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Examination of Iodine Species in the Complex Salt Environment of Marine Aerosols

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INTRODUCTION

Iodine in aerosols within the marine boundary layer (MBL) has a complex chemistry.[1] Volatilization of biogenic organoiodine compounds from the ocean is the main source of atmospheric iodine. These compounds are photooxidized in air, yielding iodine atoms and other reactive intermediates that are involved in ozone depletion[2] and aerosol formation reactions[3] within the MBL. However, the lack of measurements of individual iodine species in aerosols proves to be a major limitation to understanding the complex multiphase cycling of iodine (Pechtl et al., 2007).[4]

In this analysis, samples of MBL aerosols collected at a coastal California site are examined for levels of iodide and iodate using both single quadrupole and triple stage quadrupole mass spectrometers. The high concentrations of sulfate, nitrate, and chloride in the marine aerosol matrix make conventional conductivity quantification of iodine species problematic. The combination of separation using an ion-exchange column with the specificity of mass spectrometry provides a simple and rapid method for the detection of trace anions and removes the hindrance of matrix interference.

EXPERIMENTAL

- **Hardware**

Chromatography System:

Dionex ICS-3000 Ion Chromatography System consisting of:

DP Dual Pump module

EG Eluent Generator

DC Detector/Chromatography Compartment with conductivity detection

AS Autosampler

Columns and Accessories

IonPac® AG19 guard column, 2.1 x 50 mm

IonPac AS19 analytical column, 2.1 x 250 mm

ASRS® 300 Self-Regenerating Suppressor®, 2 mm

EGC II KOH Eluent Generator Cartridge

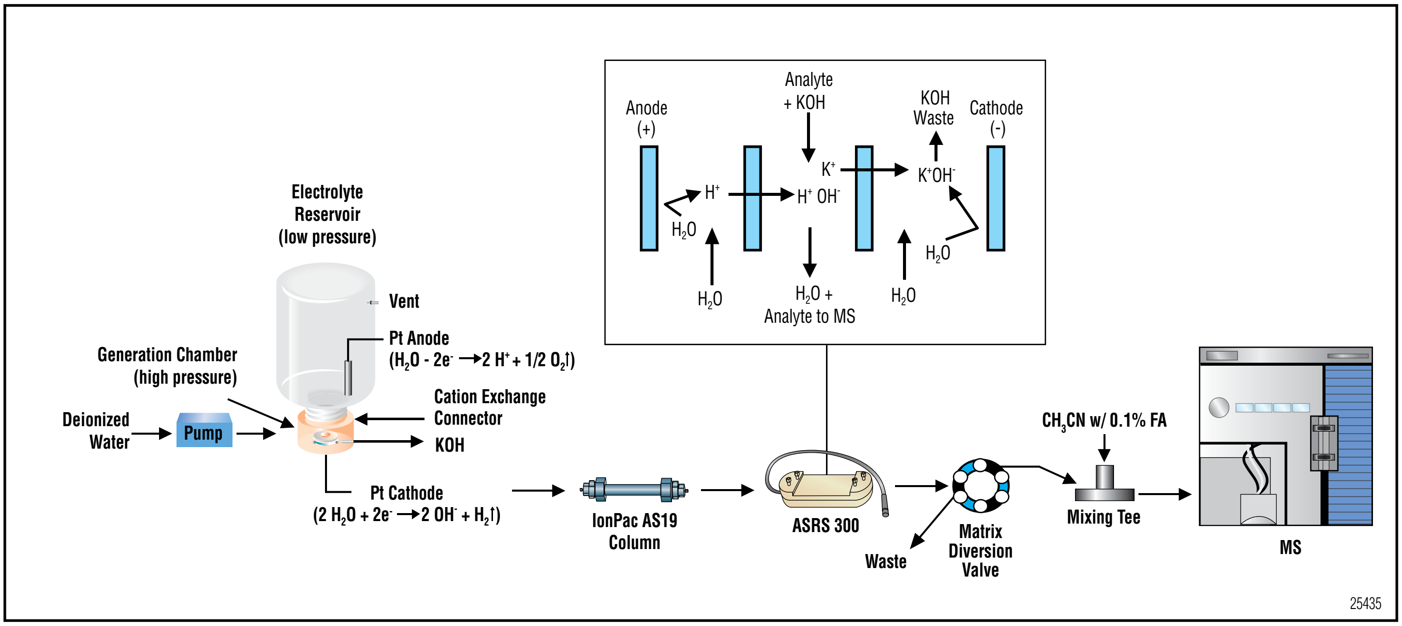

Figure 1. Eluent generation technology allows automatic production of high-purity IC eluents. The system is designed so the pump delivers deionized water to an eluent generator cartridge (EGC). The cartridge electrolytically converts the water into hydroxide eluent. After separation on the column, the eluent enters a suppressor (ASRS 300). The suppressor electrolytically exchanges the potassium ion of the KOH eluent with a hydronium ion. This exchange lowers the total background conductivity, and makes the separation compatible with a mass spectrometer.

• Mass Spectrometers:

MSQ Plus™ mass spectrometric detector-single quadrupole mass spectrometer

Thermo Fisher Scientific TSQ Quantum Access™ mass spectrometer- triple quadrupole mass spectrometer

• Software

Chromeleon® 6.8 SP2b Chromatography Management Software

Xcalibur™ 2.0.7 mass spectrometry data system software (Thermo Fisher Scientific)

• Solutions and Standards

Perchlorate ISTD, Dionex Corporation, P/N 062923

Sodium chloride, JT Baker
Sodium sulfate, EM Science
Sodium carbonate, EM Science
Ammonium nitrate, EM Science
Acetonitrile, HPLC Grade, JT Baker
Formic acid, Fisher Scientific

• LC Conditions

Mobile Phase:	Potassium hydroxide (electrolytically generated)
Gradient:	0–10 min, 5 mM KOH
	10–20 min, 5–47 mM KOH
	20–23 min, 60 mM KOH
Column Temperature:	30 °C
Flow Rate:	250 µL/min
Suppressor:	ASRS 300 operated at 60 mA
Injection Volume:	100 µL
Postcolumn Addition:	150 µL/min of acetonitrile with 0.1% formic acid

• MS Conditions

MSQ Plus:

ESI negative ionization mode

Source temperature:	500 °C
Gas flow:	5 bar
Needle Voltage:	3 kV

Compound	SIM *m/z*	Cone Voltage	Span (Da)	Dwell Time (s)
Iodate	175	75	0.5	0.3
Iodide	127	70	0.5	0.3
Perchlorate-ISTD	107	75	0.5	0.3

Full scan: 10–180 amu in 0.4 s

TSQ Quantum Access:

ESI negative ionization mode

Spray Voltage:	4100 V
Source Temperature:	290 °C
Aux Gas:	15 (arbitrary units)
Ion Sweep Gas:	2 (arbitrary units)
Sheath Gas:	40 (arbitrary units)
Collision Gas Pressure:	1.5 mTorr

Compound	Parent Mass	Product Mass	Collision Energy	Tube Lens
Iodate	174.889	158.920	29	96
Perchlorate-ISTD	107.129	89.300	29	96

Iodide was analyzed in SIM mode for m/z *127.1 and a tube lens of 96.*

SAMPLE PREPARATION:

Samples of marine aerosols were collected at Zuma Beach in Malibu, California in October 2006. The sampling and extraction were per the method described by Keene, et al.[5] Samples were collected on Whatman® 41 filters (Whatman Inc., Florham Park, NJ). The filters were extracted in deionized water by sonication in polyethylene syringes. The extract was filtered through a syringe filter (Acrodisc®, Pall Corporation, East Hills, NY). Samples were not subjected to further treatment prior to injection on the IC/MS or IC/MS/MS system.

ANALYSIS

Aliquots were separated with a potassium hydroxide gradient on an IonPac AS19 anion-exchange column (Dionex, Sunnyvale, CA). The high salt mobile phase was suppressed post column using an ASRS 300 electrolytic suppressor (Dionex, Sunnyvale, CA). A matrix diversion valve (MDV) diverted the flow to waste during periods of high sample matrix. Prior to introduction into the mass spectrometer, the second pump of the DP supplied postcolumn addition of acetonitrile with 0.1% formic acid. The organic solvent assisted in the desolvation of the eluent in the source and acted as a make up flow when the eluent was diverted to waste. Samples were examined using a single quad MSQ Plus mass spectrometer (Thermo Fisher Scientific, San Jose, CA) and a triple stage quadrupole TSQ Quantum Access mass spectrometer (Thermo Fisher Scientific, San Jose, CA) in negative electrospray ionization mode.

RESULTS

The chemistry of the column provided resolution between the major matrix peaks of chloride, nitrate, carbonate, and sulfate (Figure 2). Separation of all compounds was executed in less than 20 min. Calibration curves were generated on both the single and triple quadrupole instruments. The single quad MSQ Plus was used for the preliminary examination of iodide and iodate. The detection range was 1–100 ppb on the MSQ Plus with r^2 values of 0.9985 for iodate and 0.9983 for iodide (Figure 3). For final quantification, data was run on the triple quadrupole instrument, TSQ Quantum Access. The calibration range was 100 ppt–50 ppb with r^2 values of 0.9991 for iodate and 0.9978 for iodide (Figure 4).

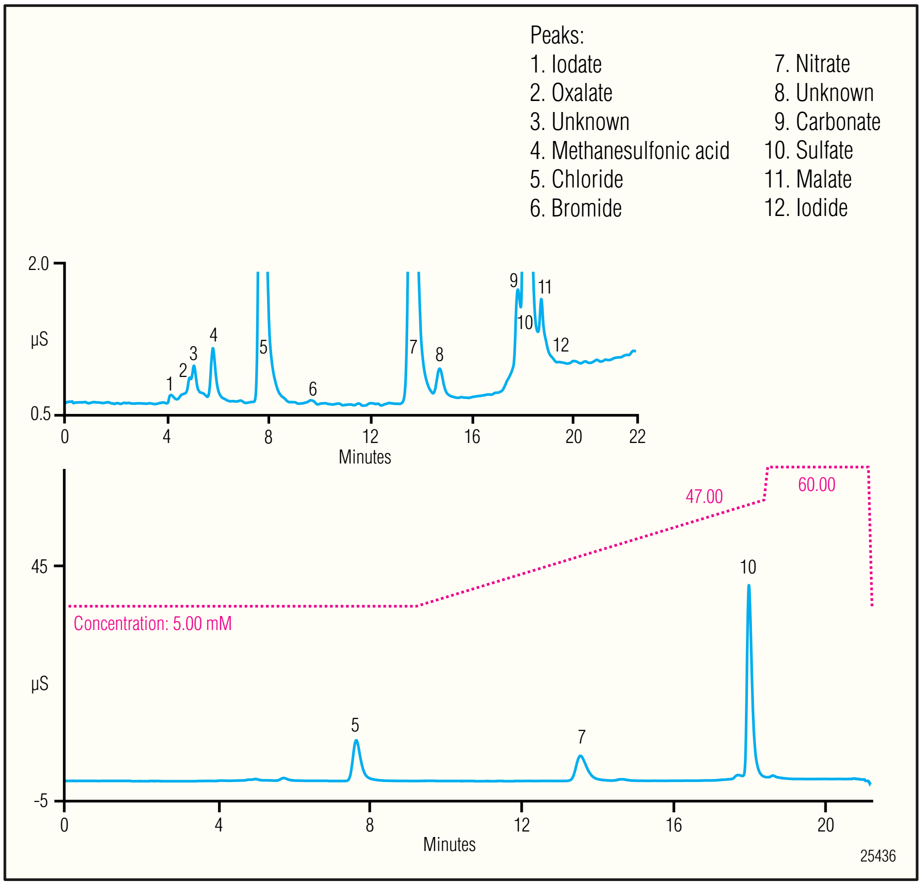

Figure 2. Conductivity detection shows the high anionic matrix of sea water aerosols. The gradient separates the sea water aerosol matrix analytes from the analytes of interest. Amplification of the baseline of the conductivity trace shows how the matrix interferes with quantification of basic anions such as iodate and iodide (peaks 1 and 12).

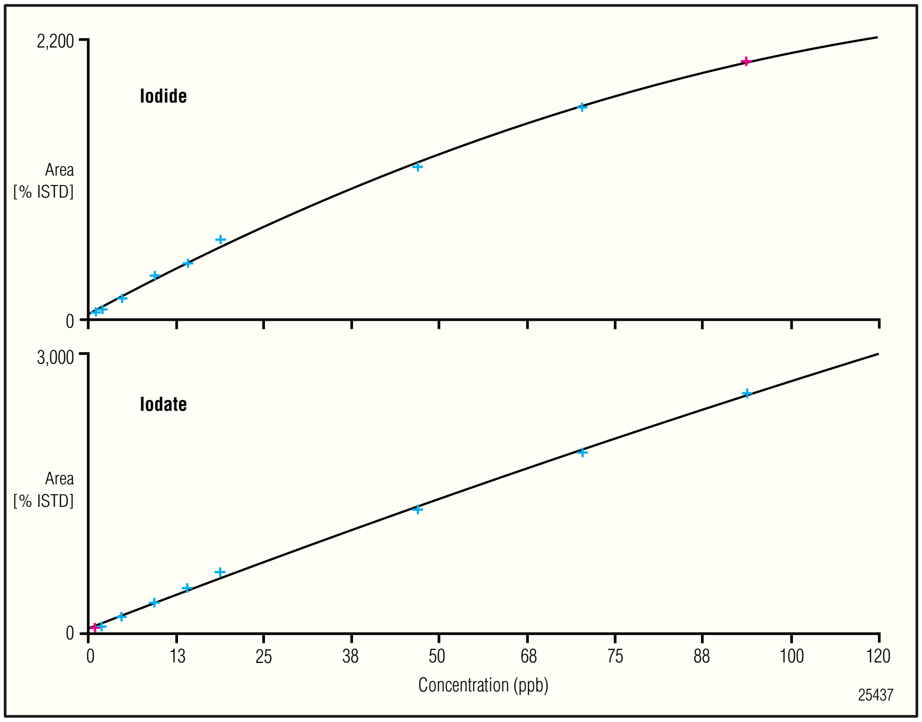

Figure 3. A quadratic fit with a correlation coefficient of 0.9983 was achieved for iodide (SIM of 127 Da) on the MSQ Plus (top trace). A quadratic fit with a correlation coefficient of 0.9985 was achieved for iodate (SIM of 175 Da) on the MSQ Plus (bottom trace).

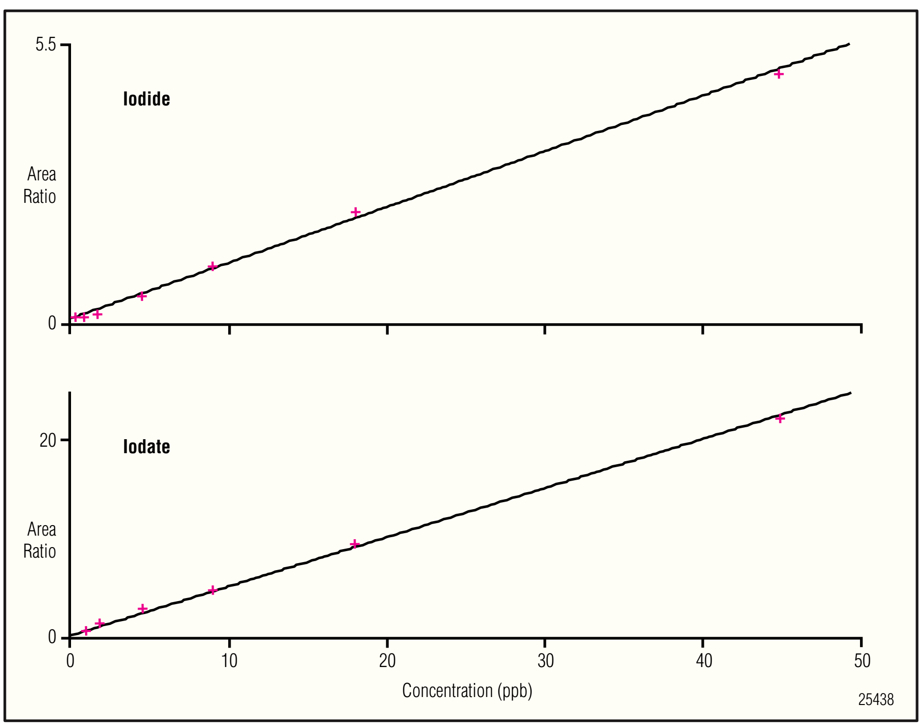

Figure 4. A correlation coefficient of 0.9991 was achieved for iodate examining the transition of 175 –> 158 Da on the TSQ Quantum Access (top curve). A correlation coefficient of 0.9978 was achieved for iodide examining the SIM of 127 Da (bottom curve).

A calculated MDL of 528 ppt for iodide and 432 ppt for iodate is expected with a triple stage quadrupole mass spectrometer. Method detection limit was calculated by 7 replicate injections of 2.5 ppb iodate and iodide and the equation MDL= $t_{99\%} \times S_{(n=7)}$, where: t is Student's t at 99% confidence intervals ($t_{99\%, n=7} = 3.143$) and S is the standard deviation.

Recoveries of 2.5 ppb iodate and iodide spiked into a simulated matrix of 100 ppm each chloride, sulfate, and carbonate showed a recovery of 105 ± 6% in matrix for iodide for 7 replicate injections. Replicate injections of iodate in matrix gave recoveries of 68% ± 8.

Isotopically labeled perchlorate ($Cl^{18}O_4$) was used as an internal standard in the analysis. All samples were spiked with 1 ppb of heavy perchlorate. The SRM transition of 107.1 –> 89.3 was monitored.

DISCUSSION

The selected column provided sufficient capacity, resulting in excellent separation of matrix ions from the analytes of interest. To provide for a more robust analysis and minimize source contamination of the mass spectrometer, the MDV diverted flow from the mass spectrometer while the matrix peaks eluted.

Although the single quadrupole allowed quantification to the low ppb range, the use of the triple stage quadrupole mass spectrometer with SRM experiments allows more sensitive and specific quantitation for the analytes. When analyzing low levels of iodate in the MSQ Plus (such as sample Unknown 1), interference was observed (Figure 5). It is believed that this additional peak at *m/z* 175 was due to extraneous material originating from the filter. This was deduced from the fact that water blanks did not show an additional peak, but filter water blanks showed the impurity. When running SRM scans on the TSQ Quantum Access triple quadrupole instrument, no additional peaks were observed in the trace for iodate. The contaminant peak did not show the transition of 175 –> 158, therefore the contaminant response was eliminated (Figure 6).

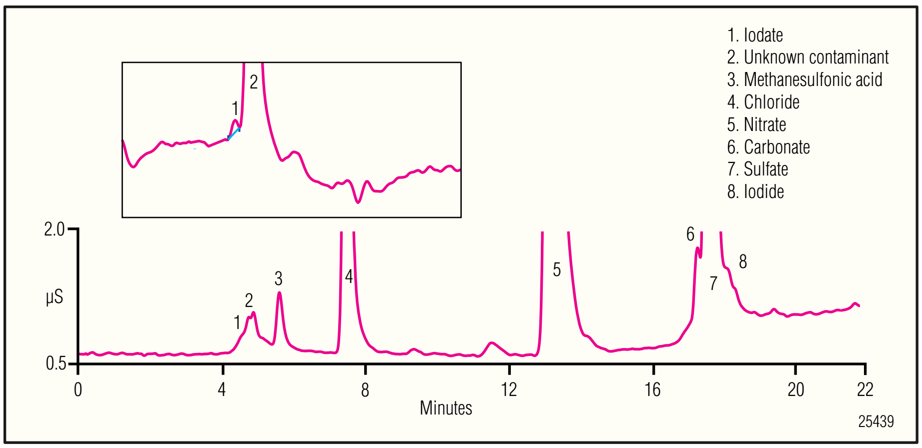

Figure 5. The conductivity trace (top chromatogram) shows the complicated matrix of sea water aerosols (sample Unknown 1). The advantage of mass spectrometry is the ability to focus on the mass-to-charge ratio of the specific analyte. When run on the MSQ Plus, a large interference peak also appears in the SIM trace of iodate at 175 Da, making low level detection difficult (bottom chromatogram).

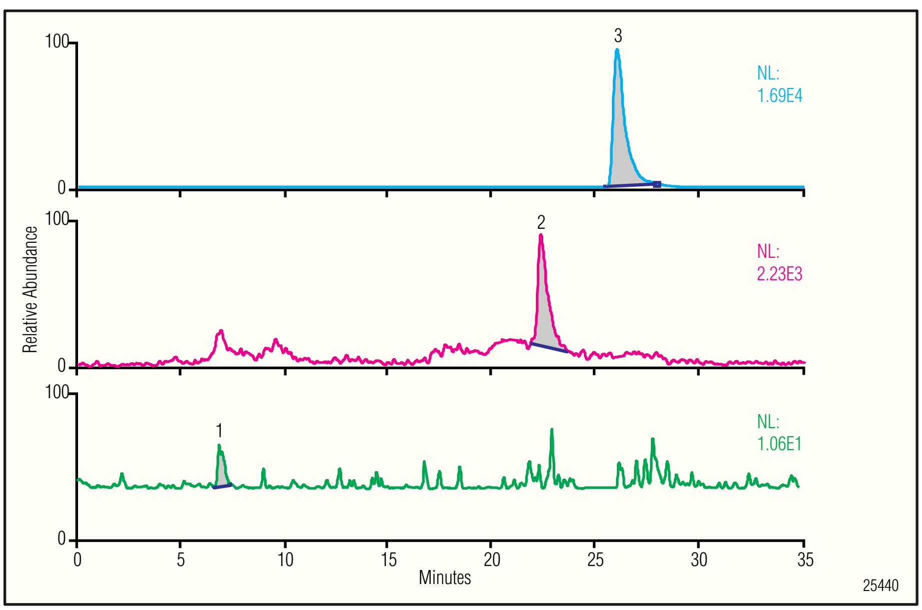

Figure 6. Examination of the data generated by the TSQ Quantum Access for sample Unknown 2 does not show interference of iodate detection at the low levels (bottom trace) found in marine aerosols. Iodate concentration was below the detection limit. The middle trace shows the response of iodide in sea water. Iodide concentration was calculated to be 620 ppt. The top trace shows the response of the 1 ppb $Cl^{18}O_4$ internal standard.

Full scan data collected from the single quadrupole instrument shows that identification of other anionic analytes is possible (e.g. bromide, bromate). Previous experiments (Cavalli, S. et al., 2005) show bromate quantitation by IC/MS.[6]

While the recoveries were low for the iodate samples spiked in matrix, it is believed that this could be remedied with the use of a stable labeled internal standard for iodate. In this method, a stable labeled standard of perchlorate was used. As perchlorate elutes at the end of the analysis, one minute after the iodide peak, it may not be the best suited internal standard for iodate, which elutes at the beginning of the analysis.

CONCLUSION

This technique provides a robust method for quantifying iodine species in a complex, high salt matrix without sample pretreatment. The advantage of an ion chromatography system equipped with an ion-exchange column allows for complete separation of iodate and iodine from the matrix of sea water aerosols. Quantitation curves generated on the MSQ Plus and TSQ Quantum Access mass spectrometers show excellent linearity. The use of a triple stage quadrupole instrument provides detection of low level iodate and iodide without any interference from the highly complex matrix.

If quantification of further analytes in sea water, such as bromate, is desired, these analytes may be detected in the mass spectrometer without any modification to this LC separation method.

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