Application Notebook

IC-MS Environmental Applications - Water Testing

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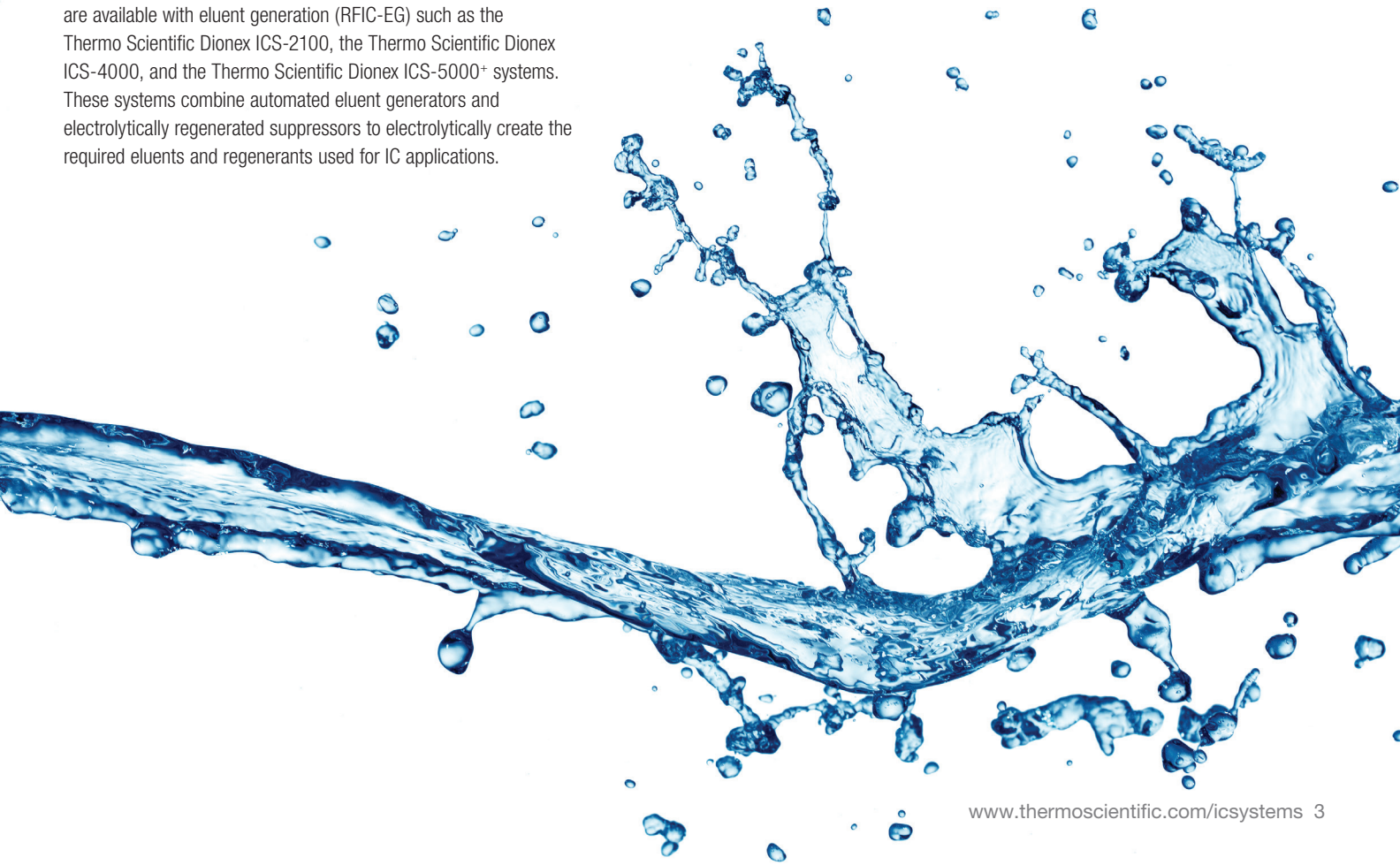
Environmental Sample Analysis using IC-MS

Trace analysis for environmental samples is especially challenging since it requires sensitive detection but also removal of matrix interferences. Ion-exchange chromatography coupled with mass detection (IC-MS) is an ideal solution for many critical contaminants. The specificity and selectivity of ion-exchange has a greater resolving power for ionic contaminants than reversed phase separations which do not take advantage of anion- or cation-exchange selectives. Conversely, mass spectrometry (MS) methods have been developed for the analysis of organic compounds using reversed-phase separations that provide simultaneous mass accuracy and confirmation. High-ionic strength matrices also cause significant signal suppression in the mass detector. A strategy often applied is the use of ion pairing agents and ionic compounds containing a hydrocarbon chain that imparts certain hydrophobicity, forcing ion pair retention on a reversed-phase column. However, ion pairing agents are typically strong acids, with potential to damage the electrospray ionization (ESI) source within the MS detector or cause signal suppression. For these reasons, the coupling of ion-exchange with MS detection has been problematic in the past.

Fortunately, there is an IC-MS solution to overcome many of these separation and detection challenges. The Thermo Scientific™ Dionex™ Reagent-Free™ Ion Chromatography (RFIC™) system was developed primarily for the separation of anions and cations through ion-exchange-based separations using conductivity detection. By utilizing a Dionex RFIC system, you gain premier technology for ease of use, improved gradient separations and low-level detection. These systems are available with eluent generation (RFIC-EG) such as the Thermo Scientific Dionex ICS-2100, the Thermo Scientific Dionex ICS-4000, and the Thermo Scientific Dionex ICS-5000+ systems. These systems combine automated eluent generators and electrolytically regenerated suppressors to electrolytically create the required eluents and regenerants used for IC applications.

The wide range of Thermo Scientific™ Dionex™ IonPac™ column choices increase your capacity and selectivity to resolve trace analytes in very challenging matrices. For example, a high column capacity allows the separation of trace contaminants in the presence of high amounts of interfering anions. During the separation, the eluent can be diverted to waste to remove interfering ions prior to detection. This improves the detection limits for the trace analyte contaminant. The continuously-regenerated suppressors desalt the mobile phase to minimize ion suppression and ensure similar response factors, even at different chromatographic conditions.



Acrylamide in Water

Introduction

Acrylamide, a known neurotoxin and human carcinogen, has been found in certain prepared foods, and has recently been included among the substances to be monitored in drinking water according to the last European Community Directive on potable water. A new method for determination of this compound based on the combination of ion-exclusion chromatographic separation and MS detection has been developed accordingly. A sample of drinking water can be directly injected onto the microbore Dionex IonPac ICE-AS1 column and detected in SIM mode by a single quadrupole system with ESI. Chromatographic conditions, such as eluent composition and flow rate, have been optimized by a Central Composite Design (CCD) experiment. Statistical analysis shows that the acetonitrile component of the eluent mixture is the variable that most readily influences retention of the acrylamide peak. After optimization of MS detection parameters, this method was validated for analysis of drinking water samples.

Analysis

Analysis was performed on a Thermo Scientific Dionex ion chromatograph coupled with the Thermo Scientific™ MSQ™ mass spectrometry detector. A 4 × 250 mm i.d. Dionex IonPac ICE-AS1 column was used with acetonitrile/formic acid eluent. The MS was operated in positive electrospray mode. Cone voltage was set at 50 V. The protonated molecular ion $[M+H]^+$ of acrylamide has been detected at a mass-to-charge ratio 72 *m/z*.

Results

The mass spectrum of acrylamide in total ion current mode is shown in Figure 1. For the quantitative measurements SIM mode at 72 *m/z* was used. The use of SIM detection mode assures better sensitivity and selectivity for this analysis. To achieve sub µg/L limits of detection, large-volume injection (up to 1 mL) was used. Recovery and repeatability were estimated at two levels (0.5 and 1 µg/L) by consecutive 10-fold injections of the samples. Recoveries were 95.5% and 97% and CVs were 16% and 12% respectively for 0.5 and 1 µg/L spiked solutions. Limit of detection (LOD) was estimated as three times the standard deviation of the sample at the lowest concentration (0.5 µg/L) or 0.20 µg/L. A chromatogram of spiked tap water is shown in Figure 2.

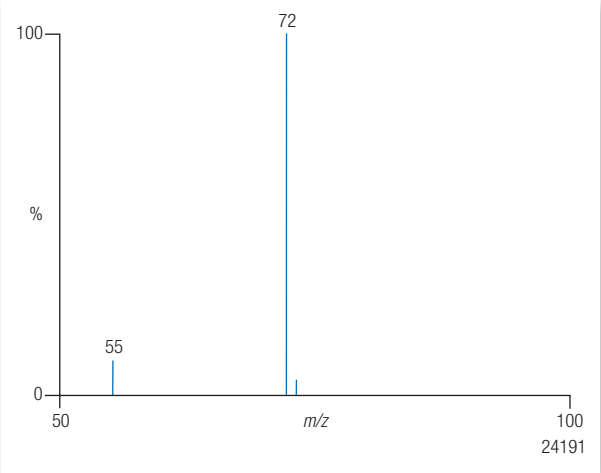


Figure 1. MS spectrum of acrylamide.

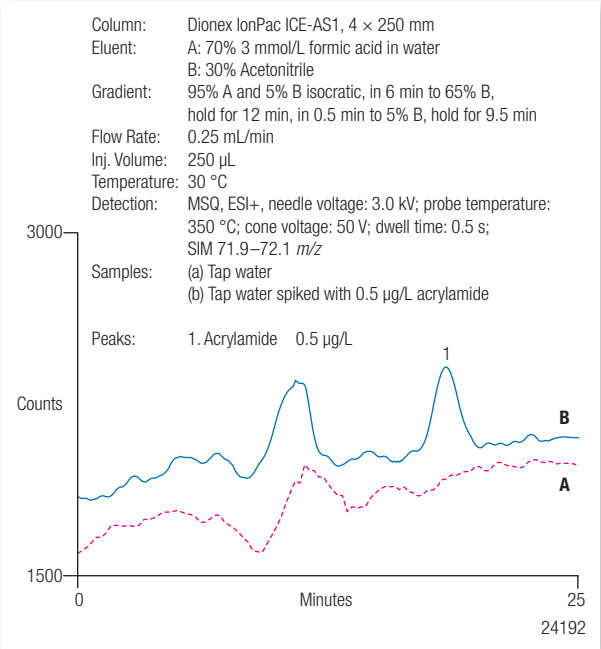


Figure 2. Chromatogram of spiked tap water.

Trace Urea in Ultrapure Water

Introduction

Low levels of many organic contaminants are found in the source waters for semiconductor manufacturing plants. Urea contamination of feed water can occur from its use as a fertilizer and subsequent runoff in water tables. Organic contaminants in ultrapure water are a concern for the semiconductor manufacturing industry because they cause interference in the etching process. Parts per billion (ppb) level monitoring of urea in ultrapure water is critical to the integrity of the photolithography process as the presence of urea can alter the photochemical properties of the photoresist on the wafer. The removal of organics at the point-of-use is necessary as these are only partially removed by conventional purification technologies.

Analysis

The ultrapure water samples were analyzed in positive ESI mode by the MSQ mass spectrometry detector after elution from the ion chromatograph using 2.5 mM MSA eluent. The eluent was prepared manually by diluting 3 mL stock of 1 N MSA solution to 1 L of eluent. Working standards of urea were prepared by appropriate dilutions of a stock 1 ppm standard. Dilutions were made using the mobile phase to ensure the pH of samples.

A low dead-volume static mixing tee was used to add 0.25 mL/min solution of acetonitrile/water (50:50) prior to the MSQ mass spectrometry detector to assist in desolvation of the eluent and in the formation of a stable electrospray. Urea was detected in the SIM mode, using the pseudo-molecular ion $(M+H)^+$ at 61 *m/z*. Conditions with the SIM trace are seen in Figure 3A. An example of a full-scan spectrum of the urea chromatographic peak is seen in Figure 3B. The spectrum also shows acetonitrile and its dimer (*m/z* 41 and 82 respectively), the pseudo-molecular ion of urea, and urea adducts with acetonitrile and MSA.

Results

One of the challenges of quantitating urea by LC-MS is retaining the analyte out of the void volume of the chromatographic system. Using the Dionex IonPac columns and with the parameters given, the analysis for urea can be accomplished in less than 5 min, with urea retained on the column 2 min out of the void.

Lower levels of detection can be reached by increasing the injected sample volume or by the additional use of sample preconcentration.

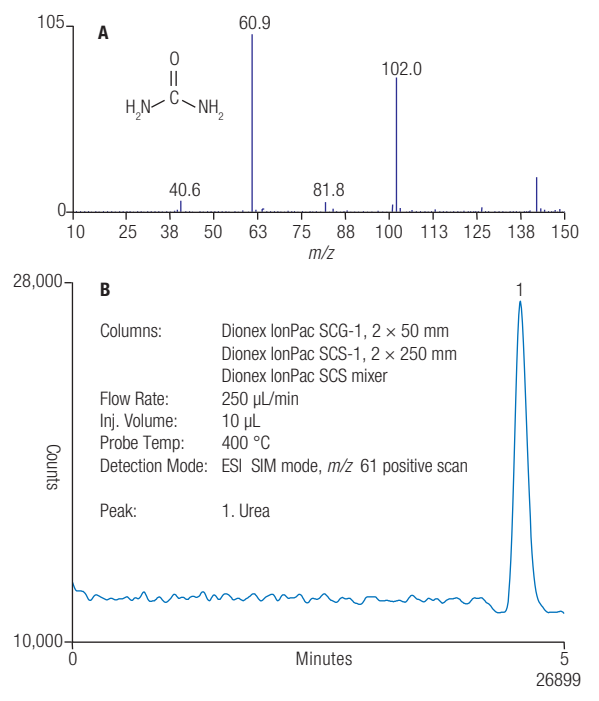


Figure 3. A) Full-scan spectrum and B) SIM trace of the urea chromatographic peak.

Common Cations and Amines

Introduction

IC has been extensively used as the preferred separation technique for ionic species such as inorganic anions/cations, small amines and organic acids, peptides and proteins, nucleic acids, and carbohydrates. In recent years, the increasing demands for higher sensitivity, selectivity, confirmative information, and structural information leads to the emergence of MS as a powerful complementary detector to conductivity, UV, and electrochemical detection.

This method demonstrates the use of IC with MS detection for the determination of six commonly seen cations and selected amines. Confirmative information was achieved using full-scan MS spectra showing positively charged cation species and characteristic adduct patterns. Quantification was achieved using SIM acquisitions for each specific analyte.

Analysis

The experiment was performed on a Thermo Scientific Dionex ICS-2000 RFIC system with separation of target analytes achieved on a Dionex IonPac CS12A-5 µm MSA selective column. The column was operated at 30 ºC with 0.5 mL/min flow rate. An eluent generator with MSA cartridge was used to generate 33 mM isocratic MSA for the elution and separation of target analytes.

The Thermo Scientific™ MSQ Plus™ single quadrupole mass spectrometer was coupled to the IC via an ESI interface, and operated in SIM mode. The external water was delivered at 1 mL/min as the regenerant for the continuous regeneration of suppressor. Isopropanol was delivered by a Thermo Scientific Dionex AXP-MS auxiliary pump at 0.2 mL/min to improve the desolvation/ionization efficiency.

Results

As seen in Figure 4, six cations were chromatographically separated and detected by the MSQ Plus single quadrupole mass spectrometer with excellent selectivity and sensitivity. The studied amines were observed co-eluting with cations. However, each of these amines was observed as a single peak in monitored SIM channels, demonstrating the great selectivity offered by mass spectrometric detection.

With mass spectrometric detection, confirmation of the analyte identity can be achieved from full-scan spectra, and quantitation can be achieved at low ppb levels with greater confidence by using selective SIM scans.

System: Dionex ICS-2000 RFIC ion chromatography system
Column: Dionex IonPac CS12A-5 µm, 3 × 150 mm with guard column, 3 × 50 mm, and a continuously regenerated cation trap column CR-CTC, 2 mm
Mobile Phase: Isocratic 33 mM MSA, electrolytically generated
Flow Rate: 0.5 mL/min
Injection Volume: 100 µL
Temperature: 30 ºC
Detection: Suppressed conductivity, external water mode
MSQ Plus mass spectrometry detector

Mass Spectrometric Conditions
System: MSQ Plus single quadrupole mass spectrometer
Interface: ESI
Solvent: 0.2 mL/min isopropanol delivered by a Dionex AXP-MS auxiliary pump
Detection Mode: Positive SIM
Needle Voltage: 2 kV
Nebulizer Gas: Nitrogen at 85 psi
Probe Temp.: 500 ºC

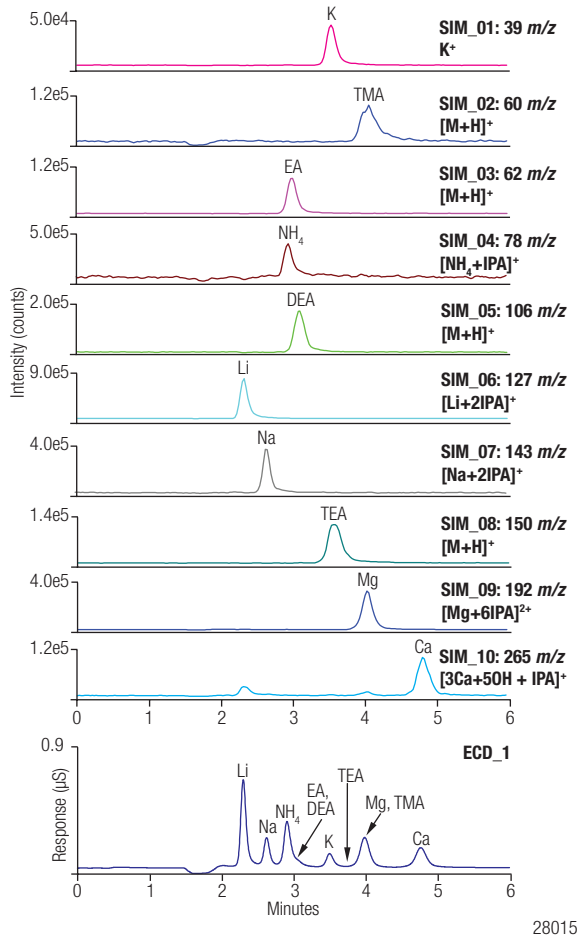


Figure 4. SIM and conductivity chromatograms of six cations and four amines.

Common Anions and Organic Acids

Introduction

MS as a detector for IC has gained popularity recently due to increasing demands for sensitivity, selectivity, confirmation of identity, and structural interpretation. Compared to other commercially available MS detectors, the MSQ Plus mass spectrometry detector offers substantially improved performance for low molecular weight analytes, and addresses most analytes for small molecule IC applications. This study demonstrates the IC-MS method using the MSQ Plus mass spectrometry detector for the determination of five common anions and selected organic acids.

Analysis

The experiment was performed on a Dionex ICS-2000 RFIC system with separation of target analytes achieved on a Dionex IonPac AS20 hydroxide selective column. The column was operated at 30 ºC with 0.25 mL/min flow rate. An eluent generator with KOH cartridge was used to generate 28 mM isocratic hydroxide for the elution and separation of target analytes.

The MSQ Plus single quadrupole mass spectrometer was coupled to the IC via an ESI interface, and operated in SIM mode. The external water was delivered at 0.5 mL/min as the regenerant for the continuous regeneration of suppressor. Acetonitrile was delivered by a Dionex AXP-MS pump at 0.22 mL/min to improve the desolvation/ionization efficiency.

Results

As seen in Figure 5, target analytes were chromatographically separated and detected by the MSQ Plus single quadrupole mass spectrometer with excellent selectivity and sensitivity. The addition of the MS detector for quantitative analysis not only significantly improves the method sensitivity, but also provides the selectivity to differentiate analyte by mass-to-charge ratio. When operated in full-scan mode for qualitative analysis, the mass spectrometric detector provides spectra for identity confirmation and structure interpretation (with the presence of fragment ions).

System:	Dionex ICS-2000 RFIC system
Columns:	Dionex IonPac AS20, 2.1 × 250 mm Dionex IonPac AG20, 2.1 × 50 mm Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column
Mobile Phase:	28 mM hydroxide generated from Thermo Scientific Dionex EGC II KOH cartridge
Flow Rate:	0.25 mL/min
Injection:	5 µL
Detection:	Suppressed conductivity, external water at 0.50 mL/min

Mass Spectrometric Conditions

System:	MSQ Plus single quadrupole mass spectrometer
Interface:	ESI
Solvent:	0.22 mL/min acetonitrile delivered by a Dionex AXP-MS auxiliary pump
Detection Mode:	Negative SIM
Needle Voltage:	1.5 kV
Nebulizer Gas:	Nitrogen at 85 psi
Probe Temp:	450 ºC

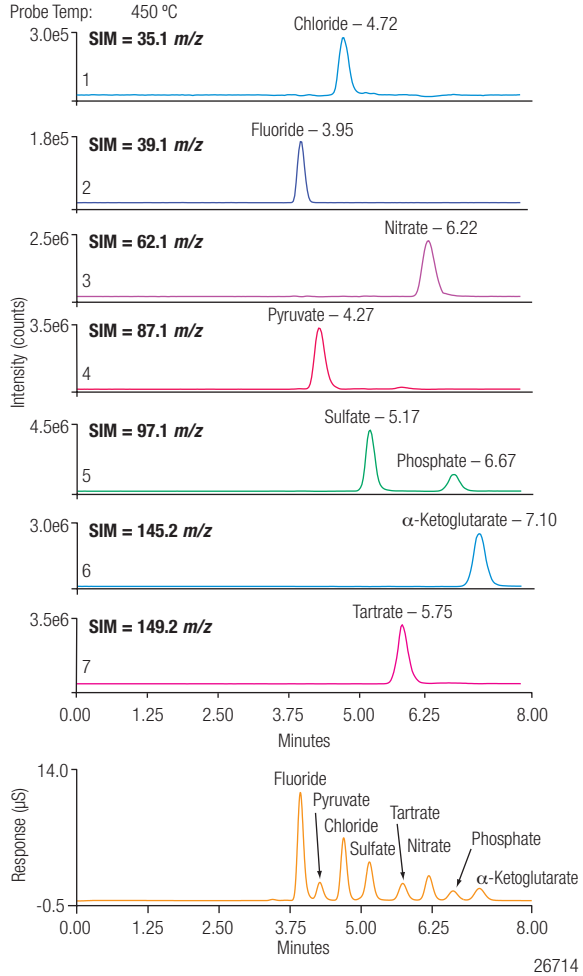


Figure 5. Conductivity and SIM chromatograms of five common anions and three selected organic acids.

Endothall in Water Samples

Introduction

Endothall is a widely used herbicide for both terrestrial and aquatic weeds. Exposure to endothall in excess of the maximum contamination level (MCL) can cause illness. Exposure to high concentrations for a short period of time can cause hemorrhaging of the gastrointestinal tract, while longer-term exposure can also affect the liver and kidney. Endothall is regulated by the U.S. Environmental Protection Agency (EPA) with an MCL at 100 ppb in drinking water, and by the California EPA at 0.58 mg/L or 580 ppb as the public health goal (PHG). Current analytical methods for quantitation of endothall in water samples described in EPA method 548.1 involves time-consuming sample preparation and derivatization followed by a 20 min analysis by GC-MS or GC-FID.

This study describes the direct analysis of trace levels of endothall in water samples by IC-MS. Water samples were directly injected for analysis and chromatographic separation was only 10 min. The MSQ Plus single quadrupole mass spectrometer was operated in SIM mode allowing minimum sample cleanup and ensuring sensitive (low ppb) and selective quantification. Isotope labeled glutaric acid (Glutarate–d_6) was used as the internal standard to ensure quantitation accuracy.

Analysis

Analyses were performed using a Thermo Scientific™ Dionex™ ICS-5000 RFIC™ system and a hydroxide selective Dionex IonPac AS16 column with a temperature of 30 °C and a flow rate of 0.4 mL/min.

A hydroxide gradient from an eluent generation KOH cartridge was used for the elution and separation of target analytes. The gradient started with 15 mM hydroxide after a 4 min equilibration, ramped up to 80 mM from 5 to 6 min and held for 3 min, and then returned to initial condition in 0.5 min. Suppressed conductivity and the MSQ Plus single quadrupole mass spectrometer were used as detectors in series.

The MSQ Plus single quadrupole mass spectrometer was coupled to the IC via an ESI interface and operated in SIM mode. IC eluent was directed to the MSQ Plus single quadrupole mass spectrometer for detection from 4.2 to 6 min, but was otherwise diverted to waste. See Figure 6 for SIM scan details.

Results

As seen in Figure 6, endothall was retained and separated from seven commonly seen anions within 10 min, and was detected with great sensitivity and selectivity using SIM acquisition. This method features direct analysis without sample pretreatment and a significant reduction in run time for improved throughput relative to GC methods. Sufficient sensitivity was achieved in this study to allow routine quantification of endothall below the lowest regulated level (100 ppb by U.S. EPA standards).

System: Dionex ICS-5000 RFIC system
Column: Dionex IonPac AS16/AG16, 2 mm
Mobile Phase: Hydroxide gradient generated from Dionex EGC II KOH cartridge

Time (min)	Conc (mM)
–4.0	15
0.0	15
5.0	15
6.0	80
9.0	80
9.5	15
10.0	15

Flow Rate: 400 µL/min
Temperature: 30 °C
Detection: Suppressed conductivity
MSQ Plus single quadrupole mass spectrometer

Mass Spectrometric Conditions
System: MSQ Plus single quadrupole mass spectrometer
Interface: ESI
Probe Temp: 500 °C
Needle Voltage: 3000 V
Solvent: 200 µL/min acetonitrile delivered by a Dionex AXP-MS pump
Matrix Diversion: Eluent to MS: 4.2 to 6.0 min
Detection Mode: SIM

Analyte	SIM (*m/z*)
Endothall	185 at 50 V
IS (glutarate-d_6)	137 at 35 V

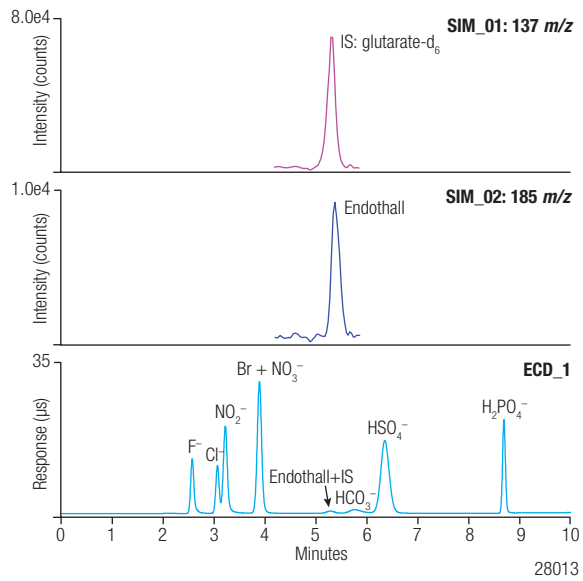


Figure 6. Analysis of endothall in water samples by IC-MS. 20 ppb endothall spiked in seven anions solution (0.2–1.5 ppm).

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