Modern Detection Systems in Ion Chromatography

This article describes the use of combined ion chromatography-mass spectrometry (IC-MS) and ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP/MS) to analyze potentially harmful compounds in the environment.

Ion chromatography (IC) with conductivity detection has been successfully used to analyze low-molecular organic compounds such as amines and organic acids, as well as anionic and cationic substances. However, due to current toxicity concerns and the consequently lowered maximum contaminant levels (MCL), analyses in complex matrices require improved sensitivity and selectivity.

The coupling of IC with multidimensional detectors such as an electrospray ionization mass spectrometer (ESI-MS) or an inductively coupled plasma mass spectrometer (ICP/MS) solves even complex separation problems, simultaneously achieving outstanding sensitivity and selectivity. Additionally, these so-called hyphenated techniques provide valuable information for an unambiguous peak identification and are less prone to matrix influences than conductivity detection. While IC-ICP/MS is used for element-specific analysis, IC-MS allows the identification of parent compounds and corresponding metabolites.

This article deals with the determination of bromate, perchlorate, and organic acids by IC-MS as well as with the detection of inorganic and organic chromium, arsenic, and selenium species by IC-ICP/MS.

Experimental

The analytical system used consisted of the 858 Professional Sample Processor and the 850 Professional IC Anion – MCS (Metrohm). The detectors were the 1100 MSD SL (MS) and the 7500 ICP/MS (Agilent Technologies). The separation columns and instrumental parameters used for IC-MS and IC-ICP/MS are listed in Tables 1 and 2, respectively.

All reagents used in this work were of the highest purity grade (puriss p.a.). The oxyhalide, chromium, arsenic, and selenium standard solutions were all purchased from Fluka (Sigma Aldrich). All solutions were prepared with deionized water with a specific resistance higher than 18 MΩ·cm.

Results and Discussion

IC-MS

Adequate chromatographic retention of the target compounds is combined with the sensitive detection of MS, providing high selectivity and sensitivity. Additionally, identification based on

	Bromate	Perchlorate	Organic Acids
Sample	10 mg/L standard	Groundwater sample	Process water sample; 1:10 dilution, dialysis.
Column	Metrosep A Supp 5-250/4.0	Metrosep A Supp 5-100/4.0	Metrosep Organic Acids - 100/7.8
Eluent	3.2 mmol/L Na_2CO_3 1.0 mmol/L $NaHCO_3$	30 mmol/L NaOH + 30% methanol	0.25 mmol/L oxalic acid
Flow	0.7 mL/min	0.8 mL/min	0.4 mL/min
ESI	13 L/min N_2, 350 °C, 60 psig, 3 kV	10 L/min N_2, 320 °C, 30 psig, 3 kV	13 L/min N_2, 350 °C, 60 psig, 3 kV
MSD	SIM neg.	SIM neg.	SIM neg.
Fragmentor	70 V	140 V	70 V

Table 1: IC conditions and MS operating parameters used for the analysis of bromate, perchlorate and the organic acids.

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simultaneous retention time matching and isotope ratios reduces the risk of incorrect peak assignment (false positives).

Bromate in Drinking Water

Bromate, a potential carcinogen, is generated by the oxidation of bromide traces during water disinfection, for example by ozonization. For drinking water and mineral water, current regulations stipulate a limit of 10 and 3 µg/L (ppb), respectively. Other oxyhalides (ClO_3^-, ClO_2^-) and standard anions (Br^-, NO_3^-, $H_2PO_4^-$, HSO_4^-) can be determined in the same run (1) (Fig. 1).

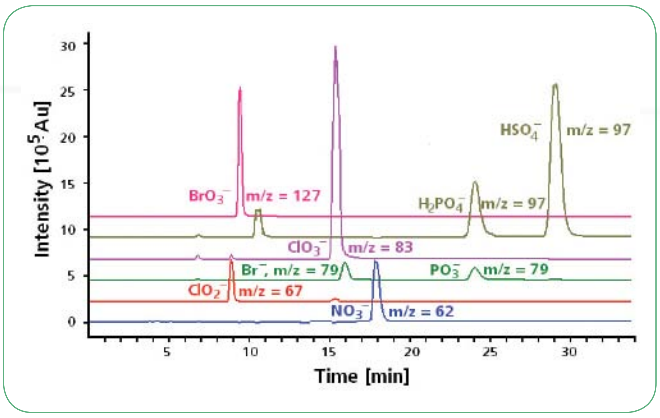

Fig. 1: MS chromatogram of a 10 mg/L standard for the standard anions and oxyhalides.

Perchlorate in Drinking Water

Perchlorate is an environmentally stable, highly water-soluble contaminant that is commonly used as an oxidant in solid fuel rocket propellants. It has been shown to competitively inhibit the transport of iodine into the thyroid gland. The Environmental Protection Agency (EPA) developed an IC-ESI-MS method (EPA 332) for drinking water with a detection limit in the sub-µg/L range. Figure 2 displays two overlaid chromatograms, one of a slightly contaminated groundwater sample and one of the same sample spiked with 1 µg/L of perchlorate (2,3).

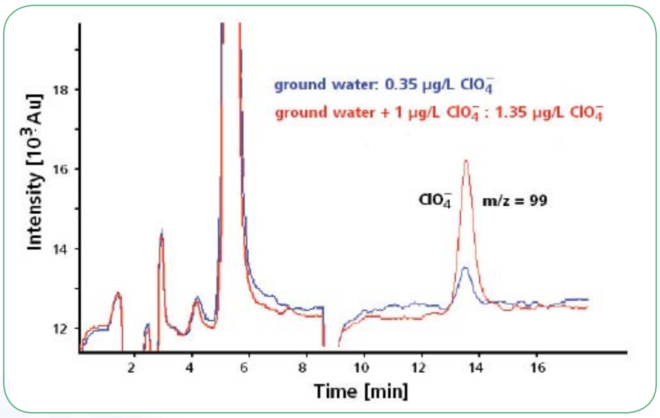

Fig. 2: MS chromatogram of an unspiked and spiked (with 1 µg/L perchlorate) groundwater sample. Because of the higher isotopic abundance of the ^{37}Cl isotope, only the SIM trace m/z 99 is displayed.

Organic Acids in Produced Water

Produced water is water trapped in underground reservoir rocks that is brought to the surface along with the crude oil and gas. Besides dispersed oil droplets and significant amounts of inorganic ions, produced water contains dissolved organic acids, mainly stemming from the degradation of organic matter. Generally, these acids point to the presence of oil.

The analytical challenge consists in detecting sub-mg/L quantities of carboxylates in the presence of very high concentrations of sodium and chloride. As Figure 3 demonstrates, IC-MS coupling allows reliable quantification of carboxylic acids, such as acetate, propionate, and butyrate in the presence of a high salt matrix containing approximately 100 g/L chloride.

IC-ICP/MS

The "zero tolerance" policy concerning chromium, arsenic, and selenium compounds in drinking water has led to IC-ICP/MS becoming one of the most prominent detection methods for trace metals in environmental samples. The advantage of this technique is that it can distinguish between different oxidation states and chemical forms of a particular element. This approach is called speciation analysis. Individual concentrations of element-containing species are, from the toxicological point of view, far more significant than total element concentrations as different valence states of an element have different properties. Chromium, arsenic, and selenium species can either be identified by their retention times or isotopic ratios.

Chromium

Chromium compounds are used in dye and pigment production, in cement, in tanning, as mordant, wood preservatives, and as efficient

	Chromium	Arsenic	Selenium
Sample	0.1 µg/L standard solution	1 µg/L standard solution	0.1…10 µg/L standard solution
Column	Agilent Cr Column G3268A	Metrosep Anion Dual 3-100/4.0	Metrosep Anion Dual 3 - 100/4.0
Eluent	5.0 mmol/L EDTA (pH = 7)	1.3 mmol/L Na_2CO_3 2.0 mmol/L $NaHCO_3$	2.6 mmol/L Na_2CO_3 4.0 mmol/L $NaHCO_3$
Flow	1.2 mL/min	0.8 mL/min	0.8 mL/min
ICP/MS	Reaction mode with H_2	Collision mode with He	Without reaction or collision mode
m/z	52*	75*	78**

*isotope of highest abundance
**isotope providing best performance under the given conditions

Table 2: IC conditions and ICP/MS operating conditions used for the analysis of chromium, arsenic, and selenium.

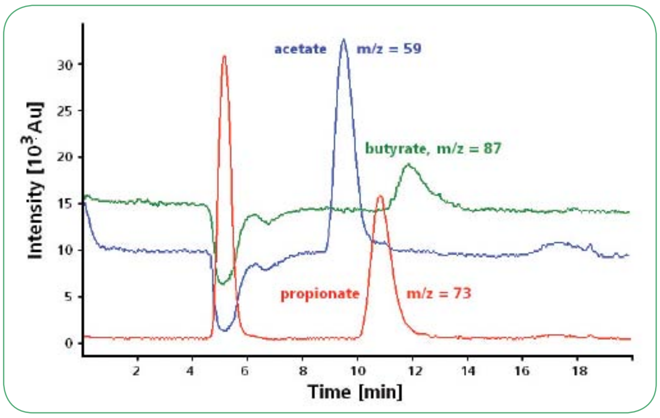

Fig. 3: MS Chromatogram of a produced water sample containing 428.4 mg/L acetate, 9.3 mg/L propionate, and 2.6 mg/L butyrate.

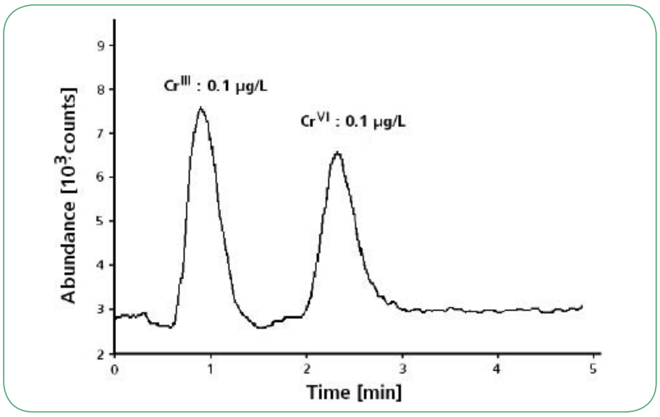

Fig. 4: Separation and detection of chromium(III) and chromium(VI), each at a concentration of 0.1 µg/L.

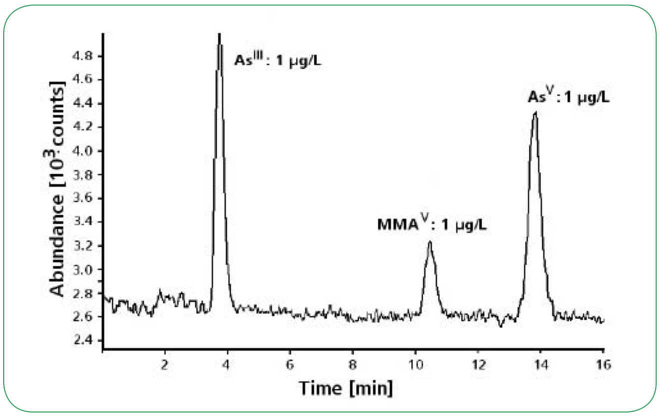

Fig. 5: Separation and detection of arsenious acid (As^{III}), monomethylarsonic acid (MMA^{V}) and arsenic acid (As^{V}), each at a concentration of 1 µg/L.

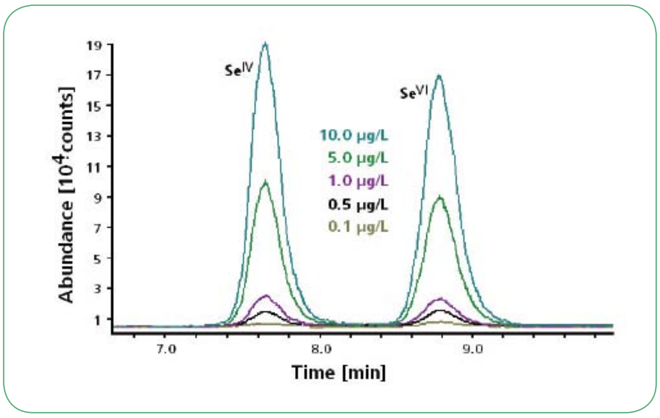

Fig. 6: Separation and detection of selenium(IV) and selenium(VI) at concentrations between 0.1 and 10 µg/L.

corrosion inhibitors. While chromium(III) is an essential trace element for humans, all forms of hexavalent chromium are regarded as highly toxic and carcinogenic. Accordingly, EPA has fixed the MCL of chromium(VI) at 100 µg/L. Figure 4 shows the chromatogram of a 0.1 µg/L standard with the trivalent and hexavalent chromium peaks (4).

Arsenic

Arsenic is the twentieth most abundant element in the earth crust, ubiquitously found in a high number of minerals. It is used in pesticides, wood preservatives, semiconductors, etc. Its use as a weed killer and rat poison illustrates its high toxicity. Additionally, inorganic arsenical derivatives are considered carcinogens and probably teratogens. Therefore, 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 characteristics. IC-ICP/MS allows, based on structural data, the separation and unambiguous identification, of different arsenic species in inorganic and organic forms (5) (Fig. 5).

Selenium

Because selenium compounds also differ strongly in their toxicity, speciation analysis is of paramount importance (Fig. 6). Selenium is used in food supplements, photographic processes and electronics. Selenium is an essential trace element for humans and animals. Its uptake occurs mainly through food (grains, cereals, and meat) and water. Elevated concentrations, however, are considered to adversely affect health (MCL = 50 µg/L). An increasing number of biogeochemical research papers suggest that selenium compounds have severe impacts on aquatic wildlife (6).

Conclusions

The coupling of highly efficient ion chromatography (IC) to multidimensional detectors such as a mass spectrometer (MS) or an inductively coupled plasma mass spectrometer (ICP/MS) significantly increases sensitivity while simultaneously reducing matrix interference.

IC-MS can detect several oxyhalides, such as bromate and perchlorate, in the sub-ppb range. Additionally, organic acids can be precisely quantified through mass-based determination even in the presence of high salt matrices.

By using of IC-ICP/MS, different valence states of chromium, arsenic, and selenium in the form of inorganic and organic species can be sensitively (0.01-0.1 µg/L) and unambiguously identified in one single run. Moreover, IC-ICP/MS is a valuable tool for the robust and sensitive analysis of transition metals.

References

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