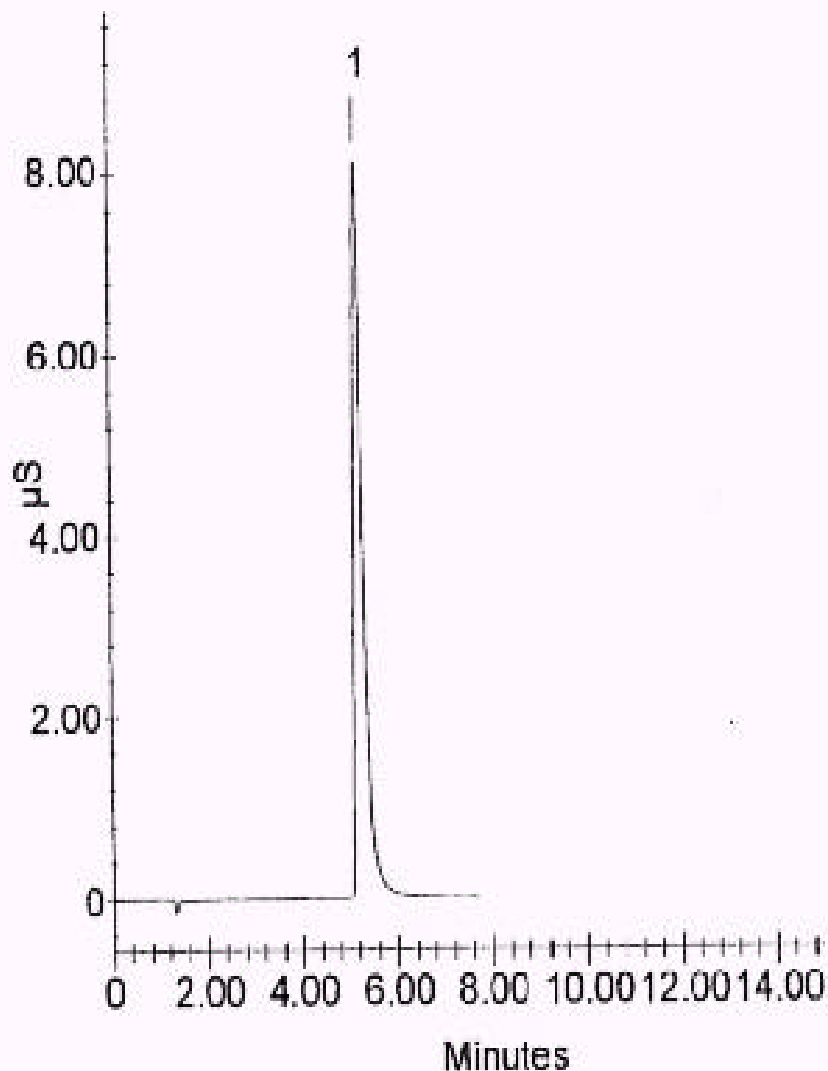
Detection:

Suppressed conductivity, ASRS

AutoSuppression™ recycle mode

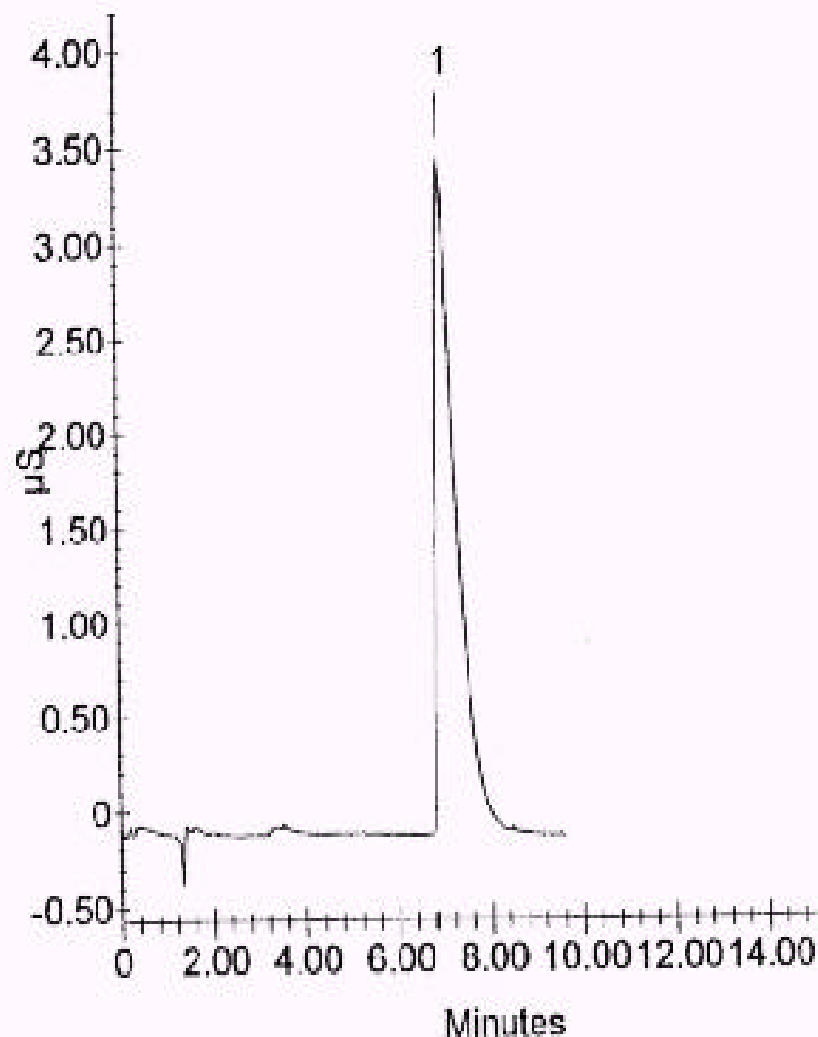
Peaks:

1. ClO₄⁻ 20 ppm



Perchlorate on the AS11 Column w/o Solvent

AS11, 25uL, 20ppm ClO₄⁻



Column:	AS11 Column
Eluent:	100 mM Sodium hydroxide
Flow rate:	1 mL/min
Inj. Volume:	25 μL
Detection:	Suppressed conductivity, ASRS AutoSuppression™ recycle mode
Peaks:	1. ClO ₄ ⁻ 20 ppm

CDHS PERCHLORATE METHOD

- Large loop (740 uL) injection
- Separation on AS5 anion-exchange column
- Eluent of 120 mM NaOH/2 mM p-cyanophenol
- Suppression using AMMS with 35 mM sulfuric acid regenerant
- Measurement using conductivity detector

CDHS PERCHLORATE METHOD SUMMARY

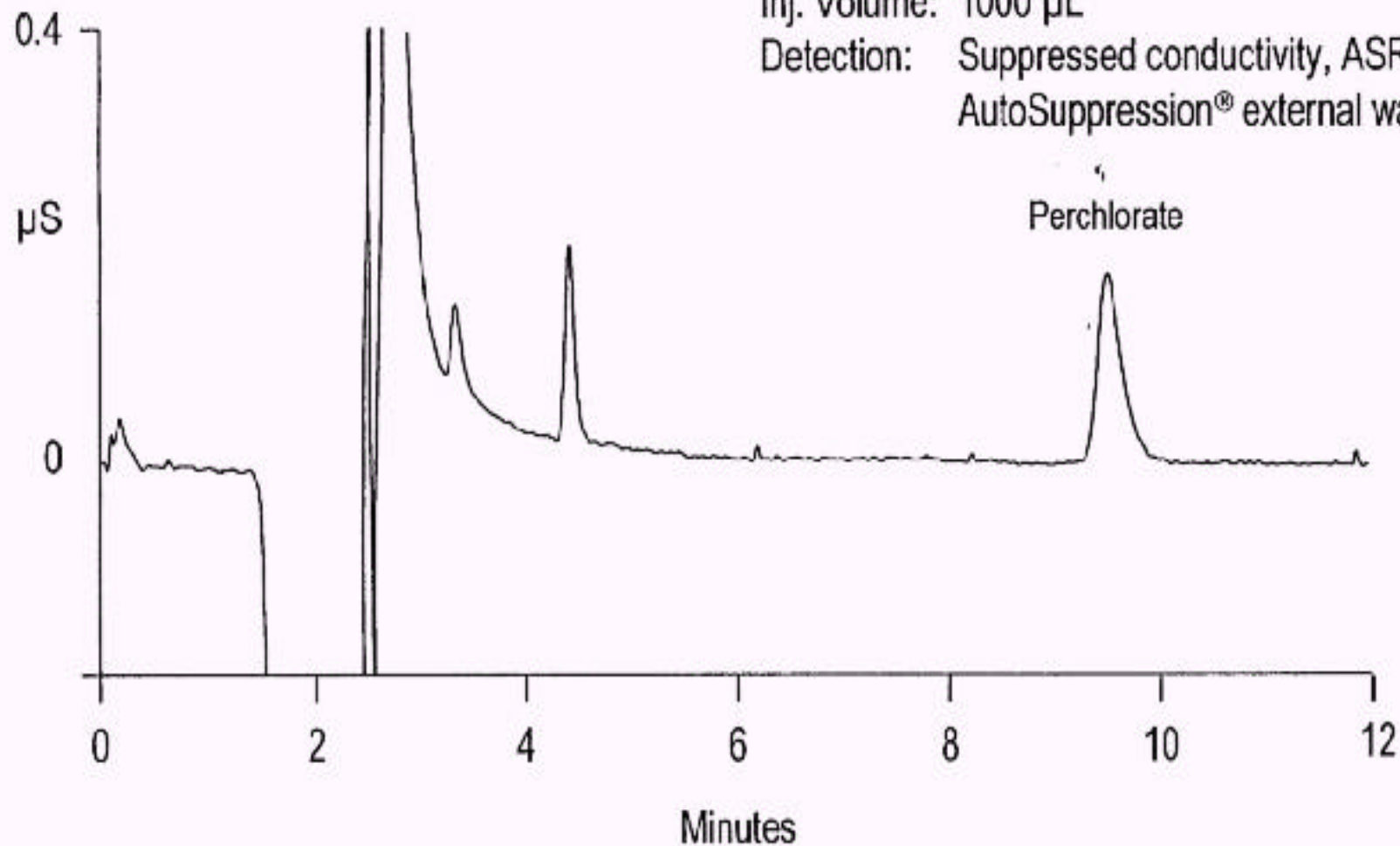
- MDL in reagent water is 0.7 ug/L (ppb)
- MRL in reagent water is 4.0 ppb
- Linear calibration range of 2 to > 100 ppb
- Recovery of perchlorate spikes at the 1-4 ppb level in the range of 87 - 98%

OPTIMIZED DIONEX PERCHLORATE METHOD

- Large loop (1000 uL) injection
- Separation on AS 11 anion-exchange column
- Eluent of 100 mM NaOH (no modifier required)
- Suppression using ASRS with AutoSuppression in external water mode
- Measurement using conductivity detector

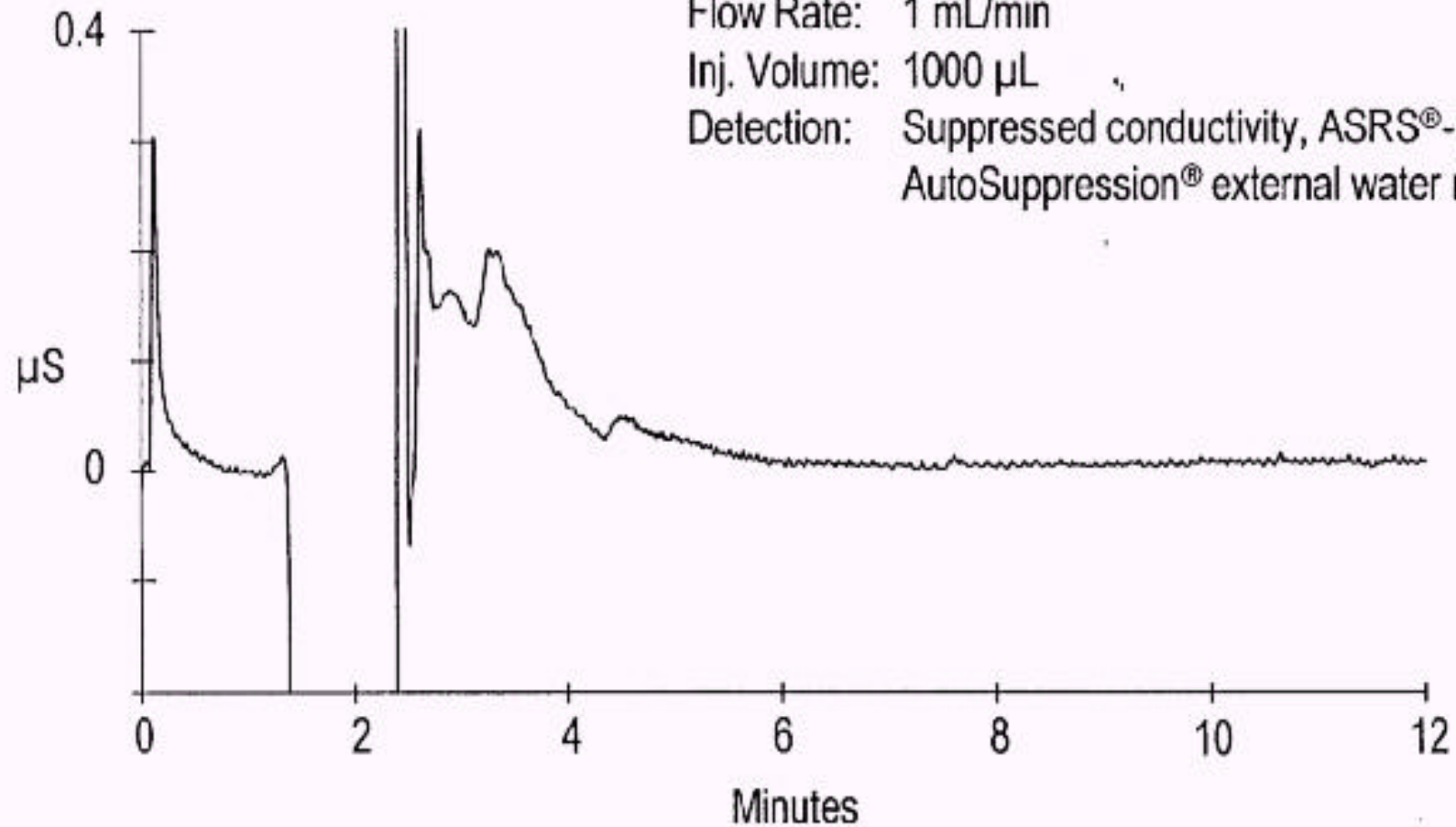
Perchlorate Standard at CA Action Level (18 ppb)

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 μ L
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



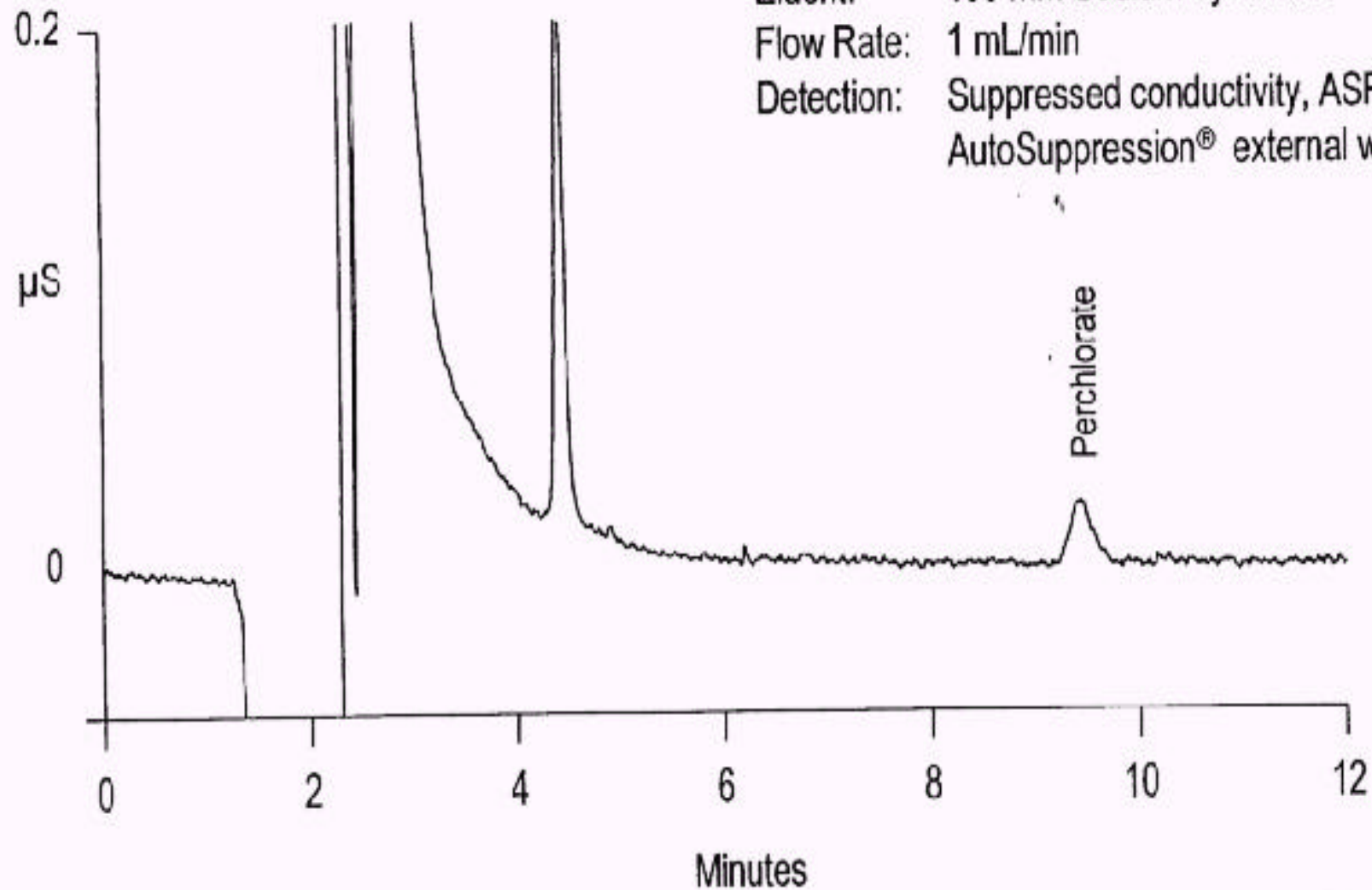
Blank (No Perchlorate) Injection

Column: IonPac® AG11, AS11; DX-120 System
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 μ L
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



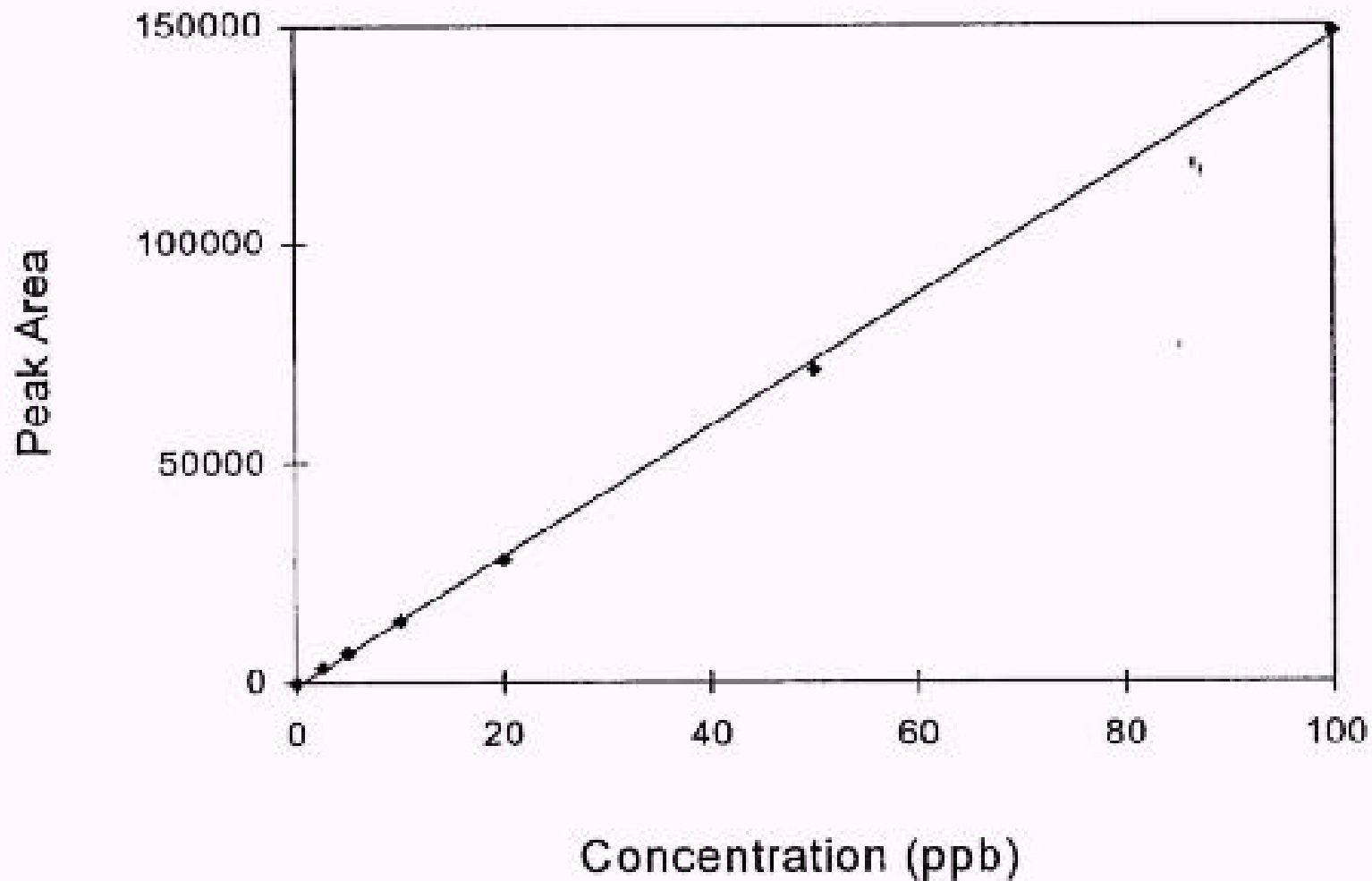
2.5 ppb Perchlorate in Reagent Water

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



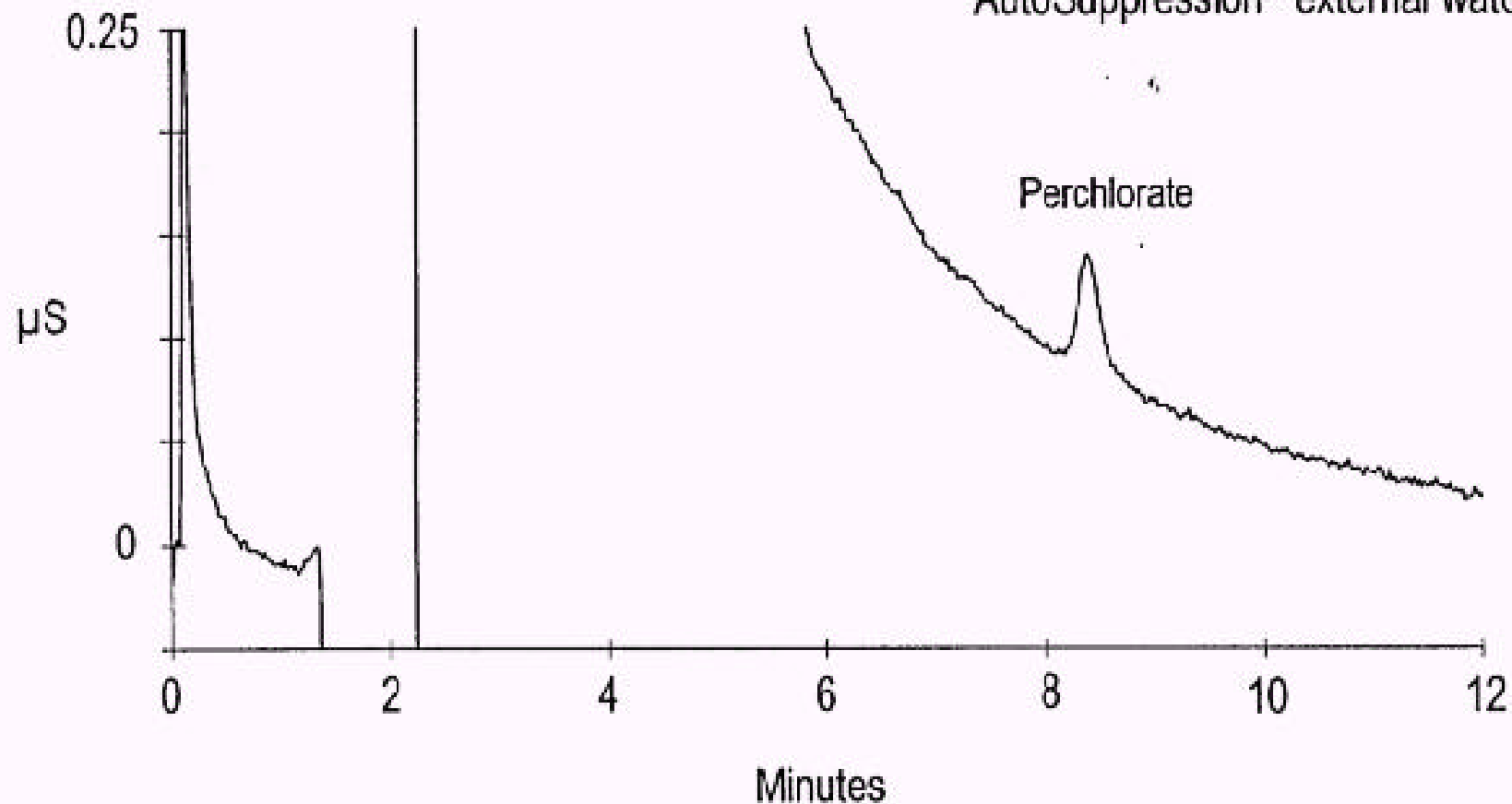
Perchlorate Calibration Curve

2.5 to 100 ppb, $R^2 = 0.9996$



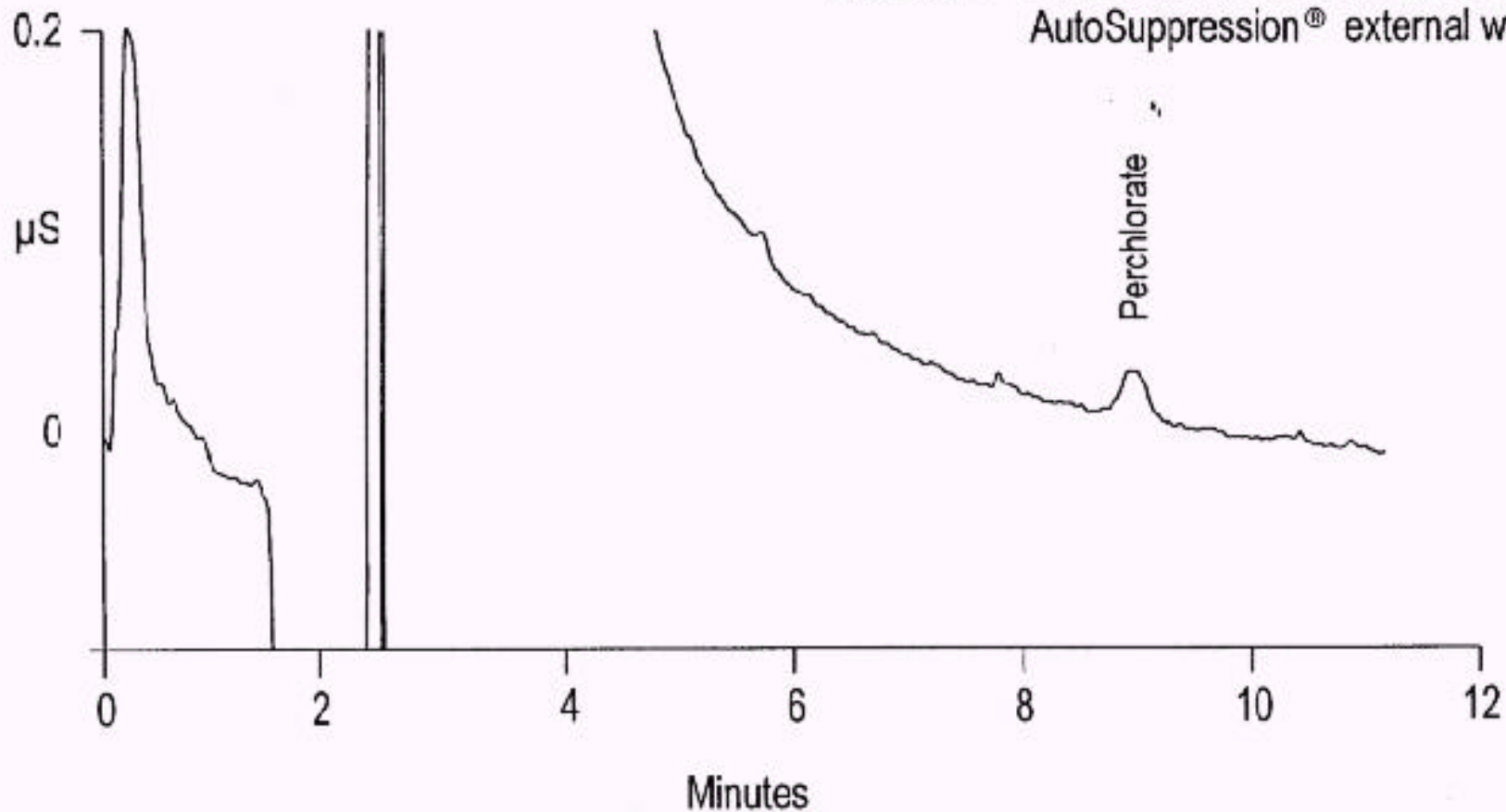
Tap Water Spiked with 4.0 ppb Perchlorate

Column: IonPac® AG11, AS11; DX-120 System
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



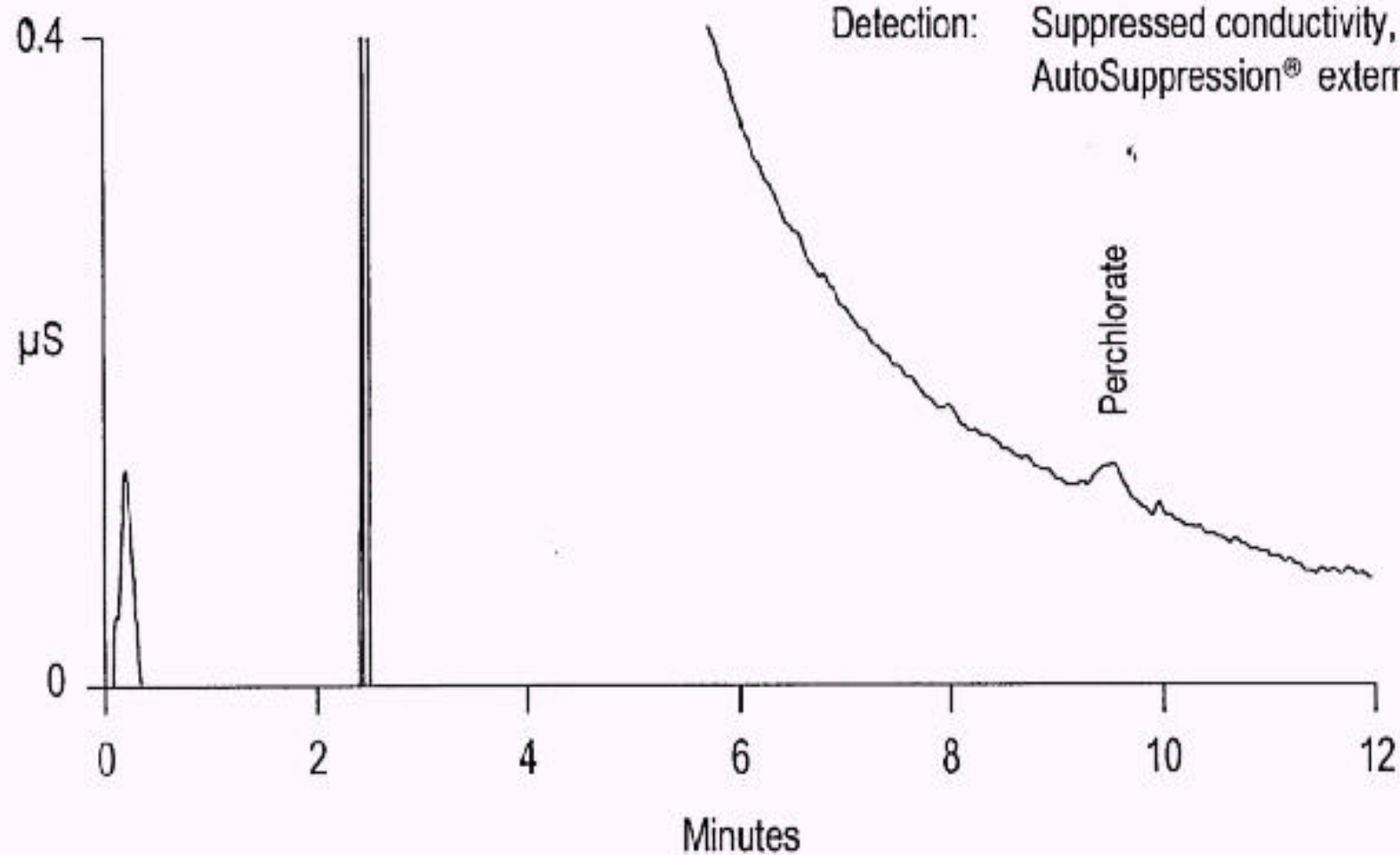
Tap Water Spiked with 2.5 ppb Perchlorate

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



2.5 ppb Perchlorate in High (700 ppm) Sulfate

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 1 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



OPTIMIZED PERCHLORATE METHOD SUMMARY

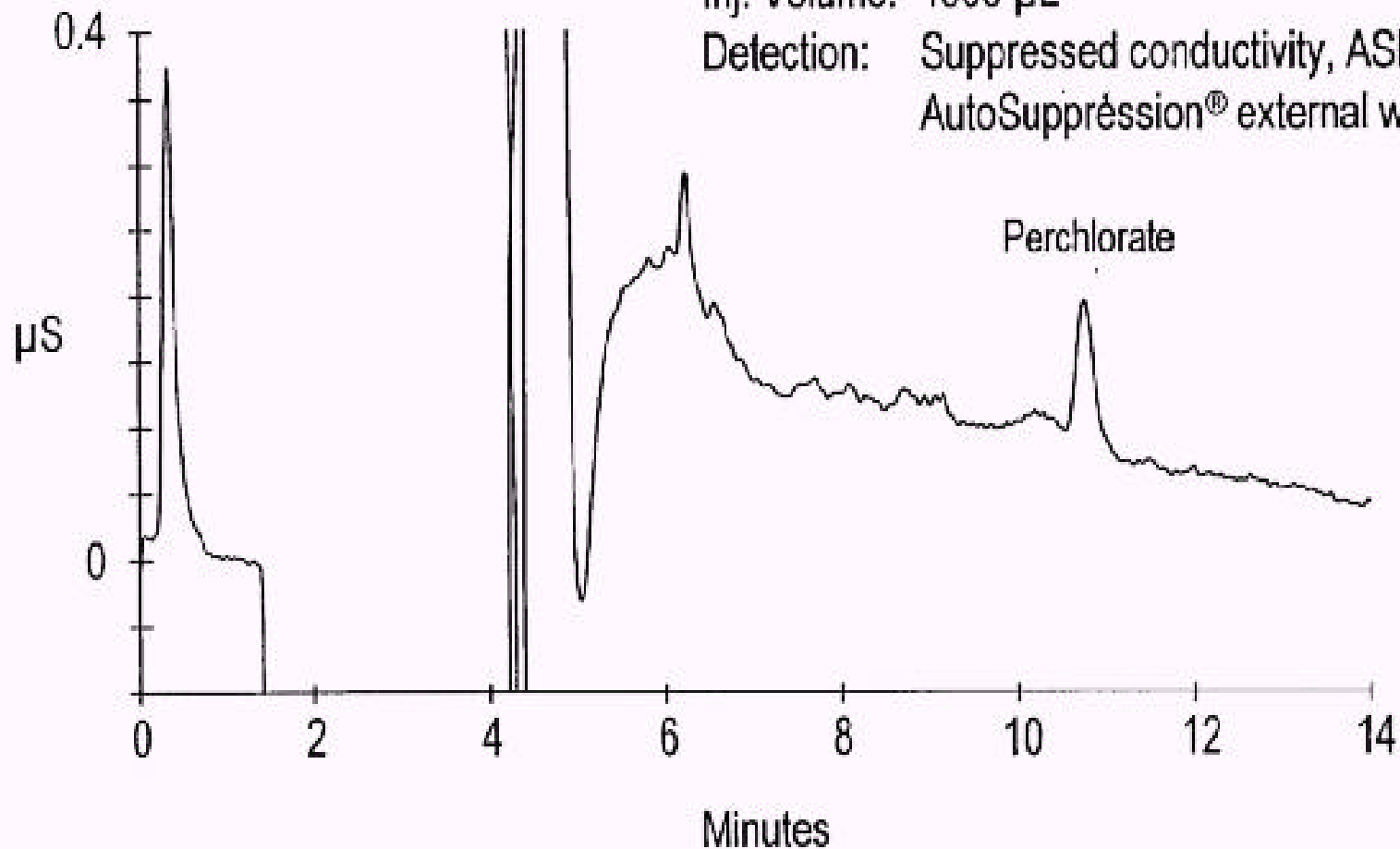
- MDL in reagent water is 0.25 ug/L (ppb)
- MRL in reagent water is ~ 1.0 ppb
- Linear calibration range of 2 to 100 ppb
- Recovery of perchlorate spikes at 2.5 ppb level in the range of 98 - 99%

PERCHLORATE - FURTHER WORK

- Application Laboratory participation in Collaborative Laboratory Study (Col-Lab-I)
- WQTC method presentation
- Use of 2mm AS11 column
- AWWARF project (RFP 2508) collaboration?
- Development of new polarizable anion column
- Application of EG40 to perchlorate analysis

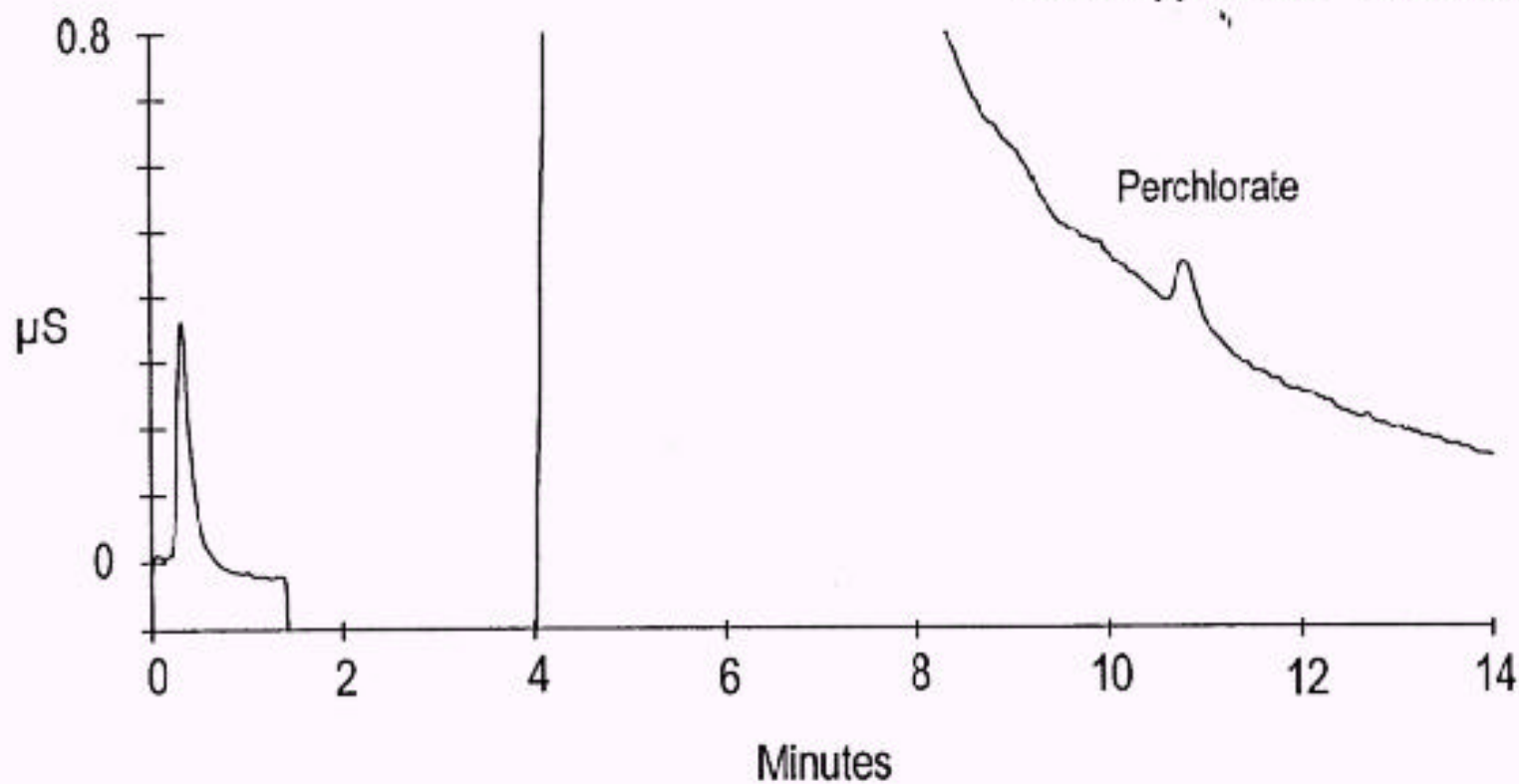
2.5 ppb Perchlorate in Reagent Water, 2mm column

Column: IonPac® AG11, AS11
Eluent: 100 mM Sodium hydroxide
Flow Rate: 0.25 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



Tap Water Spiked with 2.5 ppb Perchlorate

Column: IonPac® AG11, AS11 - 2mm
Eluent: 100 mM Sodium hydroxide
Flow Rate: 0.25 mL/min
Detection: Suppressed conductivity, ASRS®-II
AutoSuppression® external water mode



CONCLUSIONS

- Optimized, interference free method for analysis of low ug/L perchlorate in ground and tap water
- Method based on 1000 uL injection, AS11 column, 100 mM NaOH eluent and suppressed conductivity detection using ASRS
- MDL of 0.25 ug/L, MRL of ~ 1.0 ug/L
- Linear calibration range of 2 to 100 ug/L
- Recovery of 98-99% at 2.5 ug/L level

GLOSSARY OF TERMS

- **Ion Chromatography** - Separation-based technique for the analysis of ionic species; typically uses suppressed conductivity detection
- **Eluent** - Ionic solution used to “elute” or push ionic species through analytical (separator) column
- **Analytical Column** - Resin filled tube which separates ionic species (based on ion exchange interactions) into discrete bands prior to detection
- **Suppressor** - Membrane-based device used to reduce eluent conductance and enhance target analyte sensitivity
- **MDL** - Method Detection Limit. Students t-test at the 99% confidence limit applied to 7 replicate injections at ~3x detection limit
- **MRL** - Minimum Reporting Limit. Minimum quantifiable level which may be reported; typically 5x the MDL

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