Ion Chromatographic Methods Update: Perchlorate, Bromate and More

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DIONEX

Presentation Outline

- Other Anions and Cations of Environmental Interest
- Perchlorate Methods Update
  - Historical Perspective from last EPA Region VI QA Conference
  - Review current issues driving Perchlorate method development
  - Method 314.1 – IC suppressed conductivity with pre-concentration technique and confirmatory column
  - Method 330.0 – IC/MS and IC/MS-MS
  - Method 331.0 – LC/MS and LC/MS-MS
- Conclusion
- Acknowledgements

Selected Updates to EPA Methods Using RFIC™

- AS18 and new AS19 column for Method 300.0 (A)[1] and 300.1 (A)[1]
- New AS19 column for common anions and oxyhalides using Methods 300.0 (B)[2] and 300.1 (B)[2]
- CS16 column using ASTM Method 6919-03[3] for cations by RFIC
- Perchlorate
  - Method 314.1[4]: Preconcentraion/Matris Rinse RFIC
    - New Cryptand C1 concentrator column
    - AS16 and New AS20 analytical columns
  - IC/MS for perchlorate
  - IC/MS–MS for perchlorate

[1] EPA approved for drinking water and wastewater compliance monitoring
[2] EPA approved for disinfection by-product
[3] EPA proposed for drinking water and wastewater compliance monitoring
[4] Method using cooperatively developed by EPA and Dionex

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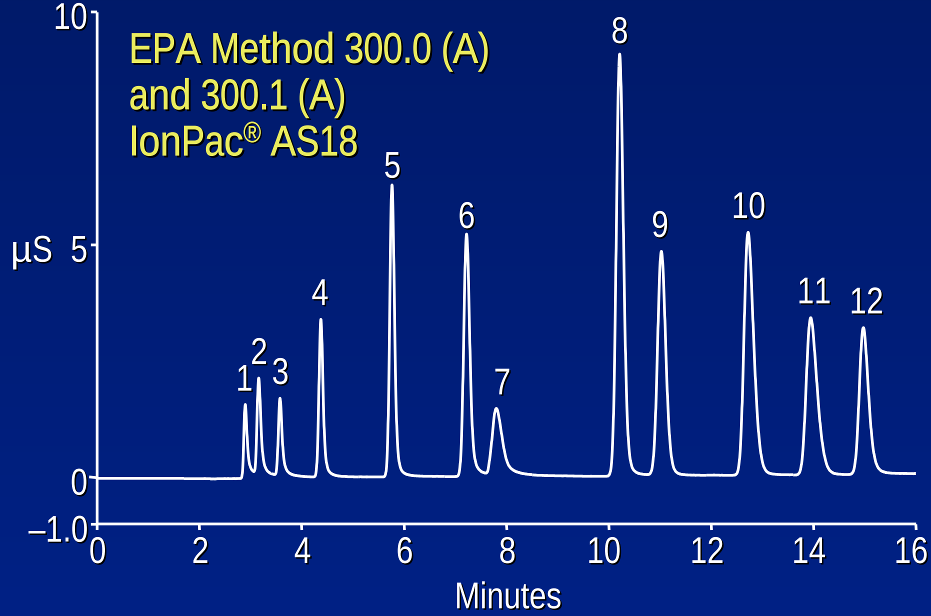
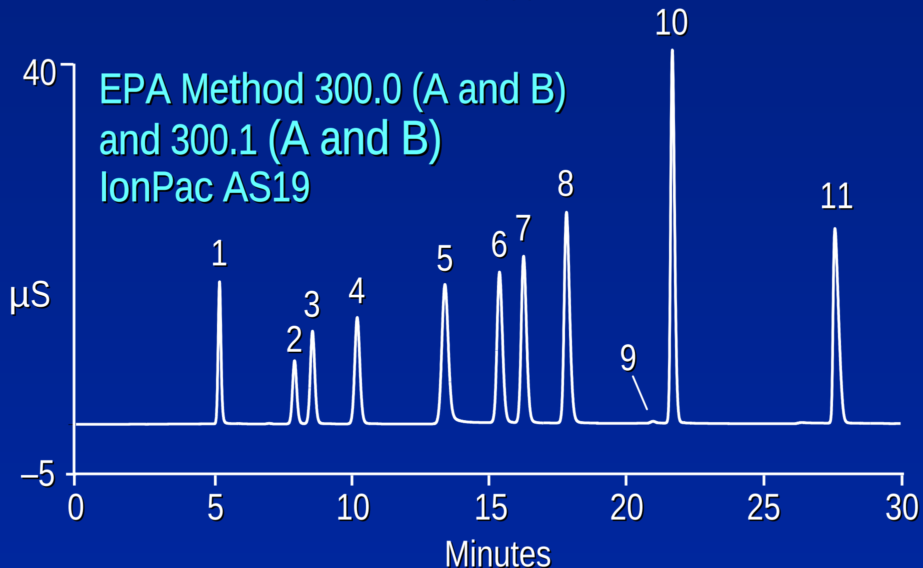
RFIC™ for EPA Anion Methods



Peaks:		
1.	Fluoride	0.5 mg/L (ppm)
2.	Acetate	2.5
3.	Formate	1.0
4.	Chlorite	5
5.	Chloride	3
6.	Nitrite	5
7.	Carbonate	20
8.	Sulfate	10
9.	Bromide	10
10.	Nitrate	10
11.	Chlorate	10
12.	Phosphate	10



Peaks:		
1.	Fluoride	2 mg/L (ppm)
2.	Chlorite	10
3.	Bromate	20
4.	Chloride	6
5.	Nitrite	15
6.	Chlorate	25
7.	Bromide	25
8.	Nitrate	25
9.	Carbonate	–
10.	Sulfate	25
11.	Phosphate	40

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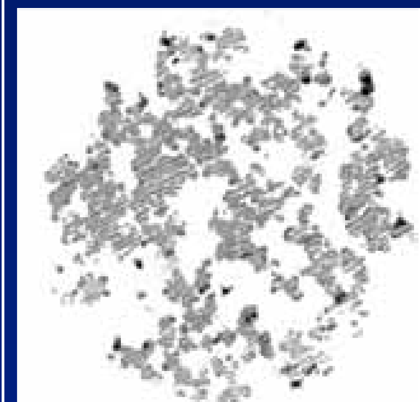
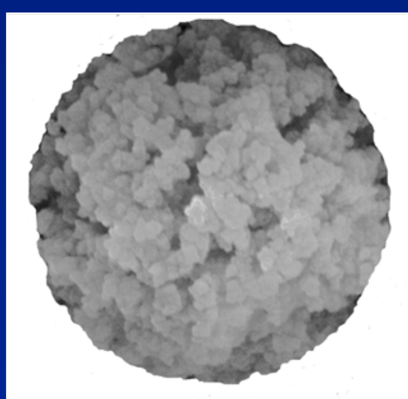
Preparation and Anatomy of AS9HC Resin

TEM of bead crossection



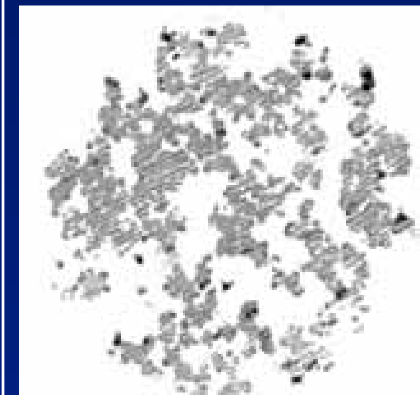


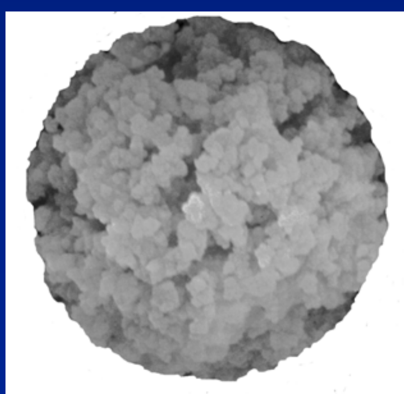
SEM of SMP bead

Cartoon of surface modification

Preparation and Anatomy of AS19 Resin

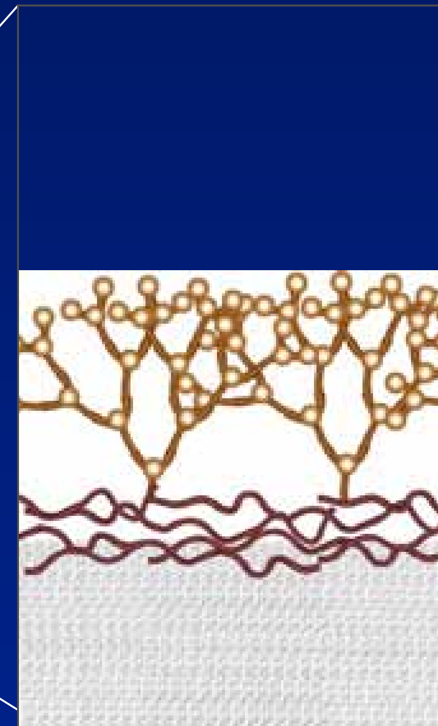
TEM of bead crossection



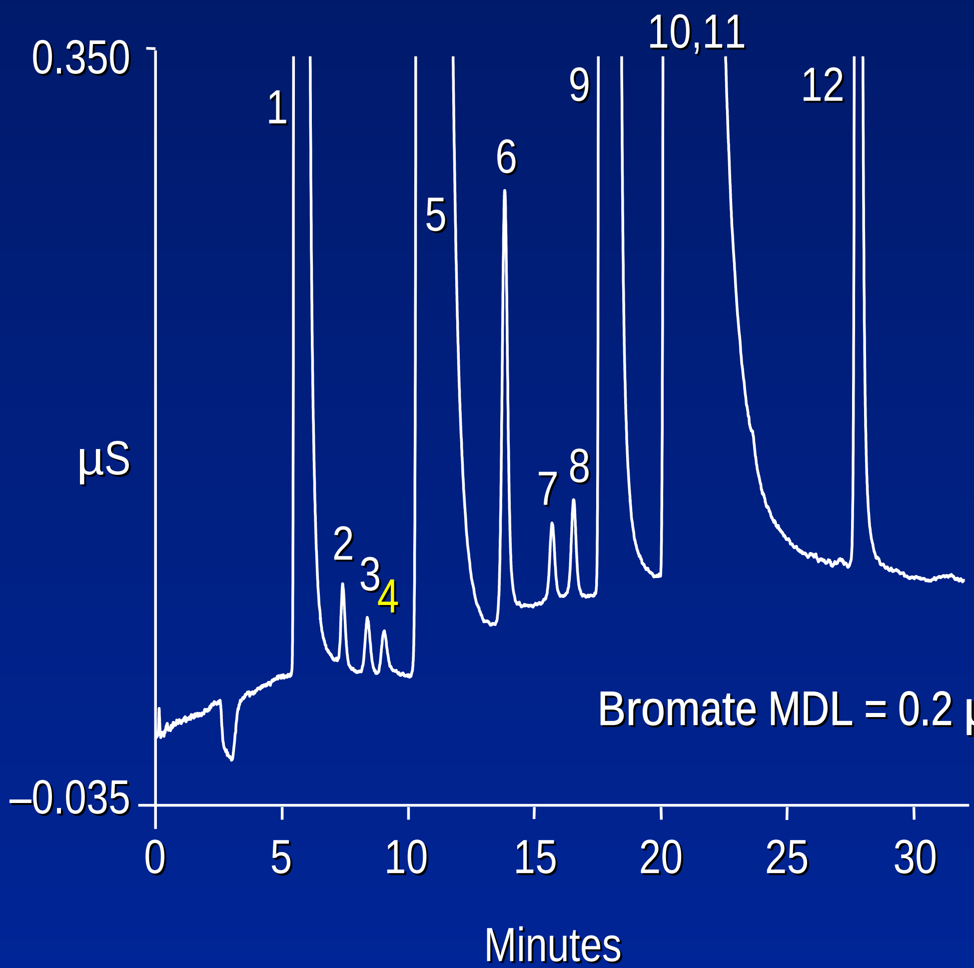


SEM of SMP bead

Cartoon of surface modification



Determination of ppb Bromate in Drinking Water



Bromate MDL = 0.2 µg/L

MDL = SD x t_s (n = 7), t_s = 3.14

Column: IonPac® AG19, AS19, 4 x 250 mm
Eluent : Potassium hydroxide: 10 mM from 0 to 10 min, 10–45 mM from 10 to 25 min
Eluent Source: EGC II KOH cartridge with CR-ATC
Flow Rate: 1.0 mL/min
Temperature: 30 °C
Suppressor: ASRS® ULTRA II, 4 mm, AutoSuppression® external water mode, 300 mA
Injection Vol.: 500 µL

Peaks:

		mg/L (ppm)
1.	Fluoride	1
2.	Formate	–
3.	Chlorite	0.005
4.	Bromate	0.005
5.	Chloride	50
6	Nitrite	0.005
7.	Chlorate	0.005
8.	Bromide	0.005
9.	Nitrate	10
10.	Carbonate	25
11.	Sulfate	50
12.	Phosphate	0.2

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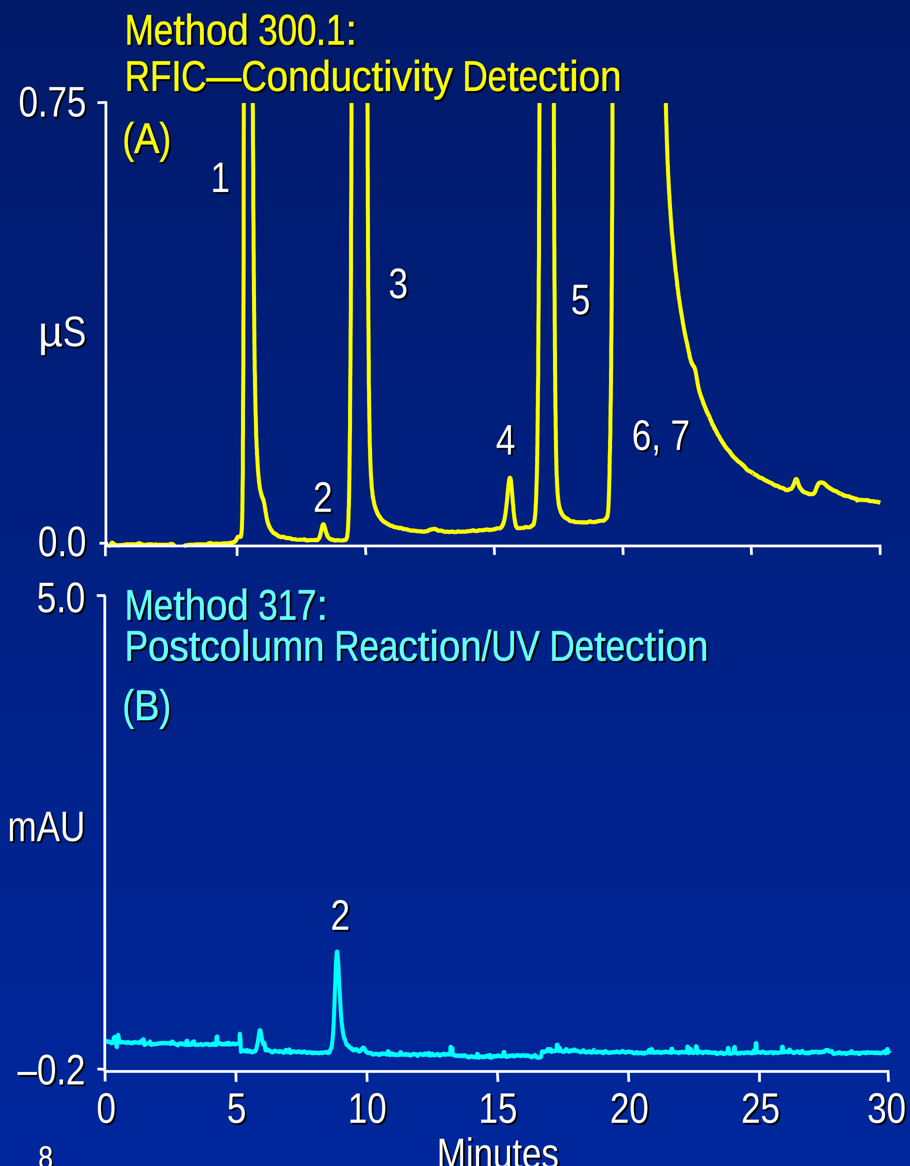
Bromate in Bottled Drinking Water Using RFIC™—Conductivity and Postcolumn Reaction Detection



Column: IonPac® AG19, AS19, 4 mm

Eluent: 10 mM KOH from 0 to 10 min
10–45 mM from 10 to 25 min

Eluent Source: EG50 with CR-ATC

Temperature: 30 °C

Flow Rate: 1 mL/min

Inj. Volume: 250 µL

Detection: (A) Suppressed conductivity,
ASRS® ULTRA II, 4 mm, ext. water mode
(B) Absorbance, 450 nm

Postcolumn Reagent: o-Dianisidine

PCR Flow Rate: 0.54 mL/min

Postcolumn Heater: 60 °C

Peaks:	(A)	(B)	
1. Fluoride	0.45		mg/L (ppm)
2. Bromate	0.010	0.010	
3. Chloride	5.7		
4. Bromide	0.018		
5. Nitrate	3.1		
6. Carbonate	—		
7. Sulfate	10.0		

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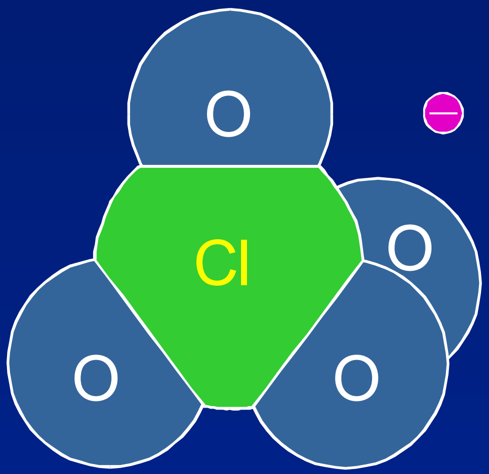
Presentation Outline 2003
Historical Perspective

- The Perchlorate Issue
- Review of EPA Method 314.0
- Status of IC Conductivity Method
  - Suppressor Improvements for Better Sensitivity
  - Sample Pretreatment for Matrix Removal and Detection Limit Enhancement
  - Second Column Confirmation with the Cryptand A1 Column
  - Automated Sample Preconcentration for Matrix Removal and Lower Detection Limits
- Status of IC-MS Method Development
  - Performance Enhancement with Matrix Diversion (MD)-IC-MS
  - Improve Electrolytic Suppressor for MD-IC-MS
  - Performance Enhancement with Solvent Wash MD-IC-MS
  - IC-MS/MS Collaborative Study, Preliminary Data

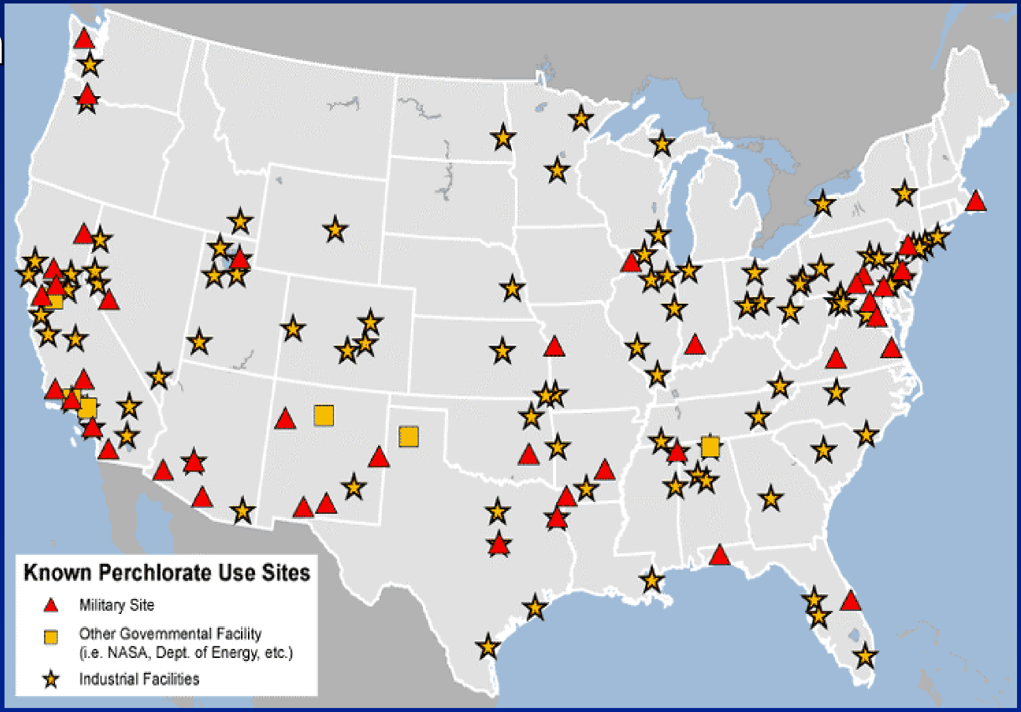
Perchlorate
General Chemistry

- The perchlorate anion (ClO_4^-) is a tetrahedral array of oxygen atoms around a central chlorine atom.
- The oxidation state of the chlorine is +7
- Perchlorate is a strong oxidizing agent (slightly weaker than dichromate or permanganate)
- Perchlorate reduction is extremely nonlabile (slow) and "rarely" observed in chemical systems
- Perchlorate is not reduced in 0.1-4.0 M acid;
- Other than some bacterial systems, perchlorate reduction is not observed
- *Perchlorate is very stable in the chromatographic conditions encountered IC applications (i.e. sample matrix and eluents)*



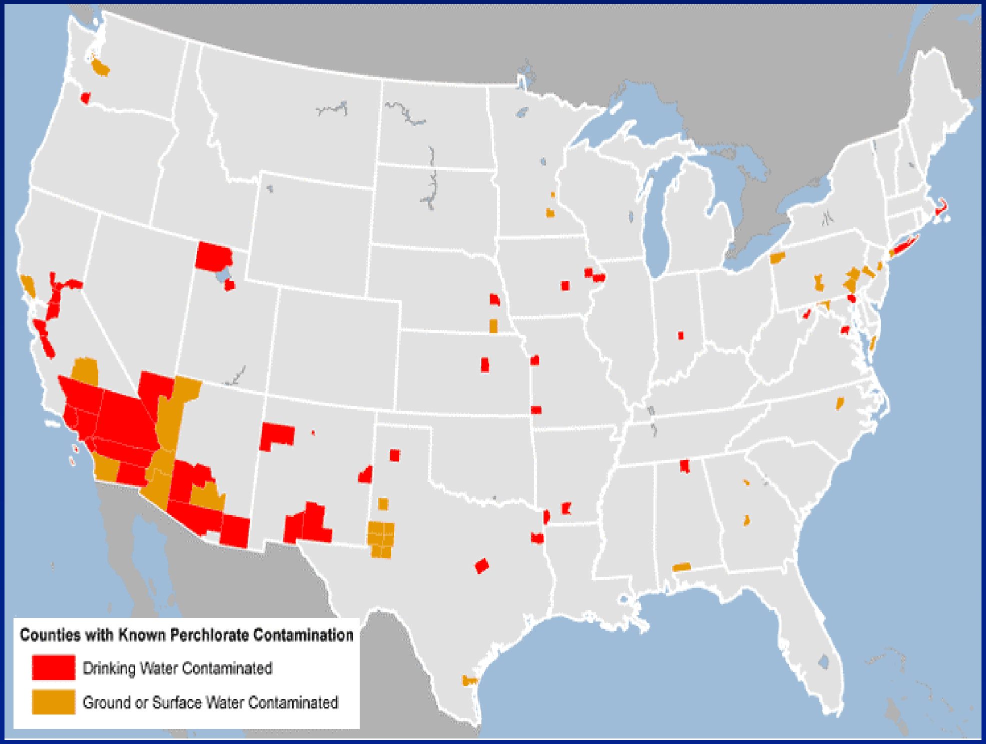
Sources of Perchlorate Contamination

- Rocket fuel production and waste disposal
- Munitions and explosives production and waste disposal
- Fireworks production, use and disposal
- Road flare production and disposal
- Hazardous waste disposal sites
- Phosphoric acid added to food and beverage products
- Indiscriminate chemical disposal



Where Perchlorate Has Been Found in Significant Concentrations (>1 ppb)

- Drinking water
  - Twenty states in the U.S.
- Aquifers associated with disposal sites
- Lakes and rivers associated with contaminated aquifers
  - Lake Mead (NV)
  - Colorado River (NV, CA, AZ)
- Crops irrigated by contaminated water
- Other foods (e.g., milk)

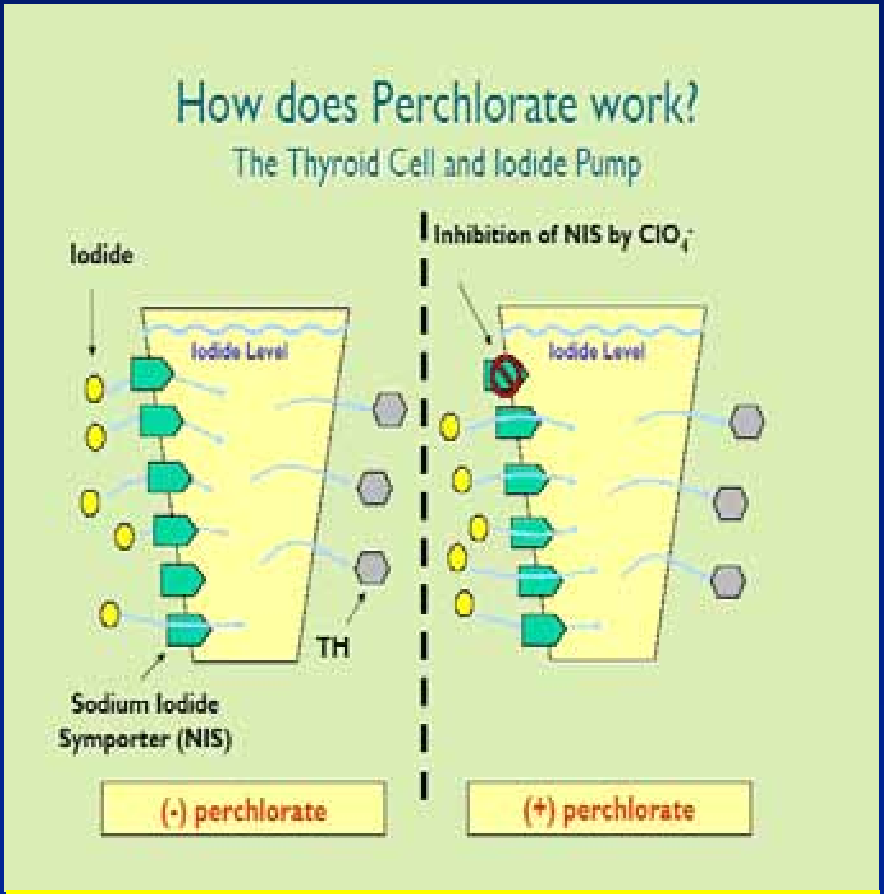


Perchlorate Health Issues*

"Perchlorate interferes with the iodide uptake into the thyroid gland."

- Interferes with thyroid hormone production
- Interferes with thyroid regulation of metabolism
- Interferes with neurological development of fetus and newborn
  - Behavior changes
  - Delayed development
  - Decreased learning capability
- Changes in thyroid hormone levels may result in thyroid gland tumors

* U.S. EPA website (www.epa.gov)



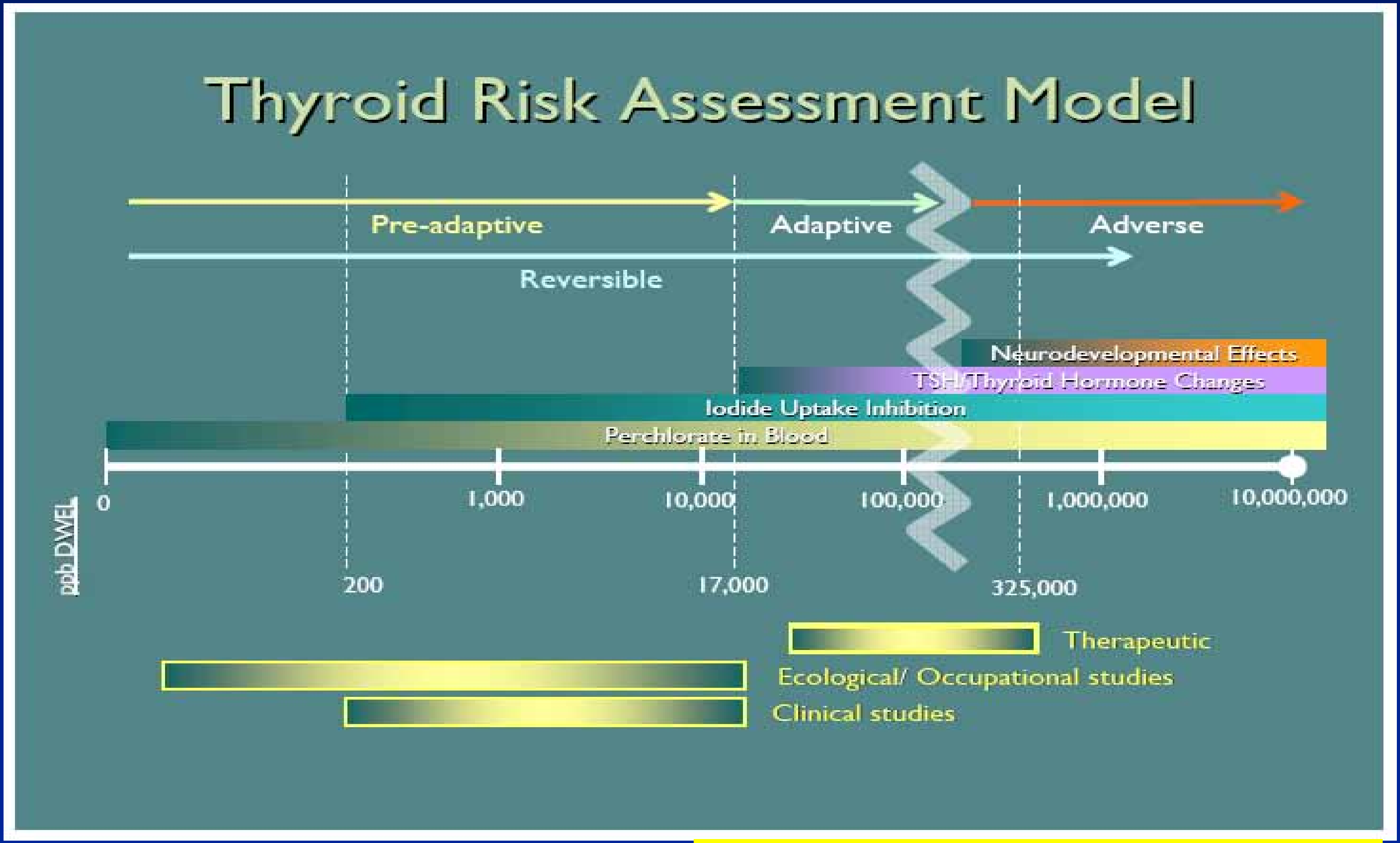
Courtesy of Richard Pleus, Intertox

Perchlorate—Preliminary Draft Toxicity Assessment

- EPA Draft Reference Dose (RfD)*
  - Exposure level, without appreciable risk of adverse affects over a lifetime: 0.00003 mg/kg/day
- Assessment considered perchlorate effect on:
  - Developing nervous system, including sensitive subgroups
  - Thyroid tumors
- Assumptions in conversion of RfD to drinking-water-equivalent level
  - 70 kg body weight
  - 2 L of water consumption per day
- EPA proposed drinking water limit = 1 µg/L (ppb)

* U.S. EPA website (www.epa.gov)

Another Perspective



Courtesy of Richard Pleus, Intertox

U.S. EPA Unregulated Contaminant Rule (UCMR)

- Initial UCMR I (1999) monitoring requirement
  - Required major drinking water utilities to monitor and report perchlorate levels for two years
  - Must use EPA Method 314.0 to quantify perchlorate
- UCMR II update (est. 2005)
  - Will require major water utilities to again monitor and report perchlorate levels in finished drinking water
  - Must use one of these EPA methods*:

    Method 314.1** – IC-Suppressed Conductivity (preconcentration)

    Method 330.0** – IC-MS or IC-MS-MS

    Method 331.0** – LC-MS-MS

    Note: Must be able to quantify sub-ppb of perchlorate, even in a matrix with 1000 ppm, each, chloride, bicarbonate, and sulfate

* *If Perchlorate >1 ppb, must ensure the value is really perchlorate by analyzing with a confirmatory method*

** *Under joint development with EPA and Dionex*

Review of EPA Method 314.0 for Perchlorate
Revision 1.0, November 1999

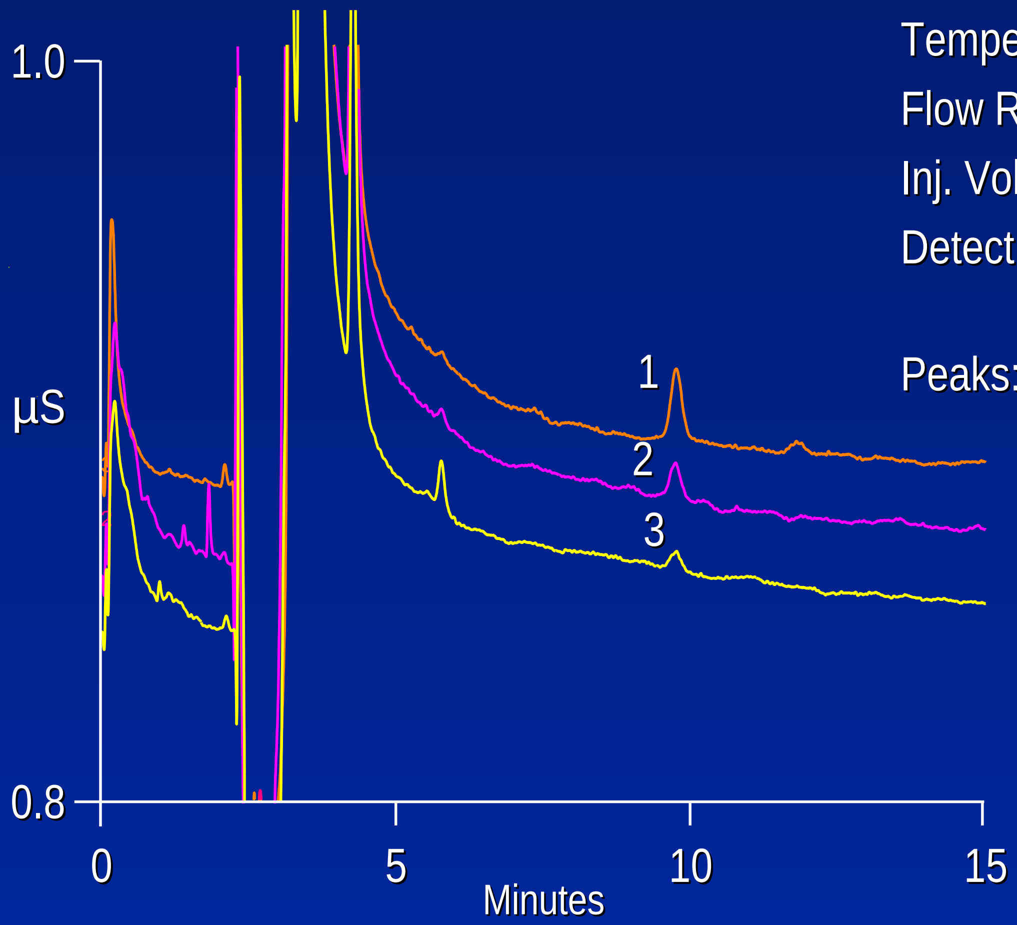
- Analytical method: ion chromatography with suppressed conductivity detection
- Key operating conditions

Column:	IonPac® AG16, AS16, 4-mm
Eluent:	50 mM sodium hydroxide
Flow Rate:	1.5 mL/min
Suppressor:	ASRS® ULTRA, external water mode
Sample Loop:	1,000 µL

- Method must deliver adequate column efficiency (peak area/height ratio – A/H) to allow quantification at the required MDL in a sample with high total dissolved solids (TDS)
- Must be able to quantify in a test matrix of chloride, carbonate, and sulfate at 600 mg/L each (TDS_{600})

Trace-Level Perchlorate Using the ASRS® ULTRA II

ICS-2000



Column:	IonPac® AG16, AS16 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 with EGC and CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Inj. Volume:	1000 µL
Detection:	ASRS ULTRA II, recycle mode

Peaks:

1. Perchlorate	2.0	µg/L (ppb)
2. Perchlorate	1.0	
3. Perchlorate	0.5	

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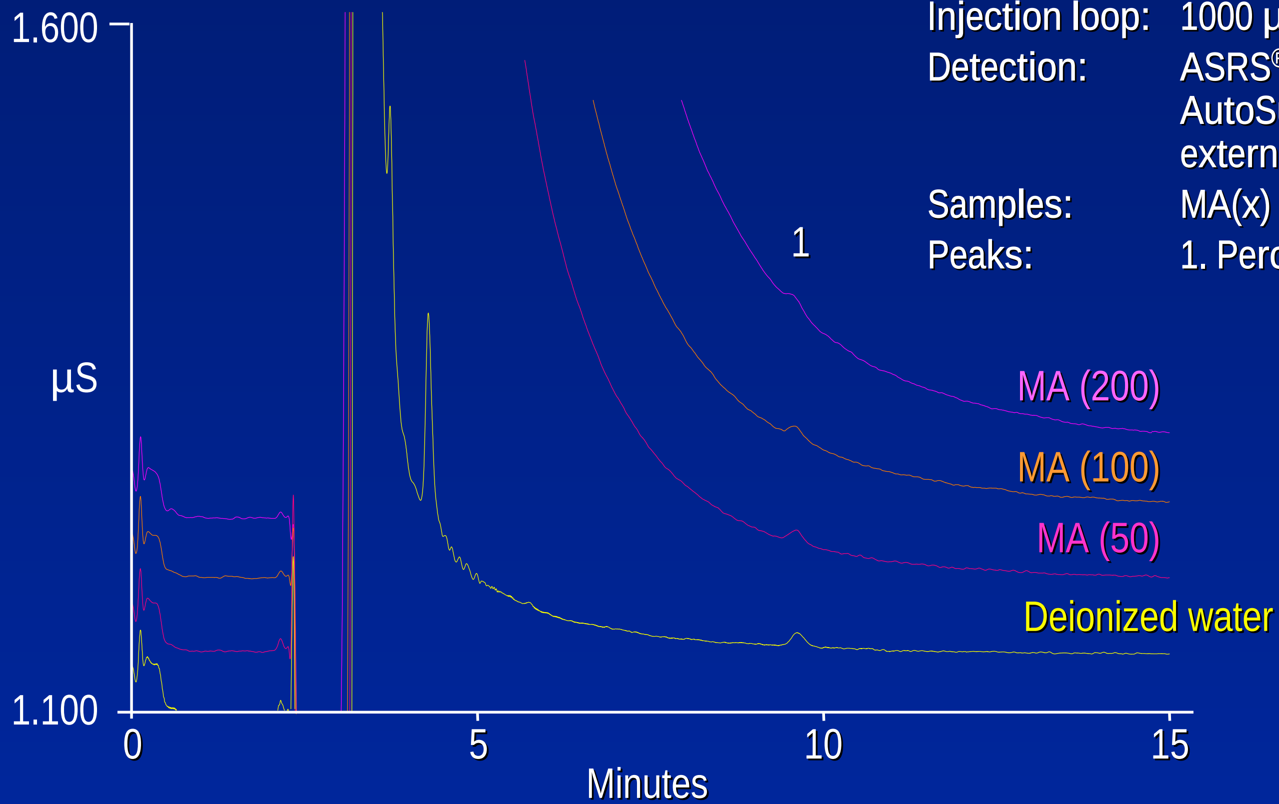
EPA Method 314.0

Determination of 1 µg/L Perchlorate with Increasing Concentrations of Chloride, Sulfate, and Carbonate

Column:	IonPac® AG16, AS16, 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 EG with CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Injection loop:	1000 µL
Detection:	ASRS® ULTRA II, AutoSuppression®, external water mode, 193 mA
Samples:	MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}
Peaks:	1. Perchlorate 1 µg/L



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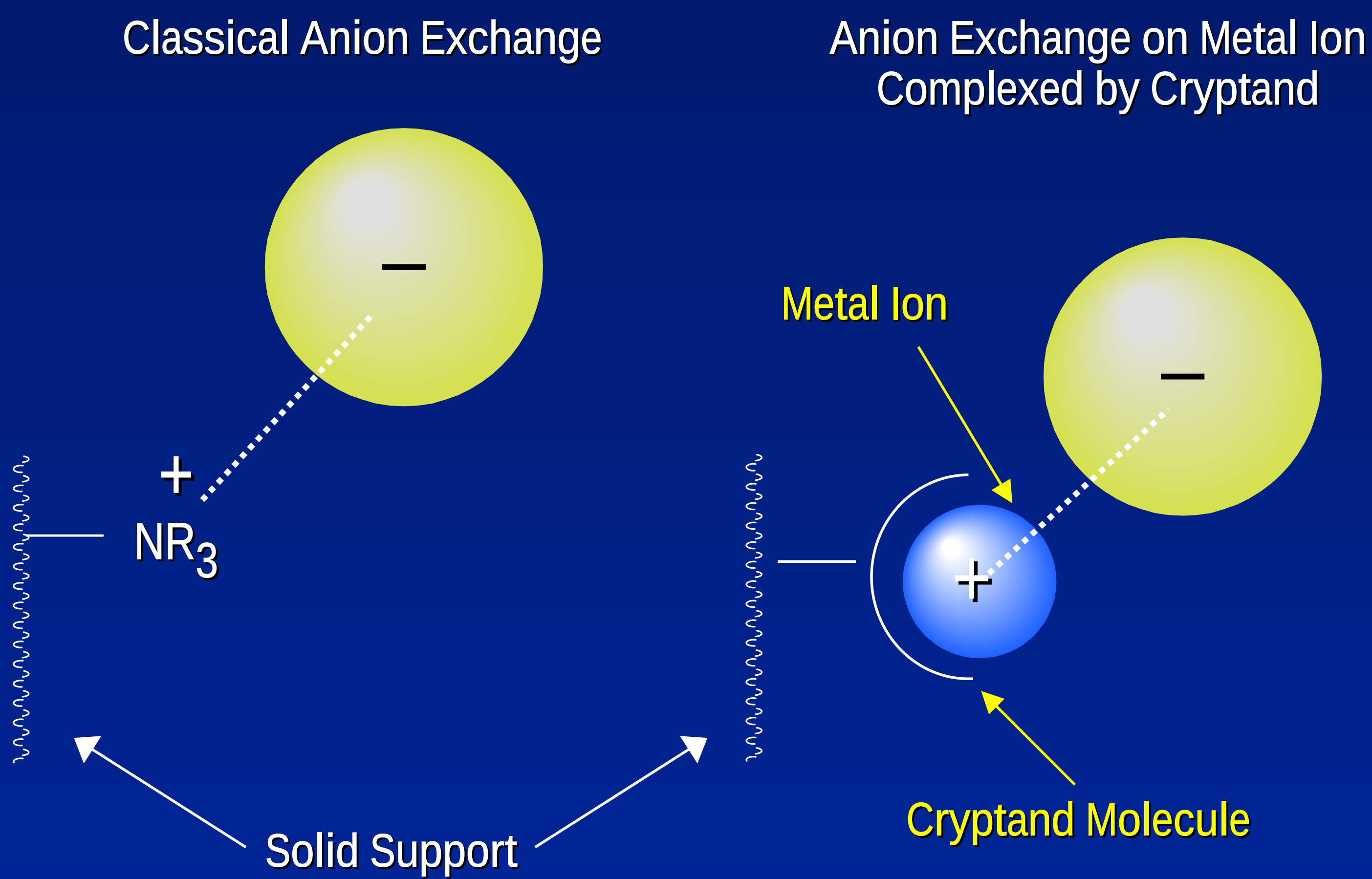
EPA Method 314.1*

Perchlorate Analysis Using RFIC™ with Preconcentration and Matrix Rinse

Eluent:	Electrolytically generated NaOH
Flow Rate:	0.25 mL / min
Preconcentration Column:	Cryptand C1
Analysis Column Set	
Primary Method:	IonPac® AG16, AS16, 2 mm
Confirmatory Method:	IonPac AG20, AS20, 2 mm
Volume Concentrated:	3 mL
Suppressor:	ASRS® ULTRA II, 2 mm
Detector:	Conductivity

* Under joint development by EPA and Dionex

Comparison of a Classical IC Trap Column and an IonPac® Cryptand C1 Concentrator Column



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Binding of Cryptand Ligand with Eluent Cations

IonPacA1 Column

Ligand (L) =

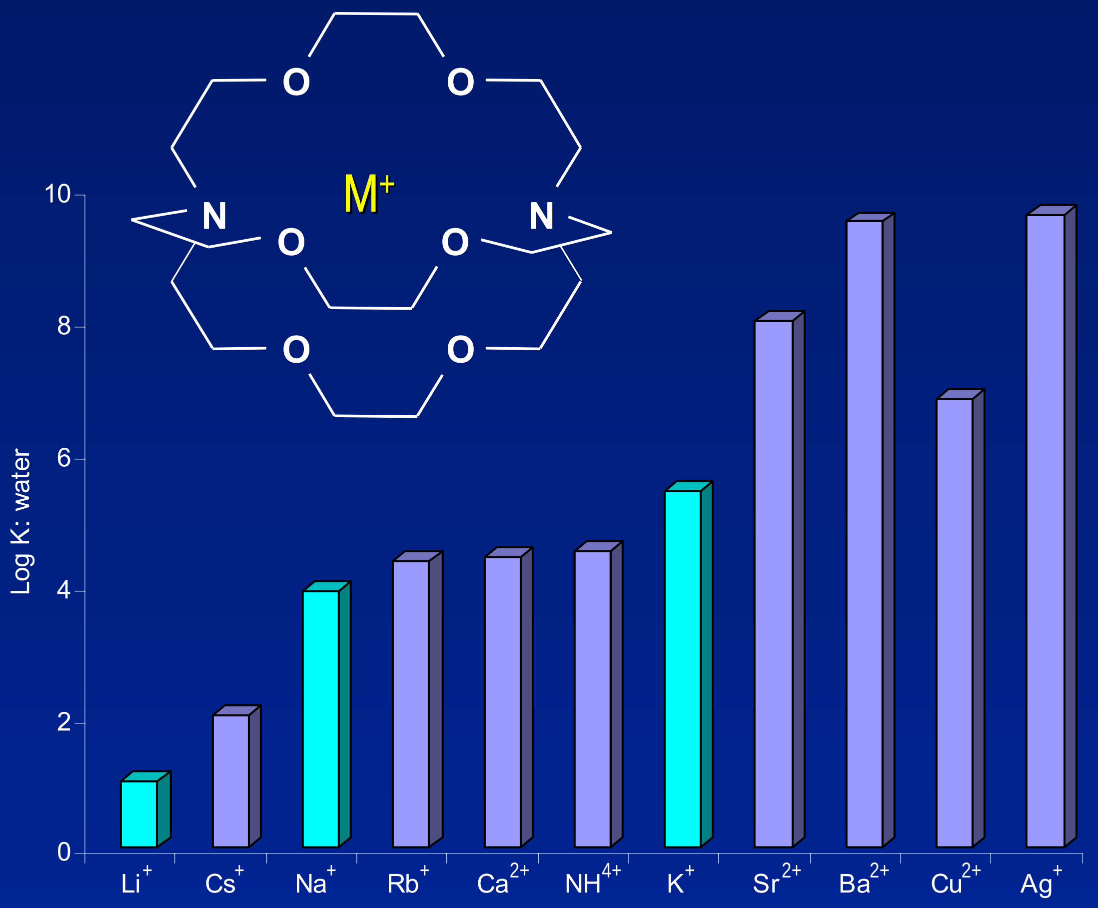
Cryptand 2,2,2

Eluent Cation (M^+) =

Li^+, Na^+, K^+ , etc.

Binding constant (K) =

$$\frac{[L - K^+]}{[L][K^+]}$$



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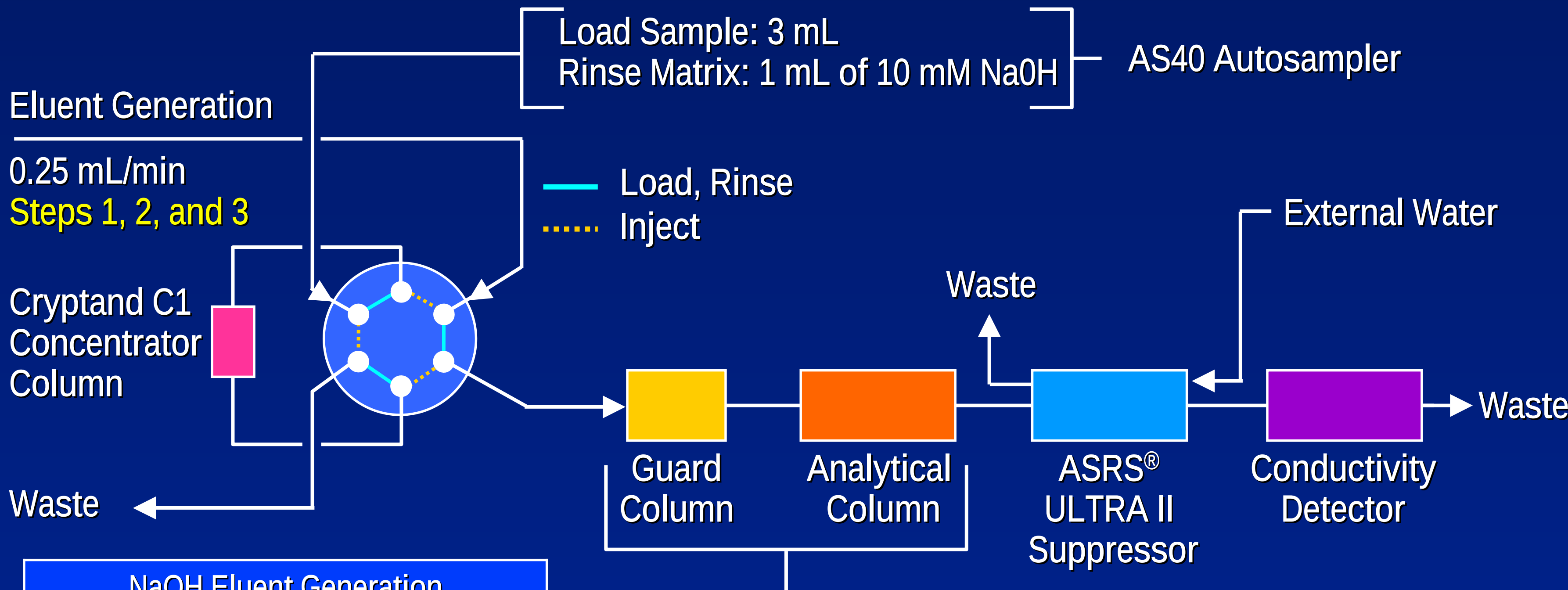
Perchlorate Analysis Using RFIC™ with Preconcentration and Matrix Rinse—EPA Method 314.1*



Primary Method — AG16, AS16 (2 x 250 mm)

Confirmatory Method — AG20, AS20 (2 x 250 mm)

NaOH Eluent Generation			
Steps	Function	Conc.	Time
1.	Perchlorate Transfer	0.5 mM	12 Min
2.	Analysis	65 mM	13 Min
3.	Column Cleanup	100 mM	5 Min

* Under joint development by EPA and Dionex

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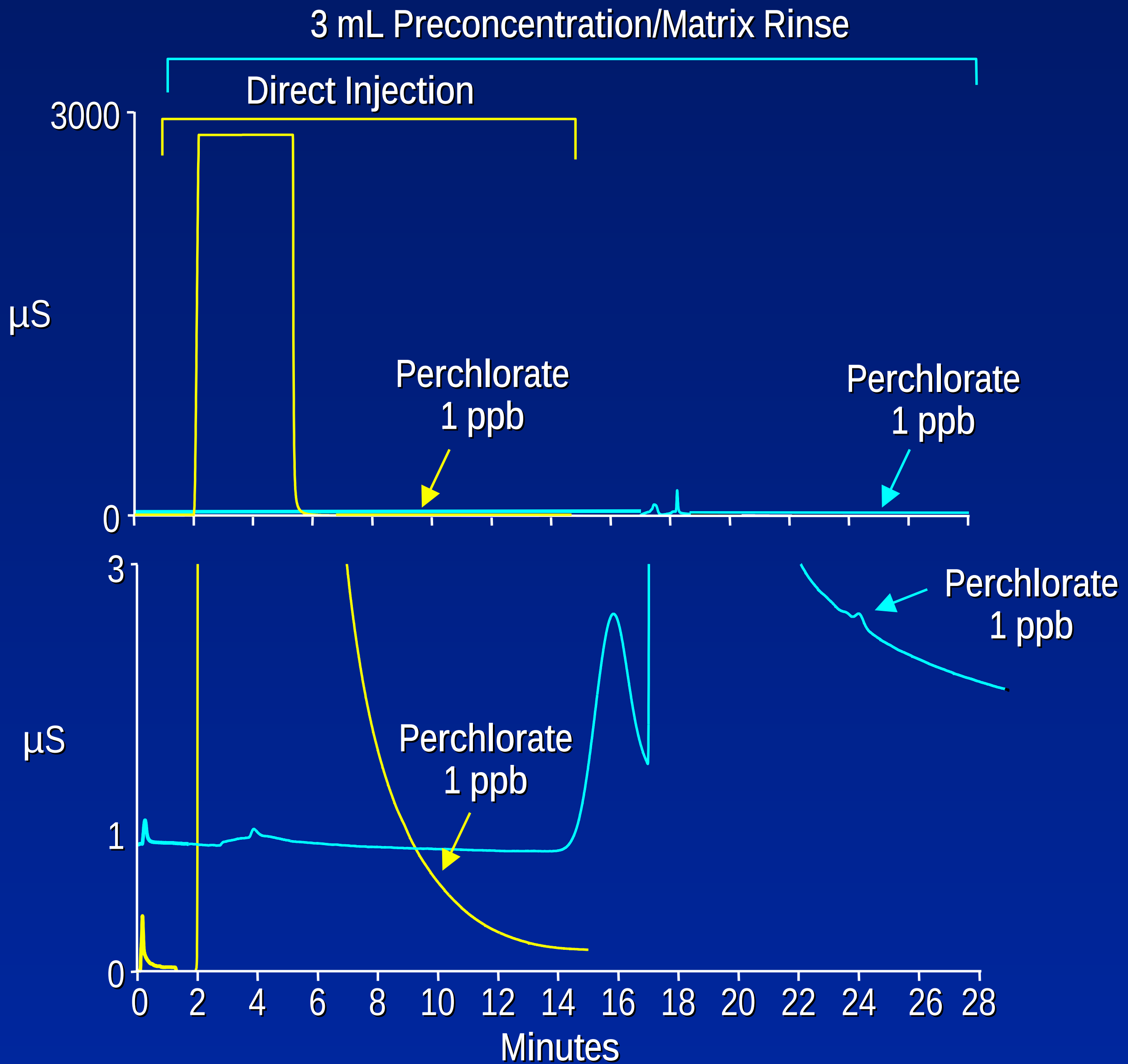
Perchlorate by Direct Injection vs Preconcentration/ Matrix Rinse



Matrix		
Chloride	1000	ppm
Bicarbonate	1000	
Sulfate	1000	

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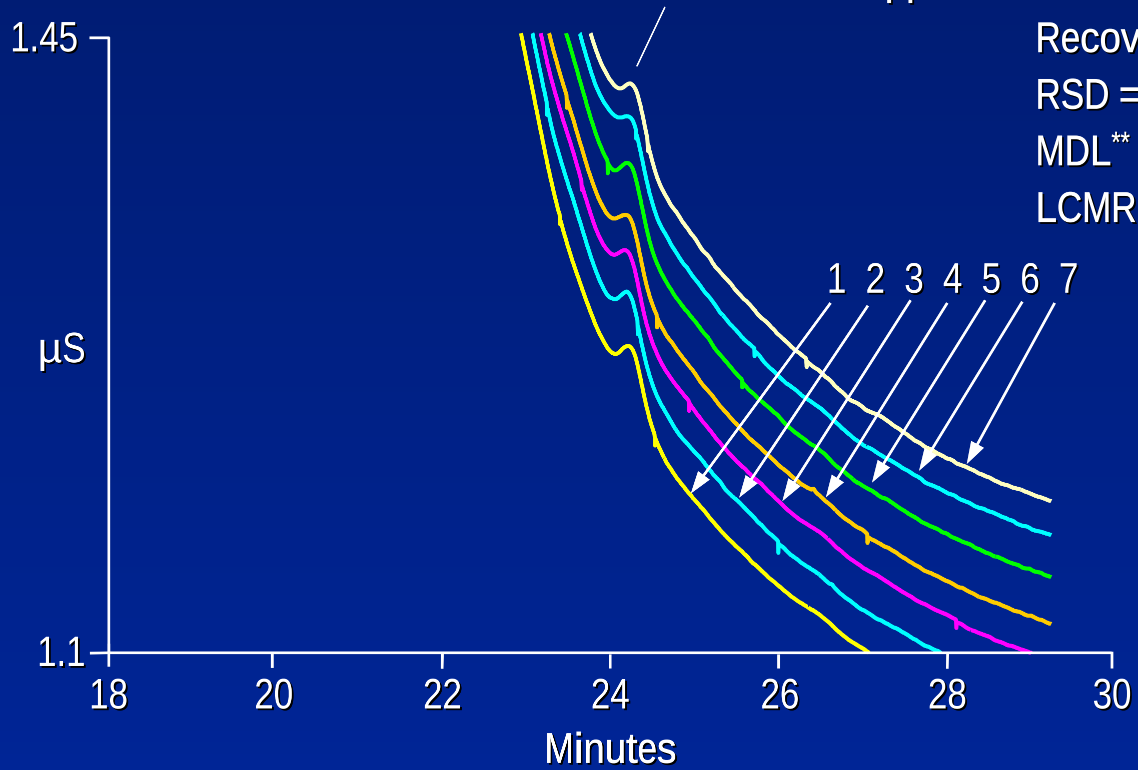
Perchlorate by EPA Method 314.1* in High Salt Matrix

Primary Method—IonPac® AS16 Column

Matrix	
Chloride	1000 ppm
Bicarbonate	1000
Sulfate	1000



Method Repeatability

Sample concentrated: 3 mL
n = 7
Ave. = 0.29 ppb
Recovery = 58%***
RSD = 4.7%
MDL** = 0.04 ppb
LCMRL = <0.100

***Recovery within EPA Guidelines

* Under joint development by EPA and Dionex

** MDL = SD x t_s (n = 7), t_s = 3.14

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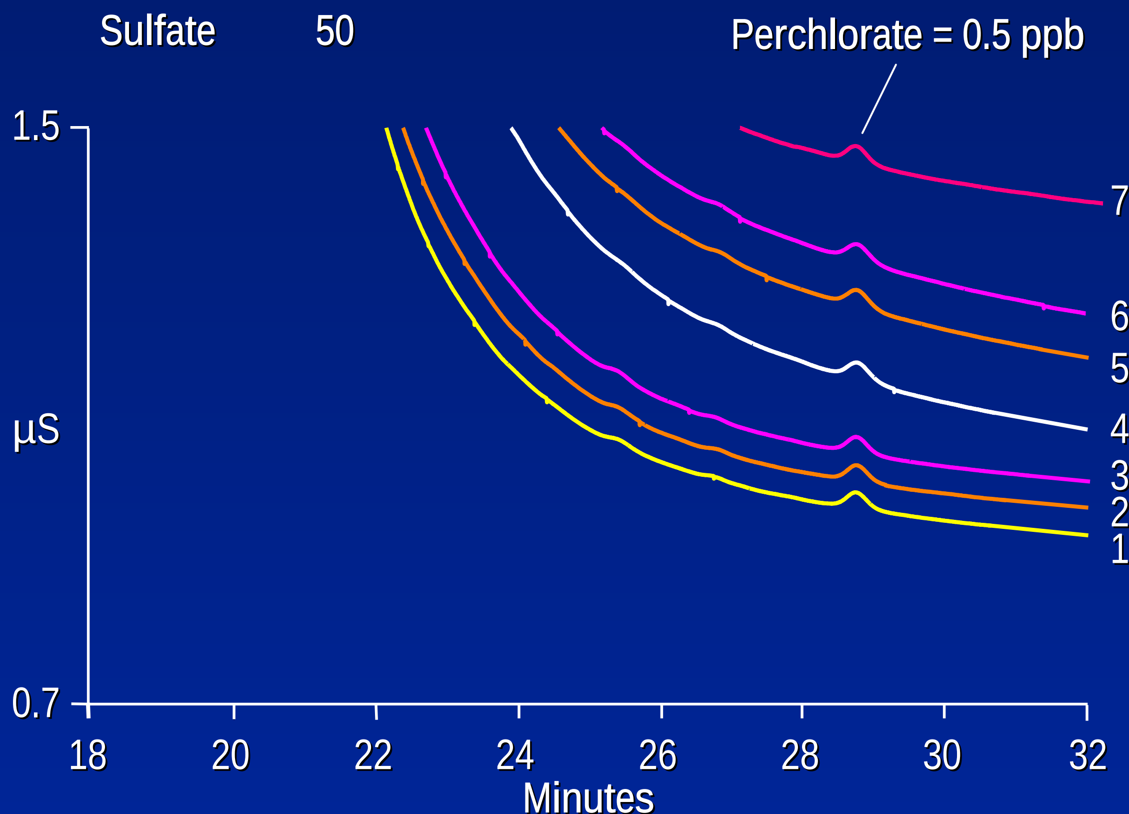
Perchlorate by EPA Method 314.1* in Drinking Water

Confirmatory Method—AS20 Column

Matrix		
Chloride	50	ppm
Bicarbonate	50	
Sulfate	50	



Method Repeatability

Sample concentrated: 3 mL

n = 7

Ave. = 0.46 ppb

Recovery = 92%***

RSD = 4.3%

MDL** = 0.06 ppb

LCMRL = <0.100

***Recovery within EPA Guidelines

* Under joint development by EPA and Dionex

** MDL = SD x t_s (n = 7), t_s = 3.14

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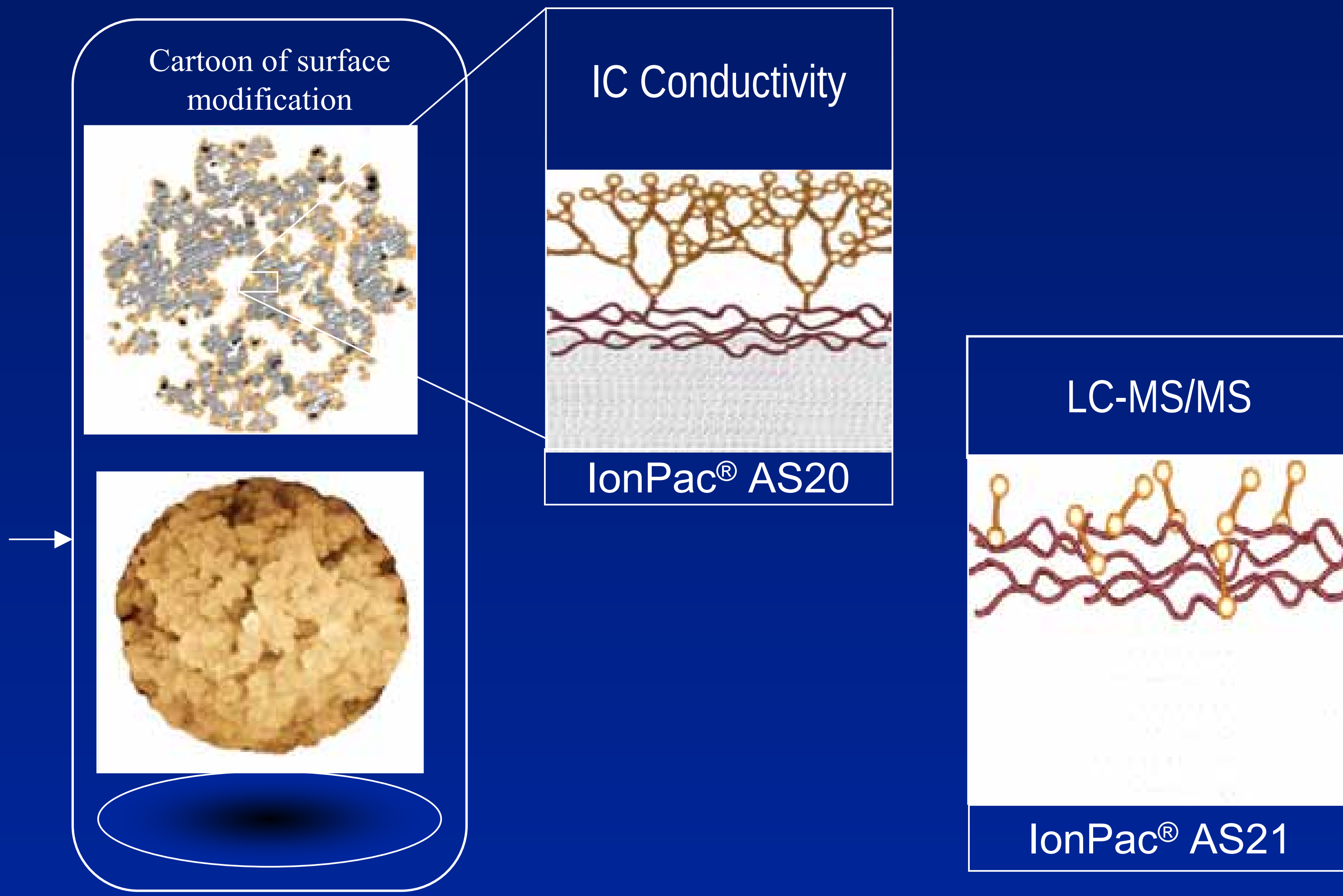
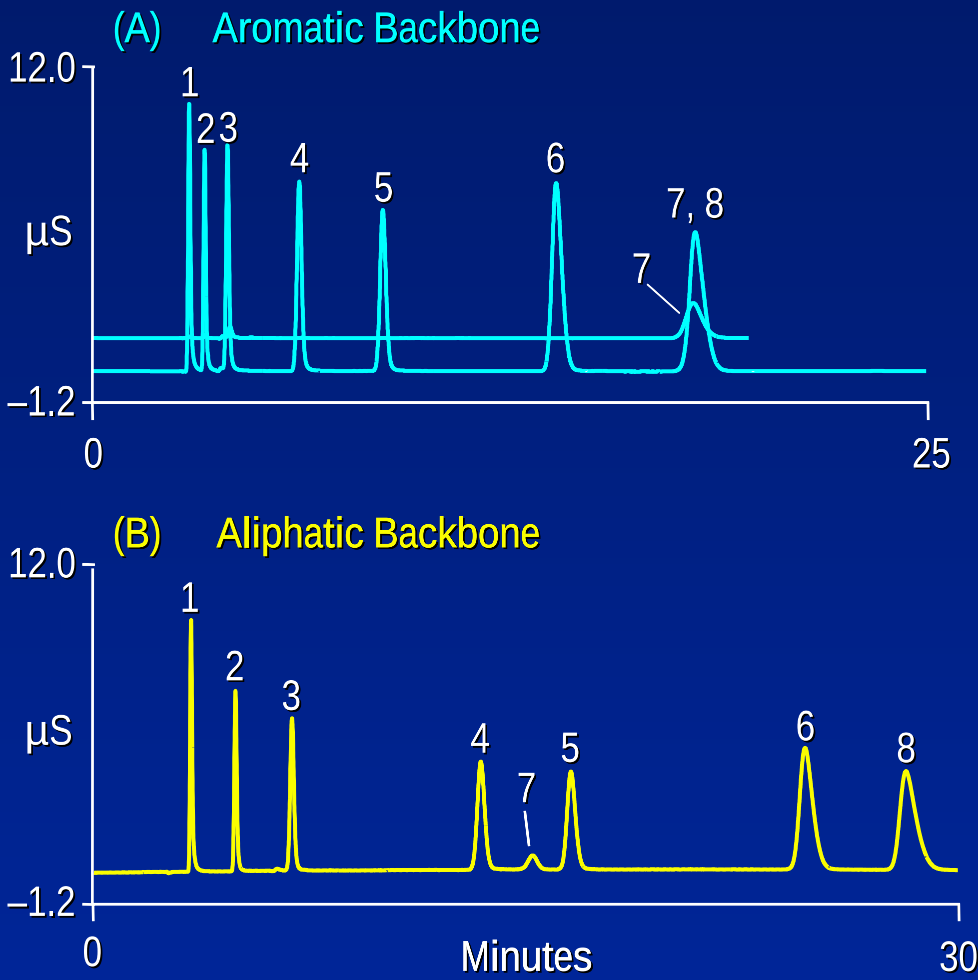
Customized Column Selectivity for Perchlorate IC and LC-MS Methods



Comparison of Primary and Confirmatory Column Performance When Using EPA Method 314.1* for Perchlorate



Columns:	(A) IonPac® AS16, 2 x 250 mm
	(B) IonPac AS20, 2 x 250 mm
Eluent:	NaOH (A) 35 mM
	(B) 25 mM
Eluent Source:	EGC II NaOH
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, ASRS® ULTRA, 2 mm, AutoSuppression® recycle mode
Peaks:	1. Fluoride
	2. Chloride
	3. Sulfate
	4. Thiosulfate
	5. Iodide
	6. Thiocyanate
	7. 4-Chlorobenzene sulfonate
	8. Perchlorate

* Under joint development by EPA and Dionex

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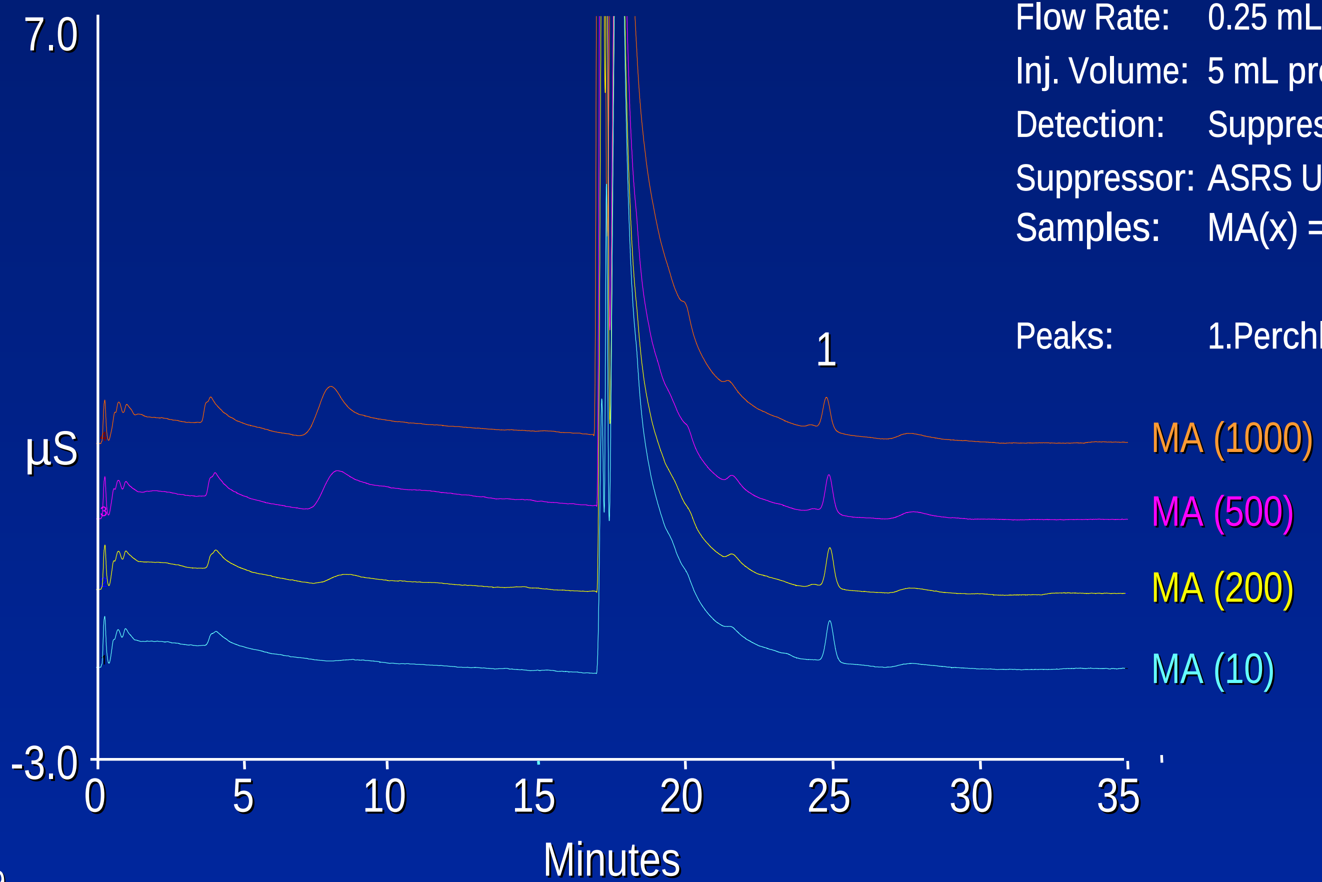
Recovery of Perchlorate Spike From High-Ionic-Strength Water Matrices



Column: IonPac® AG16, AS16, 2 mm
Eluent: 60 mM potassium hydroxide (EG50)
Temperature: 30 °C
Flow Rate: 0.25 mL/min
Inj. Volume: 5 mL preconcentrated on 09-42C 4 x 35 mm
Detection: Suppressed conductivity
Suppressor: ASRS ULTRA® II 2 mm, recycle mode
Samples: MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}

Peaks: 1.Perchlorate 2 µg/L

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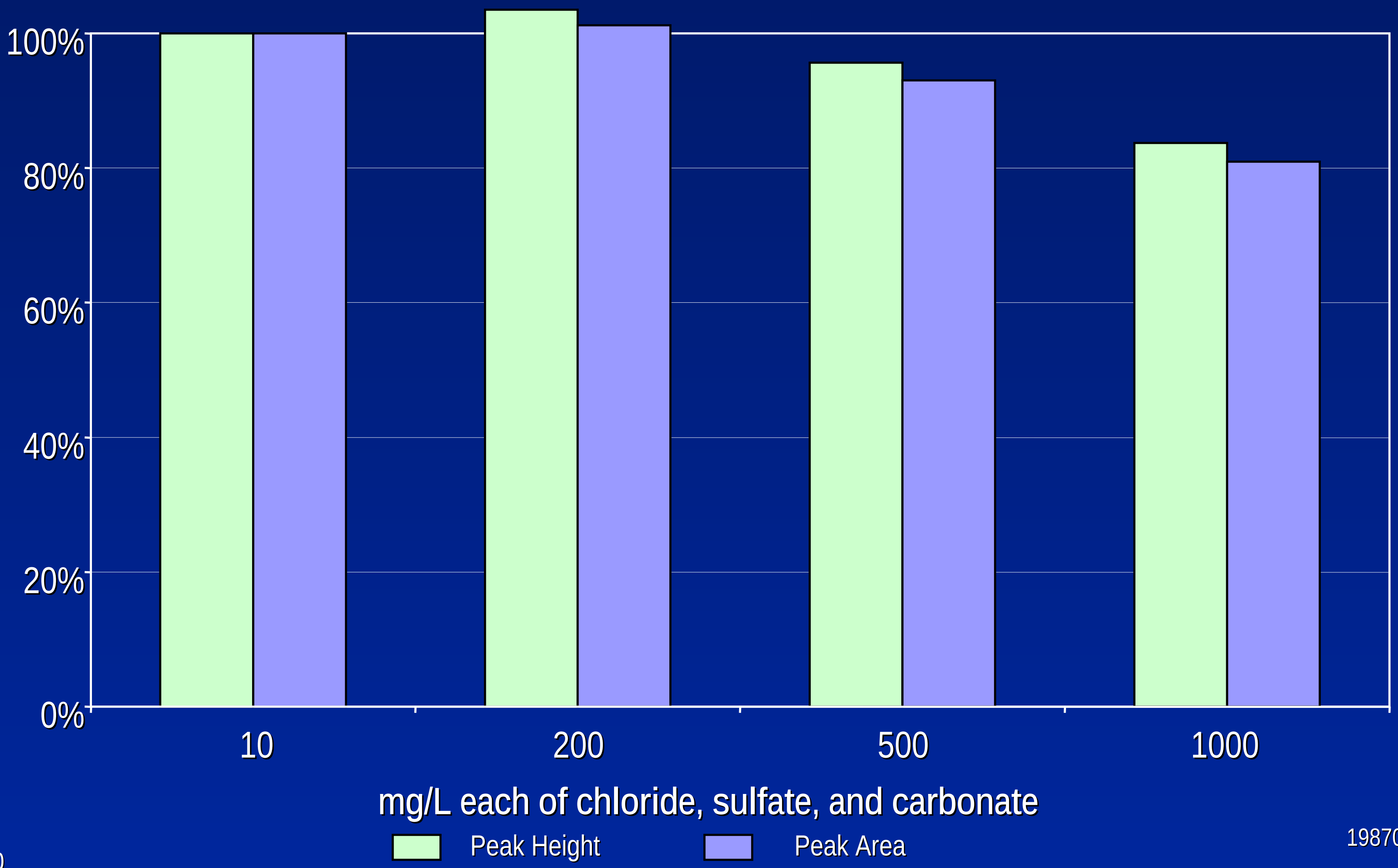
Recovery of 2 ppb Perchlorate in HIW Matrices

Cryptand 09-42C 4 x 35 mm
5 mL concentrated with 1-mL of 10 mM NaOH rinse



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EPA Method 330.0*

Perchlorate Analysis Using RFIC™ with Matrix Diversion, Solvent Wash, and MS Detection

Eluent:	Electrolytically generated hydroxide
Analytical Column Set:	IonPac® AG16, AS16, 2 mm
Injection Volume:	200 µL/min
Suppressor:	ASRS® ULTRA II, 2 mm
Diversion:	Eluent divert valve before detector to send common anions (e.g., chloride, bicarbonate, sulfate) to waste; continuous solvent wash optional
Detector:	Single quadrupole MS (ELMO option)**

Note: MS detection makes the method confirmatory

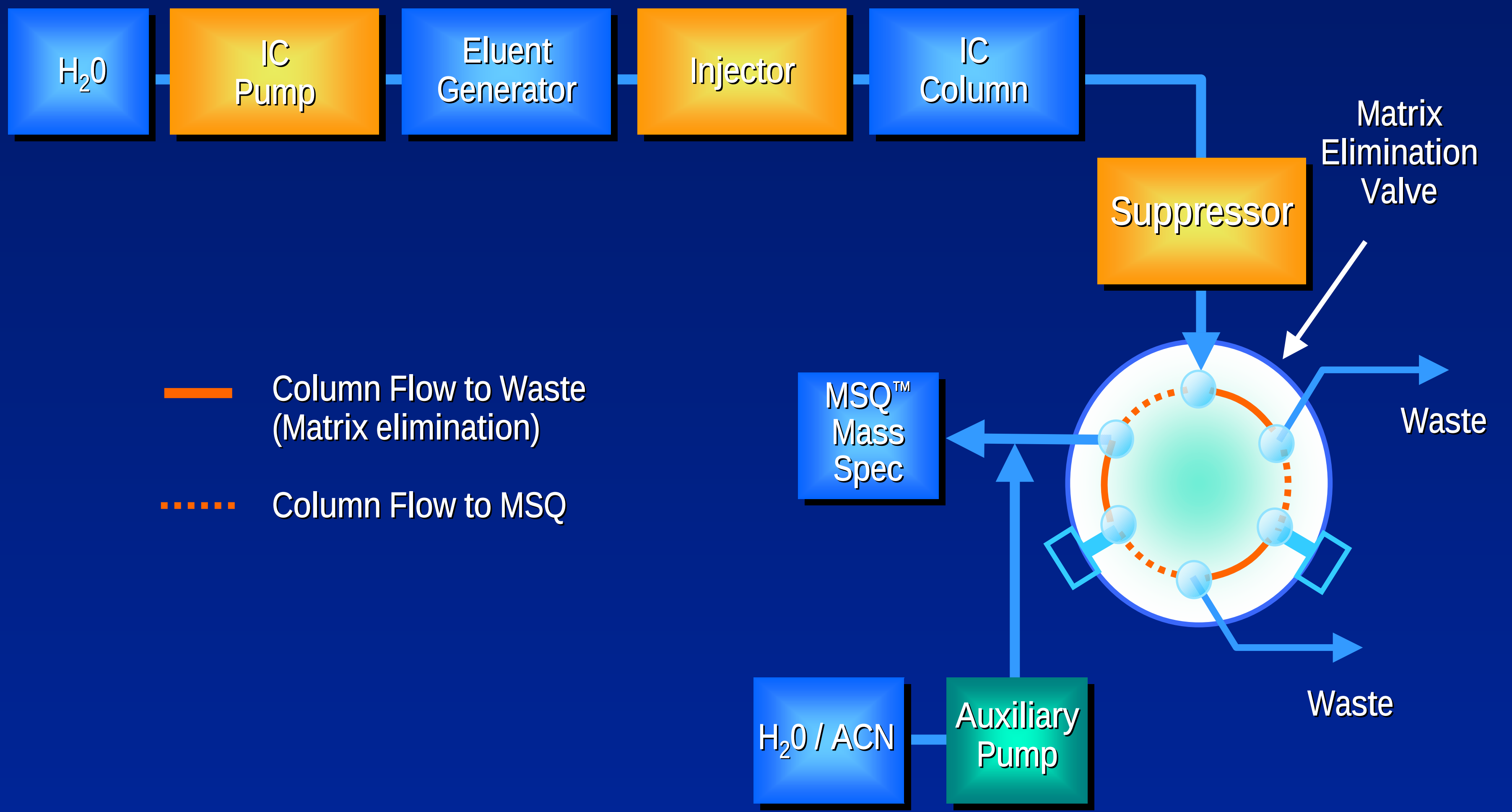
* Under joint development by EPA and Dionex

** Triple quadrupole MS-MS optional

Benefits of Combining Suppressed IC with Mass Spectrometry Detection

- Separate ionic analytes using standard IC conditions
- Suppressor permits use of high ionic strength eluents to get the benefits of high capacity columns
- Detect and identify analytes with high specificity
  - Avoid coeluting interferences to ensure accurate identification
  - Avoid background interferences to ensure highest analyte sensitivity
  - Identify analytes by mass and isotope ratios for added confirmation
  - Internal standard adds to method robustness
- Identify unknowns

EPA Method 330.0*
IC/MS System with Matrix Elimination



* Under joint development by EPA and Dionex

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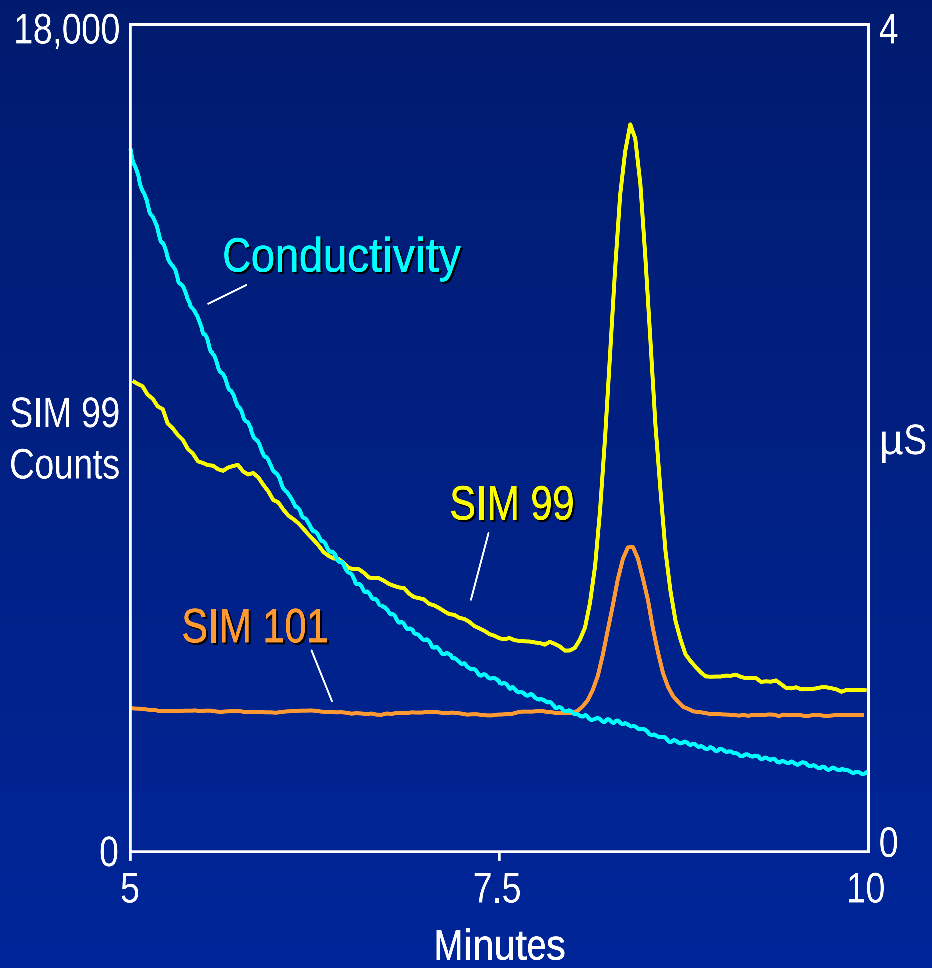
Perchlorate in California Groundwater

Using EPA Method 330.0 (IC/MS)*



Column:	IonPac® AG16, AS16, 2-mm i.d.
Suppressor:	ASRS® ULTRA, 2 mm
Eluent:	65 mM KOH (EG40)
Flow Rate:	0.30 mL/min
Inj. Volume:	250 µL
Detection:	1. Conductivity
	2. MS, SIM 99, $^{35}ClO_4^-$
	3. MS, SIM 101, $^{37}ClO_4^-$
MS Conditions:	–ESI, 70 V, 350 °C
Sample:	Groundwater diluted 1/10
Peak:	Perchlorate

$(MDL)_{99}$** = 0.04 ppb

* Method developed jointly by EPA and Dionex

** MDL = SD x t_s (n = 7), t_s = 3.14

19161

Perchlorate MS Detection Considerations

Isotope	MS SIM *m/z*	MS-MS Transitions * *m/z*	Natural Abundance	Comment
$^{35}Cl^{16}O_4^-$	99	83	67%	
$^{37}Cl^{16}O_4^-$	101	85	33%	
$^{35}Cl^{18}O_4^-$	107	89	—	Use as internal standard for MS detection
$H^{34}S^{16}O_4^-$	99	82	4%	Can be significant, for MS detection, when sample sulfate concentration is high (e.g., 1000 ppm)

* Perchlorate Ion loses one oxygen in MS-MS fragmentation
Hydrogen sulfate Ion loses an OH in MS-MS fragmentation

Continuing Improvements for MSQ™

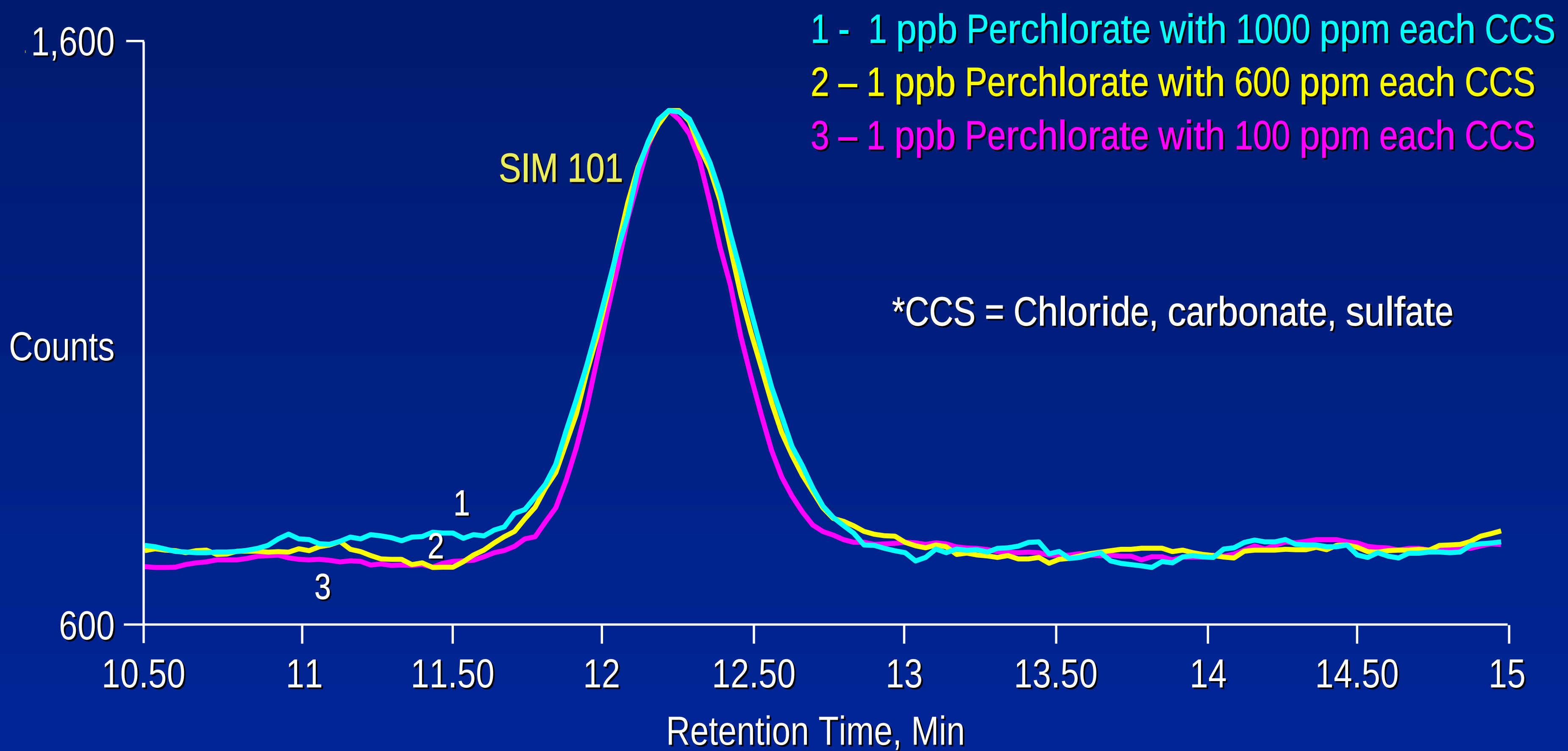
- Implementation of improved n^{th} order polynomial calibration for use in ELMO
- Implementation of improved scan speed compensation algorithm for use in ELMO
- Continued improvement in performance by collaborative work with Thermo
- Upgrade of all units to Edwards vacuum
- New software routine for detector gain optimization
- Windows XP, XC 1.4, MSQ 1.4 (Req. CM6.6SP1A)

Instrument Comparison

Parameter	MSQ	MSQ – ELMO
Mass Range	100 - 2000	15-1500 (1972)
Multiple Signal Acquisition (Number limited by CM)	32 SIM and FS Polarity switching Cone voltage	32 SIM and FS Polarity switching Cone voltage
Footprint	12" x 28"	12" x 28"
Nitrogen Consumption	<600 L/hour (active) 20-50 L/hour (stdby)	<600 L/hour (active) 20-50 L/hour (stdby)
Calibration Range	172- 1972 m/z	23-1972 m/z
Method Options	User Optimizable	User Optimizable
Mass Accuracy	0.1 amu	0.1 amu
Resolution	1 amu	1 amu
Ionization	ESI, APCI	ESI, APCI
Ion Optics	RF lens hexapole	RF lens hexapole
Mass Analyzer	quadrupole	quadrupole
Weight	132 lb.	132 lb.

Low-Level Perchlorate Analysis Using RFIC™-MD-MS with 50% Acetonitrile Solvent Wash

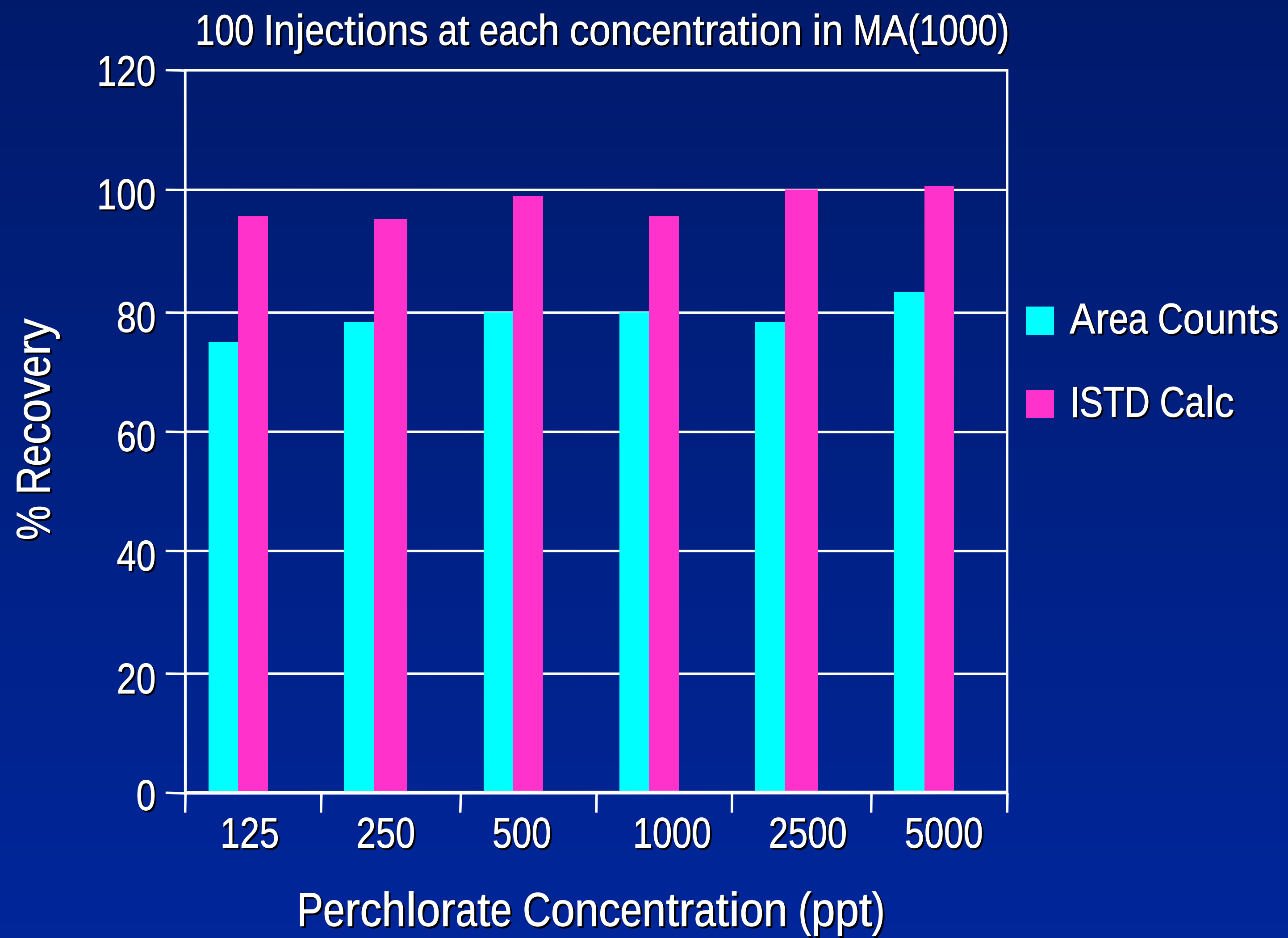
EPA Method 330.0*



* Method developed jointly by EPA and Dionex

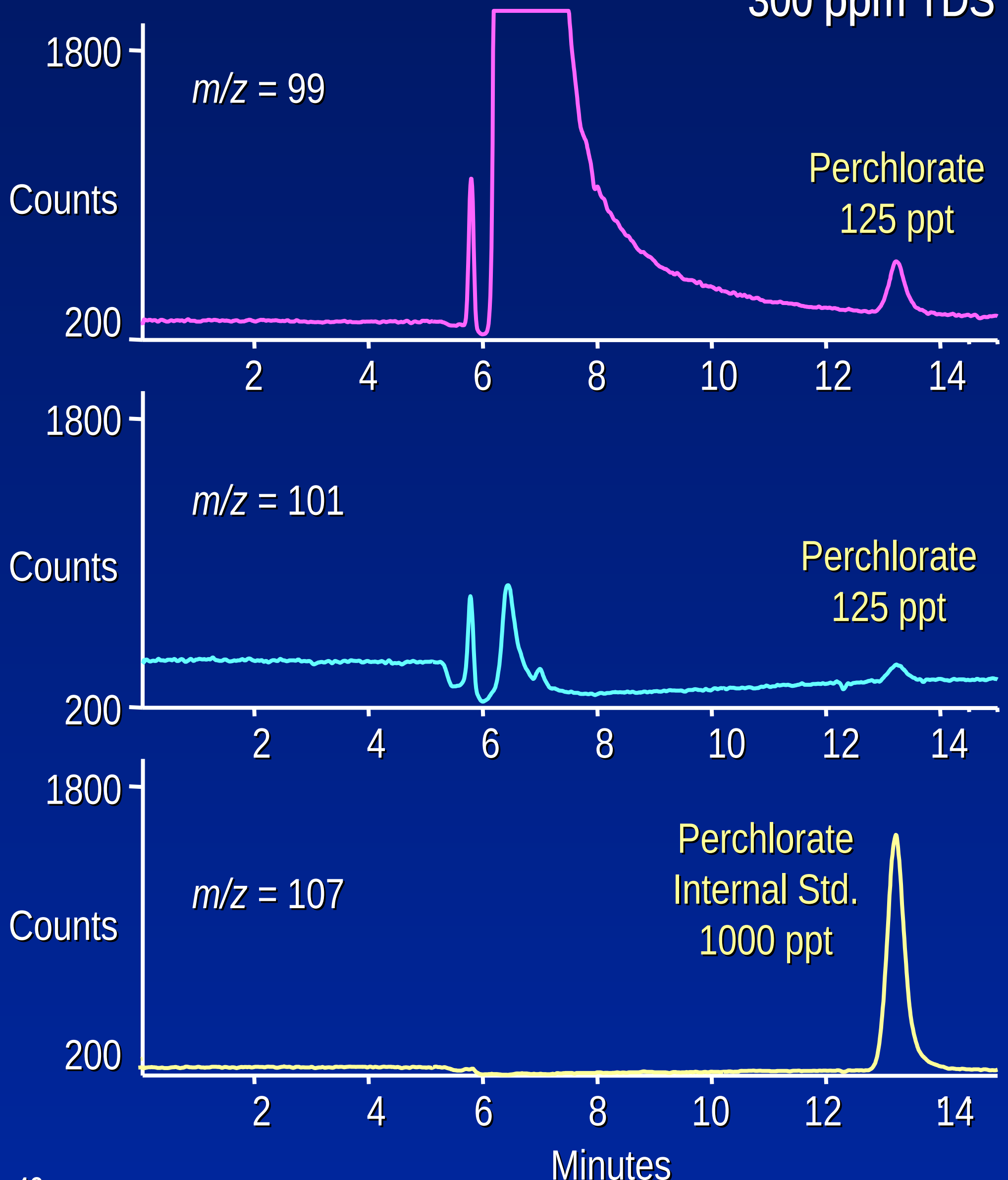
19741

Use of Perchlorate Oxygen-18 Isotope (m/z = 107) as an Internal Standard Ensures Measurement Precision



EPA Method 330.0

Perchlorate Analysis Using RFIC™ with MS Detection
300 ppm TDS Matrix



IC:	Dionex ICS-2500
Column:	IonPac® AG16/AS16
Dimension:	250 x 2 mm i.d.
Eluent:	45 mM KOH (Eluent Generator)
Suppresser:	ASRS® ULTRA II, 2 mm, external water mode, 50 mA
Injection Volume:	100 µL

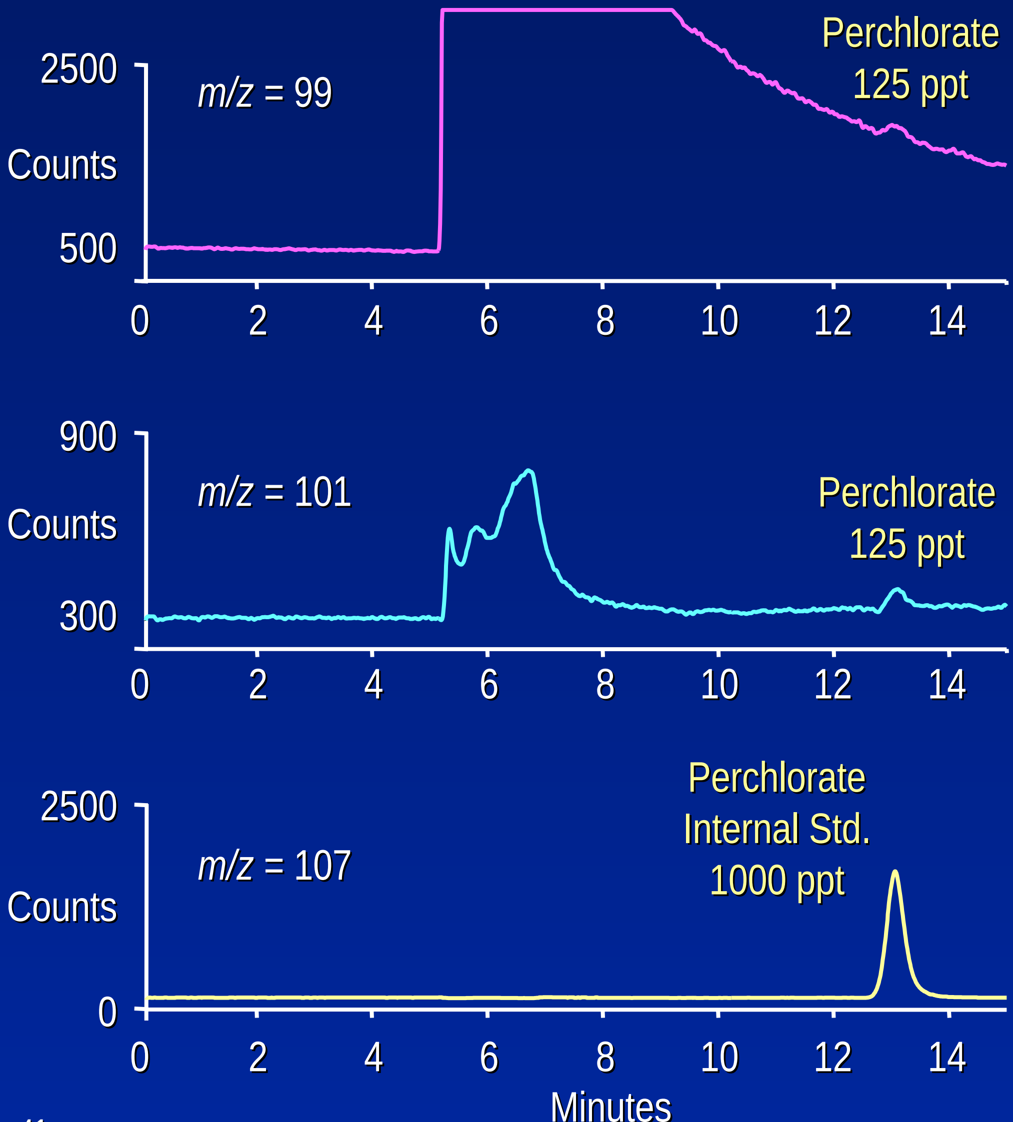
MS detection:	Agilent LC-MSD SL
ESI Mode:	Negative
Vcap:	1400 V
Fragmentor:	140 V
Dwell Time:	*m/z* 99, *m/z* 101, *m/z* 107: 1 s
Span:	Preset 0.7

Matrix	
Chloride	1000 ppm
Bicarbonate	1000
Sulfate	1000

21012

EPA Method 330.0

Perchlorate Analysis Using RFIC™ with MS Detection
3000 ppm TDS Matrix



IC:	Dionex ICS-2500
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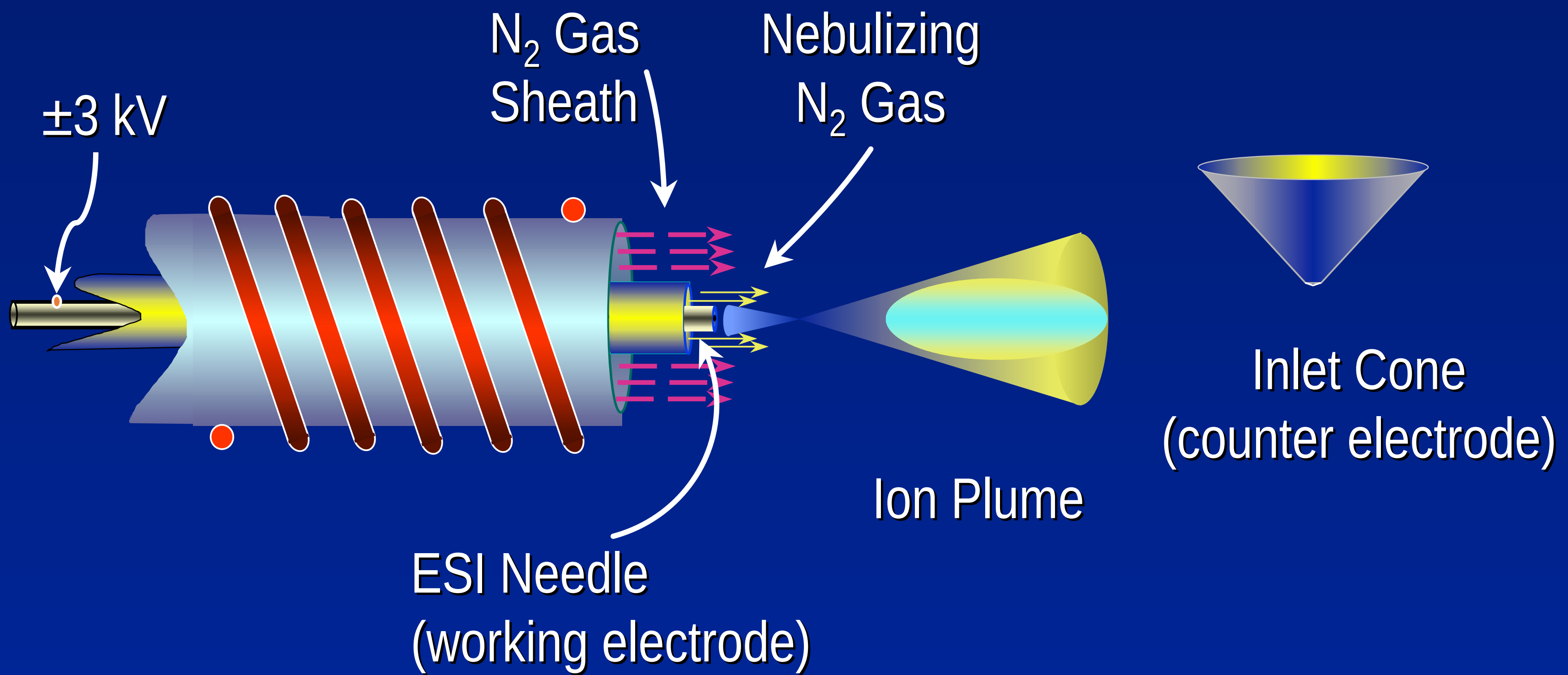
Injection Volume:	100 µL

MS detection:	Agilent LC-MSD SL
ESI Mode:	Negative
Vcap:	1400 V
Fragmentor:	140 V
Dwell Time:	*m/z* 99, *m/z* 101, *m/z* 107: 1 s
Span:	Preset 0.7

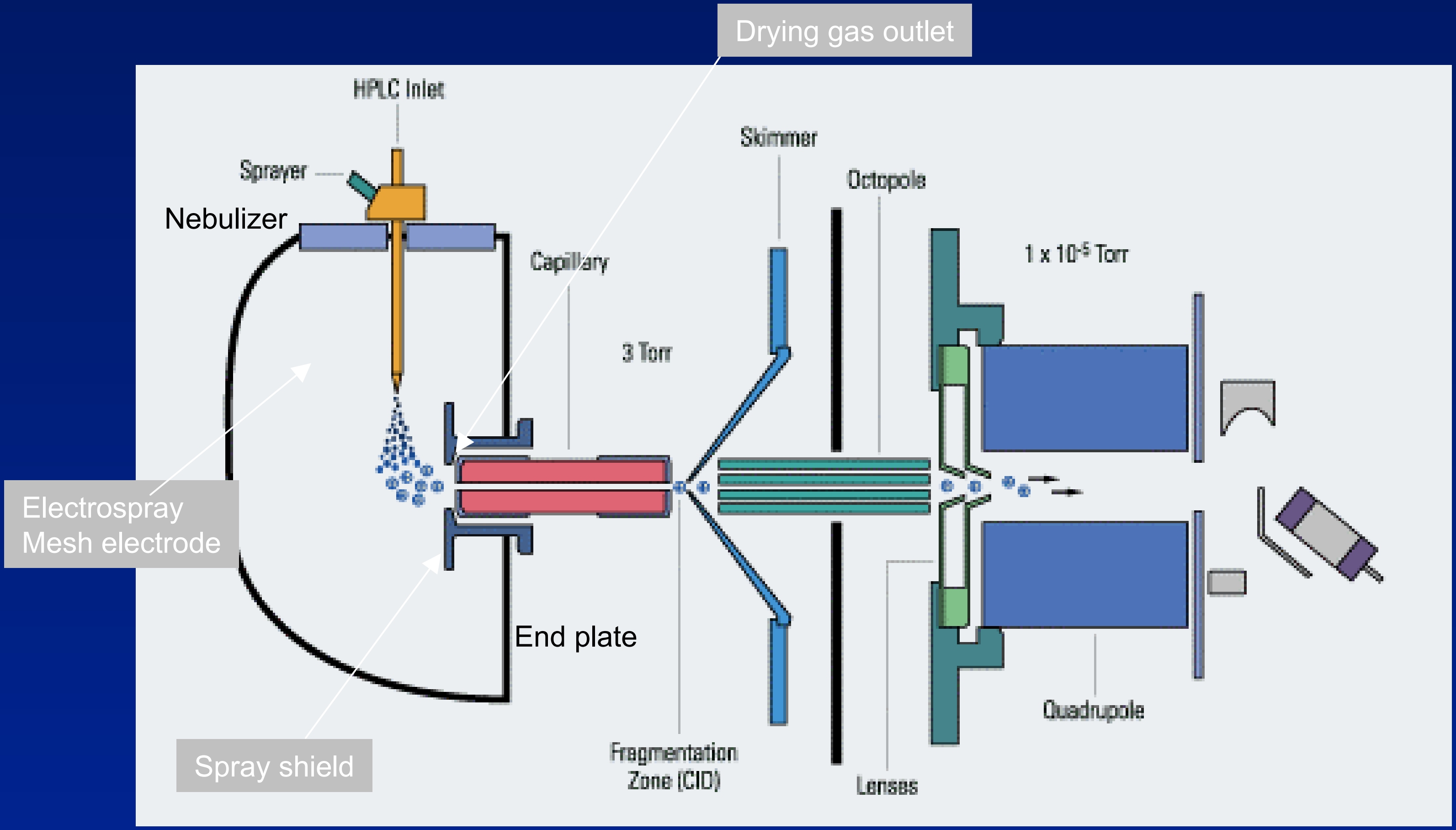
Matrix	
Chloride	1000 ppm
Bicarbonate	1000
Sulfate	1000

21013

MSQ Electrospray Inlet



MSD SL Inlet and Analyzer



Electrode, spray shield and end plate 500V less than Vcap; nebulizer and spray chamber are at ground potential; end plate and spray shield keep liquid droplets out of capillary

The combination of strong shear forces in the nebulizer, and the electrostatic field generated by the electrode draws the sample solution out and breaks it into droplets. As the droplets disperse, ions of one polarity are preferentially attracted to the surface by the electrostatic field.

Instrument Comparison

Parameter	MSQ-ELMO	MSQ	MSD SL
Mass Range	*15-1500 (1972)*	*50-1972* *(2-2000)*	***50-3000*** *(2-3000)*
Multiple Signal Acquisition	***32 SIM and FS*** *Polarity switching* *Cone voltage*	*32 SIM and FS* *Polarity switching* *Cone voltage*	*4 acquisition modes, scan, sim, frag voltage*
Footprint	*12" x 28"*	*12" x 28"*	***29" x 27"***
Nitrogen Consumption	*<600 L/hour*	*<600 L/hour*	***900 L/hour***
Calibration Range	*+ only* *23-1972*	*+ only* *172-1972*	***+ and –*** ***+120-2122;-113-2234***
Method Options	***User Optimizable***	*User Optimizable*	*Fewer options for optimization*
Mass Accuracy	0.1 amu	0.1 amu	0.13 amu
Resolution	1 amu	1 amu	1 amu
Ionization	ESI, APCI	ESI, APCI	ESI, APCI, APPI(Syagen), nano
Ion Optics	RF lens hexapole	RF lens quadrupole	octopole
Mass Analyzer	quadrupole	quadrupole	quadrupole
Weight	132 lb.	132 lb.	139 lb.

Relative Advantages for Perchlorate Analysis

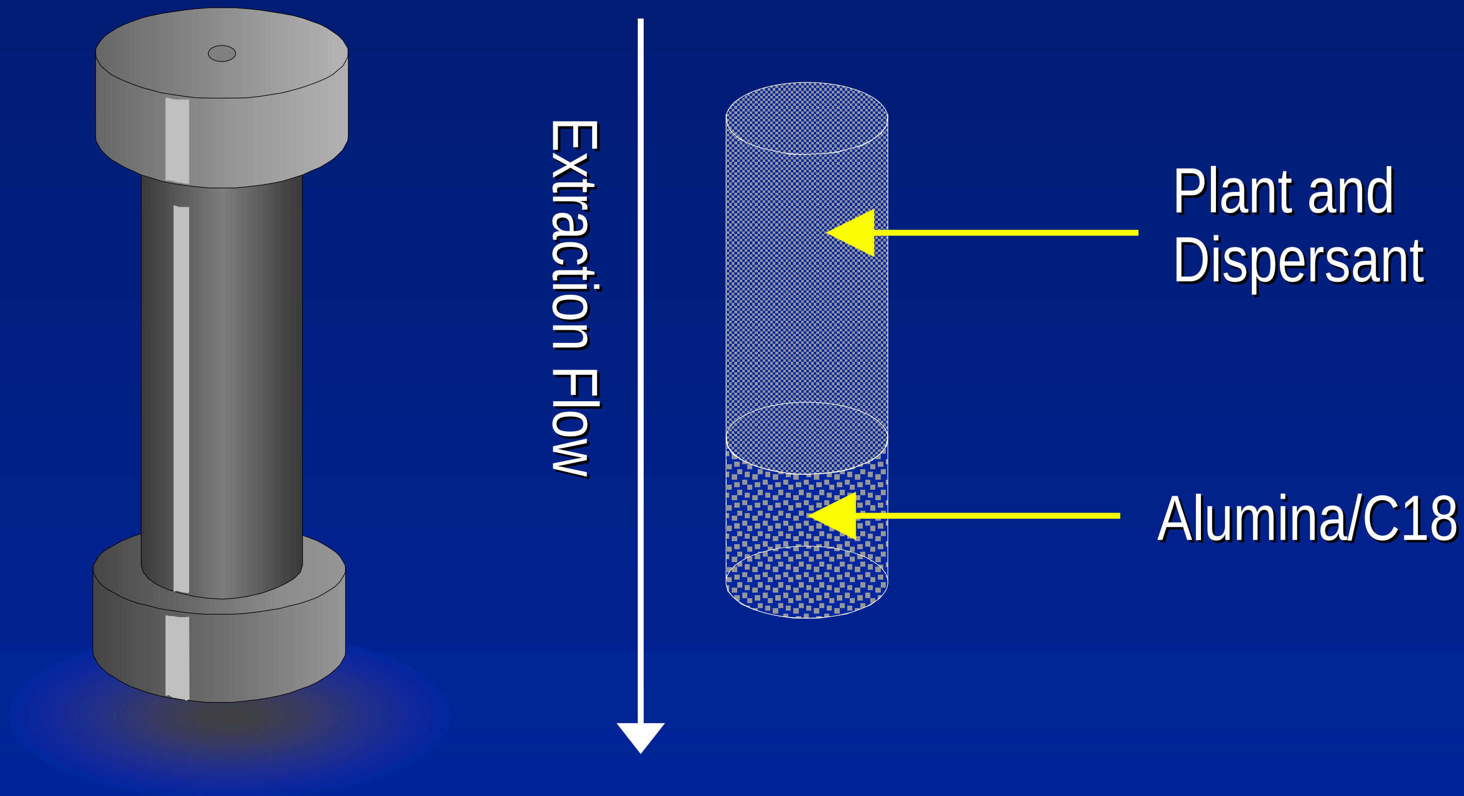
- Advantage MSQ ELMO
  - Low mass sensitivity
  - Method control
    - XCalibur allows more control of MS parameters to optimize methods
  - Full control Software
    - CM controls IC and MS
    - Adds features beyond XCalibur
  - Dionex support
    - Developed methods
    - Knowledge-base for IC-MS
  - Footprint
  - Price
  - Calibration range

- Advantage MSD SL
  - Ruggedness to short-term fouling (capillary can clog/foul)
  - Higher mass range
    - No interest for perchlorate
  - Better sensitivity (depending on application)
    - Not for perchlorate
  - Lower %RSDs
  - Separate mass calibration for +ESI and –ESI
    - +ESI not used for perchlorate

Perchlorate in Vegetables
Where IC-MS Makes a Real Difference

- Off-line cleanup investigated
- ASE® extraction using standard conditions
  - DI water, 125 °C, 1500 psi, 17 min total time
- SPE cleanup of extracts with alumina and C18
- Significantly improved results
  - Better recovery (80–100%)
  - Better precision
  - Better sensitivity

Schematic of In-Line Cleanup in ASE® Cell



ASE® with In-Line Cleanup

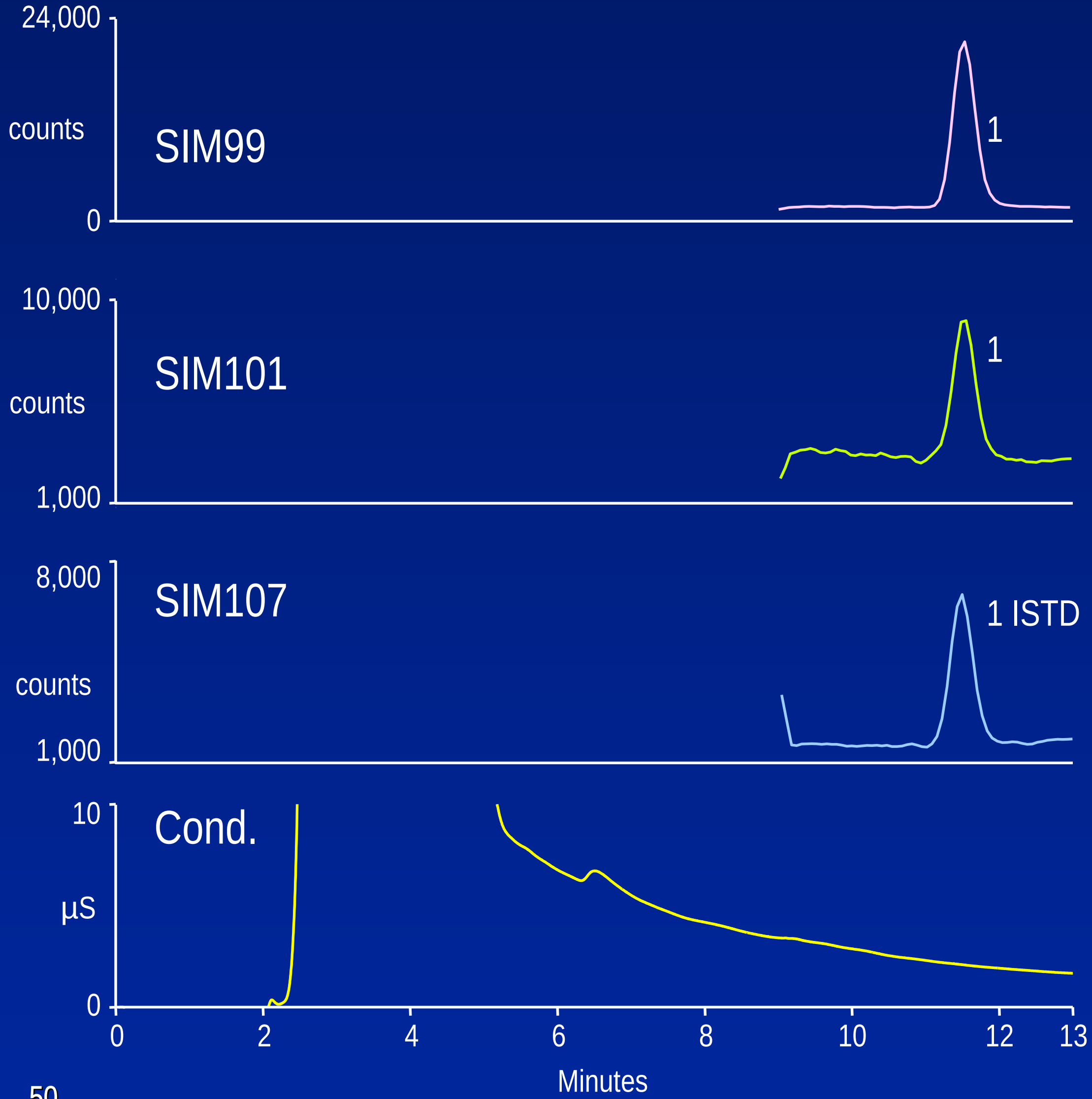
- Acidic, neutral, and basic alumina investigated
- Basic found to give best recovery with ASE
  - Acidic alumina reported in U.S. EPA methodology
- No additional salt solution needed for quantitative recovery of perchlorate
  - Sodium and ammonium nitrate, sulfate, and phosphate salts used with alumina
- Good recovery from spiked lettuce samples
  - 89% recovery, n = 3, 57 µg/kg level

Perchlorate Results with ASE® from Incurred Samples*

Sample	In-Line (mg/kg, dry basis)	Off-Line (mg/kg, dry basis)
Cabbage	36	25
Dried Soybeans	7.8	6.5

*Crops grown with water at high perchlorate levels

Perchlorate in Melon Using ASE® and IC/MS with Internal Standard



Column: IonPac® AS16, 250 x 2 mm i.d.
Suppressor: ASRS® ULTRA II, 2 mm
Eluent: 45 mM KOH (EG50)
Flow Rate: 0.3 mL/min
Injection Volume: 100 µL
Matrix Diversion: 2–9 min
Detection: 1. Conductivity
2. MS, -ESI
MS Conditions: 70 V, 450 °C, SIM 99, 101, 107
Internal Standard: 107 *m/z*
Sample: ASE extract of melon, diluted 1:2

Peaks:
1. Perchlorate, 5.8 µg/L undiluted

20297

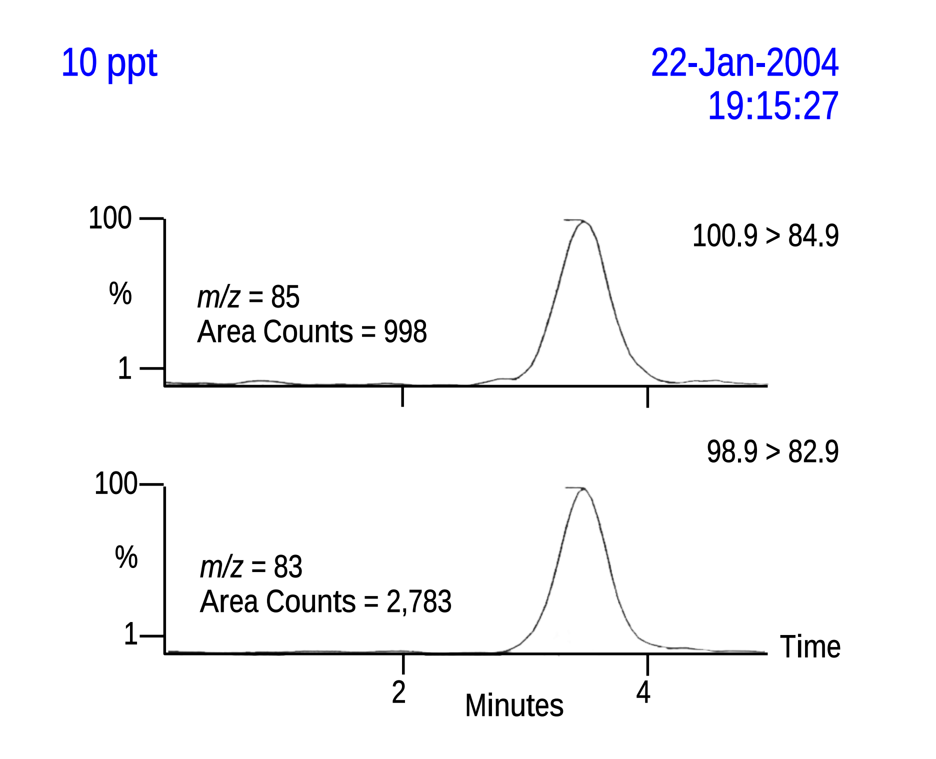
Perchlorate Results with ASE® from Incurred Samples*

Sample	In-Line (µg/kg, wet basis)
Iceberg Lettuce	7.3
Romaine Lettuce	3.9
Sweet Corn	0.2
Melon	3.5
Carrot	2.1
Alfalfa Y3	145
Alfalfa IV3	142

*Crops grown with water at low perchlorate levels

ppt-Level Perchlorate Using IC-MS-MS*

Performance After Running High TDS** Samples for Hours



True Retention Time = 10.5 + 3.5 = 14.0 min.

* Dionex ICS-2500 IC / Micromass Quattro Ultima MS-MS

** TDS = 22,600 mg/L

Data provided courtesy of Larry Penfold, Severn Trent Laboratories—Denver

IC-MS-MS Precision / Accuracy Data in High TDS Water

Test No.*	True Value (ug/L)	Mean Recovery (%)	RSD (%)
1	0.01	116.8	14.9
2	0.25	99.2	2.71
3	0.5	93.6	2.84

Day2 &Day3:

- Spikes prepared in water with 22,600 mg/L TDS
- No pretreatment
- 8 replicates tested per concentration, 4 on each of 2 days
- O-18 labeled perchlorate used as internal standard

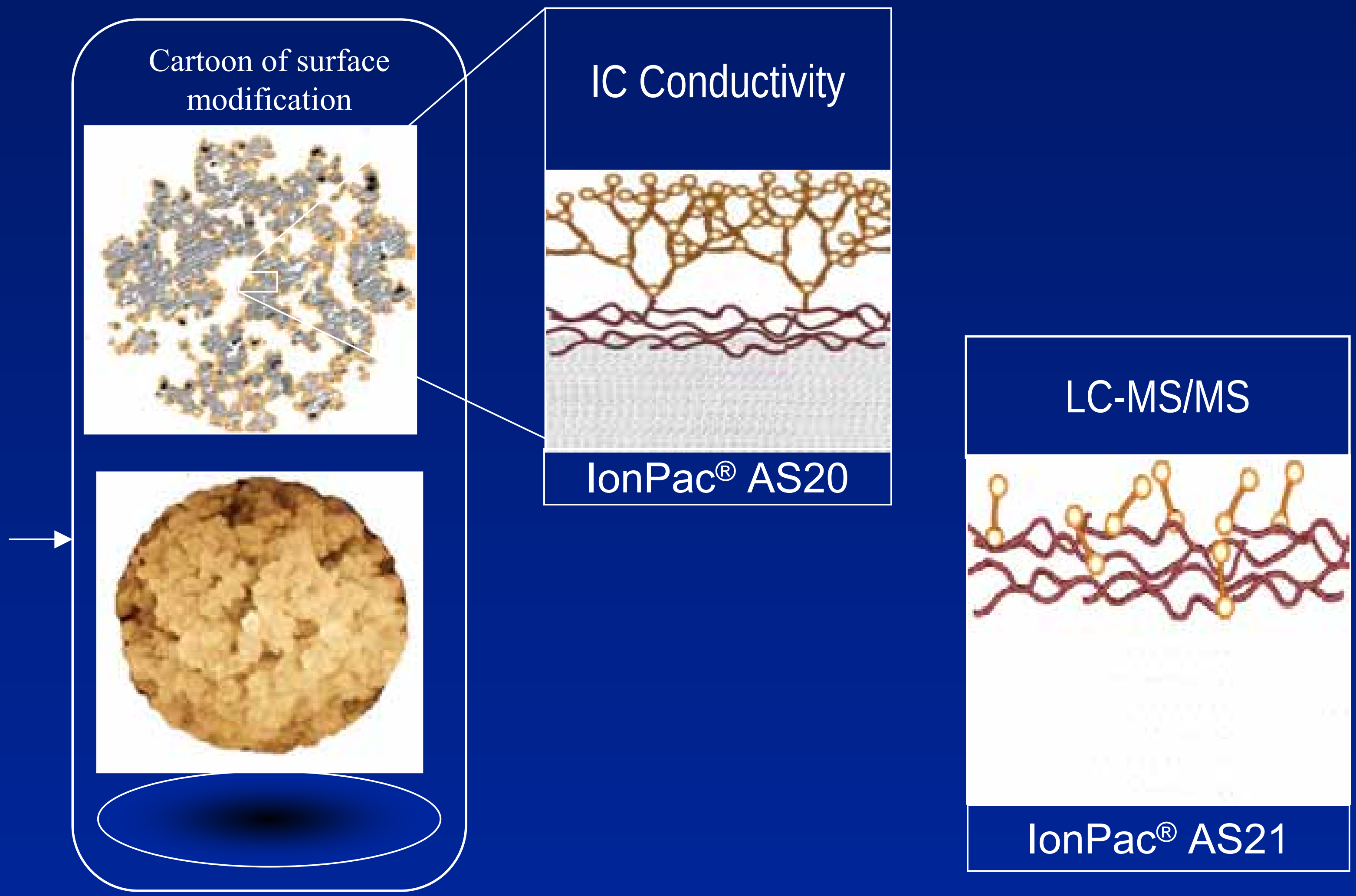
EPA Method 331.0*

Perchlorate Analysis Using Ion-Exchange Separation, Matrix Diversion, and MS-MS Detection

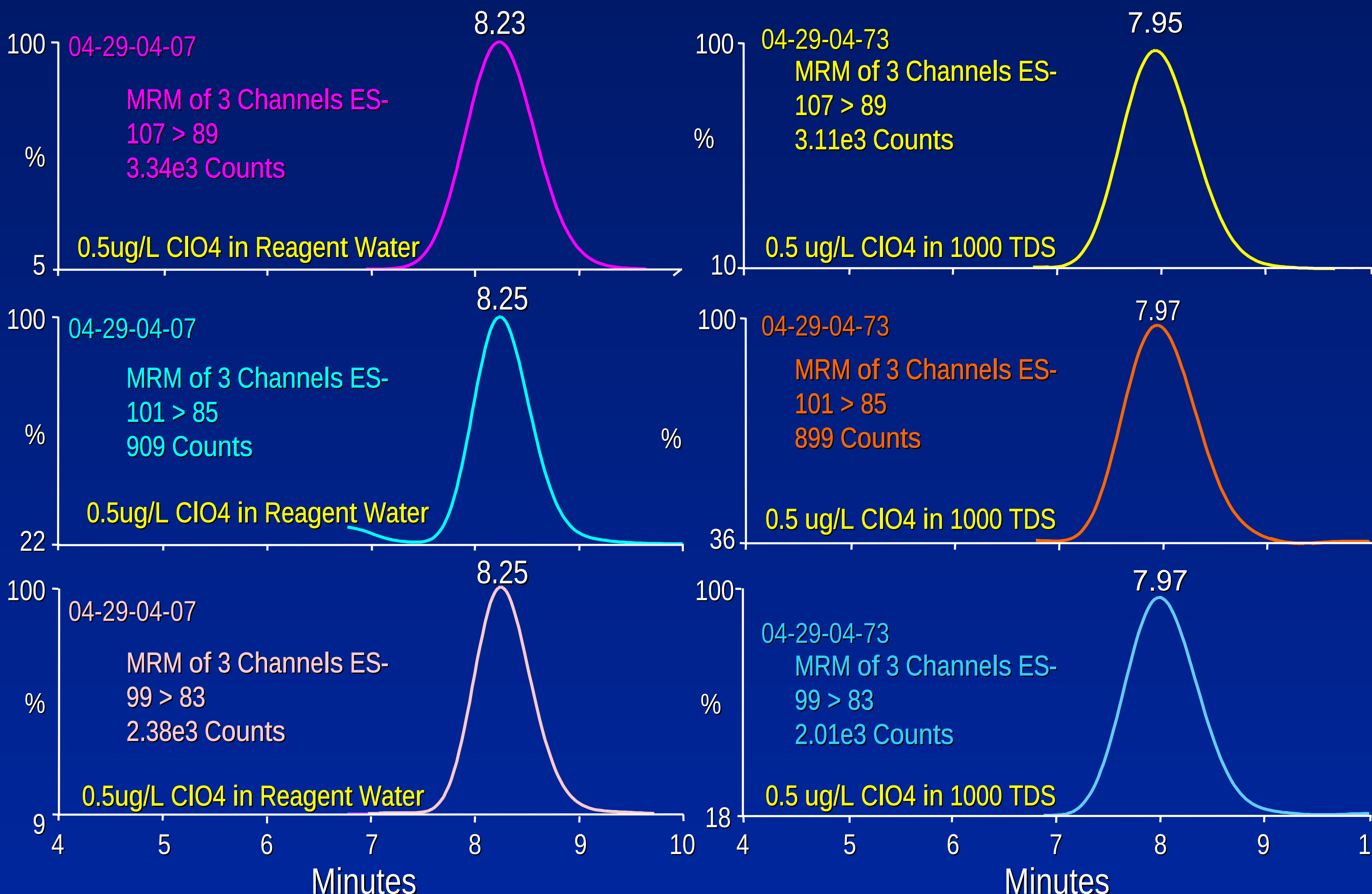
Eluent:	200 mM methyl amine
Flow Rate:	0.2 mL/min
Analysis Column:	IonPac® AS21, 2 mm
Diversion:	Eluent divert valve before detector to send common anions (e.g.,chloride, bicarbonate, sulfate) to waste
Detector:	Triple quadrupole MS-MS

* Under joint development by EPA and Dionex

Customized Column Selectivity for Perchlorate IC and LC-MS Methods



Perchlorate Analysis Using EPA Method 331.0
(LC-MS-MS)



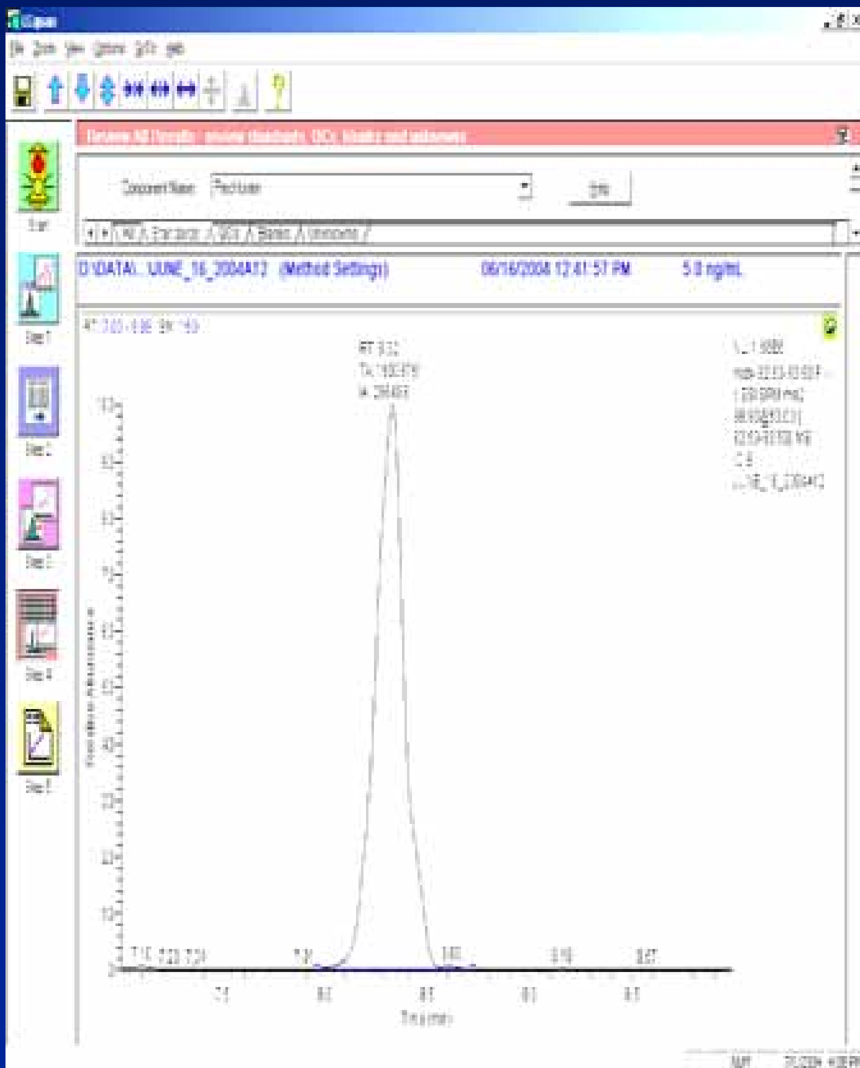
Perchlorate Analysis Using EPA Method 331.0*

	Cinn. Tap Native (µg/L)	Cinn. Tap 1.0 (µg/L) MS	% REC
Run-1	1.2	2.1	90.6%
Run-2	1.1	2.1	97.2%
Run-3	1.1	2.1	104%
Run-4	1.2	2.2	102%
Run-5	1.1	2.2	107%
AVG	1.1	2.1	
STD	0.04	0.05	
RSD	3.7%	2.4%	
	Reagent 0.5 (µg/L)	1000 TDS 0.5 (µg/L)	1000 TDS 5.0 (µg/L)
Run-1	0.54	0.59	5.3
Run-2	0.47	0.59	5.2
Run-3	0.51	0.56	5.0
Run-4	0.55	0.54	5.3
Run-5	0.51	0.53	5.2
AVG	0.52	0.56	5.2
STD	0.03	0.03	0.10
RSD	5.8%	5.2%	1.9%

* Under joint development by EPA and Dionex

Data provided courtesy of Steve Wendelken-Shaw Environmental

Separation of Perchlorate using LC-MS/MS



Column:	IonPac® AS21, 2 x 250 mm	
Eluent :	200 mM Methylamine, pH 2.0	
Flow Rate:	350 µL/min	
Injection Vol.:	100 µL	
Temperature:	30 °C	
Peaks:	1.Perchlorate	5 µg/L (ppb)
MS/MS Cond:	-ESI MS2, 40 V, 350 °C SRM 99 m/z at 50 V > 83 m/z	

Data Courtesy of Peter Philbrook, Region 1

New Perchlorate Method Performance

Method	Operating Mode	LCMRL*
314.1	Preconcentration (3 mL) with matrix rinse, suppressed conductivity detection	0.1 ppb
330.0	Direct injection (200 µL) with matrix diversion, IC-MS or IC-MS-MS detection	0.04 ppb
331.0	Direct injection (200 µL) with matrix diversion, LC-MS or LC-MS-MS detection	0.02 ppb

* Lowest Concentration Method Reporting Limit

Conclusion

- All-new perchlorate methods:
  - Meet sub-ppb MRL requirements of anticipated UCMR update
  - Allow quantification of perchlorate at sub-ppb levels, even in high TDS samples
  - Use ion-exchange separation
  - Provide perchlorate confirmation
    - ✓ Method 314.1 with AS16 and AS20 column
    - ✓ Method 330.0 and 331.0 by MS and MSMS

Acknowledgements

- US EPA
  - David Munch
  - Elizabeth Hedrick
- Shaw Environmental and Infrastructure
  - Barry Pepich
  - Herb Wagner
  - Steve Wendelken
- Dionex
  - Column Development
    - Chris Pohl
    - Charanjit Saini
    - Andy Woodruff
  - Method Development / Validation
    - Dave Thomas
    - Brian De Borba
  - Market Development
    - Doug Later
    - Bob Joyce
  - MS Technology
    - Roseanne Slingsby
    - Bill Schnute