

Hyphenated techniques as modern detection systems in ion chromatography

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Summary

The coupling of highly efficient ion chromatography (IC) to multi-dimensional detectors such as a mass spectrometer (MS) or an inductively coupled plasma mass spectrometer (ICP/MS) significantly increases sensitivity while simultaneously reducing possible matrix interference to the absolute minimum. By means of IC/MS several oxyhalides such as bromate and perchlorate can be detected 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 means of IC-ICP/MS different valence states of the potentially hazardous chromium, arsenic and selenium in the form of inorganic and organic species can be sensitively and unambiguously identified in one single run.

Introduction

Historically ion chromatography (IC) using conductivity detection has been successfully used for the analysis of ionic (anions and cations) and polar substances (e.g. organic acids or sugars). However, due to current toxicity concerns, analyses in complex matrices require improved sensitivities and selectivities.

The coupling of IC with multi-dimensional 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 sensitivities and selectivities. 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 presentation deals with the determination of bromate, perchlorate and organic acids by IC/MS as well as the detection of inorganic and organic chromium, arsenic and selenium species by IC-ICP/MS.

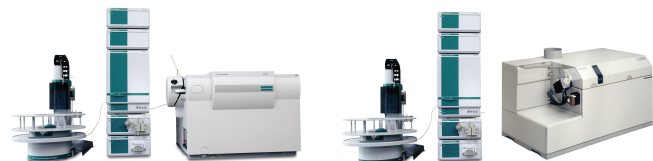
System setups

IC/MS

- 818 Advanced IC Pump
- 819 Advanced IC Detector
- 820 IC Separation Center
- 830 Advanced IC Interface
- 833 Advanced IC Liquid Handling Pump Unit
- 838 Advanced IC Sample Processor
- 1100 MSD SL, Agilent Technologies

IC-ICP/MS

- 818 Advanced IC Pump
- 819 Advanced IC Detector
- 820 IC Separation Center
- 830 Advanced IC Interface
- 833 Advanced IC Liquid Handling Pump Unit
- 838 Advanced IC Sample Processor
- 7500 ICP/MS, Agilent Technologies



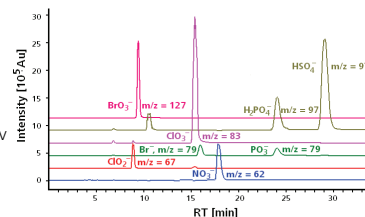
IC/MS

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 ppb, respectively. Other oxyhalides and standard anions can be determined in the same run.

10 ppm standard solution

Column: Metrosep A Supp 5 – 250
Eluent: 3.2/1.0 mmol/L Na₂CO₃/NaHCO₃
Flow: 0.7 mL/min
ESI: 13 L/min N₂, 350 °C, 60 psig, 3 kV
MSD: SIM neg.
Fragmentor: 70 V

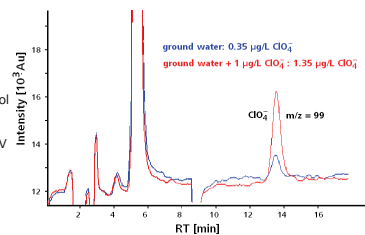


Perchlorate in drinking water

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. Recently, the Environmental Protection Agency (EPA) developed an IC/ESI-MS method (EPA 332) for drinking water with a detection limit in the sub-ppb range.

Groundwater sample

Column: Metrosep A Supp 5 – 100
Eluent: 30 mmol/L NaOH + 30% methanol
Flow: 0.8 mL/min
ESI: 10 L/min N₂, 320 °C, 30 psig, 3 kV
MSD: SIM neg.
Fragmentor: 140 V

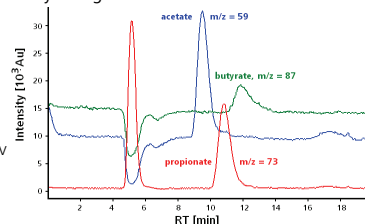


Organic acids in process water

The IC/MS coupling allows to reliably quantify carboxylic acids such as acetate (428.4 ppm), propionate (9.3 ppm) and butyrate (2.6 ppm) in the presence of a high salt matrix containing approximately 100 g/L chloride.

Process water sample of the oil industry

Sample prep.: 1:10 dilution, dialysis
Column: Metrosep Organic Acids – 100
Eluent: 0.25 mmol/L oxalic acid
Flow: 0.4 mL/min
ESI: 13 L/min N₂, 350 °C, 60 psig, 3 kV
MSD: SIM neg.
Fragmentor: 70 V



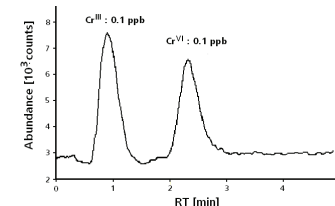
IC-ICP/MS

Chromium

Chromium compounds are used in dye and pigment production, in tanning, as mordants, wood preservers and as an effective corrosion inhibitor. While chromium(III) is an essential nutrient for humans, all forms of hexavalent chromium are regarded as highly toxic and carcinogenic. Accordingly, the EPA has set the Maximum Contaminant Level (MCL) to 100 ppb.

0.1 ppb standard solution

Column: Agilent Cr Column G3268A
Eluent: 5.0 mmol/L EDTA (pH = 7)
Flow: 1.2 mL/min
Derivat.: EDTA, 3 h at 40 °C
ICP/MS: Reaction mode with H₂
m/z: 52

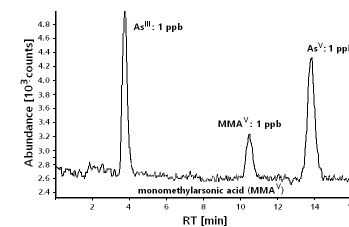


Arsenic

Arsenic is known as a human carcinogen and poison. Therefore, the EPA proposes a maximum allowable drinking water concentration of 10 ppb. 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 forms can be separated and unambiguously identified based on structural data.

1 ppb standard solution

Column: Metrosep Anion Dual 3
Eluent: 1.3/2.0 mmol/L Na₂CO₃/NaHCO₃
Flow: 0.8 mL/min
ICP/MS: Collision mode with He
m/z: 75



Selenium

Selenium is an essential trace element. Its uptake mainly takes place through food (grains, cereals and meat) and water. However, concentrations above the MCL of 50 ppb are considered to adversely affect health.

0.1...10 ppb standard solution

Column: Metrosep Anion Dual 3
Eluent: 2.6/4.0 mmol/L Na₂CO₃/NaHCO₃
Flow: 0.8 mL/min
ICP/MS: Without reaction or collision mode
m/z: 78

