Mercury and arsenic speciation analysis by IC-ICP/MS

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Ion Chromatography

Summary

By means of IC-ICP/MS, different valence states of arsenic and mercury in the form of inorganic and organic species can be sensitively and unambiguously identified in one single run. Determination of common arsenic species in biological matrices is straightforward and can be performed down to the sub-ppb level.

Species transformations of mercury that occur during several sample preparation techniques, however, require the use of specific isotope dilution mass spectrometry (SIDMS). This work illustrates the decisive advantage that Environmental Protection Agency (EPA) Method 6800 (SIDMS) 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 utilization of SIDMS will increase and that this valuable tool for optimizing and validating trace-metals-speciated sample preparation will gain much wider acceptance by analytical chemists.

Introduction

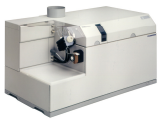
Ion chromatography (IC) with conductivity detection has been successfully used to analyze polar compounds, such as organic acids, as well as anionic and cationic substances. However, a higher sensitivity and selectivity are required to test for potentially toxic substances with low maximum contaminant levels (MCLs).
This can be achieved by coupling IC to an inductively coupled plasma mass spectrometer (ICP/MS). IC-ICP/MS shows outstanding sensitivity and selectivity, is less prone to matrix influences than conductivity detection and can differentiate between different oxidation states. However, during sample collection and preparation some heavy metal species undergo interconversion from one form to another. Depending upon the pH and the redox potential, chromium, for example, can interconvert bi-directionally between Cr^{3+} and the highly toxic and carcinogenic Cr^{6+}.
Similarly, mercury tends to undergo various transformations when released into the environment. It is found in several forms, particularly as elemental mercury (Hg^0), inorganic mercury (Hg^{2+}), and biologically active organic mercury (methylmercury CH_3Hg^+). By introducing enriched isotopic species spikes into the analytical process, one can correct for and measure interconversions to derive true concentrations of the species. This is the key feature of the speciated isotope dilution mass spectrometry (SIDMS) protocol recently published in EPA method 6800.

This article describes the determination of organic and inorganic mercury and arsenic compounds via IC-ICP/MS. While arsenic compounds were analyzed without applying SIDMS, several commonly used extraction techniques used for mercury speciation in biological samples are evaluated by applying both SIDMS and external calibration.

Instrumentation

- 850 Professional IC Anion – MCS
- 858 Professional Sample Processor
- 7500 ICP/MS, Agilent Technologies



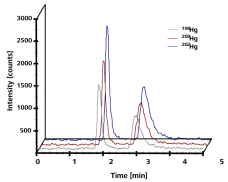


Mercury

Hg^{2+} and CH_3Hg^+ compounds were quantified in Tuna Fish Tissue Certified Reference Material (ERM-CE464) by external calibration and EPA 6800 protocol specifications, spiking the sample before the extraction with $^{199}Hg^{2+}$ and $CH_3{}^{200}Hg^+$ and application of SIDMS equations. The double-spike approach allows tracking of any artefact stemming from methylation/demethylation reactions.

ICP/MS									Separation conditions			
Operational conditions						Measurement parameters						
RF power	Plasma gas flow	Auxiliary gas flow	Nebulizer	Spray chamber	Sample and skimmer cones	Monitoring isotopes	Acquisition mode	Integration time per mass / Replicates / Total analysis time	Column	Eluent	Flow	Loop
1475 W	Ar 15 L min^{-1}	Ar 1 L min^{-1}	Quartz, concentric	Quartz	Ni, 1.1/0.8 mm	^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg	Time-resolved analysis	0.2 s / 1 / 300	DVB-C18 150 × 4.6 mm, 2 µm	50 mmol/L pyridine 0.5% (w/v) cysteine 5% (v/v) methanol pH = 3	1 mL/min	100 µL

The IC-ICP/MS chromatogram was recorded under the conditions indicated above and shows the separation of the divalent mercury ion from methylmercury (both 10 µg/L). The chromatograms obtained at different masses were shifted for clarity.



	Extraction Conditions [°C]	[min]	Procedure	External calibration Hg^{2+}	CH_3Hg^+	Sum of species	EPA method 6800 (SIDMS) Hg^{2+}	CH_3Hg^+	Sum of species
				0.12[b]	5.12 ± 0.16[a]	5.24 ± 0.10[a]	0.12[b]	5.12 ± 0.16[a]	5.24 ± 0.10[a]
				as Hg, mg/kg		mg/kg		mg/kg	
A	70	180	Sonication/water bath 25% (w/v) KOH in MeOH	0.06 ± 0.02[b]	5.05 ± 0.13	5.11 ± 0.13	0.07 ± 0.02[b]	5.22 ± 0.31	5.29 ± 0.31
B	70	180	Sonication/water bath 25% (w/v) TMAH in MeOH	0.12 ± 0.03[b]	5.05 ± 0.18	5.17 ± 0.18	0.07 ± 0.03[b]	5.20 ± 0.18	5.27 ± 0.18
C	180	20	Microwave 5% (w/v) TMAH in MeOH	0.18 ± 0.05[b]	4.88 ± 0.17	5.06 ± 0.18	0.30 ± 0.07[b]	5.18 ± 0.13	5.48 ± 0.15
D	25	5	Sonication bath 5 mol/L HCl	0.07 ± 0.02[b]	4.29 ± 0.39	4.36 ± 0.39	0.13 ± 0.05[b]	5.11 ± 0.38	5.24 ± 0.38
E	180	20	Microwave 4 mol/L HNO_3 (EPA 3200)	0.06 ± 0.04[b]	3.94 ± 0.12	4.00 ± 0.13	0.11 ± 0.07[b]	5.60 ± 0.33	5.71 ± 0.34
F	165	10	Microwave Glacial CH_3COOH	0.35 ± 0.08[b]	3.29 ± 0.14	3.64 ± 0.16	0.27 ± 0.12[b]	5.12 ± 0.19	5.39 ± 0.22
G	60	120	Water bath 1% L-cysteine hydrochloride	0.45 ± 0.10[b]	4.87 ± 0.20	5.32 ± 0.22	1.05 ± 0.14[b]	5.08 ± 0.25	6.13 ± 0.29
H	37	120	Hybridization oven Enzymatic digestion with protease XIV	0.16 ± 0.07[b]	4.42 ± 0.14	4.58 ± 0.16	0.07 ± 0.02[b]	5.22 ± 0.31	5.29 ± 0.31

[a]certified methyl mercury and total mercury content in Tuna Fish Tissue Certified Reference Material (ERM-CE464) supplied by IRMM (Geel, Belgium)
[b]inorganic mercury concentration was calculated as the difference between certified total mercury and methylmercury concentrations

The results demonstrate that SIDMS is a powerful method that facilitates the determination of mercury species with high precision, accuracy, and correction for species transformations. While procedure G, for example, showed inorganic mercury contamination in the extracting reagent, the alkaline extraction procedures (A, B, and C) yielded results that agreed well with the 95% confidence levels of the certified values.

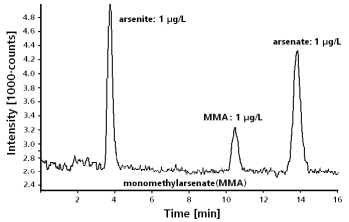
		Extraction procedure A	B	C	D	E	F	G	H
Transformation [%]	Methylation	5 ± 3	6 ± 2	3 ± 2	5 ± 3	18 ± 4	4 ± 2	4 ± 3	4 ± 2
	Demethylation	6 ± 1	4 ± 1	6 ± 2	3 ± 1	0.8 ± 0.6	27 ± 5	4 ± 1	1.4 ± 0.5

Arsenic

Arsenic is known as a human carcinogen and poison. Accordingly, the EPA proposes a maximum allowable drinking water concentration of 10 µg/L. In environmental and biological samples, more than 20 arsenic species have been identified. Depending on their binding characteristics, they have different toxicities and chemical behavior. Especially the trivalent arsenic species are highly toxic. Through the use of IC-ICP/MS, different arsenic species in inorganic and organic form can be separated and unambiguously identified based on structural data.

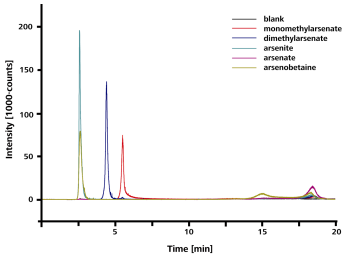
1 µg/L standard solution

Column:	Metrosep Anion Dual 3
Eluent:	1.3/2.0 mmol/L Na_2CO_3/$NaHCO_3$
Flow:	0.8 mL/min
ICP/MS:	Collision mode with He
m/z:	75



10 µg/L standard solution

Column:	Metrosep A Supp 15 - 150/4.0
Eluent:	8 mmol/L NH_4NO_3, pH = 8.3
Flow:	0.7 mL/min
ICP/MS:	Without reaction or collision mode
m/z:	75



Under these conditions arsenobetaine (ASB) is not separated from the trivalent arsenic species. However, ASB interference can be overcome by changing the chromatographic conditions.

Acknowledgements

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