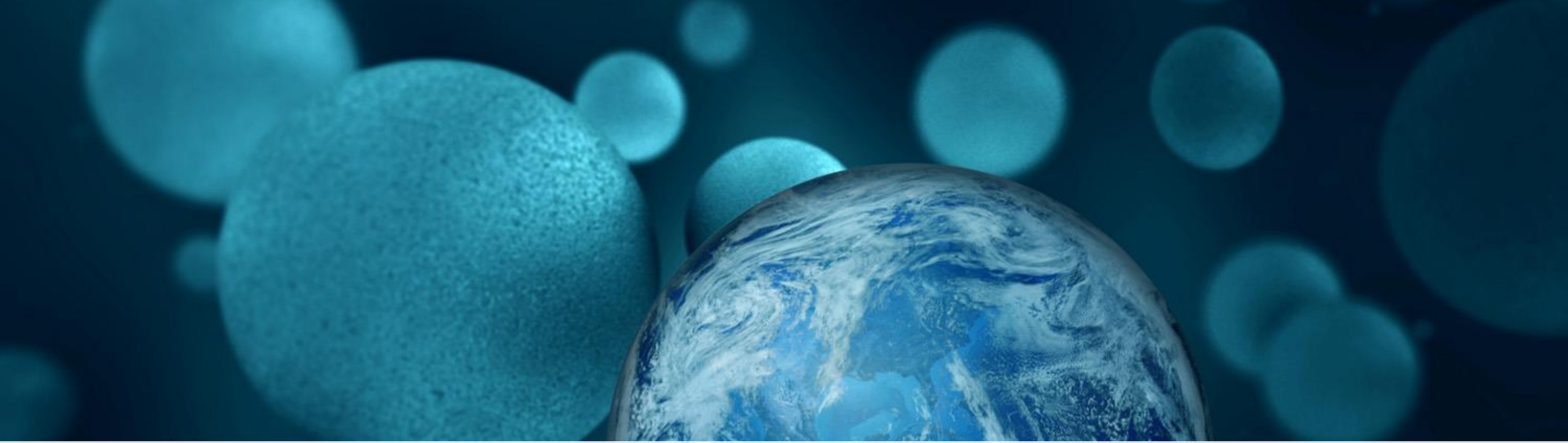

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Ion Chromatography products, IC and IC/MS applications for environmental and food safety laboratories

Roman Repas
Technical Sales Manager IC/SP, Emerging Markets
Thermo Fisher Scientific GmbH Dreieich, Germany

Agenda

Overview of IC/SP portfolio

IC systems overview

Analysis of inorganic anions and low concentrations of oxyhalides

IC/MS introduction

IC/MS applications for environmental and food safety laboratories

2019 IC/SP Portfolio

ISQ EC MS

ASE 350

Autotrace 280

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Ion Chromatography Systems

RFIC

HPIC

Dionex Aquion

Dionex Integrion

Dionex ICS-4000

Dionex ICS-6000

Dionex Aquion IC

- reliable IC system with straightforward operation
- for IC users in budget limited labs
- built on a compact platform
- low operating costs

Dionex Integrion HPIC

- for routine users who run an established method
- efficient IC analyses with comprehensive applications solutions
- interactive wellness features

Dionex ICS-4000 Capillary HPIC

- for high throughput labs
- reduce cost of system operation
- producing less waste

Dionex ICS-6000 HPIC

- for IC users in routine and research
- flexible, robust system
- ultimate in productivity
- modular IC configurable as a single or dual channel system
- interactive wellness
  troubleshooting knowledgebase
  consumables installation guidelines
- smart monitoring

Dionex ICS - 6000 IC System Detectors

Conductivity

Detection of anions and cations with suppressed conductivity detection

ICP-MS

Elemental speciation coupled with high sensitivity

Spectrophotometric

Selective determination of UV and visible absorbing compounds that allows post-column and pre-column derivatization techniques

Electrochemical

Selective and sensitive detection of electroactive compounds

Mass Spectrometry

Determine ionic and polar compounds that other techniques just can't match

Dionex IC Autosamplers

Thermo Scientific Dionex **AS-DV Autosampler**

Entry Level

- Carousel Type
- 50 x 5 mL PolyVials
- 50 x 0.5 mL PolyVials
- Filter Caps
- Full Loop, Concentrator
- Simultaneous Injection
- Optional 6-port/10-port Valve

Thermo Scientific Dionex **AS-HV Autosampler**

High Volume

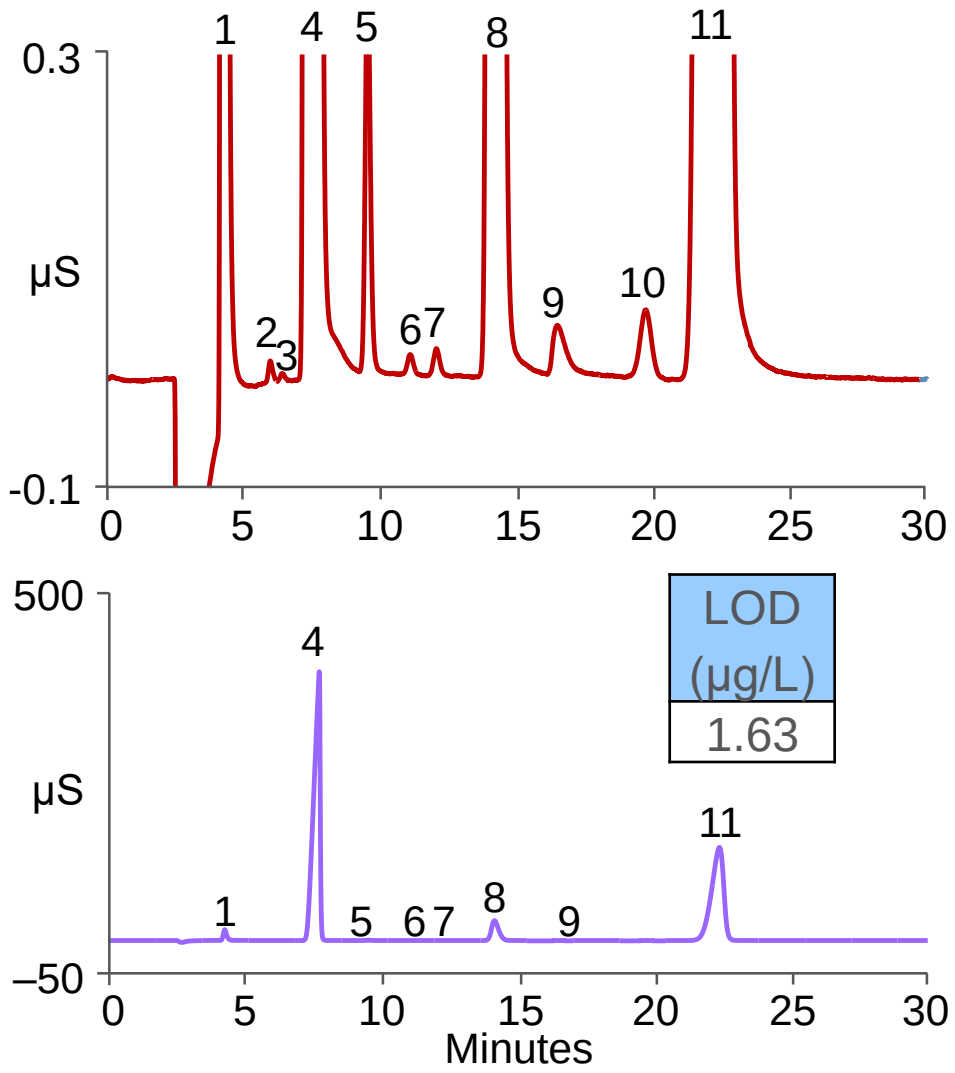
- X0Z-Type
- 24 x 250 mL TCF
- 15 x 250 mL Bottles
- Full Loop Injection, Concentrator Loading
- Simultaneous Injection
- Peristaltic Pump for sample loading and Needle Port Rinse

Thermo Scientific Dionex **AS-AP Autosampler**

For IC, BioIC, and Cap IC

- Carousel-Type
- 81 x 10 mL Vials
- 120 x 1.5 mL or 0.3 mL Vials
- 3 x 96 Well Plates
- 3 x 384 Well Plates
- Full/Partial Loop, Limited Sample, Concentrator Loading
- Push and Pull Loop injection
- Tray Thermostat
- Optional Injection Valve
- Optional Diverter Valve
- Optional Fractionation valve
- Sequential Injection
- Simultaneous Injection
- Autodilution

Determination of Trace Concentrations of Bromate Using Prepared Eluents (Isocratic)



Columns: Dionex IonPac AG23, AS23, 4 mm

Eluents: 4.5 mM Sodium carbonate/
0.8 mM Sodium bicarbonate

Temperature: 30 °C

Flow Rate: 1.0 mL/min

Inj. Volume: 200 µL

Detection: Suppressed conductivity, Dionex ASRS, 4 mm, AutoSuppression™, external water mode

Peaks:

1. Fluoride	1.0	mg/L (ppm)
2. Chlorite	0.01	
3. Bromate	0.005	
4. Chloride	50	
5. Nitrite	0.1	
6. Chlorate	0.01	
7. Bromide	0.01	
8. Nitrate	10	
9. Carbonate	50	
10. Phosphate	0.1	
11. Sulfate	50	

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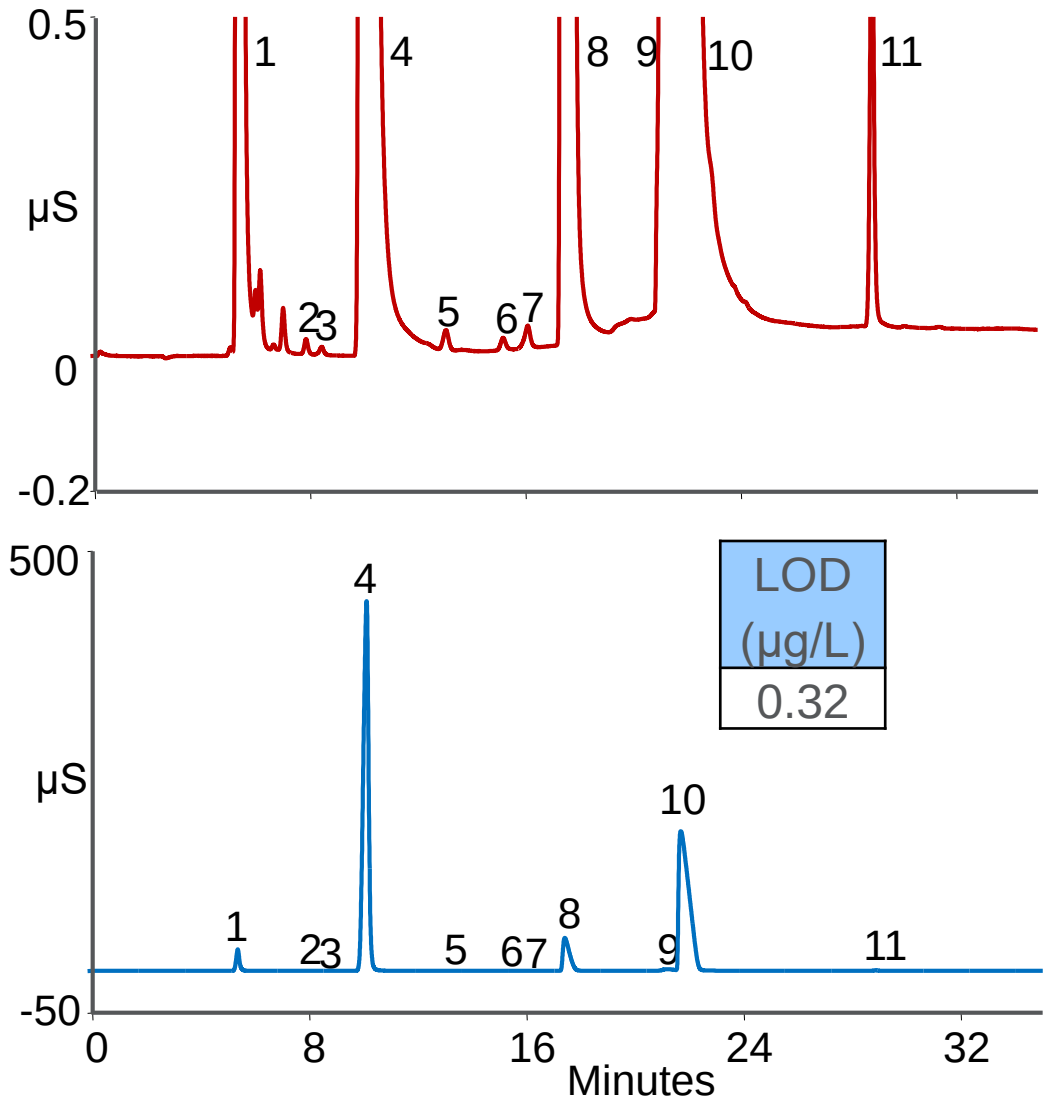
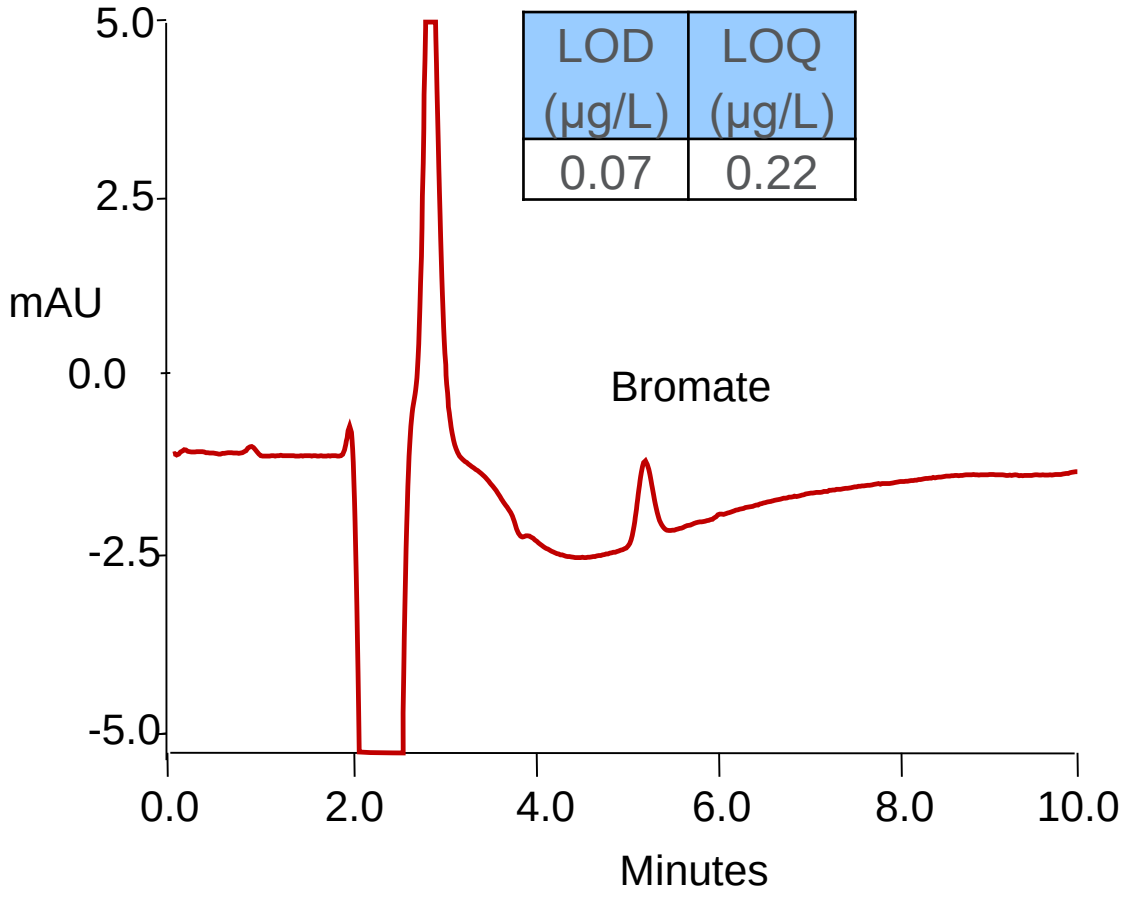
Bromate in Simulated Drinking Water



System:	Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC system
Column:	Thermo Scientific™ Dionex™ IonPac™ AS19-4µm + guard (4 × 250 mm)
Eluent :	10 mM KOH from 0 to 10 min, 10–45 mM KOH from 10 to 25 min
Eluent Source:	Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge
Flow Rate:	1.0 mL/min
Inj. Volume:	200 µL
Temperature:	30 ˚C
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500 suppressor, 4 mm AutoSuppression, recycle mode
Sample:	Simulated Drinking Water

Peaks:		
1. Fluoride	1.0	mg/L
2. Chlorite	0.005	
3. Bromate	0.005	
4. Chloride	50.0	
5. Nitrite	0.005	
6. Chlorate	0.005	
7. Bromide	0.005	
8. Nitrate	10.0	
9. Carbonate	25.0	
10. Sulfate	50.0	
11. Phosphate	0.20	

Bromate Determination with Acidic Eluent - ISO 11206



LOD (µg/L)	LOQ (µg/L)
0.07	0.22

Column:	Thermo Scientific™ Dionex™ CarboPac™ PA1 (4 × 250 mm)
Eluent:	200 mmol/L MSA
Flow:	1 mL/min
Injection vol.:	500 µL
Detection:	UV 352 nm (after PCR)
Temperature:	30 °C
PCR:	
Solution A:	0.27 mol/L KI, 0.05 mmol/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Flow	0.3 mL/min
Reaction coil:	375 µL
Bromate	1.2 µg/L

Reaction at Ambient Temp., and no Interferences from Chlorite
Cycle Time: 18 minutes

What is IC-MS?

Mass spectrometry (MS), as a detection technique for ion chromatography (IC), has recently gained popularity due to the increasing demand for sensitivity, selectivity, confirmation of identity, and structural interpretation.

IC-MS

- Increases analytical confidence by providing sensitive detection and mass confirmation in addition to retention time often without the need for sample pre-treatment
- Suitable for a wide range of applications including organic acids, perchlorate, polar pesticides, polar metabolites, amines, carbohydrates

Environmental
- Government municipalities
- Contract laboratories
- Utility providers
- Regulators (EPA)

Food & Beverage
- Contract laboratories
- Beverage manufacturers
- Regulators (FDA)
- Academic researchers

Pharma/Biopharma
- Pharmaceutical co.
- CROs
- Academic researchers
- Regulators (FDA)

IC-MS

Single quadrupole MS offers:

- Higher sensitivity and more accurate quantitation than conductivity detection
- Chromatographic peak mass confirmation, eliminating false negatives and false positives

Primary Applications

- Perchlorate (AU72507, AN72587)

MS is a more selective detector than conductivity in that it monitors the mass/charge ratio (m/z) of the analyte and can provide lower detection limits in high-ionic-strength matrices than conductivity; allows quantification of perchlorate at 99/101 m/z in high-ionic strength matrices at low ppb level

- Cations and small amines (AN72609, AB72405)

Because the mass range of these analytes is usually below 100 mass-to-charge ratio (m/z) an ideal MS detector for these analyses will have the features of mass accuracy and high mass transmission efficiency in the low mass range (15–100 m/z) while maintaining the necessary mass resolution

- Determination of Common Anions and Organic Acids using IC-MS (AN243)

IC-MS/MS

Coupling IC with the highly selective detection of a triple quadrupole mass spectrometer allows:

- Unambiguous identification of substance peaks
- Reduction of matrix interference effects, which improves the sensitivity and lowers the detection limits

Primary applications

- Polar pesticides in water
  - Glyphosate and AMPA in water (AN666)
    - The analysis of glyphosate and other polar compounds presents a difficult analytical challenge. Their polarity does not allow the direct analysis by reversed-phase HPLC, so alternative methods need to be applied.
    - Ion chromatography is the preferred separation technique for polar ionic analytes. Mass spectrometry offers very low detection limits and high detection selectivity. The system robustness allows the analysis of food and environmental samples.
- Disinfection byproducts in drinking water
  - HAAs in water (AN630, AN65196)
    - By comparison to the conventional EPA methods using GC with ECD, the combination of ion chromatography and mass spectrometry (IC-MS and IC-MS/MS) offers sensitive and rapid detection without the need for sample pretreatment.

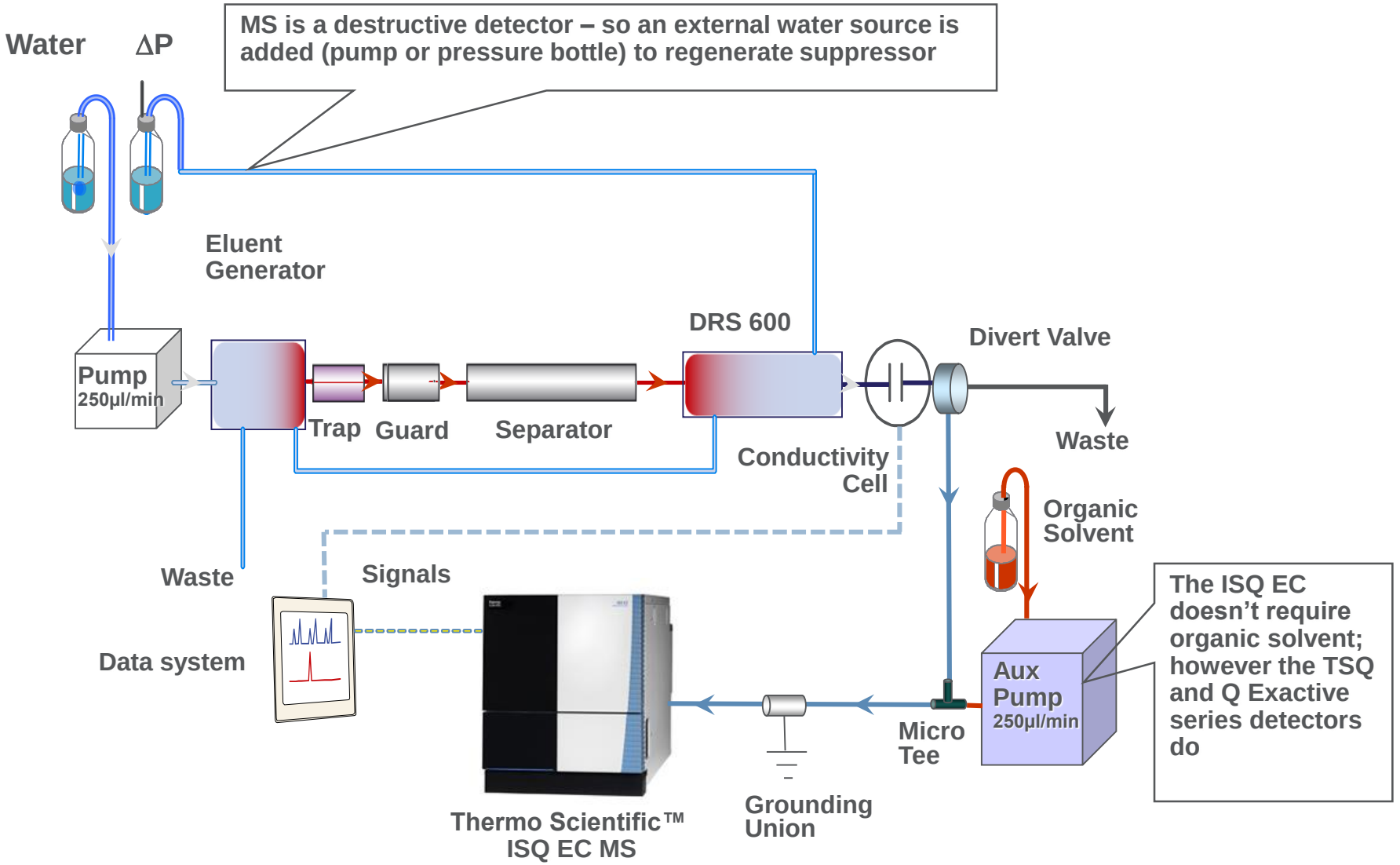
IC-HRAM

High Resolution Accurate Mass (Thermo Scientific Orbitrap) spectrometers generate high-resolution and accurate-mass data, thereby enhancing specificity in trace analyte detection, characterization, and quantitation.

Primary applications

- Metabolomics
  - The outstanding resolution of IC has led to the differentiation of many isobaric and isomeric polar metabolites. In addition, IC has shown broad coverage of glycolysis and the tricarboxylic acid cycle (TCA cycle) intermediates. Significant changes of TCA cycle metabolites in cancer stem cells versus non-stem cancer cells were observed
- Food Safety
  - Anionic pesticides in Fruits and Vegetables - quantification and identification of pesticides found regularly in samples in addition to automated qualitative screening of unexpected pesticide residues
- Lithium Ion battery Degradation Products
  - IC combined with HRAM effectively characterizes ionized/ionizable components in electrode samples from aged Li Ion batteries

IC-MS Technology: System Schematic



Thermo Scientific ISQ EC/EM Single Quadrupole Mass Spectrometers

- For ion chromatography (IC-MS) and liquid chromatography (LC-MS)
- Built for **routine** analysis and long term signal stability
- Controlled by Thermo Scientific™ **Chromeleon™** Chromatography Data System (CDS)

Thermo Scientific™ ISQ™ EC Single Quadruple Mass Spectrometer

- Mass range 10-1250 m/z
- HESI only
- Perfect for IC-MS or LC-MS

Thermo Scientific™ ISQ™ EM Single Quadruple Mass Spectrometer

- Mass range 10-2000 m/z
- HESI and APCI Options
- Perfect for LC-MS

Performance and Specifications

Specification	ISQ EM	ISQ EC
Mass Range (m/z)	10 – 2000	10 – 1250
Source Type	ESI and ESI/APCI	ESI
Supported Modes	Full scan / SIM	
Flow Rate	Up to 2 mL/min	
Scan Rate, max (Da/s)	Up to 20,000	
SIM Sensitivity (ESI+)	10 pg Reserpine	
	SN > 400:1	
SIM Sensitivity (ESI-)	20 pg Nitrophenol	
	SN > 500:1	
SIM Sensitivity (APCI+)	10 pg Reserpine	n/a
	SN > 1000:1	n/a
SIM Sensitivity (APCI-)	20 pg Nitrophenol	n/a
	SN > 80:1	n/a
Polarity Switching	Yes, 25 ms	
Mass Resolution	Unit (≤ 1.0 Da)	
Mass Accuracy	< ± 0.1 Da	
Mass Stability	< 0.1 Da over 48 h	
Digital Dynamic Range	$> 10^7$	
Power	110–240 VAC 50/60Hz	

- ✓ Enhanced low mass detection for IC/MS
- ✓ Optional larger mass range and ESI/APCI combination source
- ✓ Very fast scanning for better UHPLC compatibility
- ✓ Fast polarity switching for experiments with positive and negative scans
- ✓ Global power supply with 110V – 240V built-in support

Outstanding performance and speed

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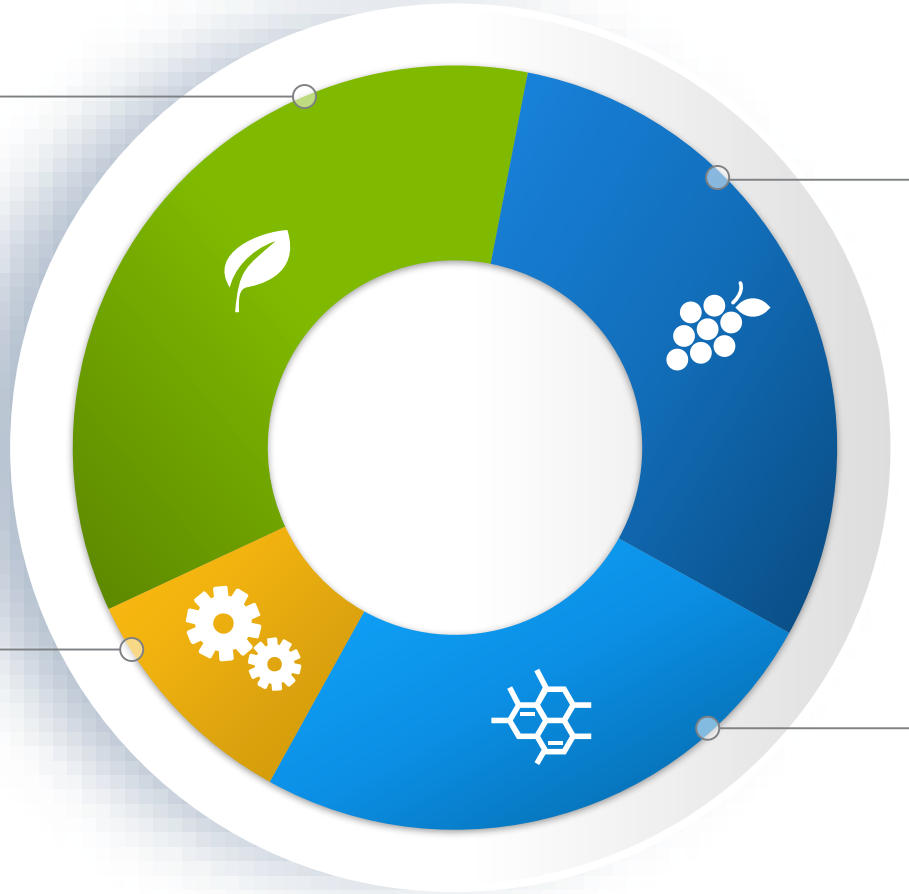
IC-MS Applications

Environmental

- Haloacetic acids in drinking water (EPA Method 557)
- Perchlorate in drinking water
- Bromate in drinking water

Industrial Manufacturing

- Corrosive anions in petrochem
- Process water
- Li-ion batteries



Food and Beverage

- Glyophosate, Glufosinate/AMPA (ionic pesticides)
- Perchlorate in vegetables
- Organic acids (“Food-omics”)
- Anions in brewing industry

Metabolomics

- Sugar phosphates
- Sugar amines

IC-MS Application Notes

- AN151 – Determination of Perchlorate in Environmental Waters by IC-MS
- AN243 – Determination of Common Anions and Organic Acids using IC-MS
- AN263 – Determination of Endothall in Water
- AN269 – Identification and Quantification at ppb Levels of Common Cations and Amines by IC-MS
- AN276 – Direct Determination of Fluoroacetic Acid in Water by IC-MS
- AN409 – Determination of Acrylamide in Water
- AN454 – Analysis of Haloacetic Acids in Drinking Water by IC-MS/MS
- AN479 – Quantification of Polyphosphonates and Scale Inhibitors in High Ionic Strength Matrix Effluents Using IC- MS/MS
- AN491 – Analysis of Glyphosate and AMPA in Environmental Water by IC-MS/MS
- AN622 – Pathway-Targeted Metabolomic Analysis in Oral/Head and Neck Cancer Cells using IC-MS
- AN630 – EPA Method 557 – Analysis of Haloacetic Acids, Dalapon, and Bromate in Drinking Water by IC-MS/MS
- AN661 – Fast routine analysis of polar pesticides in foods by suppressed ion chromatography and mass spectrometry
- AN666 – Routine analysis of polar pesticides in water at low ng/L levels by IC-MS/MS
- AN1000 – Determination of Small Organic Acids in Sea Water by IC-MS

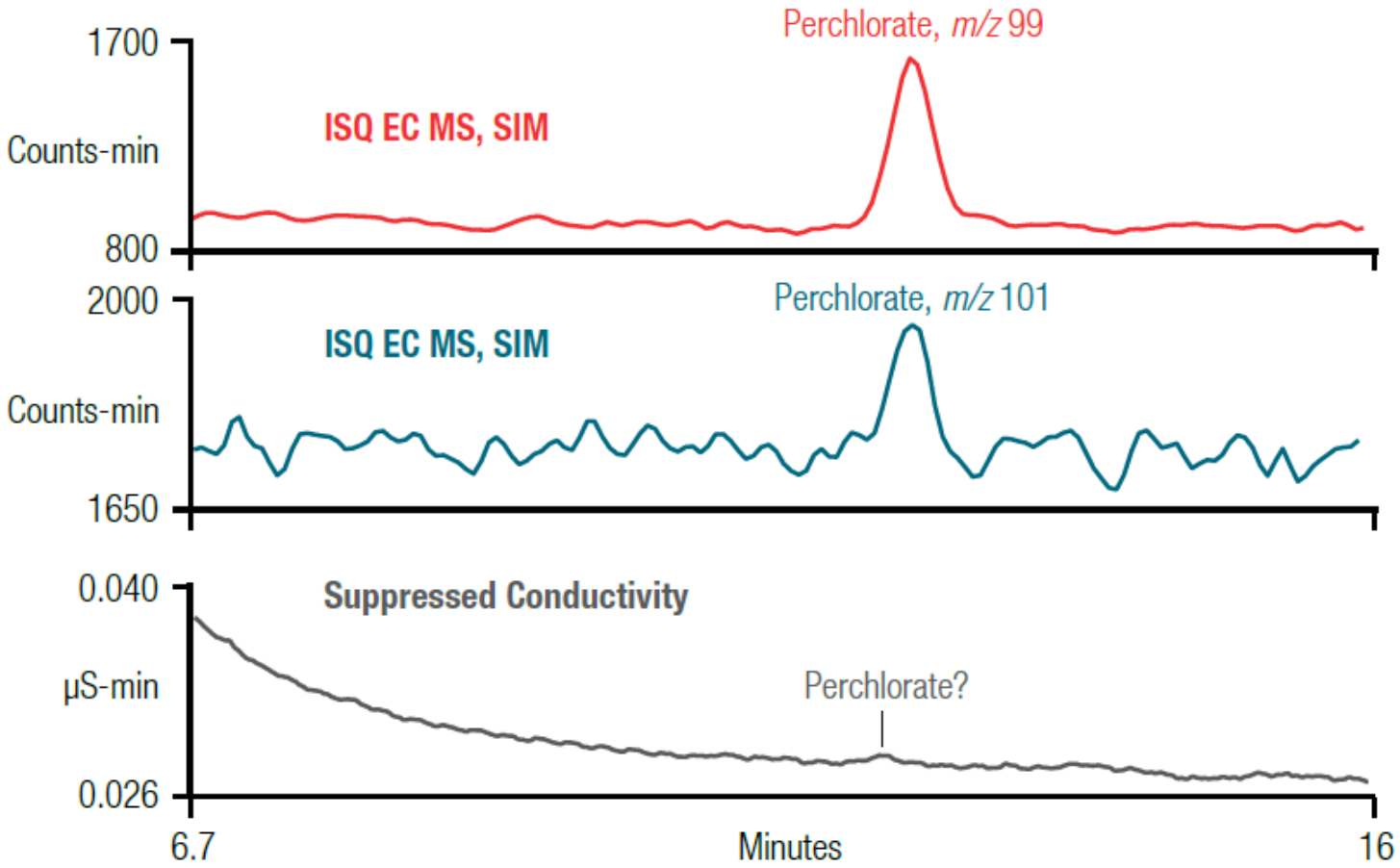
IC-MS Application Notes

- AN65196 – Tomorrow's quantitation with the TSQ Fortis mass spectrometer: robust, reproducible quantitation workflows of haloacetic acids, bromate, and dalapon in water according to EPA Method 557
- AN65201 – Tomorrow's quantitation: robust, reproducible quantitation workflows of perchlorate in water with IC-MS/MS
- AN72587 – Determination of perchlorate by U.S. EPA Method 332.0 using a compact ion chromatography system coupled with mass spectrometry
- AN72609 – Using Ion Chromatography with Electrospray Ionization Mass Spectrometry for the Determination of Cations and Amines in Alkanolamine Scrubbing Solutions
- AN72482 – Determination of urea in ultrapure water by IC-MS/MS
- AB104 – Determination of 32 Low Molecular Mass Organic Acids in Biomass by IC-MS
- AB72363 – Detection of common organic acids using a compact IC system coupled with MS
- AB72403 – Fast determination of inorganic cations and low mass amines in a spoiled grape juice sample using IC-MS
- AB72404 – Fast determination of inorganic cations and low mass amines in a spoiled cranberry juice sample using IC-MS
- AB72405 – Fast determination of inorganic cations and low mass amines in freshly prepared and moldy green tea samples using IC-MS
- AB72406 – Fast determination of low mass, inorganic cations in a ground water sample using IC-MS
- AB72454 – Detection of oxyhalides using a compact IC system coupled with MS

IC-MS Application Notes

- AU72507 – Determination of perchlorate in environmental waters using a compact ion chromatography system coupled with a single quadrupole mass spectrometer
- PN72144 – The analysis of polar ionic pesticides by ion-exchange chromatography tandem mass spectrometry
- PN85795 – Determination of Ultratrace Level Perchlorate in Liquid and Powdered Baby Formula

IC-MS: Improved Low-Mass Sensitivity in Drinking Water



Required LODs are not achievable by Conductivity Detection alone

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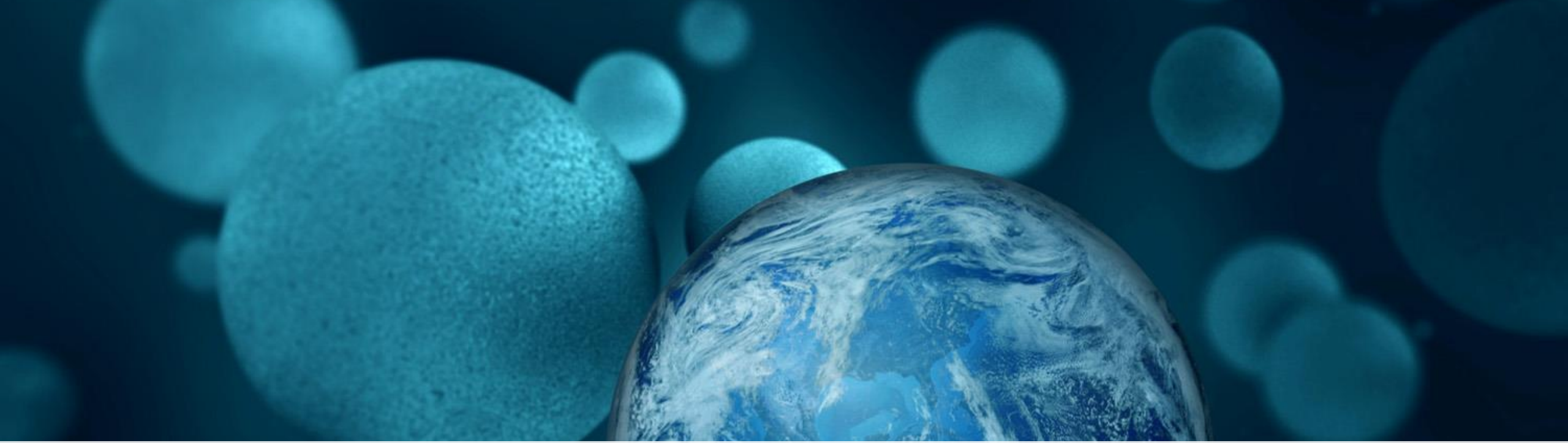

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Fast Analysis of Haloacetic Acids, Bromate and Dalapon Using Ion Chromatography Coupled with Mass Spectrometry

Disinfectant Byproducts (DBPs) Regulation

- Total Trihalomethanes (TTHMs) in 1970s
- 1998 U.S. EPA Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule:
  - Seven new regulations, including HAA5 and bromate
  - Monitoring of HAA5 at all plants that disinfect with chlorine
  - Report total MCAA, MBAA, DCAA, DBAA, and TCAA
  - Maximum Contamination Level (MCL) = 0.060 mg/L annual average
  - MCL Goal (MCLG): DCAA should not be present; TCAA < 0.030 mg/L
- 2006 U.S. EPA Stage 2 D/DBP Rule: Reduced MCLG
  - Total HAA5 MCL < 0.060 mg/L
  - MCAA < 0.07 mg/L; TCAA < 0.02 mg/L
  - DCAA should not be present

Haloacetic Acids (HAA5 and HAA9)

Acid	Abbreviation	Chemical Formula	pKa	Boiling Point °C
Monochloroacetic acid	MCAA*	$ClCH_2CO_2H$	2.86	187.8
Dichloroacetic acid	DCAA *	Cl_2CHCO_2H	1.25[a], 1.29[b], 1.30[c]	194
Trichloroacetic acid	TCAA *	Cl_3CCO_2H	0.63[a], 0.65[b], 0.70[c]	197.5
Monobromoacetic acid	MBAA *	$BrCH_2CO_2H$	2.87[a], 2.86[b], 2.7[c]	208
Dibromoacetic acid	DBAA *	Br_2CHCO_2H	1.47	238
Tribromoacetic acid	TBAA	Br_3CCO_2H	0.66	245
Bromochloroacetic acid	BCAA	$BrClCHCO_2H$	1.40	103.5
Dibromochloro acetic Acid	DBCAA	Br_2ClCCO_2H	0.03	217
Dichlorobromoacet-ic acid	DCBAA	Cl_2BrCCO_2H	NA	NA

* MCAA, DCAA, TCAA, MBAA, DBAA are collectively referred to as HAA5

Summary of EPA Methods for HAAs (& Bromate, Dalapon)

Technique	EPA Method	Thermo Scientific™ Dionex™ IonPac™ Columns	MDL (ppb)
1) Liquid/Liquid Extraction 2) Derivitization 3) GC-ECD	552.2 552.3	GC-ECD	Mono: 0.13–0.20
			Di: 0.02–0.08
			Tri: 0.03-0.10
IC-MS, IC-MS/MS	557	Thermo Scientific™ Dionex™ IonPac™ AG24 precolumn + Thermo Scientific™ Dionex™ IonPac™ AS24 separation column (2 mm i.d.)	Mono: 0.06–0.20
			Di: 0.02–0.11
			Tri: 0.04–0.09
2D-IC Suppressed Cond. (direct)	557.1	First dimension: Dionex IonPac AG24A precolumn + Dionex IonPac AS24A separation column (4 mm i.d.)	Mono: 0.17–0.45
			Di: 0.06–0.13
		Second dimension: Thermo Scientific™ Dionex™ IonPac™ AG26 precolumn + Thermo Scientific™ Dionex™ IonPac™ AS26 separation column(0.4 mm i.d.)	Tri: 0.08–0.27

METHOD 557: Determination of 9 HAAs, Bromate and Dalapon in Drinking Water by IC with Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS)

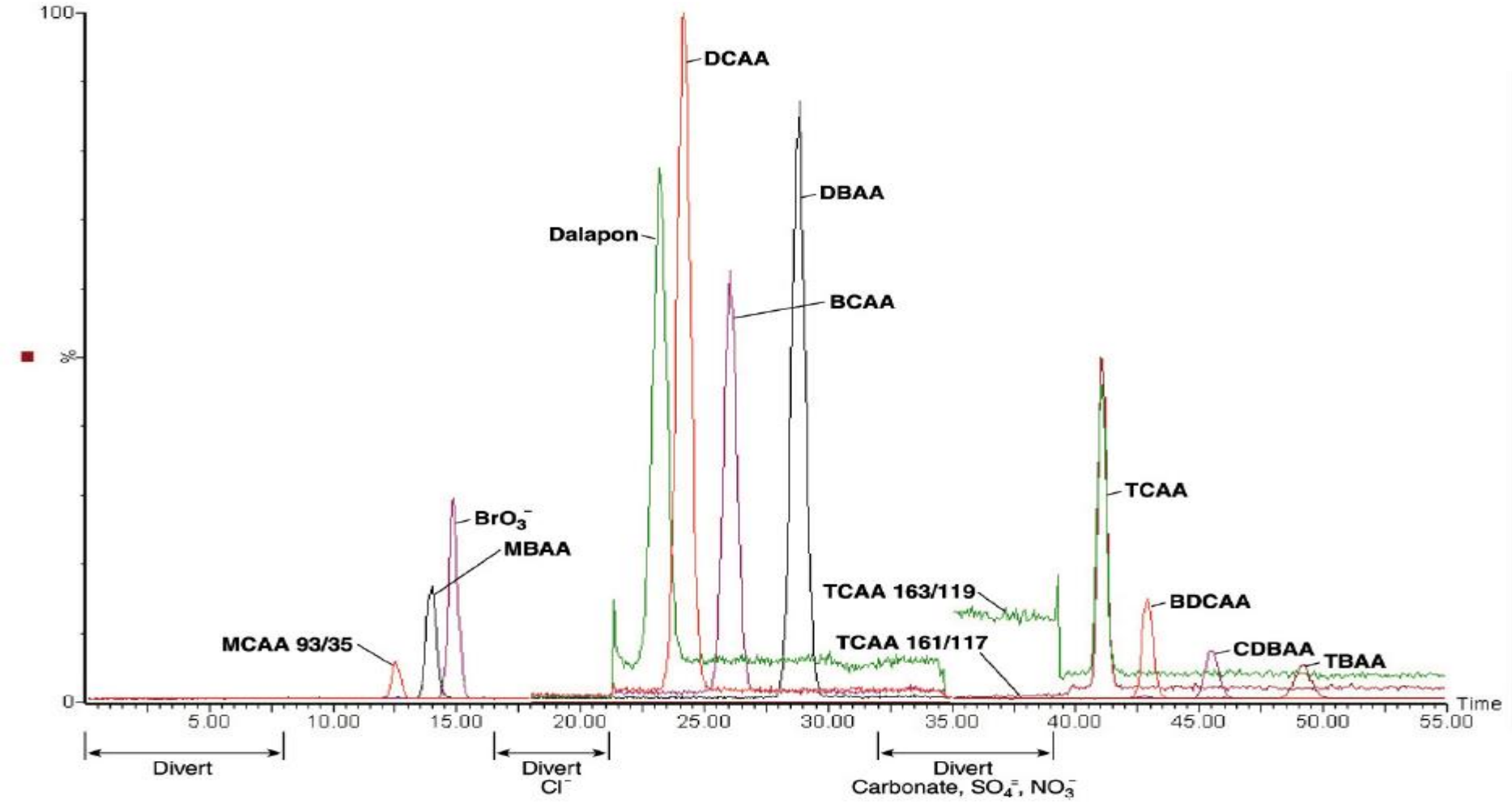

Figure 2. Dionex AS24 column: procedural calibration standard (5 µg/L).

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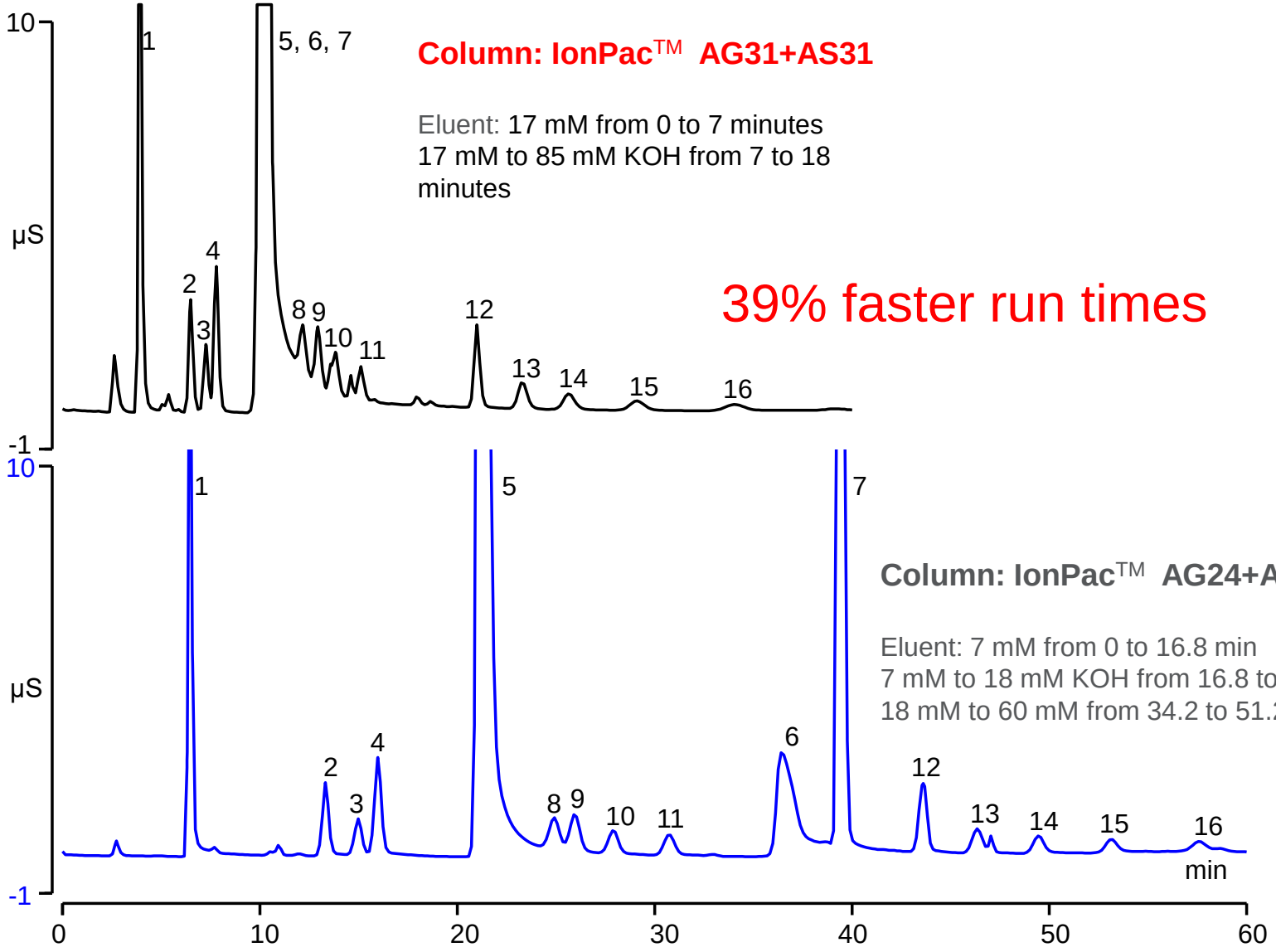
Separation of Haloacetic Acids, Dalapon, and Bromate in a Drinking Water Sample



Column:	See Chromatogram
Eluent :	See Chromatogram
Eluent Source:	Dionex™ EGC-500 KOH cartridge
Flow Rate:	0.30 mL/min
Inj. Volume:	100 µL
Temperature:	15 ˚C
Detection:	Suppressed Conductivity, Dionex ADRS 600 2mm AutoSuppression, recycle mode
Sample	Municipality Drinking Water Spiked with 9HAAs, Dalapon and Bromate

Peaks (Standard):	mg/L
1. Fluoride	NQ
2. Monochloroacetate	1.0
3. Monobromoacetate	1.0
4. Bromate	1.0
5. Chloride	NQ
6. Sulfate	NQ
7. Carbonate	NQ
8. Dalapon	1.0
9. Dichloroacetate	1.0
10. Bromochloroacetate	1.0
11. Dibromoacetate	1.0
12. Nitrate	NQ
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

NQ: Not Quantified

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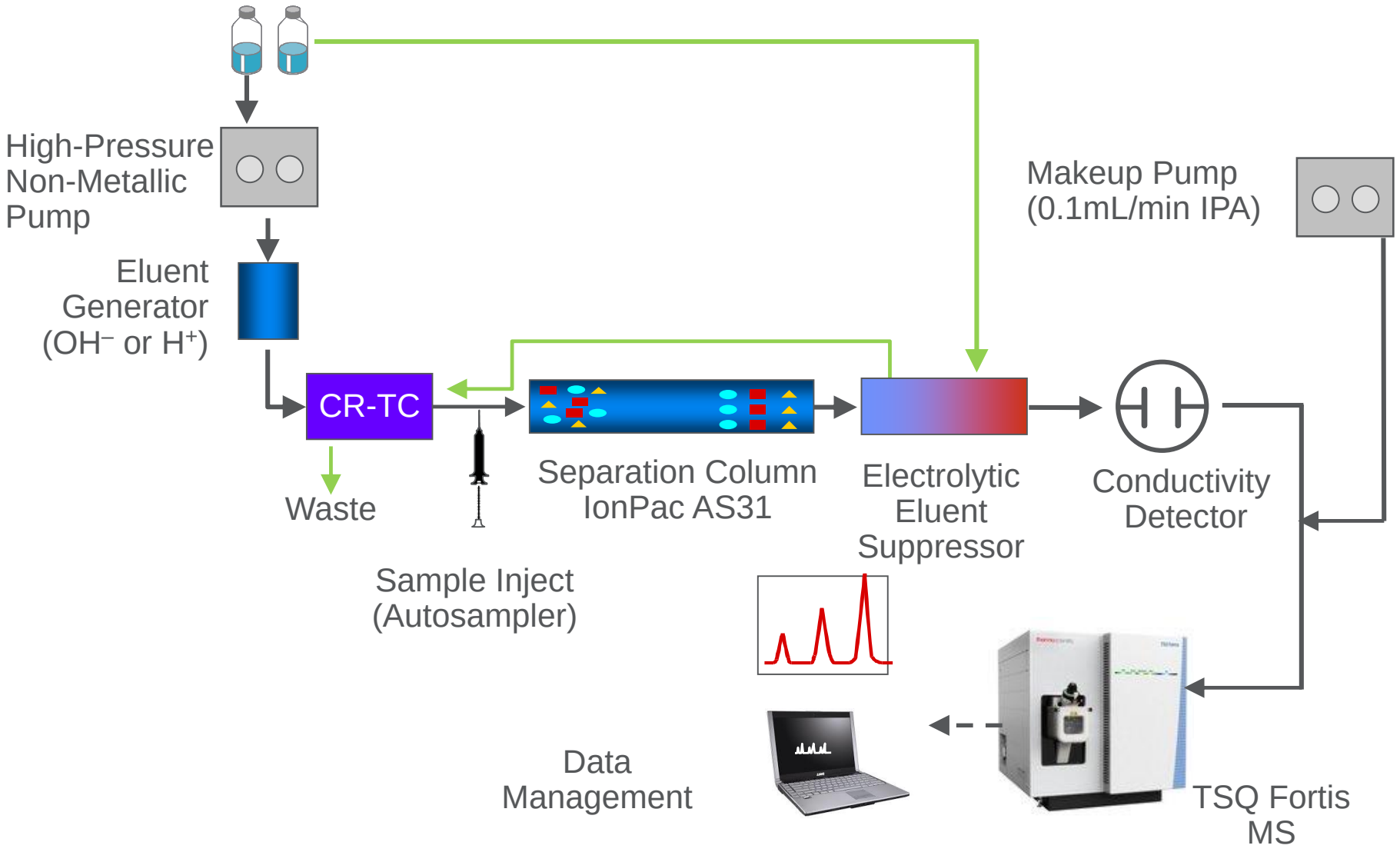
IC-MS System Setup Using a Dionex™ IonPac™ AS31 Column



Dionex IonPac AS31: HAA Analysis Low Temperature Requirement

- Operates at 15°C
  - Minimize potential for HAA degradation
  - Thermo Scientific ICS-5000^{+} or ICS-6000 HPIC system with **low temperature DC** required

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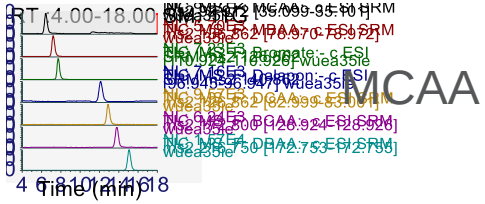
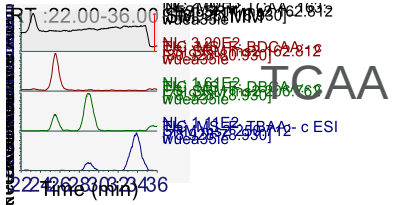
IC-MS Results for 9 HAAs, Dalapon and Bromate



MCAA



TCAA

MBAA

Bromate

Dalapon

DCAA

BCAA

DBAA

BDCAA

DBCAA

TBAA

Concentrations of 9 HAAs, Dalapon and Bromate are 5 ppb in 100 mg/L NH_4Cl

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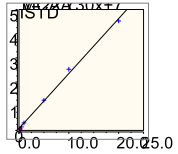
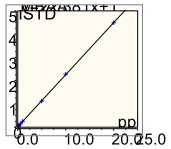
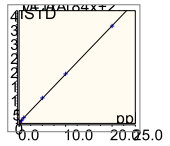
Calibration Curves: Five Regulated HAAs, Bromate, and Dalapon



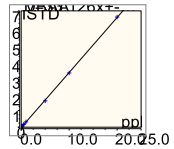
MCAA



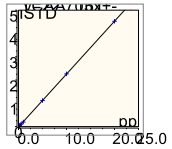
MBAA



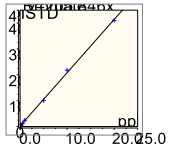
DCAA



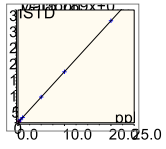
DBAA



TCAA



Bromate



Dalapon

Linear curves obtained from 0.25-20 ppb with all R^2>0.99 for five regulated HAAs, Bromate and Dalapon

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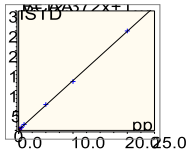
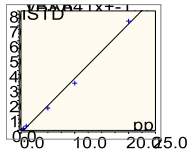
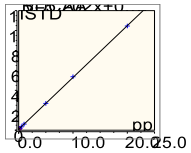
Calibration Curves : BCAA, BDCCA, DBCAA, and TBAA



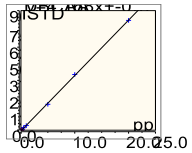
BCAA



TBAA



DBCAA



TBAA

Linear curves obtained from 0.25-20 ppb with all R^2>0.99 for the other 4 unregulated HAAs

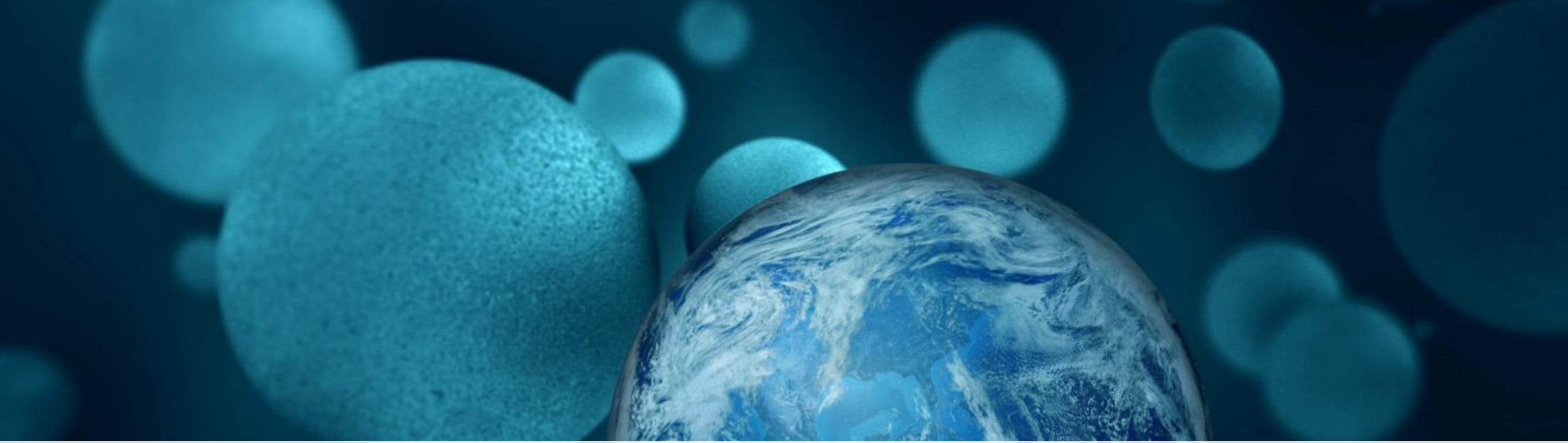
IC-MS Method Detection Limits Obtained Using Dionex™ IonPac™ AS31Columns

MDL (µg/L, n=7)	Abbreviation	EPA Calculated DL	AS31 Calculated DL
Monochloroacetic acid	MCAA	0.2	0.19
Monobromoacetic acid	MBAA	0.064	0.021
Bromate	Bromate	0.02	0.014
Dalapon	Dalapon	0.038	0.079
Dichloroacetic acid	DCAA	0.055	0.019
Bromochloroacetic acid	BCAA	0.11	0.086
Dibromoacetic acid	DBAA	0.015	0.009
Trichloroacetic acid (163/119)	TCAA	0.09	0.073
Bromodichloroacetic acid	BDCAA	0.05	0.087
Chlorodibromoacetic acid	DBCAA	0.041	0.19
Tribromoacetic acid	TBAA	0.067	0.067

Comparable MDLs obtained for the target analytes

Summary

- Thermo Scientific™ Dionex™ IonPac™ AS31 columns are packed with a novel anion exchange resin developed specifically for faster analysis of haloacetic acids (HAAs), bromate, and dalapon.
- AS31 columns have high ion exchange capacity and allow large loop injections for trace analysis (µg/L) without sample pre-treatment.
- AS31 columns operates at 15 °C and about 3200 psi, so a Thermo Scientific Dionex ICS-5000+ or ICS-6000 HPIC system is required.
- AS31 columns can meet or exceed the performance requirements of EPA Method 557.
- AS31 columns deliver 39% faster run times relative to IonPac AS24 columns, reducing the EPA Method 557 run time from 57 minutes to 35 minutes



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Polar Pesticides Analysis Using Ion Chromatography Coupled with Mass Spectrometry

IC-MS/MS Configuration for Polar Pesticides Analysis

- IC-System: Dionex Integrion RFIC
  - Eluent Source: Dionex EGC 500 KOH
  - Eluent: Potassium Hydroxide
  - Suppressor: AERS 500e – 2mm External water mode regeneration
- External Pump 1 (for suppressor regeneration): Dionex AXP-MS Auxiliary pump
- External Pump 2 (for make-up flow): Dionex AXP-MS Auxiliary pump
- Autosampler: AS-AP Dionex Autosampler (PN: 074926)
- Mass Spectrometer: TSQ Quantiva

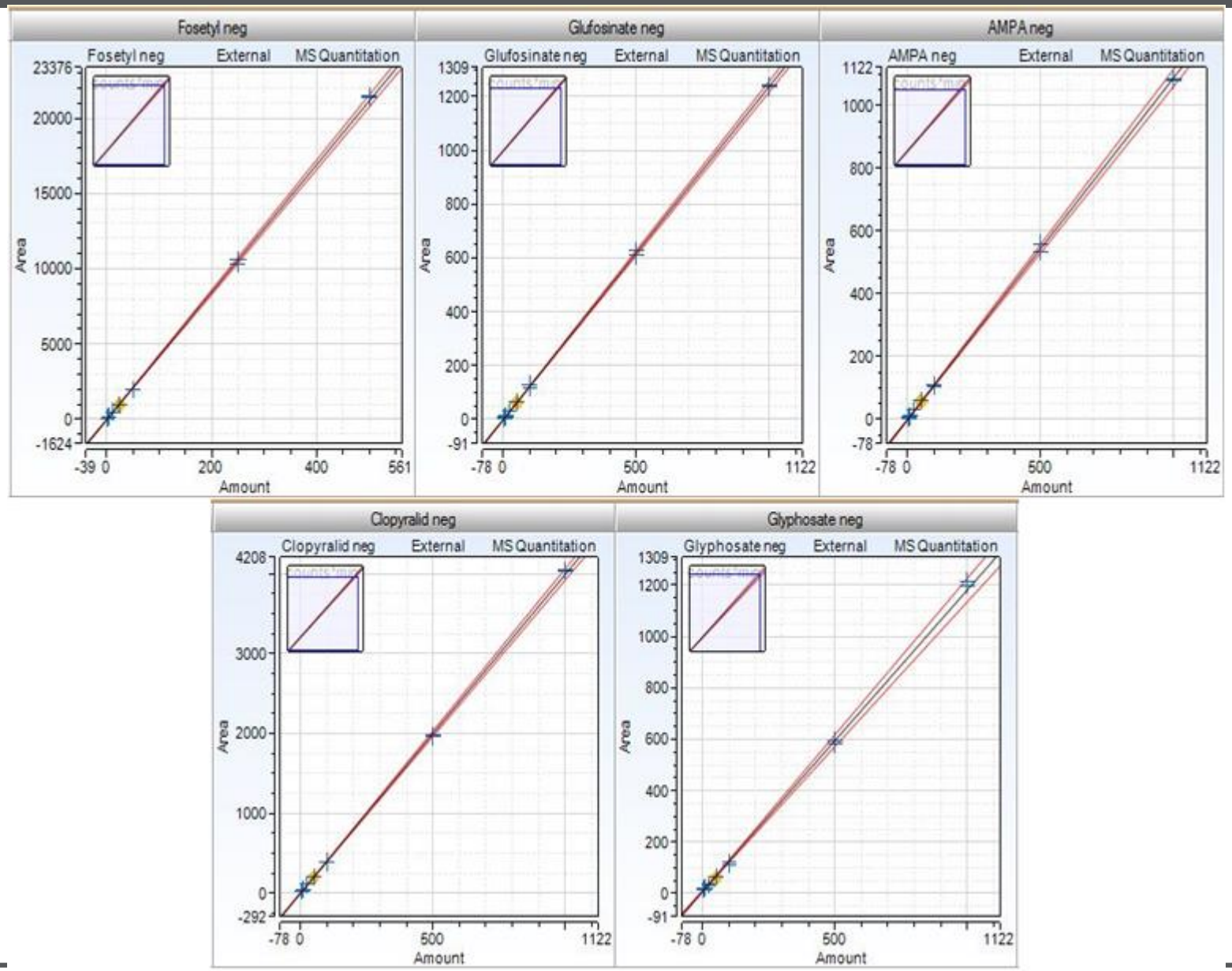
IC-MS Conditions

Column:	**AS24 (2 x 250 mm**)	Ion Source Type	H-ESI
Guard Column:	**AG24 (2 x 50 mm)**	Spray Voltage (Neg)	2800 V
Eluent:	KOH	Sheath Gas (Arb)	30
Column Temperature:	30 ºC	Aux Gas (Arb)	12
Flow rate:	0.3 ml/min	Sweep Gas (Arb)	1
Make-up flow:	0.1 ml/min	Ion Transfer Tube	340ºC
Make-up solvent:	IPA, 0.1 mL/min	Vaporizer Temperature	360 ºC
Duration:	22 min	Cycle time (s)	0.5
Injection volume:	100 µL	Q1/Q3 Resolution (FWHM)	0.7
Injection Mode:	PushFull	CID gas (mTorr)	1.5
Loop Overfill:	2.000	Source Fragmentation (V)	0
		Use calibrated RF Lens:	

IC method

Time (min)	Potassium hydroxide (KOH) (mM)	Suppressor current (mA)
0	22	25
7	25	25
7.1	40	25
9.5	40	25
9.6	80	25
10.6	80	75
14.5	80	75
14.6	100	75
17	100	75
17.1	22	75
18	22	25
20	22	25

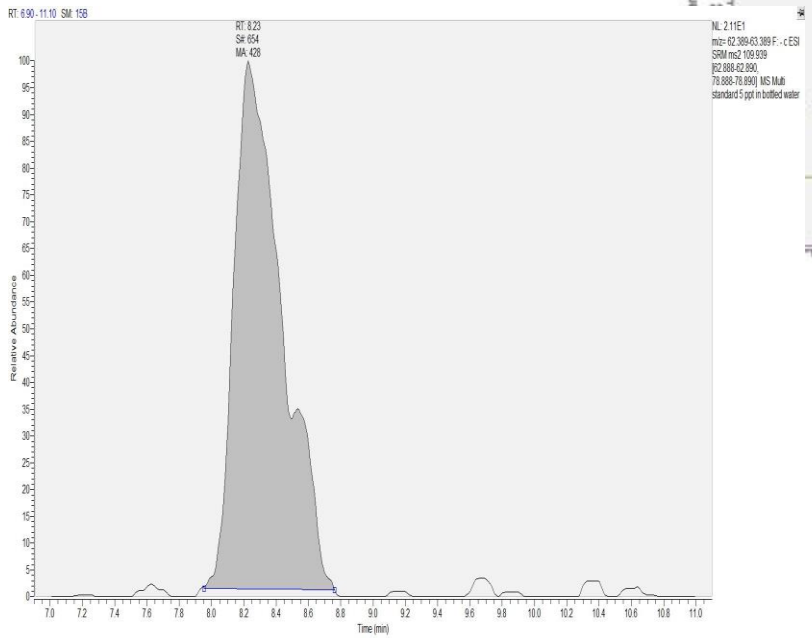
Calibration Drinking Water



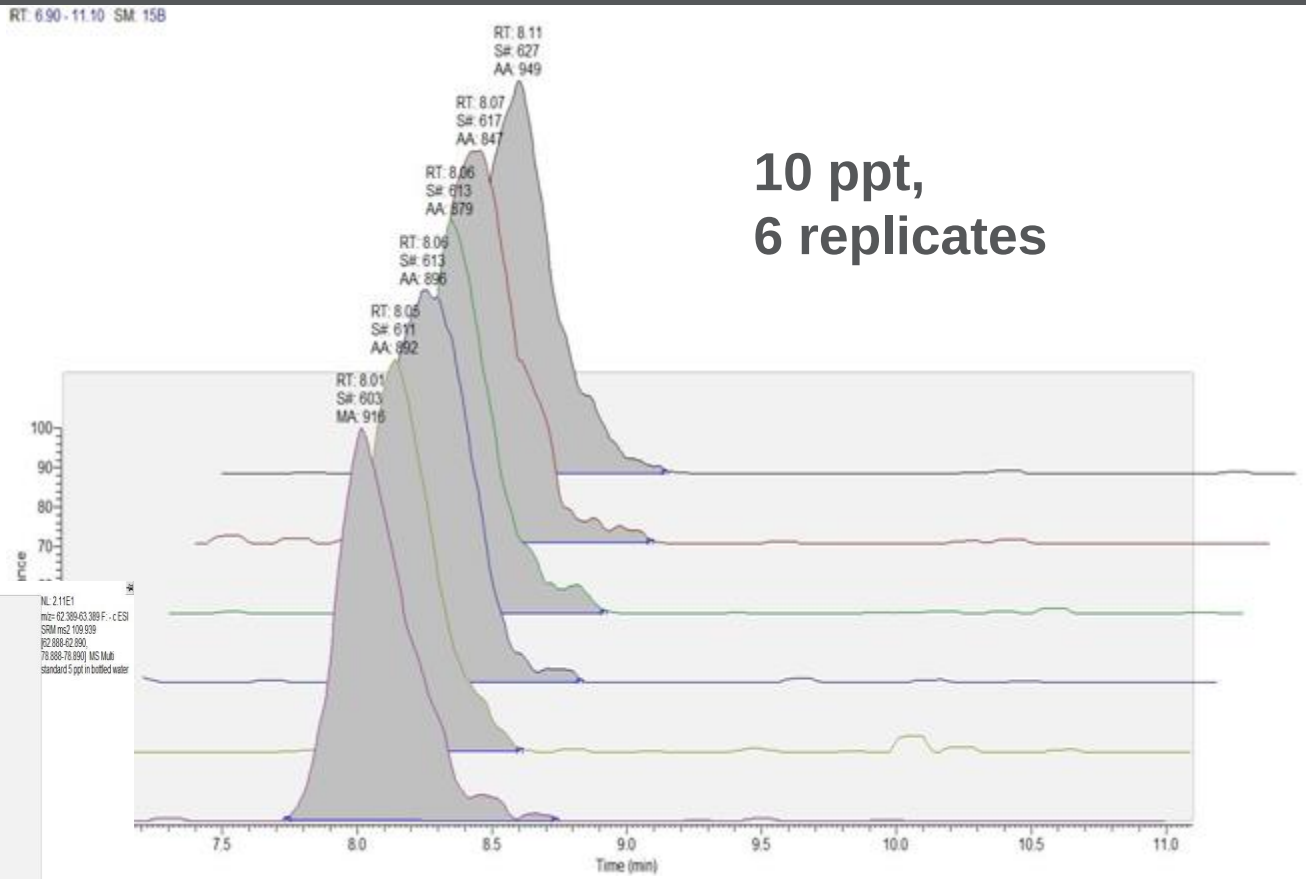
Bottled Evian Water performance

Name	LOD [ppt]	LOQ [ppt]	RSD % (10 ppt) level
Fosetyl-Al	1	2.5	5
Clopyralid	10	50	9
AMPA	2	5	9
Glyphosate	5	10	15
Glufosinate	2	5	4

Bottled water - AMPA



5 ppt



10 ppt,
6 replicates

* 6 vials in a row

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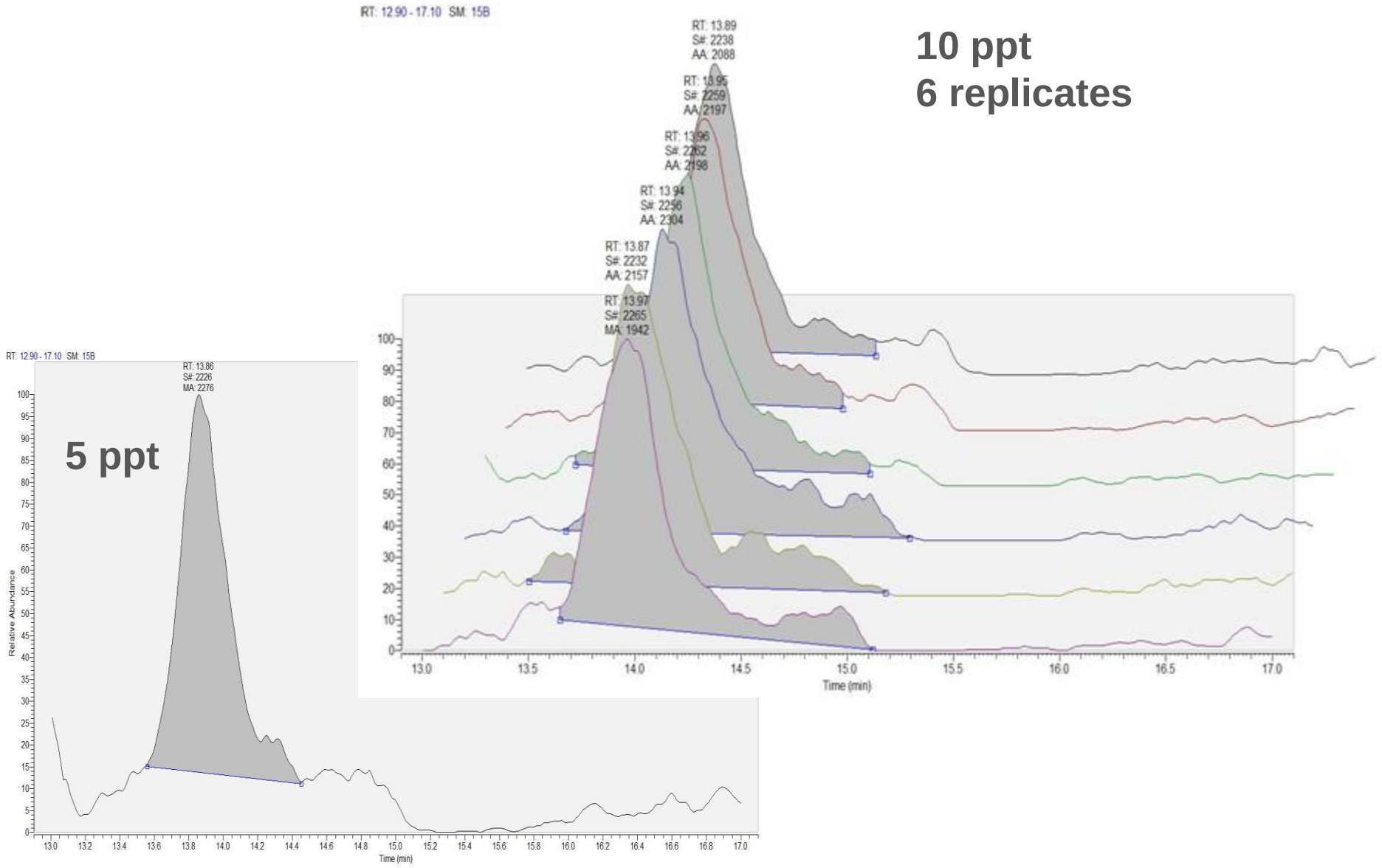
Bottled water - Glyphosate



* 6 vials in a row

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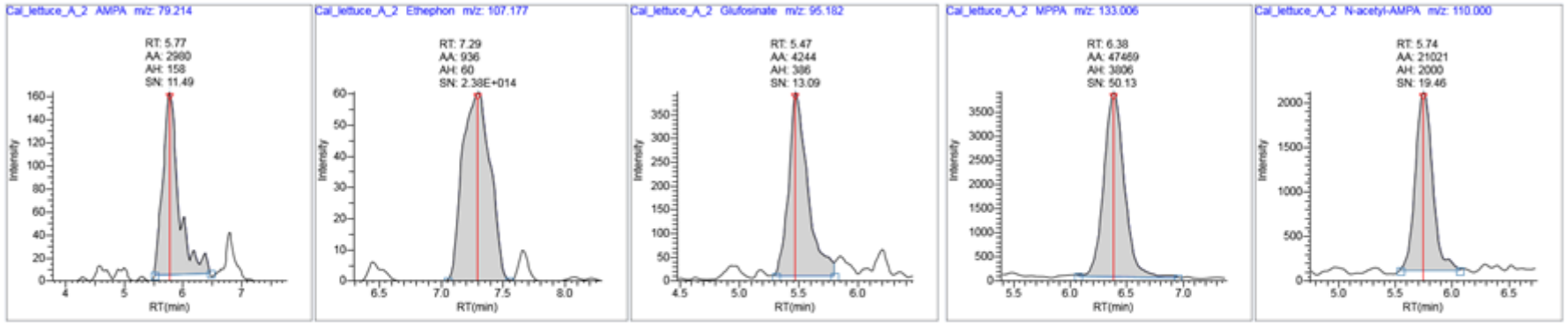
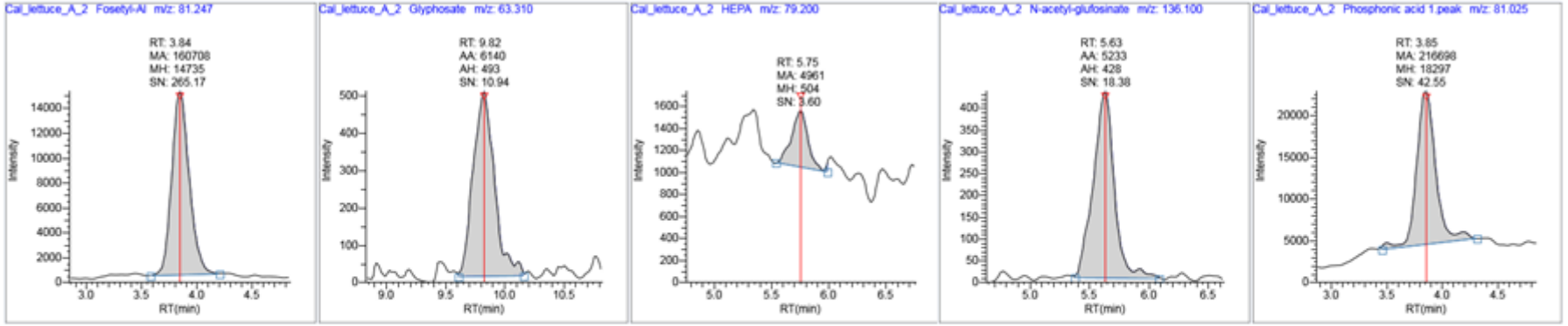
Food Analysis – Polar Pesticides by IC-MS/MS LOD and LOQ

Analyte	LOD (µg/kg)	LOQ (µg/kg)	LOD (pg on column)	LOQ (pg on column)
AMPA	10	20	100	200
Ethephon	10	20	100	200
Fosetyl-Al	10	20	100	200
Glufosinate	1	10	10	100
Glyphosate	5	10	50	100
HEPA	10	20	100	200
Maleic hydrazide	100	200	1000	2000
MPPA	1	10	10	100
N-acetyl-AMPA	1	10	10	100
N-acetyl-glufosinate	3	10	30	100
Phosphonic acid	1	10	10	100

10 ppb in lettuce



AMPA Ethephon Glufosinate MPPA N-Acetyl-AMPA



Fosetyl-Al Glyphosate HEPA N-acetyl-Glu Phosphonic acid

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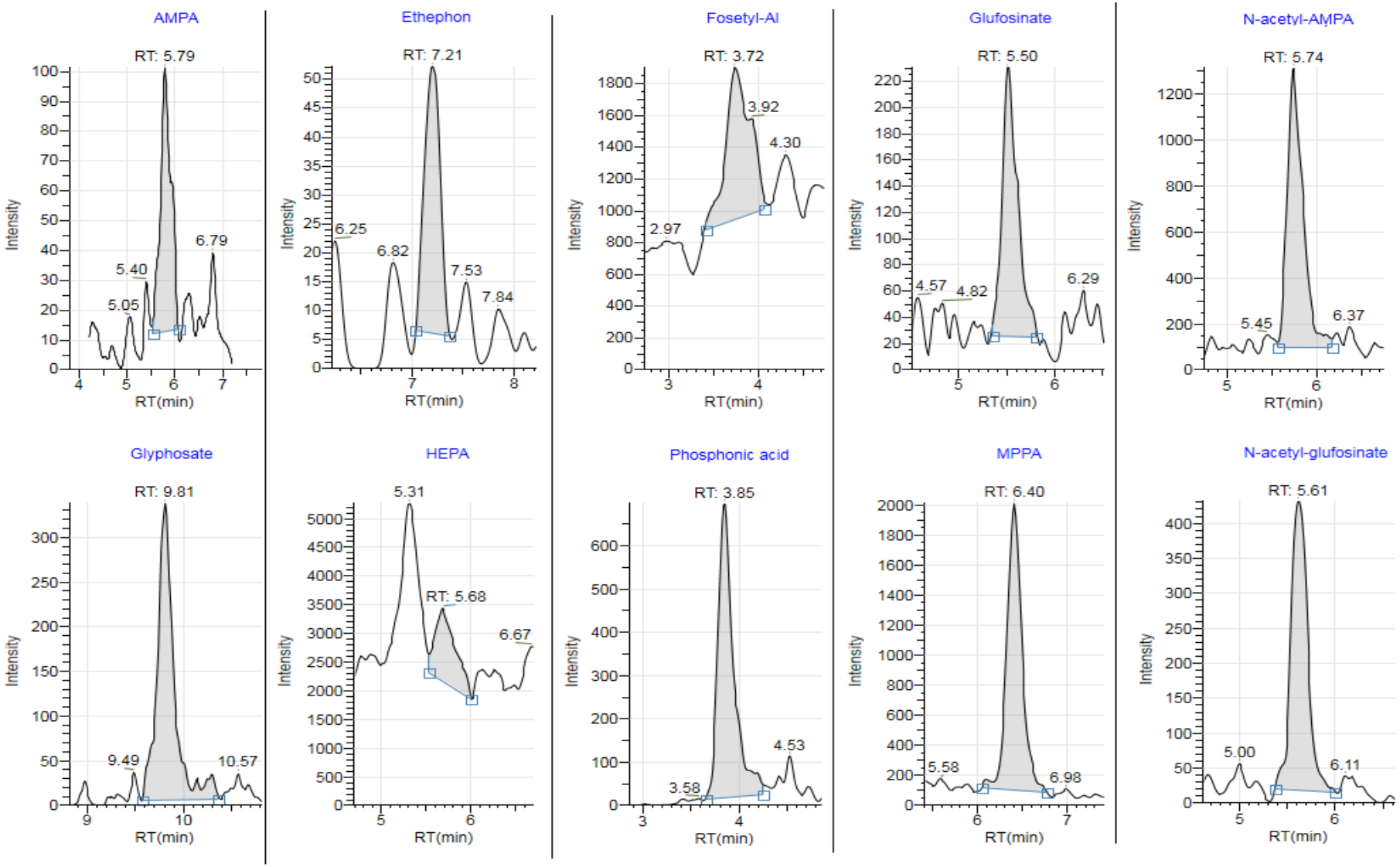
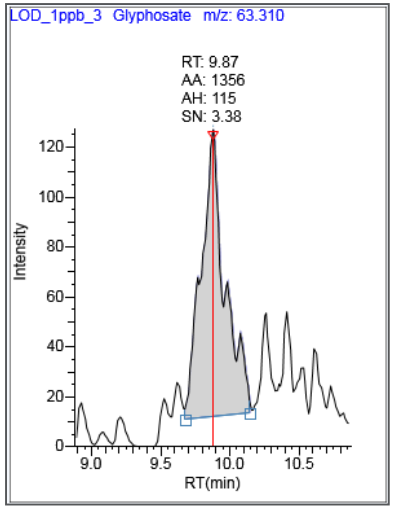
10 ppb in oranges

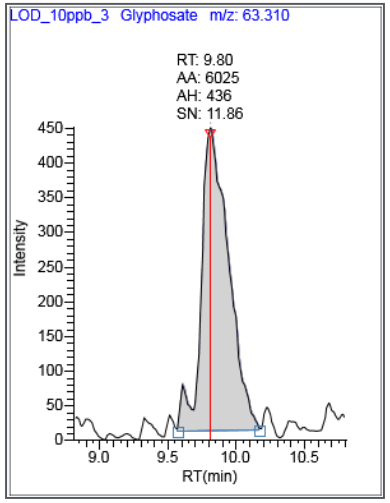


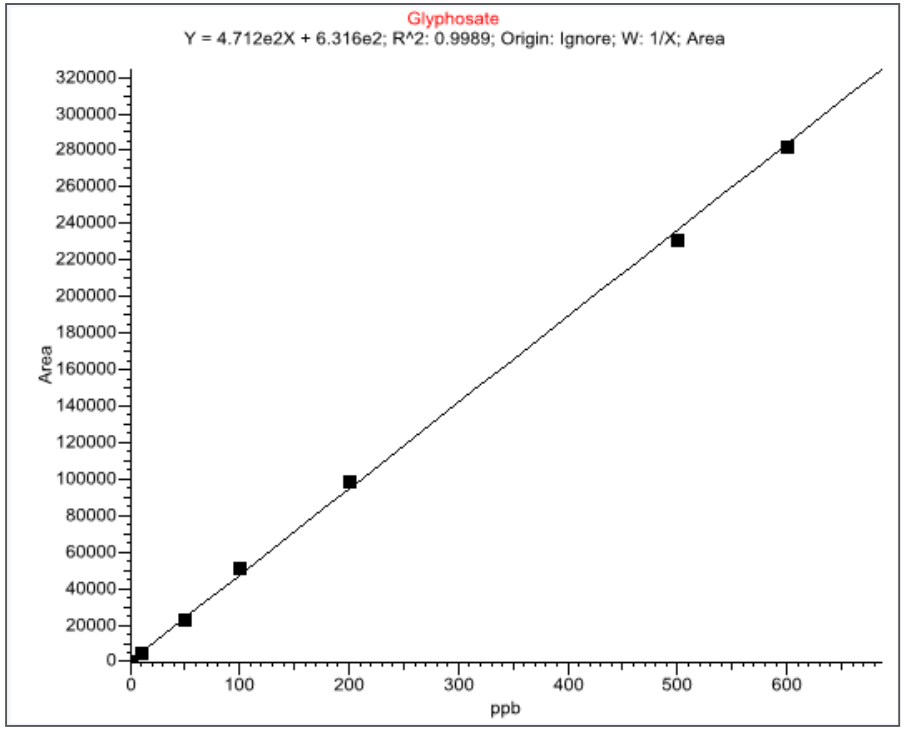
Quan Details Glyphosate in lettuce

1 ppb (LOD = 5 ppb)



LOQ – 10 ppb

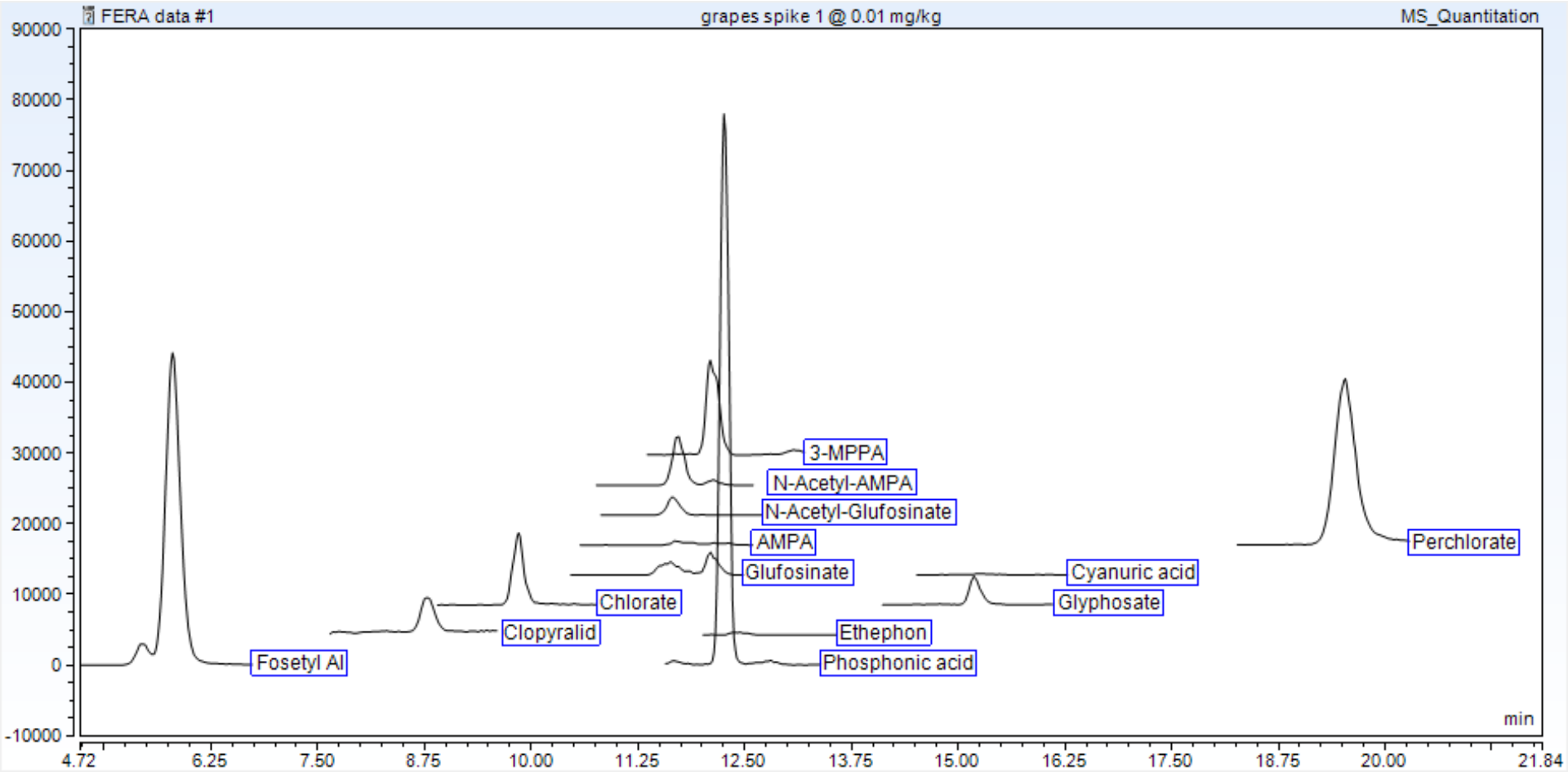




Calibration range in matrix: 10 – 600 ppb

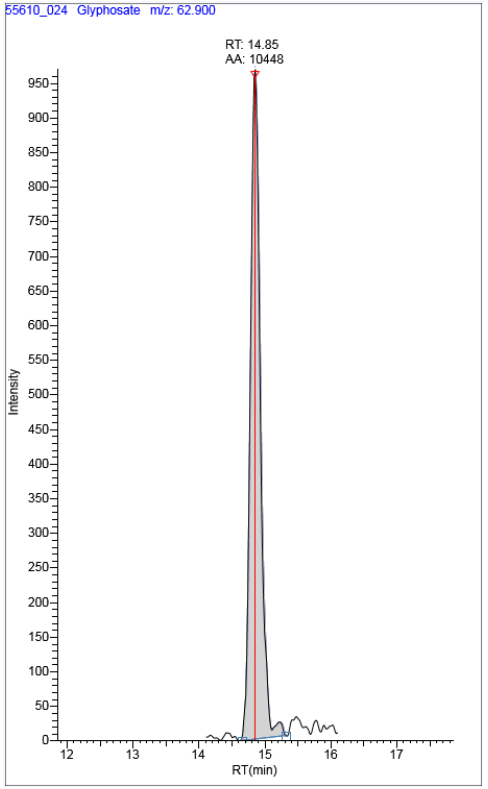
IC-MS/MS pesticide multi residue ion chromatogram

- 10 µg/kg spike in grape (Fosetyl & Phosphonic acid @ 100 µg/kg)

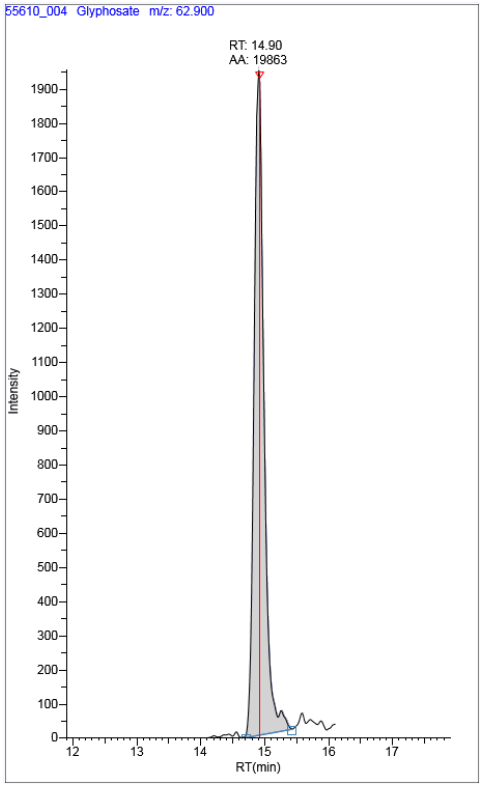


Glyphosate in Beer – No Extraction Required

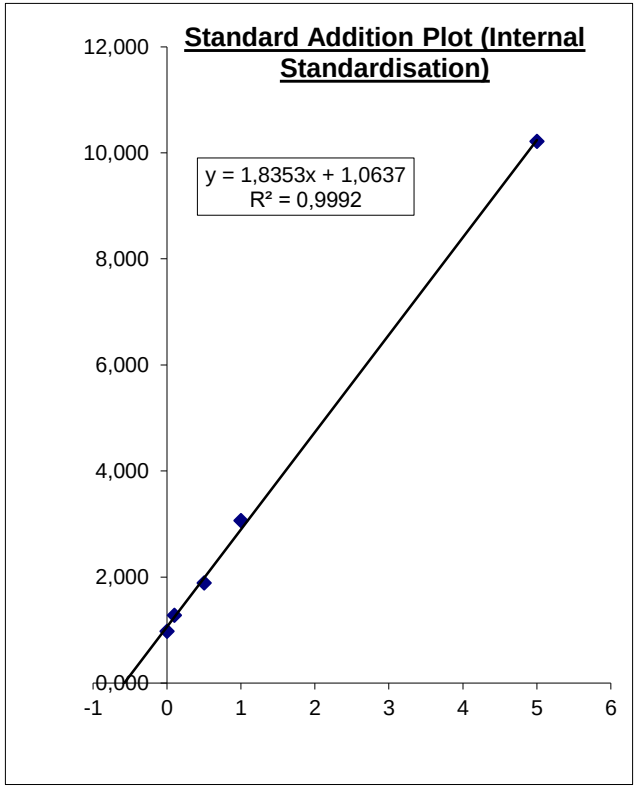
- Glyphosate incurred residue @ 0.58 µg/L



Glyphosate spike @ 0.5 µg/L



Calibration plot 0.1 – 5 µg/L spikes



- 1/10 dilution with water and internal standard added

Courtesy of Fera Science Ltd UK

Thanks for Your Attention!

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Comparing Dionex Ion Chromatography Systems

Feature	Value	Aquion	Integrion	ICS-4000	ICS-6000
High Performance Pump	Consistent, accurate results	✓	✓	✓	✓
Electrolytically Regenerated Suppressor	Saves time and money	✓	✓	✓	✓
Sample Preparation	Labor, operational, and capital savings	✓	✓	✓	✓
Eluent Generation – just add water	Increased throughput, operational savings		✓	✓	✓
Gradient Separations	Saves time and labor		✓	✓	✓
Integrated Electrochemical Cell	Capital savings, expand lab capabilities		✓	✓	✓
High Pressure IC up to 5000 psi	Increased throughput, Expanded capabilities		✓	✓	✓
Consumables Device Monitor	Maximize instrument uptime		✓		✓
Unity Remote Services	Maximize instrument uptime		✓		✓
Tablet control of system	Increased convenience		✓		✓
IC PEEK Viper Fittings	Consistent, accurate results		✓	✓	✓
Capillary IC Capability	Increased throughput, operational savings			✓	✓
Modularity	Capital savings				✓
Configurable as Independent Dual System	Capital savings				✓
Proportioned Mechanical Gradients	Expanded capabilities				✓
2-D Chromatography	Expanded capabilities				

IC-MS System Operating Conditions Using a Dionex™ IonPac™ AS31Column

Thermo Scientific™ Dionex™ ICS-6000 System and Thermo Scientific™ TSQ Fortis™ Mass Spectrometer

Column:	IonPac AS31 2 x 250 mm + 2 x 50 mm Guard
Eluent:	KOH Gradient (see Timed Events)
Suppressor:	ADRS® 600, 2-mm, external water, 0.3 mL/min
Suppressor Current:	64 mA
Analytical Flow Rate:	0.3 mL/min
Column Temp:	15 °C
Injection Volume:	100 µL
Detector:	CD, TSQ Fortis

TSQ Fortis Tune Parameters:

Ion Source Type:	H-ESI (Negative Polarity)
Spray Voltage:	3200 V
Cycle Time:	2.3 secs
Resolution:	Q1 (FWHM) 0.7
	Q3 (FWHM) 0.7
CID Gas:	2 mTorr
Sheath Gas:	50 Arb
Aux Gas :	10 Arb
Sweep Gas:	3 Arb
Ion Transfer Tube Temp:	225°C
Vaporizer Temp:	275°C

Timed Events

Time	[KOH], mM	Divert Valve
-5.0 Begin	17.0	Eluent to Waste
0.0	17.0	
5.0	17.0	Eluent to MS
7.0	17.0	
8.5		Eluent to Waste
11.1		Eluent to MS
15.6		Eluent to Waste
18.0	85.0	
21.7		Eluent to MS
35.0	85.0	Eluent to Waste
35.1	17.0	
36.0 End		

Recovery of 2µg/L HAAs, Delapon and Bromate Spiked in Reagent Water and LSSM

Analyte	Reagent Water Spiked with Analytes at 2µg/L		LSSM Spiked with Analytes at 2µg/L	
	% Recovery	% RSD (n=7)	% Recovery	% RSD (n=7)
MCAA	99.6	3.4	104.5	5.1
MBAA	101.6	3.8	103.5	4.2
Bromate	103.9	2.8	101.1	5.3
Dalapon	104.2	1.8	99.2	3.2
DCAA	109.7	1.8	110.1	2.0
BCAA	103.5	2.4	106.8	4.1
DBAA	101.7	0.6	101.0	2.8
TCAA	102.2	6.7	105.8	8.6
BDCAA	98.2	3.1	97.0	4.4
DBCAA	92.0	6.7	93.3	7.3
TBAA	92.0	3.7	98.4	7.4
AVG	100.8	3.4	101.9	4.9

All recoveries within 90-110 % with all %RSDs ≤10 to meet the EPA requirements

Recovery of 2µg/L HAAs, Delapon and Bromate in a City Tap Water Sample

Analytes	City Tap Water		City S water spiked 2µg/L	
	Conc.	%RSD	REC (%)	RSD (%)
MCAA	2.706	2.0	107.6	5.1
MBAA	0.078	4.9	104.2	4.0
Bromate	0.084	5.4	99.0	4.5
Dalapon	0.288	5.0	102.8	4.0
DCAA	12.36	0.8	107.0	2.0
BCAA	2.431	3.2	93.6	3.2
DBAA	0.339	0.4	94.8	2.2
TCAA_163	4.484	0.5	98.1	5.4
BDCAA	1.107	10	104.2	7.0
DBCAA	--	--	108.1	5.7
TBAA	--	--	102.7	5.7
AVG			102.0	4.4

- All recoveries within 90-110 % with all %RSDs ≤10 to meet the EPA requirements

Recommended IC-MS/MS configuration for polar pesticides in food

- IC-System: Dionex Integrion HPIC (PN: 22153-60208)
  - Eluent Source: Dionex EGC 500 KOH (PN: 075778)
  - Eluent: Potassium Hydroxide
  - Suppressor: AERS 500 – 2mm (PN: 082541)
    - External water mode regeneration
- External Pump 1 (for suppressor regeneration): Dionex AXP-MS Auxiliary pump (PN: 60684)
- External Pump 2 (for make-up flow): Dionex AXP-MS Auxiliary pump (PN: 60684)
- Autosampler: AS – AP Dionex Autosampler (PN: 074926)
-

IC-MS/MS Conditions

- Column: AS24 (2 x 250 mm)
- Guard Column: AG24 (2 x 50 mm)
- Eluent: KOH
- Injection volume: 10 µL
- Column Temperature: 21 ºC
- Flow rate: 0.3 ml/min
- Make-up flow: 0.1 ml/min
- Make-up solvent: CH_3OH

Time (min)	Concentration of KOH in eluent (mM)
0	25
0.2	25
11	80
11.1	100
12.5	100
12.6	25
17.0	25

- Ion Source Type: H-ESI
- Spray Voltage (Neg): 2500V
- Sheath Gas (Arb): 20
- Aux Gas (Arb): 5
- Sweep Gas (Arb): 0
- Ion Transfer Tube: 329ºC
- Vaporizer Temperature: 400 ºC
- Dwell Time (ms): 10
- Q1/Q3 Resolution (FWHM): 0.7
- CID gas (mTorr): 1.5
- Source Fragmentation (V): 0
- Use calibrated RF Lens: YES

Recovery and Repeatability

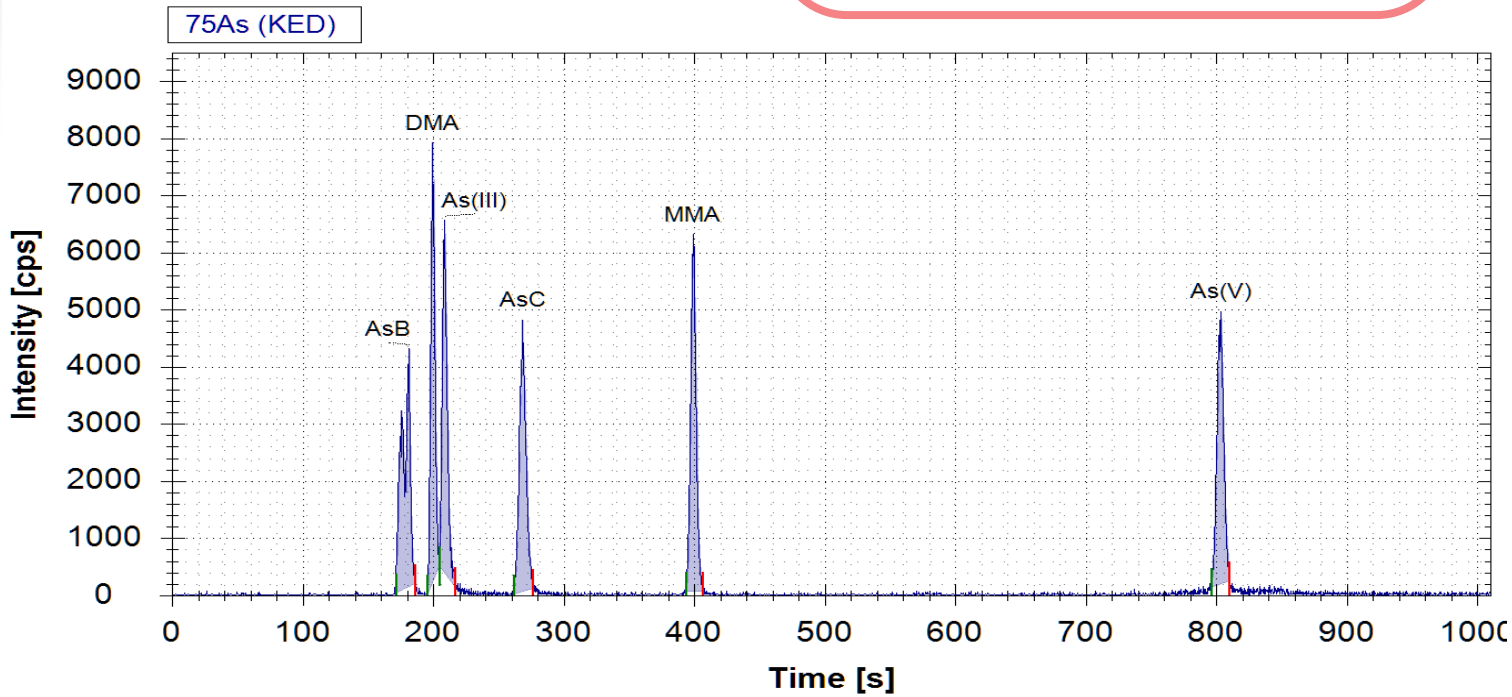
- 3 levels: 50, 200 and 500 µg/kg
- 6 repetitions at each level

Analyte	Level 1 (in ppb)		Level 2 (in ppb)		Level 3 (in ppb)	
	REC %	RSD %	REC %	RSD %	REC %	RSD %
AMPA	84	14	85	8	80	3
Ethephon	120	10	88	5	92	12
Fosetyl-Al	98	16	97	12	82	3
Glufosinate	101	4	93	8	86	3
Glyphosate	88	12	83	10	81	3
HEPA	118	7	93	9	81	4
Maleic hydrazide	51	245	0	-	40	117
MPPA	116	4	98	8	81	3
N-acetyl-AMPA	95	8	89	9	79	2
N-acetyl-glufosinate	93	8	91	8	84	2
Phosphonic acid	115	11	99	11	81	3

IC coupled to ICP-MS

Narrow peak width enables high signal to noise, resulting in lower LODs

Improved column chemistry provides better resolution even for closely eluting peaks



BENEFITS

- Completely **metal-free** flow path
  - Less contamination
  - Lowest chemical noise
  - Better S/N
  - Lower LOD
- Narrower bore columns (2 mm ID)
  - Narrower peak shapes
  - Better S/N

Metal-free flow path ideal for metal speciation applications

IC-MS Application Notes

	ISQ EC	TSQ Fortis TSQ Quantis TSQ Altis	Q Exactive Q Exactive Focus/Plus
Integrion	AN151 AN243 AN269 AN276 AN409 AN72587 AN72609 AB104 AB72363 AB72403 AB72404 AB72405 AB72406 AB72454 AU72507	AN243 AN263 AN269 AN479 AN491 AN661 AN65201 AN72482 PN72114 PN85795	AN491 AN661 PN72114

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IC-MS Application Notes

	ISQ EC	TSQ Fortis TSQ Quantis TSQ Altis	Q Exactive Q Exactive Focus/Plus
ICS-6000	AN151 AN243 AN269 AN276 AN409 AN1000 AN72587 AB104 AB72363 AB72403 AB72404 AB72405 AB72406 AB72454 AU72507	AN243 AN454 AN263 AN269 AN479 AN491 AN630 AN661 AN65196 AN65201 AN72482 PN72114 PN85795	AN491 AN622 AN661 PN72114

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