

Summary

The combination of ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP/MS) provides a rapid, reliable, and sensitive speciation analysis of wastewater-relevant free and complexed gadolinium compounds. IC-ICP/MS proceeds without costly sample preparation and provides important information on the entry, degradation, and fate of contrast media in (waste)water. The method is also highly suitable for determining compounds containing gadolinium in biological matrixes such as urine or blood.

Additionally, IC-ICP/MS is a powerful tool for monitoring iodine-containing ionic oxidation by-products that form during ozonation of iodinated X-ray contrast media.

Introduction

In recent decades, surveillance and protection of aquatic resources have been steadily improved to ensure safe drinking water supplies. Besides the inorganic, physical, and microbiological water quality, attention has increasingly focused on organic substances in water. Formerly, sum parameters such as dissolved organic carbon (DOC) or absorbable organic halogen compounds (AOX) were used to describe the water quality. In the 1990s, the coupling of liquid chromatography to mass selective detectors became feasible and thus allowed the ultratrace detection of myriads of single organic compounds in water. This was a quantum leap forward in monitoring environmental contaminants in general and in monitoring pharmaceuticals in particular. Among the latter, there are the biologically inert iodinated X-ray contrast media (ICM) and gadolinium chelates, which are used as contrast media in magnetic resonance imaging. These contrast media are applied in high amounts and are excreted in unmetabolized form via urine into wastewater. They are suspected to be nondegradable in most conventional water treatment plants and consequently accumulate in aquatic systems. While considered harmless to the human body, their long-term effects on the environment are still unknown, for which reason their removal is mandatory.

The addition of competitive Fe³⁺ ions in the flocculation step enhances the displacement of gadolinium from its chelate complexes. Thereby, highly toxic Gd³⁺ ions are released. Similarly, ICMs are commonly destroyed by oxidative treatment technologies using ozonation or UV radiation. Instead of complete ICM mineralization, ozonation leads to several unidentified iodine-containing ozonation by-products (OBPs) of unknown toxicity.

In laboratory studies, the effects of flocculation and ozonation were evaluated, respectively, for gadolinium-containing (e.g., Gadovist, Magnevist) and iodine-containing (e.g., Iomeprol, Amidotrizoic Acid) contrast media. Speciation analysis of iodinated and gadolinium species was performed using IC-ICP/MS.

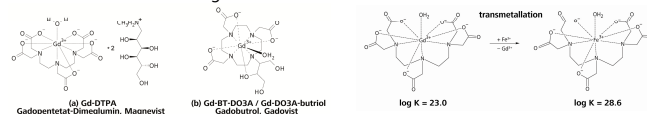
Analytical setup

- 850 Professional IC
- VG PQ ExCell ICP-MS (not shown)



Gadolinium-containing contrast media

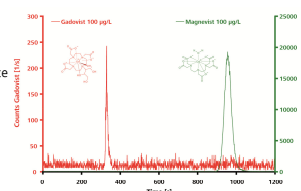
Depending on the thermodynamic complex stability, addition of the trivalent metal salts within the flocculation process produces transmetallation in the gadolinium chelates and consequently results in the release of toxic gadolinium ions. Using aqueous solutions of the model components Gadovist and Magnevist (each 1 mg/L), the present study looks at the extent to which the bench-scale Fe³⁺ flocculation liberates free gadolinium ions.



a) Anion-exchange column for the analysis of the Gd complexes

Overlay of a chromatogram of a 100 µg/L Gadovist and a 100 µg/L Magnevist solution

Column: Metrosep A Supp 3 - 250/4.6
Column temp.: 25 °C
Eluent: 7.2 mmol/L sodium carbonate
 6.8 mmol/L sodium hydrogen carbonate
Flow: 1.0 mL/min
Loop: 100 µL
RF power: 1200 W
Plasma gas flow: Ar, 13 L/min
Auxiliary gas flow: Ar, 1 L/min
Nebulizer gas flow: Ar, 1 L/min
Detection, m/z: ¹⁵⁶Gd, ¹⁵⁸Gd, ¹⁶⁰Gd

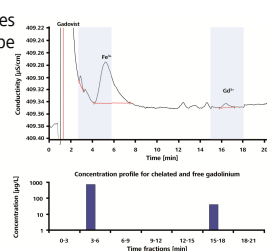


b) Cation-exchange column for the analysis of Fe³⁺ and Gd³⁺

The electrically neutral Gadovist complex elutes with the injection peak and can therefore be found in an early eluting fraction.

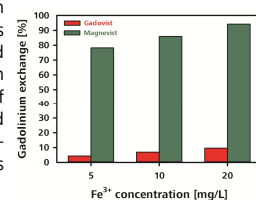
1 mg/L Gadovist solution, 5 mg/L Fe³⁺

Column: Nucleosil 5 SA - 125/4.0
Column temp.: 30 °C
Eluent: 10 mmol/L 2-hydroxyisobutyric acid
 2 mmol/L ethylenediamine
Flow: 1.5 mL/min
Loop: 100 µL



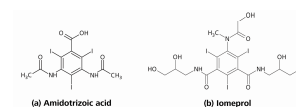
Gadolinium displacement

For both Magnevist and Gadovist, gadolinium displacement increases as Fe³⁺ concentration rises. The extent of this exchange, however, is very pronounced for Magnevist (> 80%) and relatively small for Gadovist (< 10%). The reason lies in the structure: the linear DTPA ligand of Magnevist provides less shielding for the Gd atom than the crown-ether-like polyamino-polycarboxylic acid ligand of Gadovist, which is spherically arranged around the gadolinium ion.



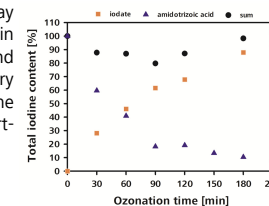
Iodinated X-ray contrast media

Aside from the destruction of pathogenic bacteria and other microorganisms, water ozonation aims at the degradation of organic compounds. Applying a dissolved ozone concentration of 3 mg/L, the impact of bench-scale ozonation on unbuffered aqueous solutions of the ICMs, Amidotrizoic acid and Iomeprol, (both ≈ 20 mg/L) was evaluated.



a) Ionic Amidotrizoic acid

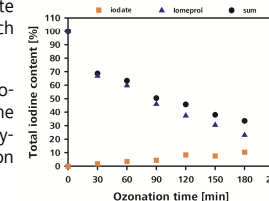
With proceeding ozonation time, concentration of amidotrizoic acid decreased in the same way as iodate concentration increased. After 120 min ozonation, approx. 8% of nondegraded ICM and 95% iodate were found, resulting in a recovery rate of approx. 103%. Ozonation cleaves the aromatic carbon-iodine bond leading to short-lived iodide that is directly ozonated to iodate.



b) Nonionic Iomeprol

Iomeprol degradation proceeds much faster than iodate formation. After 120 min ozonation, 84% of Iomeprol was degraded, whereas iodate concentration only increased to 14%, which means a recovery rate of only 30%.

In accordance with the ion-exchange chromatogram, the poor recovery is attributed to the formation of still unknown ozonation by-products (OBPs) other than iodate. Identification of these OBPs is a major future research task.



Overlay of three chromatograms obtained for a 100 µg/L iodate/iodide standard and two ozonated (60 and 120 min) aqueous Iomeprol solutions (20.4 mg/L)

IC Column: Metrosep A Supp 3 - 250/4.6
Column temp.: 30 °C
Eluent: 7.2 mmol/L sodium carbonate
 0.8 mmol/L sodium hydrogen carbonate
Flow: 1.0 mL/min
RF power: 1200 W
Plasma gas flow: Ar, 13 L/min
Auxiliary gas flow: Ar, 1 L/min
Nebulizer gas flow: Ar, 1 L/min
Detection, m/z: 127

