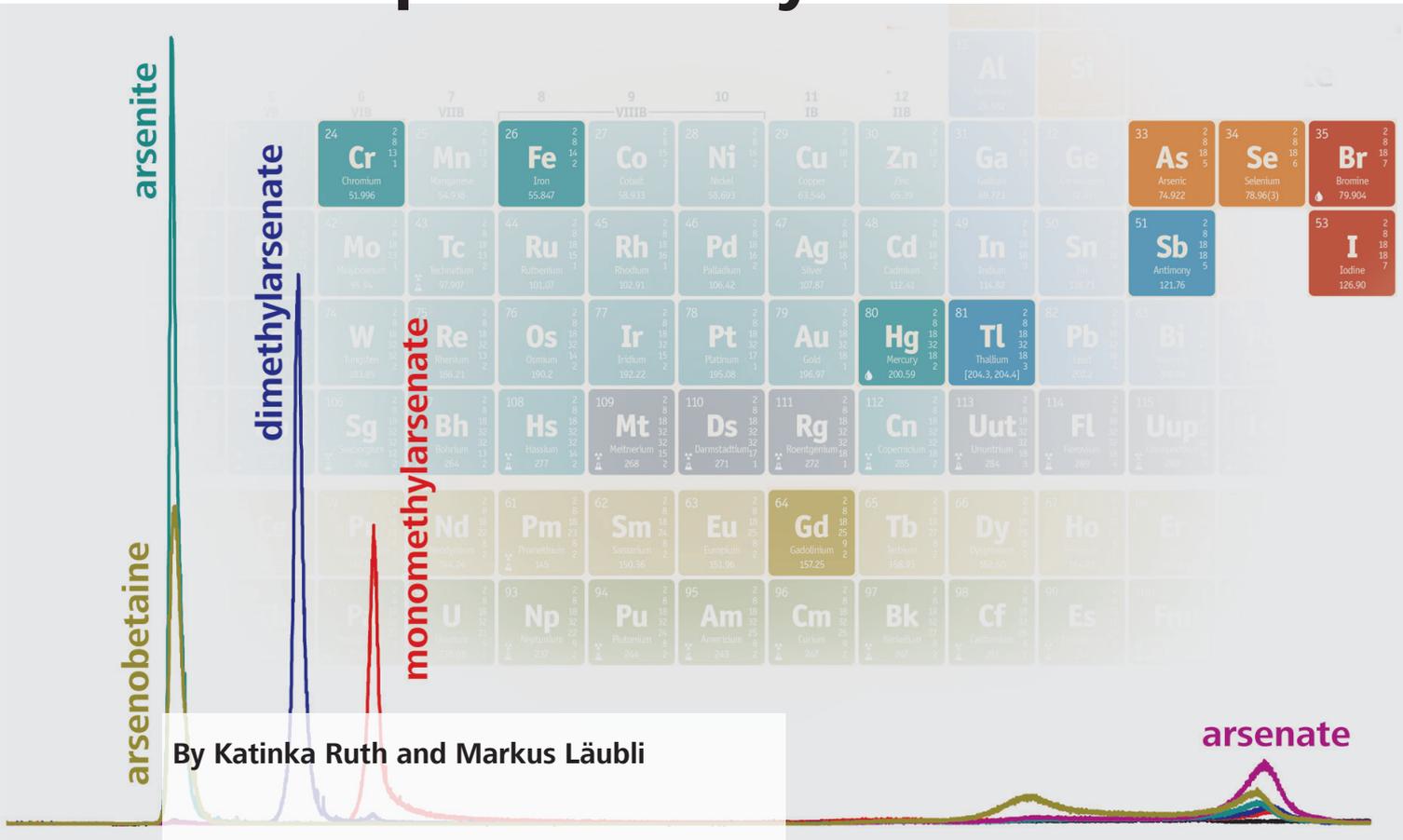


## Coupling of ion chromatography and inductively-coupled plasma mass spectrometry



By Katinka Ruth and Markus Läubli

Online hyphenation of ion chromatography (IC) to inductively coupled plasma mass spectrometry (ICP/MS) is a powerful instrumental tool to handle some of the most challenging analytical tasks. Reliable determination of elemental composition, oxidation states, and chemical binding is crucial to judge toxicity in environmental investigations, water quality control, pharmaceutical and medical analysis, as well as the food and beverage industry.

# Metrohm White Paper

## Content

<b>1</b>	<b>Introduction to IC-ICP/MS</b>	<b>1</b>
1.1	Norms and standards	1
1.2	Ion chromatography instrumentation	2
1.3	ICP/MS instrumentation	3
<b>2</b>	<b>Chromium</b>	<b>4</b>
2.1	Chromium species in soil, solid samples, and pharmaceuticals according to US EPA 6800	4
2.2	Chromate in HCl eluates with Inline Preconcentration, Matrix Elimination, and ICP/MS detection	5
2.3	Chromium species in dietary supplements using speciated isotope dilution mass spectrometry	6
2.4	Chromate in NIST SRM 2701 by speciated isotope dilution mass spectrometry according to US EPA 6800	7
2.5	Speciation of Cr(III) and Cr(VI) by microbore column	8
<b>3</b>	<b>Arsenic</b>	<b>9</b>
3.1	Inorganic arsenic species in dietary supplements using gradient ion chromatography	9
3.2	Mercury and arsenic speciation analysis	10
3.3	Simultaneous speciation of arsenic and selenium species in petroleum refinery aqueous streams	11
3.4	Simultaneous determination of arsenic and selenium species in fish tissues	12
<b>4</b>	<b>Mercury</b>	<b>13</b>
4.1	Mercury and arsenic speciation analysis	13
4.2	Mercury species in crude oil by speciated isotope dilution	14
4.3	Mercury species transformations in human hair using speciated isotope dilution mass spectrometry	15
4.4	Microwave-assisted extraction protocol for analysis of total mercury and methylmercury in fish tissues	16

# Metrohm White Paper

<b>5</b>	<b>Iodine</b>	<b>17</b>
5.1	Monitoring the fate of iodinated X-ray contrast media after ozonation	17
<b>6</b>	<b>Gadolinium</b>	<b>18</b>
6.1	Gadolinium-based MRI contrast agents	18
<b>7</b>	<b>Selenium</b>	<b>19</b>
7.1	Hyphenated techniques as modern detection systems in ion chromatography	19
7.2	Simultaneous speciation of arsenic and selenium species in petroleum refinery aqueous streams	20
<b>8</b>	<b>Thallium</b>	<b>21</b>
8.1	Detection of dimethyl thallium in water samples at low concentration levels	21
8.2	Indirect anodic stripping voltammetric determination of Tl(I) and Tl(III) in Baltic seawater samples	22
<b>9</b>	<b>Iron</b>	<b>23</b>
9.1	Iron speciation in soil and other matrices using speciated isotope dilution according to US EPA 6800	23
<b>10</b>	<b>Organic compounds</b>	<b>24</b>
10.1	Aminopolycarboxylic acids in surface water using ion-exchange chromatography coupled to ICP/MS	24
<b>11</b>	<b>Antimony</b>	<b>26</b>
11.1	Sb(III), Sb(V), and Sb-containing nanoparticles in airborne particulate matter	26
<b>12</b>	<b>Bromate</b>	<b>27</b>
12.1	Ultratrace determination of bromate in drinking waters by microbore column IC	27
<b>13</b>	<b>References</b>	<b>28</b>

## 1. Introduction to IC-ICP/MS

More than ever do we need to monitor our environment for hazardous substances to protect the basis of our own existence. And more than ever should we insist on a better quality control / process control in the production of our consumer goods such as foodstuffs and pharmaceuticals. One outstanding technique for such controls is the online hyphenation of ion chromatography (IC) to inductively coupled plasma mass spectrometry (ICP/MS). IC-ICP/MS is a powerful instrumental tool to handle some of the most challenging analytical tasks.

ICP/MS can determine the total amount of a specific element in a sample with excellent detection limits (element selectivity). IC copes with species selectivity, i.e., it can separate ionic analytes according to their chemical structure (Herrmann, T.; 2006). The online coupling of IC with ICP/MS thus combines the molecular selectivity of IC with the elemental selectivity and sensitivity of ICP/MS (Knöll, J.; 2013). As toxicity not only depends on the elemental composition, but also on bioavailability, which is influenced by the oxidation states and chemi-

cal binding within the molecule, the reliable determination of these parameters offered by IC-ICP/MS is crucial in environmental investigations, water quality control, pharmaceutical and medical analysis, as well as the food and beverage industry.

Hyphenation of a high-performance IC to an inductively coupled plasma mass spectrometer significantly increases sensitivity while at the same time reducing possible matrix interferences to a minimum. IC-ICP/MS is therefore a robust technique for speciation analysis in complex matrices. Some of the most popular applications are shown in this overview.

### 1.1 Norms and standards

More and more norms arise that require the quantification of pollutants like hexavalent chromium or bromate at low concentrations. Table 1 lists a few norms and standards that suggest IC-ICP/MS as a test method.

**Table 1.** Selection of standards that suggest IC-ICP/MS as a test method

Norm	Matrix	Analyte	Detection limit
DIN EN 71 - 3 (2013) Safety of toys - Part 3: Migration of certain elements	Various toy materials in the categories a) threadbare b) dry, brittle, dusty c) liquid	Chromium(VI)	a) 0.2 mg/kg b) 0.02 mg/kg c) 0.005 mg/kg
SN/T 2210-2008 Determination of hexavalent chromium in health foods – IC-ICP/MS method	Foodstuffs	Chromium(VI)	
EPA Method 321.8 Determination of bromate in drinking waters by ion chromatography inductively coupled plasma mass spectrometry	Potable water	Bromate	0.3 µg/L
ASTM C1845 Standard Practice for The Separation of Lanthanide Elements from Uranium Matrices Using High Pressure Ion Chromatography (HPIC) for Isotopic Analyses by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Dissolved uranium materials such as nuclear fuels, uranium ores, hydrolyzed UF <sub>6</sub> , and depleted, natural, or enriched oxides/powders, or metals	Lanthanides	
EPA SW-846, Method 6800 Elemental and speciated isotope dilution mass spectrometry	Hydrosphere, Biosphere	Hg, As, Cr	

# Metrohm White Paper

## 1.2 Ion chromatography instrumentation

For hyphenated systems, intelligent instruments which allow online sample introduction, automated sample preparation, and logical decisions will become increasingly important. With the 940 Professional IC Vario system, Metrohm sets a new standard in IC. 940 Professional IC Vario stands for maximum flexibility combined with easiest operation and full reliability.

The requirements towards the analysis system vary depending on the analytes in question, the structure of the sample matrix, and the number of samples. Therefore, a system that is entirely modular by design is ideal: It fulfills current requirements while being adaptable for future analytical challenges.

If desired, the 940 Professional IC Vario system produces all solutions, including standards, fully automatically. Starting with sample injection, the system works completely autonomously. Moreover, it is self-monitoring, i.e., all system and method parameters are permanently checked. If any system component requires maintenance, the system issues a warning. This ensures superior reliability of both the system itself and the analytical results produced by it, as operator errors are virtually ruled out. Moreover, all results can be traced back to every single step of the analysis and even sample preparation. Thus, the IC system is not only suitable for complex scientific investigations but also a robust and user-friendly tool for routine analysis.

The benefits of the 940 Professional IC Vario include:

- Modular high-performance ion chromatography system
- Virtually unlimited possibilities for system configuration
- Compact dimensions, small footprint
- For routine analyses and research applications from the ng/L to the % range
- Highest sensitivity for lowest detection limits
- Intelligent system components for reliable results
- Wide range of detection options: Conductivity, UV/VIS, amperometry, ...
- Free choice of suppressor and column
- All gradient options
- Inline eluent preparation integrated in the system
- Multi-language MagIC Net software for intuitive and simple operation
- Complies with GLP and the FDA regulations
- Compatible with the unique and partly patented Metrohm Inline Sample Preparation techniques (MISP)
- Complete automation for high sample throughput
- Low maintenance costs and long lifetime
- Rugged Swiss quality





### 1.3 ICP/MS Instrumentation

Mass spectrometry with inductively coupled argon plasma is one of the most powerful methods for inorganic trace analysis. ICP/MS is superior to, e.g., ICP/AES when low detection limits are required. Ionization of metals is more efficient than ionization of other elements; hence metal ions are the most common analytes for this technique. It is routinely used for trace analysis in environmental samples, quality control in foodstuffs, as well as in medical and biological samples. The technique offers the following advantages (Herrmann, T.; 2006):

- Multi-element method for simultaneous determination of almost all elements of the periodic table
- Trace analysis with outstanding limits of detection (pg/L range)
- Dynamic measuring range of more than eight orders of magnitude
- Quick, semi-quantitative analysis with high informative value for preliminary overviews
- Capable of determining isotopic ratios and of isotope dilution analysis
- Solid, liquid, and gaseous samples can be analyzed with the correct sample preparation/introduction
- Only a small sample amount is required

In ICP/MS, samples are ionized using a plasma source whose energy supply comes from electric currents which are produced by electromagnetic induction: a time-varying electric current is passed through a coil, producing a time-varying magnetic field which in turn induces the electric currents. The inductively heated gas (mostly argon) forms a plasma when the concentration of its ions and electrons is sufficient to make the gas electrically conductive (Montaser, A.; 1992). This will ionize the sample. The generated ions are subsequently introduced into a vacuum via several stages. Lenses and skimmers focus the ion beam. As in any MS, ions are consecutively separated based on their mass to charge ratio. Quadrupole, time-of-flight, or sector field technology is used as mass analyzer. Quadrupoles are most frequently used for routine analysis.

All state-of-the-art ICP/MS instruments are equipped with remote control functionality to allow synchronization of the data acquisition with IC instruments. This is the most direct and straight-forward setup when the instruments are operated with two different softwares. There are no limitations to which two instruments can be combined.

Additional detectors like conductivity, amperometry, or UV/VIS detectors from Metrohm can easily be integrated via the IC. Their signals can be transferred to the ICP/MS software by digital-to-analog converters.

## 2. Chromium

Chromium species may exist in several oxidation states, but the hexavalent and trivalent oxidation states – Cr(VI) and Cr(III) – are the most abundant in the environment. The toxicity of chromium species depends on the species' chemistry and on its bioavailability, both of which are related to its chemical form (species) and concentration. Trivalent chromium is regarded as more stable, relatively non-toxic and known to be an essential trace nutrient in the human diet helping to maintain effective glucose, lipid, and protein metabolisms. Hexavalent chromium is considered toxic and carcinogenic because it can diffuse easily through the cell membrane and oxidize biological molecules (Rahman, G. M. M. et al.; 2012)

### 2.1 Chromium species in soil, solid samples, and pharmaceuticals with IC-ICP/MS according to US EPA 6800 Application Note [AN-M-011](#)

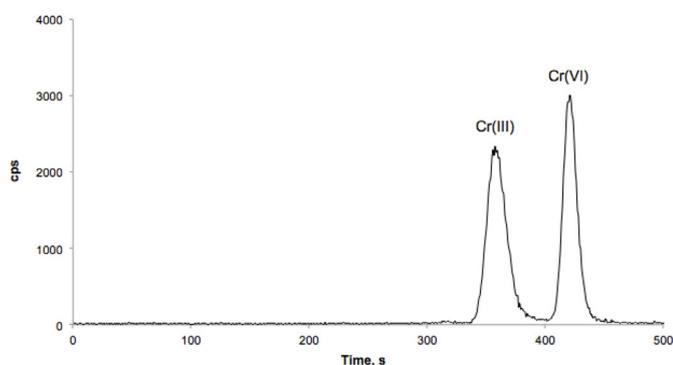
#### Introduction

While soil naturally contains a small amount of chromium (Cr) that comes from weathering of its bedrock, the element also enters the environment through anthropogenic activities. Cr(III) and Cr(VI) are the prevalent forms of Cr in the environment. The speciation analysis of Cr has received increasing interest because of the opposing properties of the two prevalent species. In soil, Cr(III) mainly occurs in the form of insoluble (hydr)oxides or adsorbed to humic acid and macromolecular clay compounds, whereas Cr(VI) occurs in anions ( $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$ ) that are mobile under most conditions. Cr(III) is relatively innocuous; in fact, it is essential for the proper functioning of organisms. However, Cr(VI) is toxic to both plants and animals because it is a corrosive, acute tissue irritant and carcinogen.

In the present study, Cr(VI) and soluble Cr(III) were simultaneously determined by IC-ICP/MS with speciated isotope dilution methodology. The soil was spiked with isotopically enriched analogues of the analytes, i.e.,  $^{50}\text{Cr(III)}$  and  $^{53}\text{Cr(VI)}$ , and both the endogenous and spiked analytes were extracted in a microwave using alkaline solution of ethylenediaminetetraacetic acid (EDTA). The extracts were analyzed by IC-ICP/MS, and the separated species were quantified using the mathematical relationships in speciated isotope dilution mass spectrometry (SIDMS, EPA Method 6800) with simultaneous correction for their method-induced transformations. Direct separation of Cr(VI) and Cr(III) by chromatography is difficult because the species are oppositely charged in solutions. A Metrohm IC with the Metrosep A Supp 4 column was used to achieve baseline separation of both species prior to analysis on an Agilent 7700 ICP/MS instrument (Figure 1). The IC and ICP/MS instruments were synchronized using remote signal.

#### Results

Baseline separation between Cr(III) and Cr(VI) was achieved in less than 10 minutes. Several standard reference materials (SRM) were analyzed in the study. The measured mass fractions of Cr(VI) in the soil SRMs statistically agreed with the certified values at 95% confidence level (CL). The soluble Cr(III) found in all the SRMs was less than 3% of the total Cr in the corresponding samples.



**Figure 1.** Standard solution containing 10.0 ng/g Cr per species. Column: Metrosep A Supp 4 - 250/4.0; eluent: 2.0 mol/L EDTA (pH 10; isocratic); flow: 0.8 mL/min; injection volume: 100  $\mu\text{L}$ ; recording time: 10 min; temperature column off; ICP/MS parameters: RF power: 1550 W, RF matching: 1.8 V; sampling depth: 8 mm; plasma gas flow rate: 15 L/min; carrier gas flow rate: 0.95 L/min; makeup gas flow rate: 0.15 L/min; collision gas (He) flow rate: 4.0 mL/min; spray chamber temperature: 2  $^{\circ}\text{C}$ ; tuning solution: 1 g/L Li, Co, Y, Ce, and Tl in 2%  $\text{HNO}_3$  solution; monitoring masses (Cr): 50, 52, and 53 amu; acquisition mode: spectrum and time-resolved analysis (TRA)

## 2.2 Chromate in HCl eluates with Inline Preconcentration, Matrix Elimination, and ICP/MS detection

Application Note [AN-M-009](#)

### Introduction

Hexavalent chromium is toxic and has been classified as carcinogenic. Consumer goods must be tested for this compound to guarantee consumer safety. In this method, acidic eluates from chalk, fabrics, ballpoint pen refills, inks, and plastics were tested for hexavalent chromium.

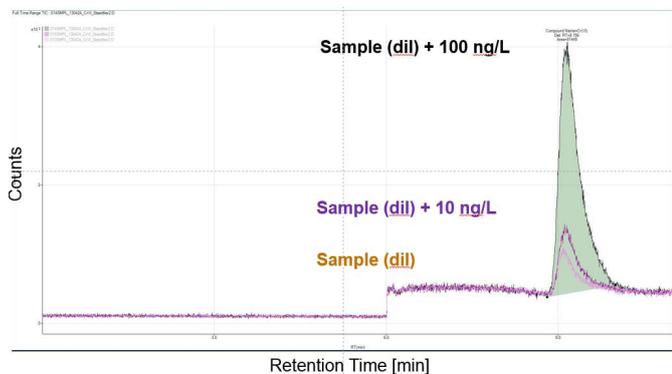
### Method

In accordance with DIN EN 71-3, 1 g sample was treated with 50 mL of 0.25% HCl. This solution was neutralized with a buffer. 2000 µL of this neutralized solution was then pre-concentrated and the matrix automatically eliminated with acetone/water. Separation was performed on a Metrosep A Supp 5 -

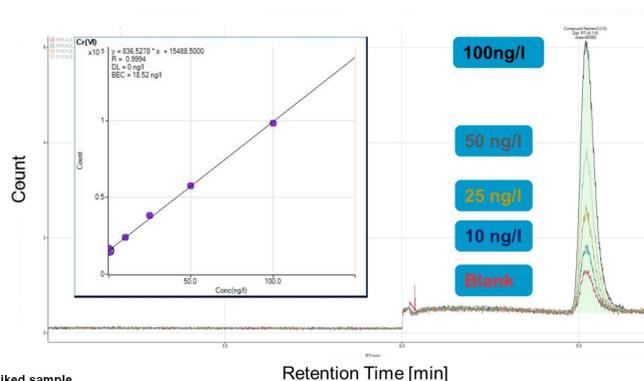
250/4.0 column with subsequent detection by ICP/MS. Only 6 min after the injection was the column outlet switched to the ICP/MS to prevent carryover of acetone into the ICP. Detection of the Cr(VI) peak took place after approx. 9 min. The mass 52 was recorded in collision mode in order to suppress ArC interference caused by the mobile phase.

### Results

Cr(VI) concentrations between 10 and 100 ng/L can be quantified with this method (Figure 2 and 3). Automated matrix elimination resulted in nearly complete removal of organic sample components, which allows analysis of samples with complex matrices and has a positive effect on the column life. The method is extremely sensitive and specific. This also calls for a clean working environment and pure chemicals to avoid Cr(VI) blank values (e.g., metal spatulas should not be used).



**Figure 2.** Spiked sample of consumer good



Spiked sample

**Figure 3.** Calibration of hexavalent chromium concentrations between 10 and 100 ng/L. Column: Metrosep A Supp 5 - 250/4.0; eluent: 15.4 mmol/L  $\text{Na}_2\text{CO}_3$ , 4.8 mmol/L  $\text{NaHCO}_3$ ; flow rate: 0.8 mL/min; injection volume: 2000 µL; m/z 52

## 2.3 Chromium species in dietary supplements using speciated isotope dilution mass spectrometry

Martone, N.; Mizanur Rahman, G. M.; Pamuku, M.; Kingston, H. (2013) *J. Agric. Food Chem.* 61(41), 9966–9976

### Introduction

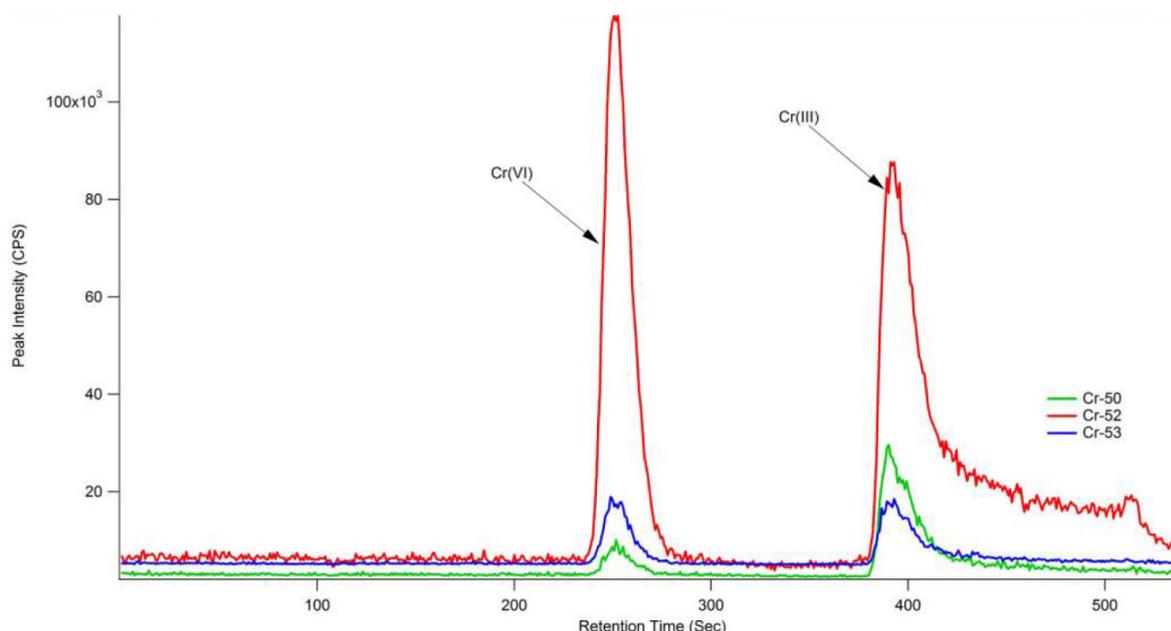
To determine the health impact of chromium in dietary supplements, Cr(III) and Cr(VI) must be independently measured and verified by mass balance (sum of both species must equal independent measurements of total chromium), as both may be present in finished products. Because Cr(III) is stable in acidic conditions and Cr(VI) in alkaline conditions, interconversions between species may occur in complex matrices and during analytical extraction, increasing the difficulty of quantification.

A study was conducted to determine Cr(VI) and Cr(III) in dietary supplements. EPA Method 3060A extraction protocol

was performed to extract Cr(VI) and EPA Method 3052 was performed on the extracted residue to digest the remaining Cr(III). Speciated isotope dilution mass spectrometry (SIDMS), as described in EPA Method 6800 (update V) was implemented with IC-ICP/MS. Method 6800 uniquely enables tracking and correcting for the bidirectional chromium interspecies conversions that occur during extraction and sample handling prior to instrumental analysis.

### Results

Mass balance results indicated that the off-the-shelf dietary supplements analyzed during this study contained hexavalent chromium ranging from below the detection limit to  $122.4 \pm 13.0 \mu\text{g/g}$ , which corresponds to 16% of the total chromium content (Figure 4). This type of variation in the final products raises public health issues and points to a need to use a robust method that can accurately and reliably analyze speciation, while correcting for species conversions.



**Figure 4.** Typical dietary supplement sample. Column: Hamilton PRP-X100 anion-exchange (150 mm  $\times$  4.6 mm, 10  $\mu\text{m}$ ); eluent A: 0.06 mol/L  $\text{HNO}_3$ , pH = 9.3; eluent B: 0.06 mol/L  $\text{HNO}_3$ , pH 1.2; flow rate: 1.0 mL/min with gradient elution; m/z 50, 52, 53

## 2.4 Chromate in NIST SRM 2701 by speciated isotope dilution mass spectrometry according to US EPA 6800 (Rahman, G. M. M. et al.; 2012)

### Introduction

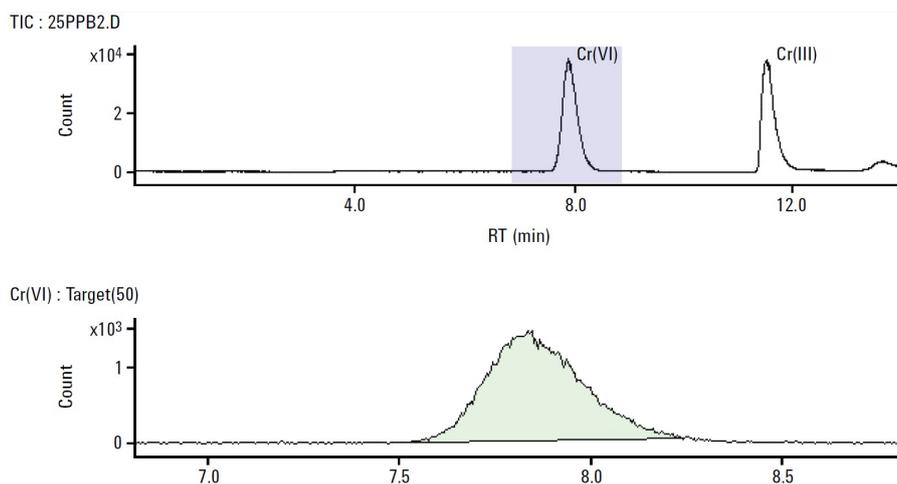
The objectives of this study were to apply EPA Method 6800, which uses speciated isotope dilution mass spectrometry (SIDMS), and to compare chromium speciation results from SIDMS with those obtained from conventional techniques.

### Results

Accurate and reproducible results at very low detection levels for both chromium species were obtained during this study

(Figure 5). The analysis time per sample was less than 15 minutes, which can be further reduced by using a shorter column. The Cr(VI) concentration agreed with the certified and reference Cr(VI) concentration for the SRM 2701. NIST's certificate of analysis for SRM-2701 states that Method 6800 SIDMS was used to determine the true value.

SIDMS possesses the unique capability to track interspecies conversions and provide the analyst with the ability to make legally defensible corrections, especially for samples with highly reactive matrices, such as chromite ore processing residue (COPR). This makes EPA Method 6800 an indispensable tool for chromium speciation.



**Figure 5.** 25 µg/L Cr(III) and Cr(VI) standard. Column: Hamilton PRP-X100 anion-exchange (150 mm × 4.6 mm, 10 µm); eluent A: 0.06 mol/L NO<sub>3</sub><sup>-</sup> (pH 9.3 adjusted with NH<sub>4</sub>OH); eluent B: 0.06 mol/L NO<sub>3</sub><sup>-</sup> (pH 1.2); flow rate: 1 mL/min; m/z 50, 52, 53

### Chromium – further applications with IC-ICP/MS

Determination of Cr(VI) in wastewater

Application Note [AN-M-008](#)

Optimization and validation of strategies for quantifying chromium species in soil based on speciated isotope dilution mass spectrometry with mass balance. Wolle, M.M.; Mizanur Rahman, G. M.; Kingston, H. M.; Pamuku, M. (2014) *J. Anal.*

*At. Spectrom.* 29(9), 1640–1647

Development of methods for the speciation of chromium in leather waste by IC-ICP/MS. Sushil, K. C. Ph.D. Thesis, Central Ostrobothnia University of applied sciences, Finland, 2010

Use of IC-ICP/MS coupling. Element species analysis of chromium. Knöll, J., Seubert, A. (2009) *GIT Labor-Fachzeitschrift* 53(3), 151–153

# Metrohm White Paper

## 2.5 Speciation of Cr(III) and Cr(VI) by microbore column

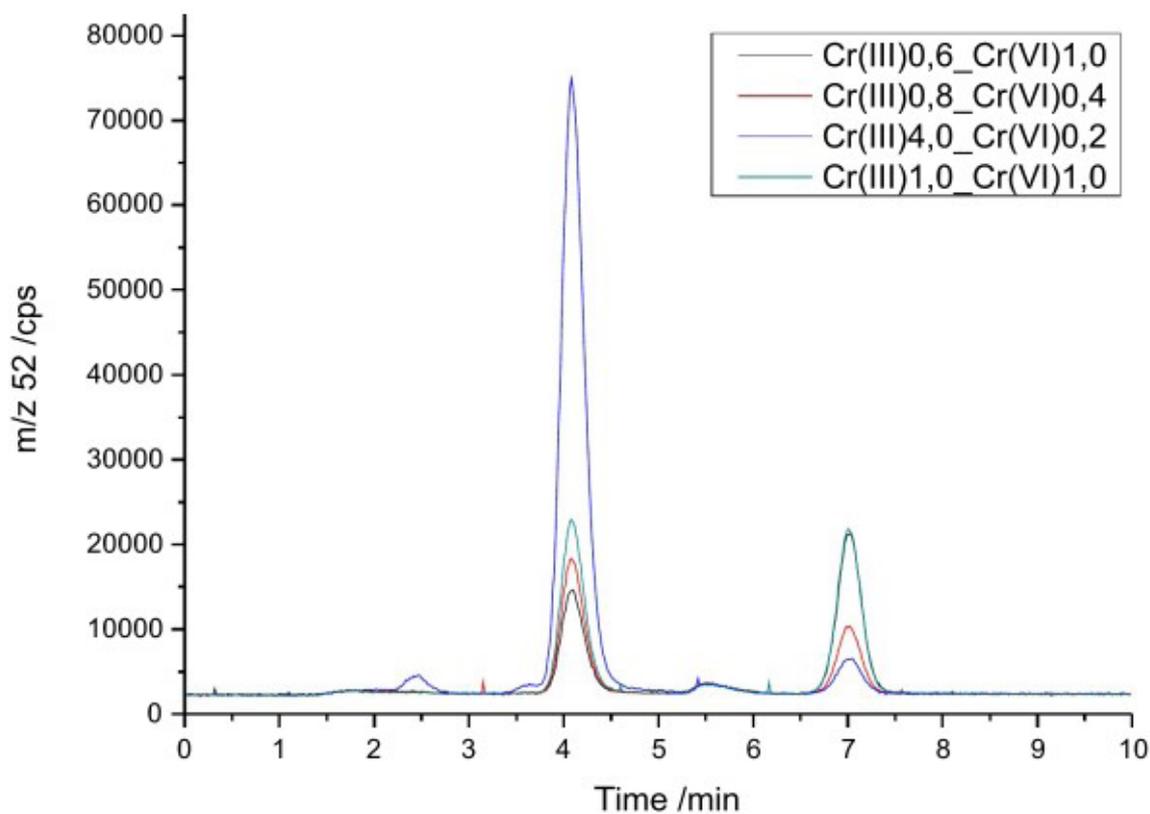
Application Note [AN-M-013](#)

### Introduction

The goal of this study was a fast separation of Cr(III) and Cr(VI) with a good resolution of both species. This was achieved with the column Metrosep Carb 2 - 100/2.0.

### Results

The two species were separated as Cr(III)-EDTA complex and chromate. The IC effluent was directly connected to the IPC-MS. The flow rate of the microbore column fitted was suitable for the ICP/MS, thus a flow splitter was not necessary. The chromatographic separation can be done within 10 minutes (conditions as mentioned in Figure 1).



**Figure 6.** Mixtures of Cr(III) and Cr(VI) with different concentrations (0.2–4.0 µg/L). Column: Metrosep Carb 2 - 100/2.0; eluent c(ammoniumnitrate) = 100 mmol/L, set to pH 9 with ammonia; flow rate 0.2 mL/min

## 3. Arsenic

Arsenic (As), a metallic element found naturally in the environment in ores and soil, may occur in both organic and inorganic forms. Inorganic arsenic, whether naturally occurring or introduced anthropogenically, is usually in the form of either arsenate As(V), which is fully oxidized, or arsenite As(III), which is partially reduced.

Inorganic arsenic is associated with excess skin, lung, liver, bladder, and kidney cancers in humans following chronic exposure. Both arsenate and arsenite are genotoxic and are capable of inducing chromosome aberrations and sister chromatid exchange in rodent and human cells. In this regard, arsenite is approximately an order of magnitude more potent than arsenate. Both forms of inorganic arsenic compromise pulmonary alveolar macrophage function at noncytotoxic concentrations, with arsenite more potent than arsenate. Both forms produce tumors following intratracheal instillation to the lungs of hamsters (Saranko, C. J.; 1998).

### 3.1 Inorganic arsenic species in dietary supplements using gradient ion chromatography and IC-ICP/MS

Wolle, M. M.; Mizanur Rahman, G. M.; 'Skip' Kingston, H. M.; Pamuku, M. (2014) *Anal. Chim. Acta* 818, 23–31

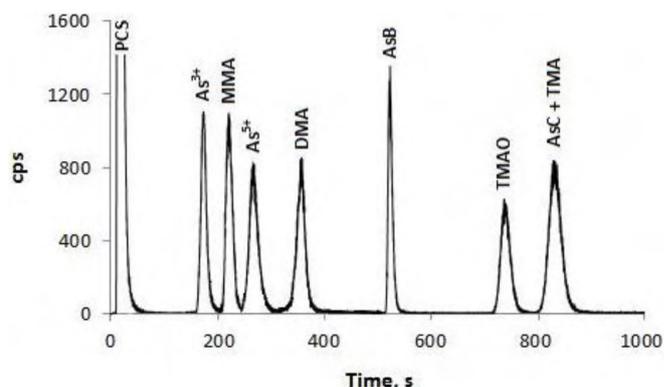
#### Introduction

Dietary supplements are often considered to be exclusively beneficial to health and free from toxic side effects. However, studies show that some supplements are contaminated with high levels of toxic substances. Arsenic is among the elements of primary concern because of its toxicity. Contamination of dietary supplements with arsenic occurs mainly through the plant materials used as ingredients. Arsenic is released into the environment through natural and anthropogenic activities, and it is taken up by plants and accumulated in their edible parts. Assessment of arsenic should be conducted based on the determination of its individual species because the element's toxicity depends on its chemical form.

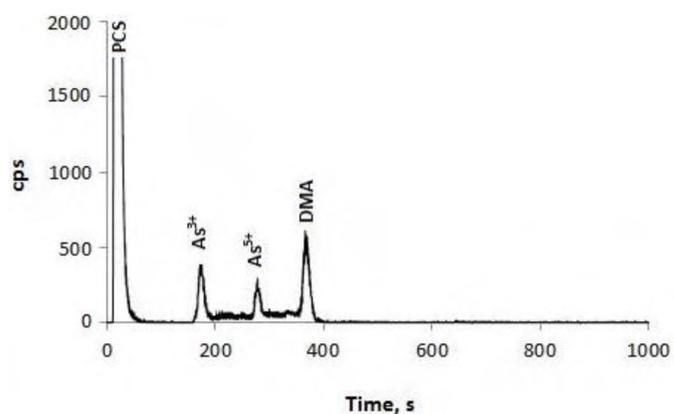
In the present study, inorganic and organic arsenic species were simultaneously extracted from dietary supplements using a microwave-enhanced protocol and were then determined by IC-ICP/MS. High-pressure-gradient IC with a Hamilton PRP-X200 cation exchange column was used to achieve baseline separation of the species prior to injection into an Agilent 7700 ICP/MS instrument. A post-column internal standard was injected using an 800 Dosino. The IC and ICP/MS instruments were synchronized using remote signal. MagIC Net software controlled the sample loading and gradient program while data handling and manipulation was done with Agilent MassHunter software.

#### Results

The chromatographic condition separated As(III), As(V), MMA, DMA, AsB and TMAO. While AsC and TMA were separated from the other species, they were not resolved from each other (Figure 7). Ten widely consumed prenatal and children's dietary supplements were analyzed using the optimized protocol. The supplements were found to have total arsenic contents in the concentration range of 59–531 ng/g. IC-ICP/MS analysis of the extracts showed that all the supplementary products contained As(III) and DMA. As(V) was found in two of the supplements, and an unknown species of arsenic was detected in one product (Figure 8).



**Figure 7.** Standard solution containing 10.0 ng/g arsenic per species, conditions as below (Figure 7).



**Figure 8.** Microwave extract generated from a prenatal supplement prepared from plant materials. The supplement was available in hard-pressed powder (tablet) form. Column: Hamilton PRP-X200 cation-exchange column; eluent A 1.0 mmol/L HNO<sub>3</sub> (pH 2.5); eluent B: 2.0 mmol/L HNO<sub>3</sub>, 20.0 mmol/L NH<sub>4</sub>NO<sub>3</sub> (pH 2.5); flow rate: 0.9 mL/min; m/z 75

## 3.2 Mercury and arsenic speciation analysis by IC-ICP/MS

Reyes, L.; 'Skip' Kingston, H. M.; Wille, A.; Knöll, J.; Steinbach, A. (2010) *American Laboratory* 9, 22–27

### Introduction

This article discusses the determination of organic and inorganic arsenic and mercury compounds by IC-ICP/MS. Arsenic species (monoisotopic) are not prone to interconversion and are thus determined by traditional speciation analysis.

### Results

IC-ICP/MS allows the separation and unambiguous identification of different arsenic species in inorganic and organic forms (Figure 9).

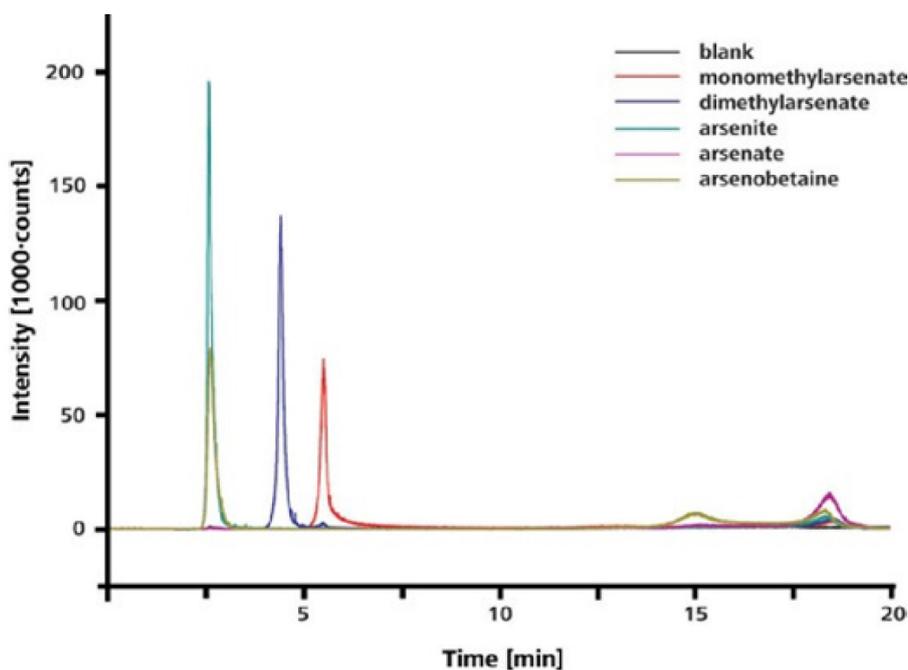
## Arsenic – further applications with IC-ICP/MS

Study on analytical methods for inorganic arsenic speciation in soil by IC-ICP/MS. Mun, S. H.; Lee, B. J.; Kim, H. S.; Cho, M. K.; Sung, J. Y. (2015)

Sulfur redox chemistry governs diurnal antimony and arsenic cycles at Champagne Pool, Waiotapu, New Zealand. Ullrich, M. K.; Pope, J. G.; Seward, T. M.; Wilson, N.; Planer-Friedrich, B. (2013) *J. Volcanol. Geotherm. Res.* 262, 164–177

Determination of arsenic and selenium species in drinking water applying IC-ICP/MS

Application Note [AN-M-010](#)



**Figure 9.** Separation and detection of arsenite, dimethylarsenate, monomethylarsenate, and arsenate. Column: Metrosep A Supp 15 - 150/4.0; eluent: 8 mmol/L  $\text{NH}_4\text{NO}_3$  (pH 8); flow rate 0.7 mL/min;  $m/z$  75

### 3.3 Simultaneous speciation of arsenic and selenium species in petroleum refinery aqueous streams

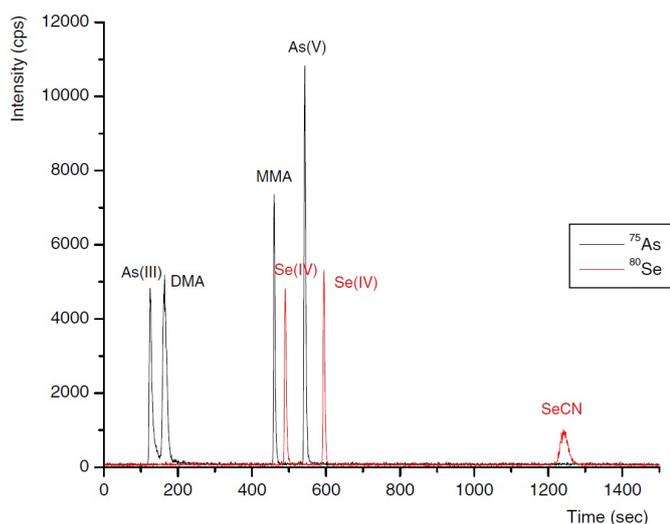
Tonietto, G. B.; Godoy, J. M.; Oliveira, A. C.; De Souza, M. V. (2010) *Anal. Bioanal. Chem.* 397(5) 1755–1761

#### Introduction

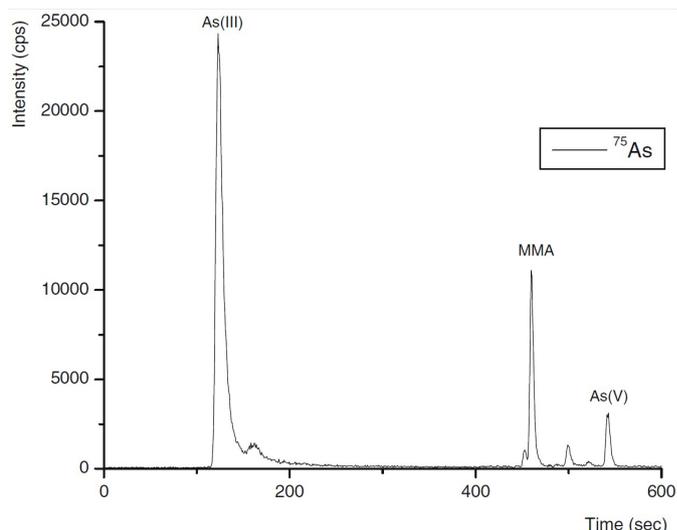
The quantitative speciation of selenium (Se) and arsenic (As) in the streamwaters of a refining process was investigated.

#### Results

Four arsenic species – arsenite As(III), arsenate (As(V)), monomethylarsinic acid (MMA), and dimethylarsinic acid (DMA) – and three inorganic Se species – selenite Se(IV), selenate Se(VI), and selenocyanate (SeCN<sup>-</sup>) – were separated in a single run by IC using gradient elution with 100 mmol/L NH<sub>4</sub>NO<sub>3</sub>, pH 8.5, adjusted by addition of NH<sub>3</sub>, as eluent (Figure 10 and 11). Repeatabilities of peak position and peak area evaluation were better than 1% and about 3%, respectively. Detection limits (defined as 3× baseline noise) were 81, 56, and 75 ng/L for Se(IV), Se(VI), and SeCN<sup>-</sup>, respectively, and 22, 19, 25, and 16 ng/L for As(III), As(V), MMA, and DMA, respectively.



**Figure 10.** Separation of the arsenic species As(III), DMA, MMA, and As(V), and the selenium species Se(IV), Se(VI), and SeCN<sup>-</sup> (5 ng of each species). Conditions as Figure 11



**Figure 11.** Arsenic species in a typical process wastewater inlet sample. Column: Metrosep A Supp 10 - 250/4.0; eluent: 100 mmol/L NH<sub>4</sub>NO<sub>3</sub> (pH 8.5, adjusted by addition of NH<sub>3</sub>); flow rate: 1 mL/min using gradient elution; m/z 75–83

## 3.4 Simultaneous determination of arsenic and selenium species in fish tissues using IC-ICP/MS

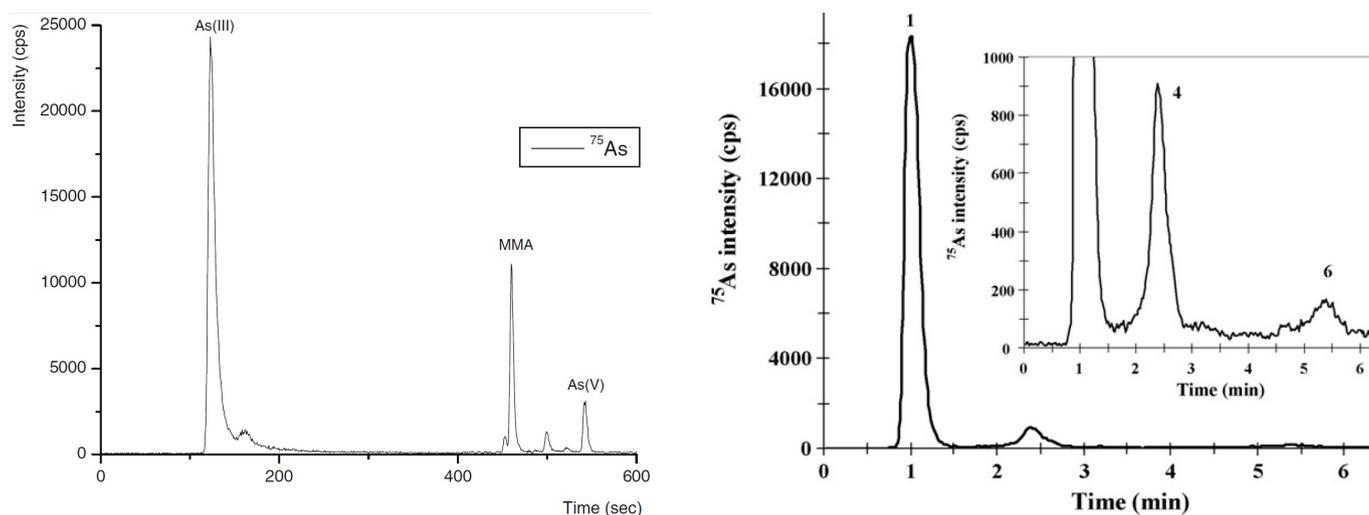
Reyes, L. H.; Mar, J. L. G.; Mizanur Rahman, G. M.; Seybert, B.; Fahrenholz, T.; 'Skip' Kingston, H. M. (2009) *Talanta* 78(3), 983–990

### Introduction

A microwave-assisted enzymatic extraction (MAEE) method was developed for the simultaneous extraction of arsenic (As) and selenium (Se) species from fish tissues.

### Results

The accuracy of the developed extraction procedure was verified by analyzing two reference materials, DOLT-3 and BCR-627. The extraction recoveries in these reference materials ranged between 82% and 94% for As. Arsenobetaine (AsB) and selenomethionine (SeMet) were the major species detected in fish tissues. In the analyzed fish extracts, the sum of arsenic species detected was in good agreement with the total As extracted (Figure 12).



**Figure 12.** IC-ICP/MS profile of enzymatic extracts of (left) BCR-627 and (right) DOLT-3 obtained by MAEE. Peak identification of the right-hand chromatogram: (1) AsBet, (4) DMA, and (6) As(V). Column: Metrosep Anion Dual 3 - 100/4.0, Metrosep Anion Dual 3 guard; eluent A: 5 mmol/L  $\text{NH}_4\text{NO}_3$ ; eluent B: 50 mmol/L  $\text{NH}_4\text{NO}_3$ , 2% (v/v) methanol (pH 8.7); flow rate: 1 mL/min; m/z 75, 77, 82

### Arsenic – further applications with IC-ICP/MS

Sulfur redox chemistry governs diurnal antimony and arsenic cycles at Champagne Pool, Waiotapu, New Zealand Ullrich, M. K.; Pope, J. G.; Seward, T. M.; Wilson, N.; Planer-Friedrich, B. (2013) *J. Volcanol. Geoth. Res.* 262, 164–177

Determination of arsenic and selenium species in drinking water applying IC-ICP/MS

Application Note [AN-M-010](#)

## 4. Mercury

Mercury is found in several forms, particularly as elemental Hg(0), inorganic Hg(II), or alkylated mercury (CH<sub>3</sub>Hg<sup>+</sup>). Of the most common mercury species found in the environment, methylmercury is considered the most toxic species. It is classified as a neurotoxin that rapidly bioaccumulates and can cause major health problems or death, even in small quantities. According to the US Food and Drug Administration (FDA), the major exposure pathway to methylmercury in humans and wildlife is through consumption of contaminated fish.

Mercury can not only be analysed in fish, but also in end-consumers (e.g., in human hair) or in potentially polluting substances (e.g., crude oil). The US Environmental Protection Agency (EPA) stipulates a reference dose for methylmercury of 0.1 µg/kg of body weight per day, while the World Health Organization (WHO) has set 1.6 µg/kg of body weight per week as the tolerable dose (Levenson, C. W., 2006).

### 4.1 Mercury and arsenic speciation analysis by IC-ICP/MS

Reyes, L.; 'Skip' Kingston, H. M.; Wille, A.; Knöll, J.; Steinbach, A. (2009) *Separation Science* 1(6), 17–21

Moritz, T.; Reyes, L. H.; 'Skip' Kingston, H. M.; Mizanur Rahman, G. M.; Czyborra, Metrohm poster [8.000.6039](#)

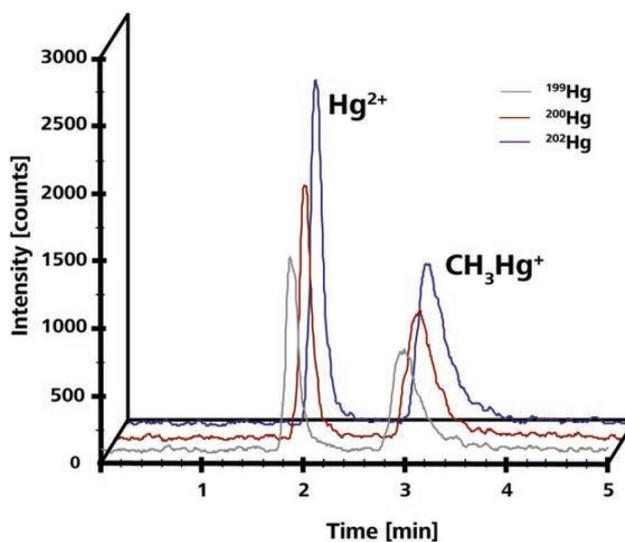
#### Introduction

Species transformations of mercury that occur during several sample preparation techniques call for the use of specific isotope dilution mass spectrometry (SIDMS). This work illustrates the decisive advantage that SIDMS, as described in Environmental Protection Agency (EPA) Method 6800, offers for studying the transformations of mercury species during sample preparation of fish tissue samples. Because of the unique features and benefits of EPA Method 6800, it is expected that use of SIDMS will increase and that this valuable tool for optimizing and validating trace-metals-speciated sample preparation will gain wide acceptance by analytical chemists.

#### Results

Separation was achieved in less than five minutes and the retention times were  $1.87 \pm 0.02$  and  $2.98 \pm 0.03$  minutes (Figure 13). Linear calibration curves for Hg(II) and CH<sub>3</sub>Hg<sup>+</sup> were obtained in the range from 1–20 µg/L. Detection limits were  $0.46 \pm 0.02$  and  $0.78 \pm 0.08$  µg/L for Hg(II) and CH<sub>3</sub>Hg<sup>+</sup>, respectively.

SIDMS is an invaluable tool for overcoming non-quantitative recoveries and species transformations observed during extraction procedures. It facilitates the determination of mercury species with high precision, accuracy, and correction for species transformations. Depending on the extraction procedure, inorganic mercury contamination in the extracting reagent could be observed. Alkaline extraction procedures, however, yielded results that agreed well with the 95% confidence levels of the certified values.



**Figure 13.** 10 µg/L Hg(II) and CH<sub>3</sub>Hg<sup>+</sup>. Chromatograms obtained at different masses were shifted for clarity. Column: DVB-C18 column, 150 × 4.6 mm, 2 µm; eluent: 50 mmol/L pyridine, 0.5% (w/v) mmol/L cysteine, 5% (v/v) methanol (pH = 3); flow rate: 1 mL/min, isocratic; m/z 199, 200, 201, 202

## 4.2 Mercury Species in crude oil by speciated isotope dilution LC-ICP/MS

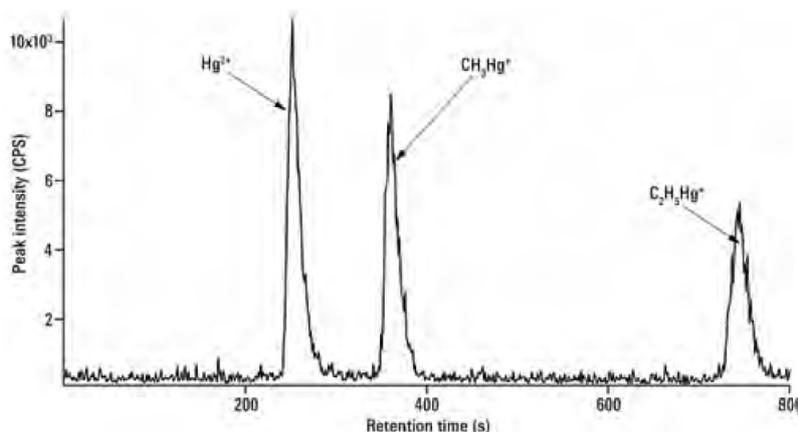
Mizanur Rahman, G. M.; Fahrenholz, T. M.; Pamuku, M.; 'Skip' Kingston, H. M. (2012) [http://www.agilent.com/cs/library/applications/5990-9473EN\\_icpmsSpeciationHB\\_lr.pdf](http://www.agilent.com/cs/library/applications/5990-9473EN_icpmsSpeciationHB_lr.pdf) (accessed Oct 7, 2016)

### Introduction

Mercury is found in a variety of chemical and physical forms in the environment arising from many sources, both natural and anthropogenic. Among the contributors of mercury to the environment, the burning of fossil fuels is a significant concern. Sources include natural gas, gas condensate, crude oil, and petroleum. All of these may contain considerable amounts of mercury. Depending on the region of its production, crude oil may contain mercury ranging from 0.1 to 20,000  $\mu\text{g}/\text{kg}$ .

### Results

HPLC-ICP/MS analysis of mercury species can be successfully used for crude oil samples by following ccf-SIDMS according to EPA Method 6800 (Figure 14). The method detection limit for  $\text{Hg}^{2+}$ ,  $\text{CH}_3\text{Hg}^+$ , and  $\text{C}_2\text{H}_5\text{Hg}^+$  was below 0.1  $\text{ng}/\text{mL}$ , thus below 1  $\text{ng}/\text{g}$  for crude oil samples.



**Figure 14.** Three mercury species (10  $\mu\text{g}/\text{L}$  each). Column: Supelcosil LC-18 (300 mm  $\times$  4.0 mm, 5  $\mu\text{m}$ ); eluent: 0.4% (w/v) L-Cysteine, 0.05% (v/v) 2-mercaptoethanol, 0.06 mol/L ammonium acetate, 5% (v/v) methanol; flow rate: 1 mL/min; m/z 199, 200, 201, 202

## 4.3 Mercury species transformations in human hair using speciated isotope dilution mass spectrometry

Mizanur Rahman, G. M.; Fahrenholz, T.; 'Skip' Kingston, H. M. (2009) *J. Anal. At. Spectrom.* 24, 83–92

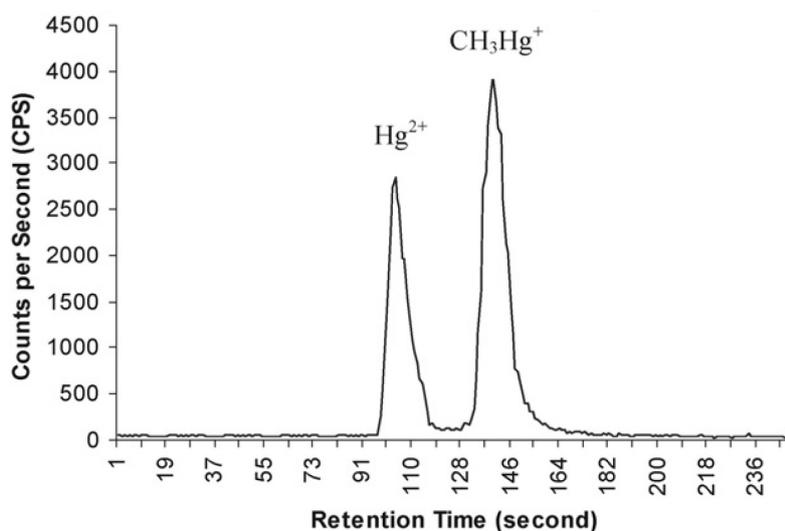
### Introduction

Nine different analytical extraction methods commonly used for mercury speciation in human hair samples were evaluated by analyzing hair certified reference material (IAEA-085) certified for the content of monomethyl mercury and total mercury. Extraction efficiencies, recoveries, and the potential of species transformations during sample processing were evaluated for each of the nine methods by applying speciated isotope dilution mass spectrometry (SIDMS) as both a quantita-

tive and diagnostic tool. The extraction methods evaluated in this study were based on acid leaching with HCl and HNO<sub>3</sub>. Detection of total mercury and of mercury species from all extraction methods was carried out by ICP/MS and high performance liquid chromatography-ICP/MS, respectively.

### Results

All of the methods tested could be corrected using isotopic correction using SIDMS protocol to prevent relative biases from being interpreted as accurate species measurement (Figure 15). This indicates that, as long as isotopic equilibration is achieved, the sample preparation and extraction errors may be corrected so that accurate and legally defensible results can be obtained.



**Figure 15.** Speciation of inorganic mercury and monomethyl mercury. Column: Nova-Pak C18 RP column, 60 Å, 4 µm, 3.9 mm × 150 mm; eluent: 0.4% L-Cysteine (pH 5); flow rate: 1 mL/min; m/z 199, 200, 202

## 4.4 Microwave-assisted extraction protocol for analysis of total mercury and methylmercury in fish tissues

Reyes, L. H.; Mizanur Rahman, G. M.; 'Skip' Kingston, H. M. (2009) *Anal. Chim. Acta* 631, 121–128

### Introduction

A rapid and efficient closed vessel microwave-assisted extraction (MAE) method based on acidic leaching was developed and optimized for the extraction of total mercury (Hg), inorganic mercury ( $\text{Hg}^{2+}$ ), and methylmercury ( $\text{CH}_3\text{Hg}^+$ ) from fish tissues.

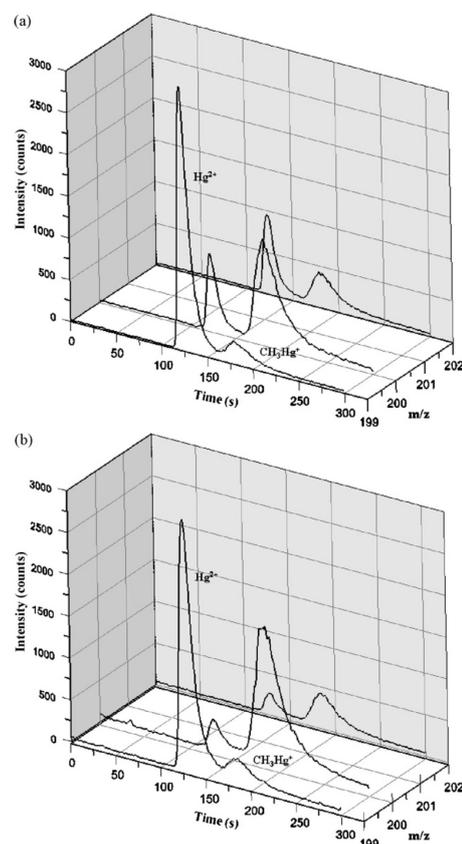
Fish consumption is the main route of methylmercury ( $\text{CH}_3\text{Hg}^+$ ) exposure in humans (85–90% of total Hg level present in aquatic organisms).  $\text{CH}_3\text{Hg}^+$ , one of the most toxic forms of Hg, is produced in aquatic ecosystems by microbial action on  $\text{Hg}^{2+}$ . It is readily bioavailable and also bioaccumulates in the food chain, reaching relatively high concentrations in large predator fish such as shark, marlin, swordfish, and some tuna species. Serious neurological damages to children and developing fetuses have been caused by ingestion of contaminated fish in the past decades (Aschner, T., 2005; Gochfeld, M., 2005; Burger, J., 2005).

### Results

An efficient and fast MAE method for the extraction of total Hg,  $\text{Hg}(\text{II})$ , and  $\text{CH}_3\text{Hg}^+$  in fish tissues was developed. The optimum conditions for the MAE were found to be 0.5 g of sample, 10 mL of solvent containing 5 mol/L HCl and 0.25 mol/L NaCl, and an irradiation time of 10 min at temperature 60 °C (Figure 16). The accuracy of the method was demonstrated by analyzing both total Hg and Hg species in different biological certified reference materials. SIDMS was successfully used as diagnostic tool to validate the MAE method.

### Mercury – further applications with IC-ICP/MS

Comparison of methods with respect to efficiencies, recoveries, and quantitation of mercury species interconversions in food demonstrated using tuna fish. Reyes, L. H.; Mizanur Rahman, G. M.; Fahrenholz, T.; 'Skip' Kingston, H. M. (2008) *Anal. Bioanal. Chem.* 390(8), 2123–2132



**Figure 16.** Dog fish liver DOLT-3 (top) and marlin fish tissue (bottom) samples spiked with  $^{199}\text{Hg}(\text{II})$  and  $\text{CH}_3^{200}\text{Hg}^+$  before MAE. Column: PS-DVB C18 RP (150mm  $\times$  4.6mm, 2  $\mu\text{m}$ ); eluent: 50 mmol/L pyridine, 0.5% (w/v) L-cysteine, and 5% (v/v) methanol (pH 3); flow rate: 1mL/min

## 5. Iodine

Iodine-containing contrast media are used in noninvasive diagnostics to assist targeted imaging (magnetic resonance imaging, or MRI for short, and X-ray examinations) of organs and to differentiate between healthy and unhealthy tissue. They are safe to be administered intravenously and orally and are excreted from the body unmetabolized after a few hours. Because of their poor biodegradability, contrast media can enter the environment, even after passing through wastewater treatment plants, and can be detected in environmental samples at elevated concentrations.

### 5.1 IC-ICP/MS for monitoring the fate of iodinated X-ray contrast media after ozonation

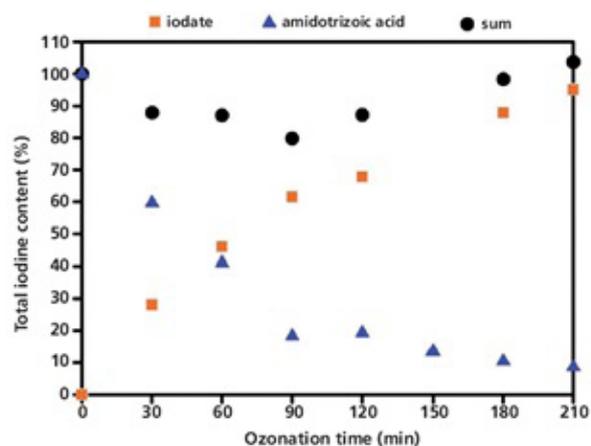
Pfundstein, P.; Martin, C.; Schulz, W.; Seitz, W.; Ruth, K. M.; Wille, A.; Steinbach, A.; Flottmann, D. (2015) *The Column* 11(16), 9–14

#### Introduction

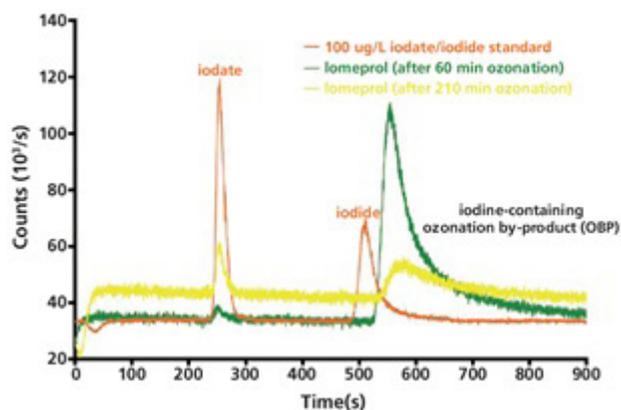
This study shows that IC-ICP/MS is suitable for monitoring iodine-containing ionic oxidation by-products that form during ozonation of iodinated X-ray contrast media, particularly, amidotrizoic acid and iomeprol. The presented method provides important information on the entry, degradation, and fate of various contaminants in (waste-)water, as well as a reduction of sample preparation time.

#### Results

The effect of ozonation treatment on iodinated X-ray contrast media can be determined from the amount of iodate produced during the treatment. Iodate was measured by IC-ICP/MS in this study. It was shown that a 210-min ozonation treatment degrades almost all of the amidotrizoic acid to iodate (Figure 17). However, when degrading iomeprol under the same ozonation conditions, 16% of the iomeprol were still present after 210 min. Degradation was not complete and proceeded via longer-lasting intermediates. Only 14% of the iomeprol had been degraded iodate. The ion chromatogram exhibits other, yet to be identified peaks that are assumed to be the result of other iodine-containing degradation products. The intact iodinated X-ray contrast media could not be detected under the chosen ion chromatographic conditions (Figure 18).



**Figure 17.** Iodine in the form of iodate and amidotrizoic acid as a function of on the duration of the ozonation process.



**Figure 18.** 100 µg/L iodate and iodide standard in comparison with an iomeprol solution (20.4 mg/L) after 60 and 210 min ozonation process. Column: Metrosep A Supp 3 - 250/4.6 or Phenomenex Envirosep-PP RP-18 125 × 4.6 mm HPLC column; eluent: 7.2 mmol/L Na<sub>2</sub>CO<sub>3</sub>, 0.8 mmol/L NaHCO<sub>3</sub>; flow rate: 1.0 mL/min; m/z 127

## 6. Gadolinium

Gadolinium contrast agents, which are predominantly administered intravenously, excel through their outstanding *in vivo* and *in vitro* stability. With a half-life of approximately 2 h, they are excreted unchanged through the kidney-urine pathway and are thus emitted into the wastewater. In municipal sewage treatment plants, where flocculation with  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  salts is performed to improve the settling behavior of dissolved and suspended colloidal material, the added trivalent metal ions compete with  $\text{Gd}^{3+}$  for the organic ligands. Depending on the thermodynamic complex stability, addition of the trivalent metal salts may lead to recomplexing (transmetallation) in the MRI contrast agents and thus release toxic  $\text{Gd}^{3+}$  ions. The metal exchange in gadolinium chelates takes place as part of iron flocculation (Künnemeyer, J., 2009; Kümmerer, 2008).

### 6.1 IC-ICP/MS analysis of gadolinium-based MRI contrast agents

Pfundstein, P.; Martin, C.; Schulz, W.; Ruth, K. M.; Wille, A.; Moritz, T.; Steinbach A.; Flottmann D. (2011) *Separation Science* 3(11), 8–14

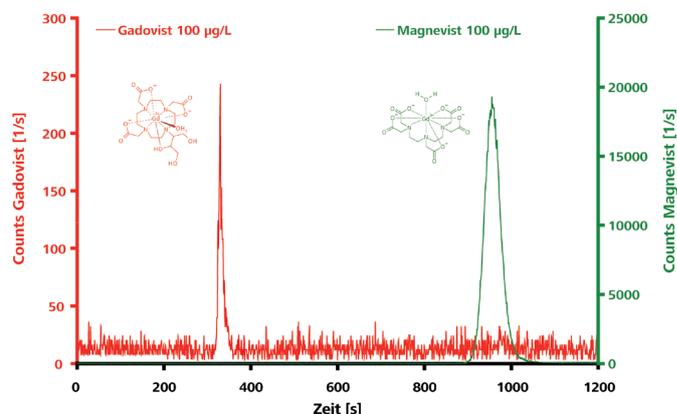
#### Introduction

This study looks at the extent to which iron flocculation performed in wastewater treatment releases toxic gadolinium ions from MRI chelates. Gadolinium speciation is performed by IC-ICP/MS.

#### Results

IC-ICP/MS analysis produces well-separated peaks for Gadovist and Magnevist on the anion-exchange column. Gadovist, being a polar, uncharged compound, elutes after only a few minutes; the twice negatively charged Magnevist, on the other hand, is more strongly retained and hence elutes much later (Figure 19). The concentrations of the competing Fe(III) and Gd(III) ions on the polyaminopolycarboxylate ligands, which reflect the extent of transmetallation, showed the increasing displacement of gadolinium as the  $\text{Fe}^{3+}$  concentration

rose. This effect was more pronounced for Magnevist than for Gadovist. According to the higher thermodynamic stability constant of the iron(III)-DTPA complex ( $\log K = 28.6$ ), Magnevist ( $\log K = 23.0$ ) can be recomplexed to approximately 80% by  $\text{Fe}^{3+}$  concentrations of just 5 mg/L (Künnemeyer, J., 2009). With an  $\text{Fe}^{3+}$  concentration of 20 mg/L, more than 90% of the chelate complexes is in the form of iron chelate complexes. By contrast, less than 10% of the  $\text{Gd}^{3+}$  ions are released from Gadovist – even at higher  $\text{Fe}^{3+}$  concentrations. The crownether-like polyaminopolycarboxylic acid ligand, which is arranged spherically around the gadolinium, effectively shields the complex center of Gadovist against competing  $\text{Fe}^{3+}$  ions, whereby transmetallation is largely prevented. By contrast, the linear DTPA ligands of Magnevist only provide weak shielding of the central atom, so that gadolinium is to a large extent substituted by iron, forming the more stable iron(III) complex (Bianchi, A., 2000).



**Figure 19.** Chromatograms of polar and electrically neutral Gadovist and of ionic Magnevist (both 100 µg/L). Column: Metrosep A Supp 3 - 250/4.6; eluent: 7.2 mmol/L  $\text{Na}_2\text{CO}_3$ , 6.8 mmol/L  $\text{NaHCO}_3$ ; flow rate: 1.0 mL/min; m/z 156, 158, 160

### Gadolinium – further applications with IC-ICP/MS

Speciation and Isotope Dilution Analysis of Gadolinium-Based Contrast Agents in Wastewater. Telgmann, L.; Wehe, C.A.; Birka, M.; Künnemeyer, J.; Nowak, S.; Sperling, M.; Karst, U. (2012) *Environ. Sci. Technol.* 46(21), 11929–11936

## 7. Selenium

Although selenium is an essential trace element, it is toxic if taken in excess. Exceeding the tolerable upper intake level of 400 micrograms per day can lead to selenosis. Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailabilities. By contrast, selenates and selenites are very toxic, having an oxidant mode of action similar to that of arsenic trioxide. The chronic toxic dose of selenite for humans is about 2400–3000  $\mu\text{g}$  of selenium per day for a long time. Selenium also occurs in organic compounds such as dimethyl selenide, selenomethionine, selenocysteine, and methylselenocysteine, all of which have high bioavailabilities and are toxic in large doses (Wilber, C. G., 1980). Hence, it needs to be monitored in various environmental samples (Tonietto, G.B., 2010).

### 7.1 Hyphenated techniques as modern detection systems in ion chromatography

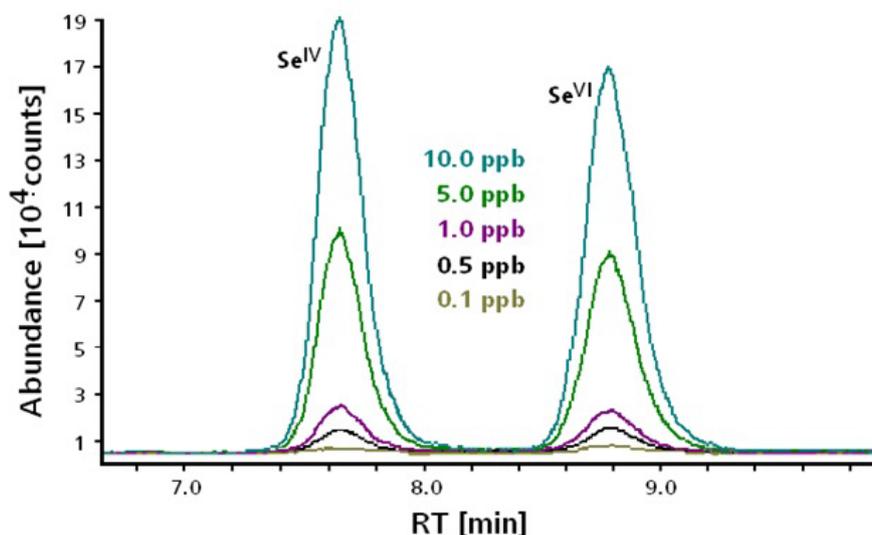
Wille, A., Czyborra, S., Steinbach, A. (2009) *The Column*, 7, 22–24

#### Introduction

In this study, a versatile method was developed to screen for Se(IV) and Se(VI) with sensitivities in the low  $\mu\text{g/L}$  range.

#### Results

Se(IV) and Se(VI) can be separated and detected with IC-ICP/MS. Because selenium compounds differ strongly from one another in their toxicity, speciation analysis is of paramount importance. The main isotope of Se is  $^{80}\text{Se}$ , but  $m/z$  80 is also the Ar-Ar-adduct; therefore, the  $m/z$  78 isotope (23.7%) of Se was measured. An alternative measurement could be done on  $m/z$  82 (8.7%), for which equal sensitivity is expected (Figure 20).



**Figure 20.** Separation and detection of Selenite Se(IV) and Selenate Se(VI) at concentrations between 0.1 and 10  $\mu\text{g/L}$ . Column: Metrosep Anion Dual 3 - 100/4.0; eluent: 2.6 mmol/L  $\text{Na}_2\text{CO}_3$ , 4.0 mmol/L  $\text{NaHCO}_3$ ; flow rate: 0.8 mL/min;  $m/z$  78

## 7.2 Simultaneous speciation of arsenic and selenium species in petroleum refinery aqueous streams

Tonietto, G. B.; Godoy, J. M.; Oliveira, A. C.; De Souza, M. V. (2010) *Anal. Bioanal. Chem.* 397(5), 1755–1761

### Introduction

Selenium usually exists in four oxidation states in the environment: selenate Se(VI), selenite Se(IV), elemental selenium Se(0), and selenide Se(II). Some oil refinery and mining wastewaters contain significant concentrations of selenocyanate ( $\text{SeCN}^-$ ). As crude oil is processed in refinery operations, selenium is concentrated in the wastewater. The treatment of waters polluted with selenium is challenging because the mobility of the different selenium species varies strongly. Conventional wastewater-treatment processes, e.g., coagulation with ferric salts, are not effective for removal of  $\text{SeCN}^-$  because of its low affinity for iron hydroxide at neutral pH.

### Results

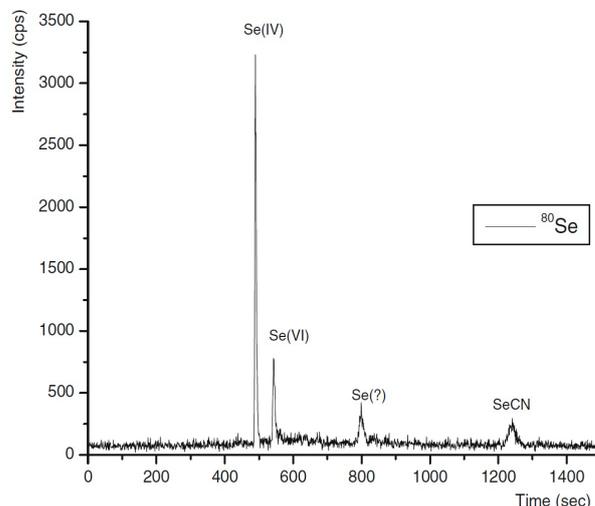
Three inorganic Se species – selenite Se(IV), selenate Se(VI), and selenocyanate ( $\text{SeCN}^-$ ) – were separated in a single run by IC using gradient elution (Figure 21) with an eluent containing 100 mmol/L  $\text{NH}_4\text{NO}_3$  at pH 8.5, adjusted by addition of  $\text{NH}_3$ . Repeatabilities of peak position and of peak area evaluations were better than 1% and ca. 3%, respectively. Detection limits (defined as  $3\times$  baseline noise) were 81, 56, and 75 ng/L for Se(IV), Se(VI), and  $\text{SeCN}^-$ .

Key conditions of the ICP/MS octapole collision/reaction cell (C/RC), including gas flow rates and ion lens voltages, were adjusted for the simultaneous removal of arsenic and selenium interferences. The effect on the detection limits achieved by using a C/RC is greater for selenium than for arsenic.

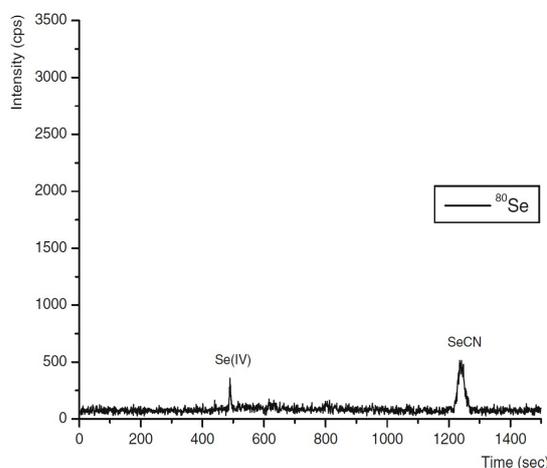
The method was successfully used to study the quantitative speciation of selenium and arsenic in petroleum refinery wastewaters (Figure 22).

### Selenium – further applications with IC-ICP/MS

Isotope Fractionation of Selenium by Biomethylation in Microcosm Incubations of Soil. Schilling, K.; Johnson, T.M.; Wilcke, W. (2013) 352, 101–107



**Figure 21.** Ion chromatogram obtained from selenium species typically found at process wastewater inlet (condition as below)



**Figure 22.** Ion chromatogram obtained from selenium species typically found at process wastewater inlet. Column: Metrosep A Supp 10 - 250/4.0; eluent A: 100 mmol/L  $\text{NH}_4\text{NO}_3$  (pH 8.5); eluent B: ultrapure water; flow rate: 1 mL/min, gradient elution; m/z 75–83

## 8. Thallium

The high environmental relevance of Thallium (Tl) is due to its elevated toxicity. Tl is emitted by various sources, including industry, mining, and waste handling. Usually, the inorganic species of thallium are considered in environmental studies. The occurrence of organic Tl species in marine ecosystems, like the dimethyl thallium cation, is under investigation. Knowledge on the environmental relevance of this organometallic compound is very restricted, which is primarily due to the lack of analytical methods to determine dimethyl thallium at low concentration levels.

### 8.1 Detection of dimethyl thallium in water samples at low concentration levels

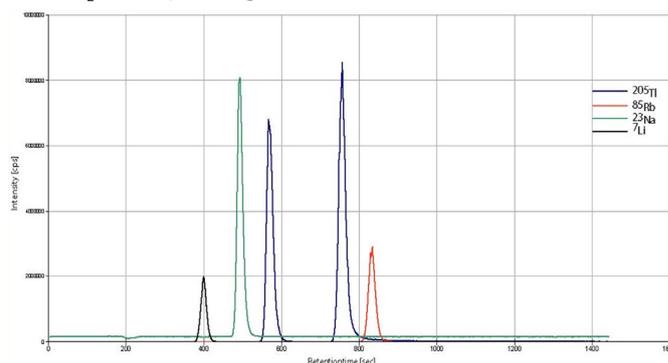
Gronen, L.; Bruchmann, M.; Sindern, S.; Heister, S.; Dreßen, S.; Schwarzbauer, J. (2012) Proceedings 13th European Meeting on Environmental Chemistry.

#### Introduction

So far, only few investigations pointed to the occurrence of an organic species of thallium in marine ecosystems, the dimethyl thallium cation  $\text{Me}_2\text{Tl}^+$ : The first evidence of its occurrence was found in 1999 by Schedlbauer and Heumann (Schedlbauer, O.F., 2000). This study aims at the development of appropriate analytical methods for the determination of dimethyl thallium at trace levels. Two different approaches were investigated, a liquid chromatography / mass spectrometry (LC/MS)-based technique and ion chromatography linked with inductively coupled plasma mass spectrometry (IC-ICP/MS). (Schedlbauer, O. F., 2000)

#### Results

The IC-ICP/MS method is suitable for the detection and quantification of  $\text{Me}_2\text{Tl}$  in standard solutions as well as in natural samples. It is the best available technique, because it minimizes the effects of sample pretreatment on the stability of the  $\text{Me}_2\text{Tl}$  complex (Figure 23).



**Figure 23.** Full IC-ICP/MS run of a 1  $\mu\text{g/L}$  23-element standard solution from Merck after addition of 1  $\mu\text{g/L}$  of Tl, Rb, and  $\text{Me}_2\text{Tl}$ , respectively. The first Tl peak is formed by  $\text{Me}_2\text{Tl}^+$  and the second one by  $\text{Tl}^+$ . The low concentration was chosen to be able to evaluate the suitability of the method for the low concentrations of  $\text{Me}_2\text{Tl}$  expected in environmental samples. Standard peak area could be used for internal standard calibration of these kinds of samples. Column: Metrosep C 4 - 250/4.0; eluent: 1.7 mmol/L  $\text{HNO}_3$ ; flow rate: 0.9 L/min

## 8.2 Indirect anodic stripping voltammetric determination of Tl(I) and Tl(III) in the Baltic seawater samples

Krasnodebska-Ostrega, B.; Paldyna, J.; Wawrzynska, M.; Stryjewska, E. (2011) *Electroanalysis* 23(3), 605–610

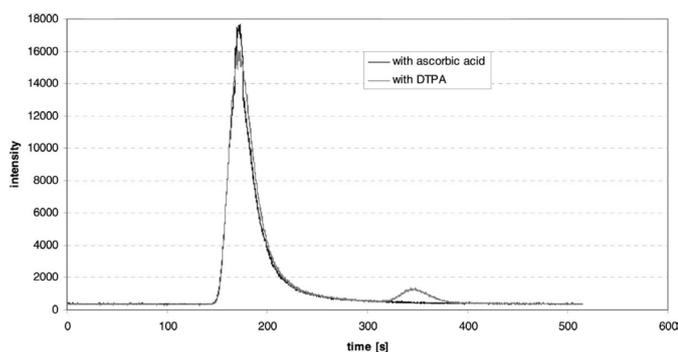
### Introduction

The oxidized forms of thallium have been found in water and in plant tissues, and the dimethyl thallium ion  $\text{Me}_2\text{Tl}$  has been detected in Atlantic seawater. The analytical procedure proposed here to analyze Tl speciation in water samples consists of chromatographic separation with subsequent detection by inductively coupled plasma mass spectrometry (ICP/MS) or by inductively coupled plasma optical emission spectrometry (ICP/OES). A microcolumn containing immobilized oxine on surfactant-coated alumina was used to retain monovalent thallium Tl(I) in the presence of EDTA. Tl(I) was thereby sepa-

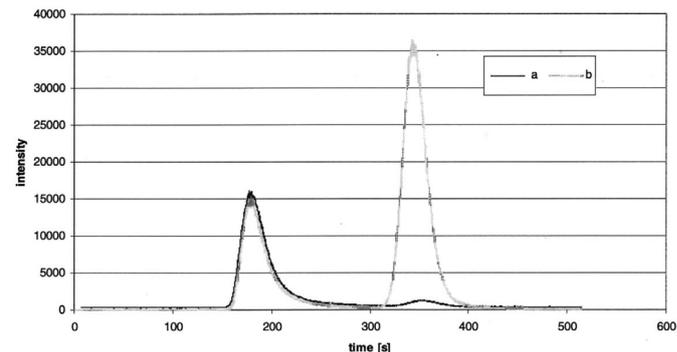
rated from other thallium species. The concentration of Tl(III) was evaluated on the basis with or without the addition of DTPA. DTPA acts as a stabilizer and prevents the reduction of Tl(III).

### Results

The Baltic seawater sample enriched with thallium was analyzed with the method proposed above. The chromatograms indicated that ascorbic acid reduced Tl(III). Reduction could be avoided by stabilization of Tl(III) with DTPA (Figure 24). Figure 25 presents chromatograms of two prepared samples containing different amounts of Tl(III). The peak of Tl(III)-DTPA was recorded at a retention time of 350 s. Chromatographic analysis of both thallium species unveiled concentrations of  $284 \pm 6$  ng/mL Tl(I) and  $24 \pm 4$  ng/mL Tl(III).



**Figure 24.** IC chromatograms of seawater spiked with standards of 280 µg/L Tl(I) and 25 µg/L Tl(III) and conserved with ascorbic acid or DTPA solution (diluted 1:10). The signals were recorded with online ICP/MS detection of  $^{205}\text{Tl}$ . Column: Hamilton PRP-X100 (250/4.1); eluent: 100 mmol/L ammonium acetate, 5 mmol/L DTPA (pH 6.2); flow rate: 1.5 mL/min



**Figure 25.** IC chromatograms of seawater spiked with standards of 280 µg/L Tl(I) and 25 µg/L Tl(III) (a) and of the same sample after addition of 500 mg/L Tl(III)-DTPA (b). Both samples were diluted 1:10. The signals were recorded with online ICP/MS detection of  $^{205}\text{Tl}$ .

### Thallium – further applications with IC-ICP/MS

Tl-speciation of aqueous samples – a review of methods and application of IC-ICP/MS/LC-MS procedures for the detection of  $(\text{CH}_3)_2\text{Tl}^+$  and  $\text{Tl}^+$  in river water. Sindern, S.; Schwarzbauer, J.; Gronen, L.; Görtz, A.; Heister, S.; Bruchmann, M. (2015) *Int. J. Environ. Anal. Chem.* 95(9), 790–807

## 9. Iron

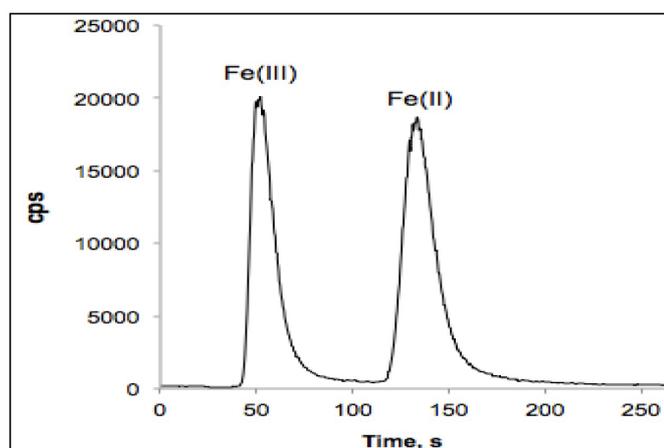
The redox speciation analysis of iron is important because the environmental behavior, uptake by plants, absorption by humans and other animals, and transport and storage of the element depend on its oxidation state.

### 9.1 Iron speciation in soil and other matrices using speciated isotope dilution according to US EPA 6800

Application Note [AN-M-012](#)

#### Introduction

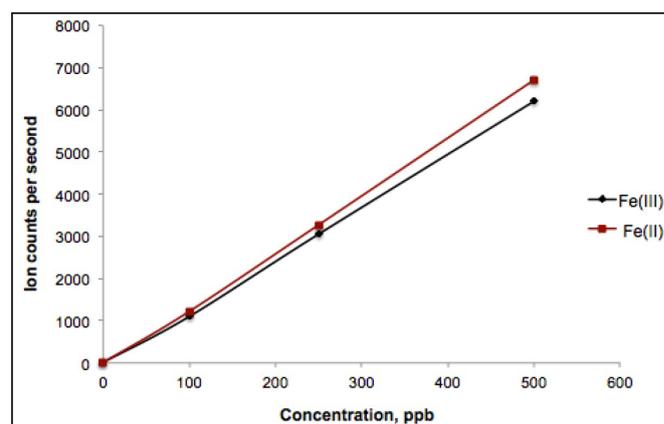
In the present study, an IC-ICP/MS method was developed for the determination of Fe(II) and Fe(III) based on in-column complexation by pyridine-2,6-dicarboxylic acid, commonly known as dipicolinic acid (DPA). DPA is a known chelator for di- and trivalent metal ions including those of iron.



**Figure 26.** Chromatogram of a standard solution containing 250.0 ng/g of Fe(II) and Fe(III) (conditions as Figure 26).

#### Results

The IC and ICP/MS instruments were synchronized by remote signal. The MagIC Net software controlled the sample loading and gradient program while data handling and manipulation were done with the Agilent MassHunter software. The chromatographic condition achieved baseline separation between Fe(II) and Fe(III) in less than 5 minutes (Figure 26). Several aqueous standard solutions and beverage samples were analyzed. In most of the samples, Fe(II) was found to be the predominant species (Figure 27). Iron is constantly interconverting between the oxidation states +2 and +3, i.e., Fe(II) and Fe(III), depending on various environmental conditions. This method provides exact quantitation of each species in soil, water, wastewater, and nutraceuticals.



**Figure 27.** Calibration curve (0.01–500 ppb). Column: Metrosep A Supp 10 S-Guard/4.0; eluent: 4.0 mmol/L DPA, 20 mmol/L ammonium nitrate (pH 4.3); flow rate: 0.8 mL/min, isocratic; m/z 56

#### Iron – further applications with IC-ICP/MS

Method development for the redox speciation analysis of iron by ion chromatography–inductively coupled plasma mass spectrometry and carryover assessment using isotopically labeled analyte analogues. Wolle, M. M.; Fahrenholtz, T.; Mizanur Rahman, G. M.; Pamuku, M.; 'Skip' Kingston, H. M.; Browne, D. (2014) *J. Chrom. A*, 1347, 69–103

## 10. Organic compounds

In recent years, IC-ICP/MS has been applied to analyze organic compounds such as pesticides and biomolecules. The technique proved suitable for molecules with relatively small masses which are present as ions. Further fields of application are the monitoring of chelating agents, which are used in many industrial processes and which could potentially pollute the environment, as well as the analysis of organophosphates in battery research (Knöll, J., 2012).

### 10.1 Aminopolycarboxylic acids in surface water using ion-exchange chromatography coupled to ICP/MS

Knöll, J.; Seubert, A. (2012) *J. Chrom. A* 1270, 219–224

Knöll, J. *Ph.D. Thesis, Philipps-Universität Marburg, Germany, 2013*

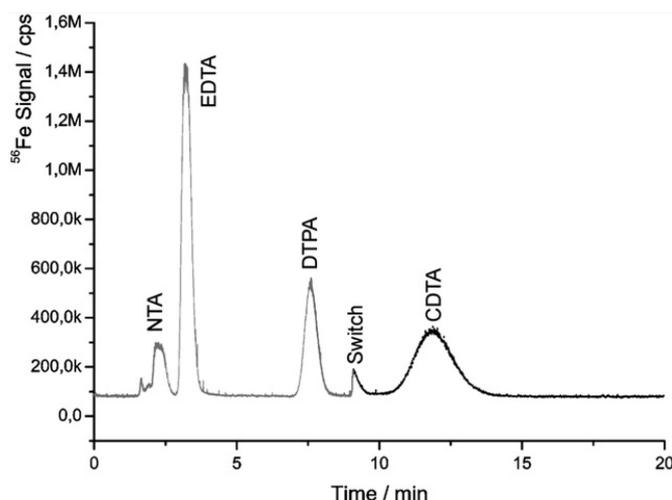
#### Introduction

Aminopolycarboxylic-acid-based chelating agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), and (1,2-cyclohexylenedinitrilotetraacetic acid (CDTA) are widely used in industrial processes and in household products. As these chelating agents pass the wastewater treatment plant unhindered, they reach surface waters, in which they are only poorly biologically degradable. Through the groundwater, they then enter the drinking water cycle. These chelating

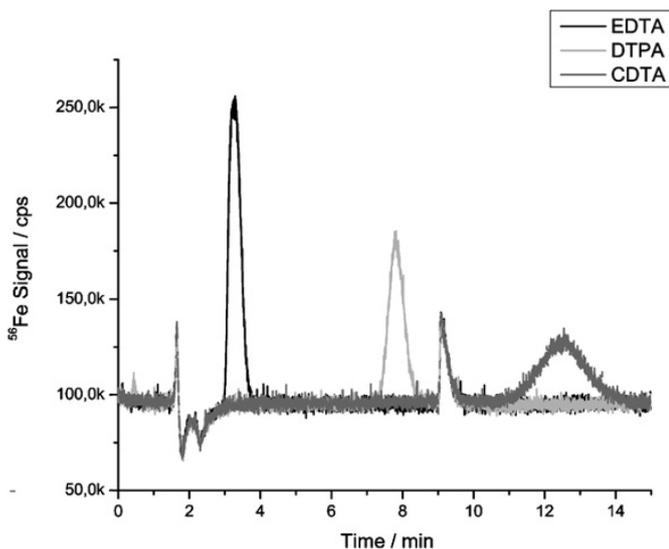
agents are usually not toxic themselves, but they are capable of mobilizing toxic metals from the sediment of rivers and making them biologically available.

#### Results

An indirect method for the determination of ultra-trace amounts of aminopolycarboxylic acids in surface water which requires only a minimum of sample preparation was developed. Metal ions are added to the water sample to transform the chelating reagents into negatively charged complexes. These are separated by ion-exchange chromatography. The central metal ion of the complex is detected by online coupled ICP/MS to deduce the concentrations of the chelating agent from this. Iron (Figure 28) and indium (Figure 29 on p. 25) as two metal ions of nominal charge +3 were investigated.  $\text{In}^{3+}$  provided the best results in terms of sensitivity with detection limits in the lower ng/L range. The trivalent complexing agent NTA could not be determined accurately because of the low retention of the complex. The indium and iron complexes of CDTA are strongly absorbed on anion exchangers and showed retention times of over 1 h. The use of column-switching reduced the retention time to less than 15 min. The method has been validated against a sample set of 62 samples which have previously been analyzed by an external water lab according to DIN EN ISO 16588 using the GC-MS method.

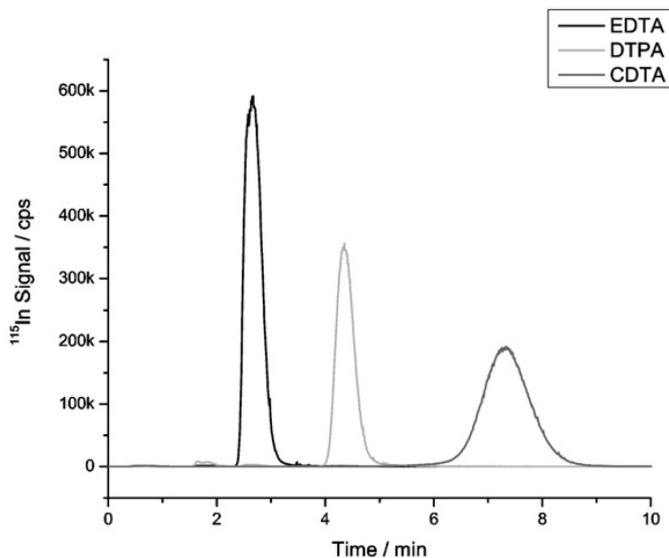


**Figure 28.** Separation of the Fe(III) complexes of NTA, EDTA, DTPA, and CDTA in less than 15 min using column-switching.



## Organic compounds – further applications with IC-ICP/MS

Two-dimensional ion chromatography for the separation of ionic organophosphates generated in thermally decomposed lithium hexafluorophosphate-based lithium ion battery electrolytes. Kraft, V.; Grütze, M.; Weber, W.; Menzel, J.; Wiemers-Meyer, S.; Winter, M.; Nowak, S. (2015) *J. Chrom. A* 1409, 201–209



**Figure 29.** Fe(III) complexes (top) and In(III) complexes (bottom) of EDTA, DTPA, and CDTA demonstrating the increased sensitivity for indium. Column 1: DV-080429-1A2 20 mm  $\times$  2 mm, PEEK, capacity 20  $\mu\text{mol}$ ; column 2: DV-080429-1A1 100 mm  $\times$  2 mm, PEEK, capacity 100  $\mu\text{mol}$ ; eluent: 20 mmol/L  $\text{NH}_4\text{NO}_3$  (pH = 2); flow rate: 0.6 mL/min; m/z 56, 115

## 11. Antimony

Antimony (Sb) is an emerging element of environmental concern because of the alarming increase in its concentration observed during the past years. This is due to the extensive industrial use of antimony; e.g., antimony compounds are employed in the production of glassware and ceramics, in brake linings, and in electronic components. Antimony-containing nanoparticles are found in urban atmospheric particulate matter (PM).

### 11.1 Sb(III), Sb(V) and Sb-containing nanoparticles in airborne particulate matter

Marconi, E.; Canepari, S.; Astolfi, M. L.; Perrino, C. (2011) *Procedia Environ. Sci.* 4, 209–217

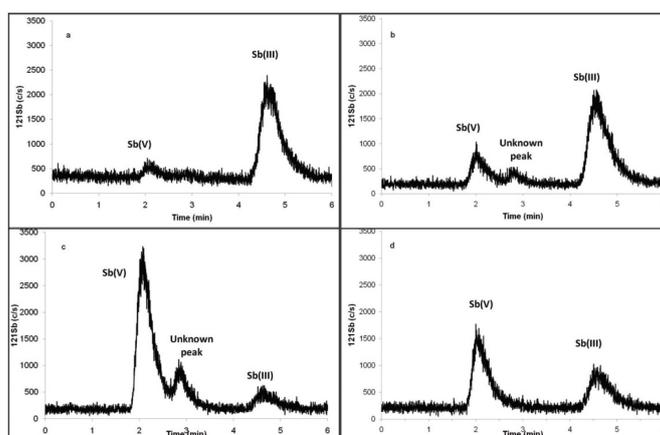
#### Introduction

Recently, a large number of studies about the environmental relevance of antimony have been published, even though many questions about its chemistry remain unanswered. It is

known that the oxidation state influences the physiological and toxicological behavior of antimony, as well as of other elements (e.g., As). Just like As, Sb(III) is more toxic than Sb(V), and  $Sb_2O_3$  is suspected of being carcinogenic in humans by the International Agency for Research on Cancer (IARC).

#### Results

The method described here allows the analysis of the two main inorganic forms of extractable antimony in atmospheric PM samples. It is fast and easily applicable to intensive monitoring campaigns. Analyses of different types of brake pads and road dust showed that brake pad abrasion is the main source of atmospheric Sb(III) in urban coarse particles and the Sb(III)/Sb(V) ratio is mainly driven by the temperature reached by the pad during the braking process (Figure 30). The spontaneous conversion of Sb(III) into Sb(V) in the atmosphere was not observed.



**Figure 30.** Separation of Sb(III) and Sb(V) by IC-ICP/MS in different samples: a–b) two different types of brake pads, c) dust from a car braking system d) road dust. Column: Metrosep A Supp 5 - 150/4.0; eluent: 10 mmol/L EDTA, 1 mmol/L potassium hydrogen phthalate (pH 4.5); flow rate: 0.7 mL/min, isocratic; m/z 121

#### Antimony – further applications with IC-ICP/MS

Relevance of Sb(III), Sb(V), and Sb-containing nanoparticles in urban atmospheric particulate matter. Canepari, S.; Marconi, E.; Astolfi, M. L.; Perrino, C. (2010) *Anal. Bioanal. Chem.* 397(6), 2533–2542

## 12. Bromate

Bromate is formed during the disinfection of drinking water by ozonation. It is potentially carcinogenic to rats and mice at mg/L levels. Newer toxicological studies have led the International Agency for Research on Cancer (IARC) to classify bromate as a group-2B carcinogen to humans with renal tumor risks at concentrations > 0.05 g/L. Therefore, the US Environmental Protection Agency (USEPA) has requested comments on setting the maximum contaminant level goal for bromate to zero.

### 12.1 Ultratrace determination of bromate in drinking waters by microbore column IC and ICP/MS

Nowak, M.; Seubert, A. (1998) *Anal. Chim. Acta* 359, 193–204

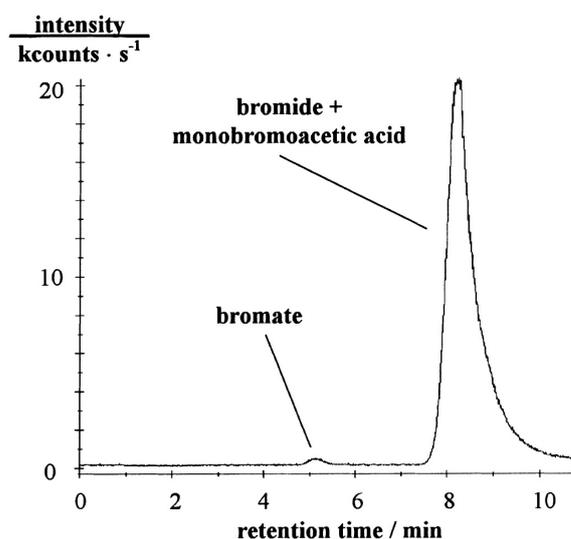
#### Introduction

The aim was to establish a method for the routine determination of bromate in drinking water using IC with mass-spectrometric detection. IC-ICP/MS was chosen because of its simplicity compared to other mass-spectrometric procedures. The method determines bromate in drinking water at concentration levels in the sub- $\mu\text{g/L}$  range. Sample pretreatment is not necessary and the analysis time for one sample is 15 min.

#### Results

A method for ultra-trace determination of bromate in drinking water by IC-ICP/MS was developed. The method uses the microbore column technique in combination with a self-made high-capacity and high-performance anion-exchanger. The high capacity of the separation column as well as an optimized elution system based on  $\text{NH}_4\text{NO}_3$  allows a direct analysis of almost every water sample without matrix elimination. What's more, the use of large injection volumes is possible. No trace enrichment is required thanks to the sensitivity of ICP/MS detection. Thus, no sample pretreatment is required.

The method detection limits for bromate in the drinking and mineral waters investigated were in the 50–65 ng/L range, corresponding to absolute detection limits of 44–58 pg. Retention of bromate as well as signal-to-noise (SNR) and signal-to-background (SBR) ratios depended on the sample composition. The within-run imprecision of the presented IC-ICP/MS coupling was 5% at a concentration of 500 ng/L bromate. The time spent on a complete analysis was 8–15 min, depending on the bromide content of the sample (Figure 31). Considering its sensitivity, precision, and analysis duration, the described IC-ICP/MS coupling is well suited for precise routine analysis of bromate in drinking waters at sub- $\mu\text{g/L}$  levels.



**Figure 31.** Separation of 1  $\mu\text{g/L}$  bromate, 100  $\mu\text{g/L}$  bromide, and 100  $\mu\text{g/L}$  monobromoacetic acid. Sample volume: 585  $\mu\text{L}$ ; column: self-made; eluents: 100 or 60 mmol/L nitric acid or 100 mmol/L hydrochloric acid, pH adjusted to 6 with ammonia (25% w/w);  $m/z$  79

## **Bromate – further applications with IC-ICP/MS**

Comparison of ion chromatographic methods based on conductivity detection, post-column-reaction and on-line-coupling IC-ICP/MS for the determination of bromate Schminke, G.; Seubert, A. (2000) *Fresenius J. Anal. Chem.* 366(4), 387–391

Trace analysis of bromate in drinking waters by means of online coupling IC-ICP/MS Seubert, A.; Nowak, M. (1998) *Fresenius J. Anal. Chem.* 360(7), 777–780

## **Further applications with IC-ICP/MS**

### **Sulfur**

Measurement of sulphur isotope ratio ( $^{34}\text{S}/^{32}\text{S}$ ) in uranium ore concentrates (yellow cakes) for origin assessment Han, S.; H.; Varga, Z.; Krajko, J.; Wallenius, M.; Song, K.; Mayer, K. (2013) *J. Anal. At. Spectrom.* 28(12), 1919–1925

### **Aluminum**

Characterization of an aluminium(III) citrate species by means of ion chromatography with inductively coupled plasma-atomic emission spectrometry detection Peukert, A.; Seubert, A. (2009) *J. Chrom. A* 1216(45), 7946–7949

## 13. References

- Aschner, M.; Syversen, T. (2005) Methylmercury: Recent advances in the understanding of its neurotoxicity. *Ther. Drug Monit.* 27, 278–283.
- Bianchi, A.; Calabi, L.; Corana, F.; Fontana, S.; Losi, Maiocchi, A.; Paleari, L.; Valtancoli, B. (2000) Thermodynamic and structural properties of Gd(III) complexes with polyamino-polycarboxylic ligands: Basic compounds for the development of MRI contrast agents. *Coord. Chem. Rev.* 204, 309–393
- Burger, J.; Gochfeld, M. (2005) Heavy metals in commercial fish in New Jersey. *Environ. Res.* 99(3), 403–412
- Dietary Supplement Fact Sheet: Selenium. US National Institutes of Health; Office of Dietary Supplements. Retrieved Oct 11, 2016.
- Gochfeld, M.; Burger, J. (2005) Good fish/bad fish: A composite benefit–risk by dose curve. *Neurotoxicology* 26(4), 511–520
- Herrmann, T. Einsatz der On-line-Kopplung von Ionenchromatographie und ICP-MS zur Bestimmung von Anionen. Diploma thesis, Philipps-Universität Marburg, Germany, 2006
- Knöll, J. Ph.D. Ultratrace determination of aminopolycarboxylic acid based chelating agents using inverse on-line coupling of IC with ICP-MS. PhD thesis, Philipps-Universität Marburg, Germany, 2013
- Knöll, J.; Seubert, A. (2012) Indirect ultra trace determination of aminopolycarboxylic acids in surface water using ion exchange chromatography coupled on-line to inductively coupled plasma mass spectrometry. *Journal of Chromatography A* 1270, 219–224.
- Kümmerer, K.; Ed. Pharmaceuticals in the environment: Sources, fate, effects, and risks. Springer-Verlag Berlin Heidelberg, 2008; 3rd ed.
- Künemeyer, J.; Terborg, L.; Meermann, B.; Brauckmann, C.; Möller, I.; Scheffer, A.; Karst, U. (2009) Speciation analysis of gadolinium chelates in hospital effluents and wastewater treatment plant sewage by a novel HILIC/ICP-MS method. *Environ. Sci. Technol.* 43(8), 2884–2890.
- Künemeyer, J.; Terborg, L.; Nowak, S.; Telgmann, L.; Tokmak, F.; Krämer, B. K.; Günsel, A.; Wiesmüller, G. A.; Waldeck, J.; Bremer, C.; Karst, U. (2009) Analysis of the contrast agent Magnevist and its transmetalation products in blood plasma by capillary electrophoresis / electrospray ionization time-of-flight mass spectrometry. *Anal. Chem.* 81(9), 3600–3607
- Levenson, C. W.; Axelrad, D. M. (2006) Too much of a good thing? Update on fish consumption and mercury exposure. *Nutr. Rev.* 64(3), 139–145.
- Montaser, A.; Golightly, D. W.; Eds. Inductively coupled plasmas in analytical atomic spectrometry. VCH Publishers, Inc.: New York, 1992.
- Rahman, G. M. M.; Martone, N.; 'Skip' Kingston, H. M. (2012) Determination of hexavalent chromium in NIST SRM 2701 by speciated isotope dilution mass spectrometry (EPA Method 6800) using IC-ICP-MS. In *Handbook of hyphenated ICP-MS applications*, 2nd edition; Agilent, 2012; pp 33–35. [http://www.agilent.com/cs/library/applications/5990-9473EN\\_icpmsSpeciationHB\\_lr.pdf](http://www.agilent.com/cs/library/applications/5990-9473EN_icpmsSpeciationHB_lr.pdf) (accessed Oct 7, 2016)
- Saranko, C. J. et al. Fact Report for toxicity of arsenite and arsenate, Florida Dept. of Health, Nov 6, 1998
- Schedlbauer, O. F.; Heumann, K. G. (2000) Biomethylation of thallium by bacteria and first determination of biogenic dimethylthallium in the ocean. *Appl. Organomet. Chem.* 14(6), 330–340
- Wilber, C. G. (1980). Toxicology of selenium: A review. *Clin. Toxicol.* 17 (2), 171–230.

# Metrohm White Paper

 **Contact:** Katinka Meike Ruth, [kru@metrohm.com](mailto:kru@metrohm.com)

