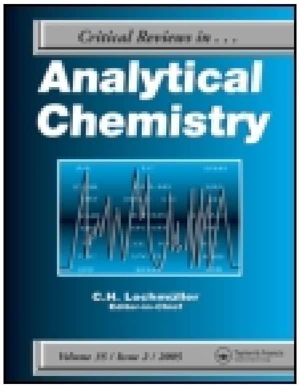

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Application of Ion Chromatography with ICP-MS or MS Detection to the Determination of Selected Halides and Metal/Metalloids Species

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Speciation analytics as determination of various forms of elements is becoming more and more popular and valuable in areas such as environmental protection, biochemistry, geology, medicine, pharmaceuticals, and food product quality control. Its growing importance is related to the fact that what often decides the toxicological properties of a given element or compound is not its total content but the presence of its various forms, especially ionic. Determination of low concentrations of analytes requires complex and sophisticated analytical methods and techniques. The latest trends in this area concern the so-called "hyphenated techniques," in which the separation and various detection methods are combined. This article is a review of possible uses of ion chromatography in combination with ICP-MS and MS detectors for the speciation analytics of selected halides as well as metals and metalloids species.

Keywords Ion chromatography, mass spectrometry, hyphenated techniques, speciation analytics, metals, metalloids, halides

INTRODUCTION

At the beginning of the twenty-first century, analytical chemistry (including environmental analytics) is facing new challenges. First and foremost, this situation is linked to the fact that new data concerning the toxicological properties and forms of elements have been appearing and that there is a necessity for the detection and determination of gradually lowering analyte concentrations, often in complex matrix samples.

The concept of speciation in chemistry is employed to determine the occurrence of a particular element in its diverse forms (at different oxidation states, in combination with various ligands, etc.) in the examined material such as food, animal tissues, or environmental samples. These forms may vary in terms of their physical and chemical characteristics or pathophysiological effects. Speciation analytics (identification and quantity analysis of individual forms of a given element) is becoming more and more important in environmental protection and medicine despite its considerable cost.

The definitions of chemical speciation found in the literature are equivocal. The terms in use are individual, group, physical, or chemical speciation (Florence and Batley, 1993). Since all these designations defined the concept of speciation differently, it was necessary to disambiguate it. The International Union of Pure and Applied Chemistry (IUPAC) identifies speciation as a process that is to prove the existence of the atomic and molecular forms of the determined analytes. The definition was specified by Caroli (1995). He described chemical speciation as the identification and verification of various forms of the analyte in terms of the threats they pose to human health.

Toxicological tests show that what often determines an element's influence on living organisms is not its complete content but the participation of its individual forms.

For that reason, knowledge of various analyte forms' occurrence is more important than information on its complete content.

Biological activity and toxicity to living organisms is demonstrated primarily by the elements existing in ionic forms. All ions of a specific element present in the environment may occur as free anions, cations, or ions bound with organic or inorganic ligands in complexes. The simplest and most popular method of sample separation into the dissolved phase (consisting of different metal ion complexes and metals adsorbed on colloidal particles) and insoluble particulates together with ions absorbed on them is called physical speciation.

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Redox speciation involves the elements that may occur at different oxidation states and consists in the determination of the concentration of the element at each oxidation state. It is especially important in the case of the elements that, depending on their oxidation state, demonstrate highly diversified toxicological characteristics in relation to living organisms.

Reducing the detection limits to extremely low levels means that it is not always possible to determine gradually decreasing amounts of the analytes in the examined samples with the analytical methods used so far. Because of that, there is a tendency to combine diverse methods and techniques together, to which the name "hyphenated techniques" is given. They most often combine separation methods (e.g., chromatographic ones) with different modes of detection (e.g., spectroscopic techniques).

A specific hyphenated technique should be selective towards the determined analytes, be sensitive in a wide range of concentrations, and should enable the best possible identification of the determined analytes.

The hyphenated techniques have important applications in speciation analytics. The growing interest in speciation issues calls for the solution of numerous analytical issues, ranging from sampling to methods facilitating the determination of particular analytes in the sample.

Applying a procedure enabling the separate determination of each individual component is an example of an ideal situation in speciation analytics, and as such it is seldom possible in practice. In the instance of environmental samples (when it is often necessary to determine trace concentrations of an analyte that is unstable and occurs in the complex matrix) it is practical to use the hyphenated techniques. They are based on the selective separation of the analyte ions and their determination with appropriate detectors.

The hyphenated techniques employed the most quickly were ones using the coupling of gas chromatography with different detectors and creating combinations such as GC-MS (gas chromatography-mass spectrometry), GC-AAS (gas chromatography-atomic absorption spectrometry), GC-AES (gas chromatography–atomic emission spectrometry) or GC-ICP-MS-TOF (gas chromatography-inductively coupled plasma-time of flight mass spectrometry) (Bouyssiere et al., 2003).

While coupling the gas chromatograph with the mass spectrometry detector was relatively simple, the large eluate volume in the case of the liquid chromatograph was a serious obstacle to the introduction of the HPLC-MS (high-performance liquid chromatography-mass spectrometry) system into the laboratory practice. For technical reasons, systems applying liquid chromatography methods to the separation of the analyzed elements such as HPLC-MS and HPLC-ICP-MS (high-performance liquid chromatography-inductively coupled plasma-mass spectrometry) appeared on the market some time afterwards.

Ion chromatography as a kind of liquid chromatography is primarily applicable to (in terms of the hyphenated techniques) inorganic ion determination (Wille et al., 2007; Michalski, 2009). Determination and separation of ions (which until recently has been thought to be difficult or even impossible to separate, especially in the case of complex matrix samples) have become more effective with the implementation of the new highly selective stationary phases in ion-exchange columns and new modes of detection. This concerns the majority of environmental samples in which the excess of some ions (most frequently, Cl^-, SO_4^{2-}, and Na^+) hampers the determination of the remaining analytes at low concentrations levels (Marheni et al., 1991).

The most popular hyphenated techniques employing ion chromatography are IC-ICP-MS (ion chromatography-inductively coupled plasma-mass spectrometry) and IC-MS (ion chromatography-mass spectrometry).

Using the IC-MS system allows not only obtaining information about the quality and quantity composition of the sample but also defining the structure of analytes and their molar weights. There is a necessity for maintaining extremely low pressure in the spectrometer while the separated ions of the analyte leave the chromatographic column under relatively high pressure. Research into such applications started as early as in the 1980s, but they have been introduced on a commercial scale only recently.

The ion source is used for transferring the eluent into the spectrometric detector. It consists in the conversion of the liquid eluent containing the analyte into its gas phase under atmospheric pressure. The analyte must be thermally stable and the eluent should vaporize without leaving salts behind. Organic solvents such as methanol and acetononitrile are sometimes added to the eluent to assist its vaporization.

Various sources of ionization may be used in HPLC-MS systems (Wille and Czyborra, 2007), including ESI (electrospray ionization), APCI (atmospheric pressure chemical ionization), and APPI (atmospheric pressure photochemical ionization).

The scope of these applications depends on the polarity and molar mass of analytes as well as on the eluent flow rate. Only the first variant of the above-mentioned ionization types is used in the IC-MS systems. ESI is the so-called soft ionization method. In contrast to other ionization methods, it is able to convert multivalent ions into the gas phase. The MS detection might be conducted in two different modes: selected ion monitoring (SIM) and scan mode (SM). In the SIM mode the information on the analyte molar mass is obtained, and the method is usually applied for quantitative analyses. In the SM method the information on retention times, mass spectra, and mass distribution is attained. This mode is primarily used in qualitative analyses.

Identification is relatively simple when it pertains to analytes with low molar mass. The identification problems concerning large molecules are chiefly related to the higher number of possibilities in terms of obtaining spectra with the same ratios of molar mass to charges.

The main applications of ion chromatography in speciation analytics can be divided into three areas:

1. Determination of nitrogen (e.g., NO_2^-, NO_3^-, NH_4^+) (Michalski and Kurzyca, 2006) and sulfur (e.g., S^{2-}, SO_3^{2-}, SO_4^{2-} $S_2O_3^{2-}$, SCN^-) (Divjak and Goessler, 1999) ions.
2. Determination of inorganic water disinfection by-products (e.g., BrO_3^-, ClO_2^-, ClO_3^-) (Michaski, 2010) and other halide ions (e.g., ClO_4^-, IO_3^-) (Dasgupta, 2006).
3. Determination of metal (e.g., Cr(III)/Cr(VI), Fe(II)/Fe(III)) and metalloid (e.g., As(III)/As(V), Se(IV)/Se(VI)) (Montes-Bayon et al., 2003; Sarzanini and Mentasti, 1997) ions.

Determination of nitrogen and sulfur ion forms has been done since the beginnings of ion chromatography and is usually carried out with the classic ion chromatograph equipped with an appropriate anion or cation exchange column and suppressed conductivity detection. From the environmental and toxicological point of view, the most important uses are halide and metal/metalloid ion determinations.

A review of references concerning the applications of IC-ICP-MS and IC-MS hyphenated techniques as well as their potential in the speciation analytics of selected ions are presented below.

DETERMINATION OF SELECTED HALIDE IONS WITH IC-ICP-MS AND IC-MS

Protecting people against health-threatening microorganisms present in drinking water requires its disinfection by means of various methods. Water chlorination is a well-known and effective technology used for many years; however, in its course dangerous by-products such as trihalomethanes can form.

Due to that fact, there has been a search for other water disinfection methods, among which ozonation has become the most popular. Even though modern water disinfection methods have their undeniable advantages, they also have certain negative aspects and limitations. They mainly involve the formation of inorganic oxyhalide by-products such as bromate, chlorite, and chlorate.

Bromate can form in raw water containing bromides that is subjected to the ozonation processes. The International Agency for Research on Cancer (IARC) classified it as a potential carcinogen (B2 group), whereas the World Health Organization (WHO) and the United States Environmental Protection Agency (U.S. EPA) initially established the bromate dose safe for a human at the level of 0.8 $\mu g/dm^3$. Owing to the lack of a simple analytical method making the determination of such low concentrations possible, the provisional permissible bromate content in drinking water was soon increased to the level of 25 $\mu g/dm^3$ (WHO, 1993). Nowadays, in most highly industrialized countries the permissible bromate content in drinking water is 10 $\mu g/dm^3$(WHO, 2005).

Ion chromatography has the most significant practical meaning when taking into account the necessity of water disinfection by-product determination at the level of $\mu g/dm^3$. The methods of bromate, chlorite, and chlorate determination in water with ion chromatography can be categorized into three groups depending on the detection mode (Michalski, 2005a):

1. Direct methods (conductivity detection);
2. Indirect methods (UV/Vis detection);
3. Hyphenated techniques (MS and ICP-MS detection).

Methods 300.0 (U.S. EPA, 1003) and 300.1 (U.S. EPA, 1997) published by the U.S. EPA as well as the method described in the ISO 15061 standard (ISO, 2001) belong to the first category. The direct methods rely on selective BrO_3^-ion separation in the presence of other anions in the sample and their detection with suppressed conductivity detection. These methods are relatively simple and inexpensive, but their main flaw is difficulty with the appropriate separation of BrO_3^- and Cl^- ions, whose concentrations in real samples differ significantly.

Regardless of the separation conditions, chlorides are leached next to bromate ions. The precondition for obtaining quantification limits at the level of a few $\mu g/dm^3$ is the appropriate separation of the BrO_3^-/Cl^- ion pair. In real samples in which the ratio of BrO_3^- ion concentration to Cl^- ion concentration exceeds 1:10,000, the chloride ions "overlapped" the bromate ion peak, which in turn hampers or even disables their separation and determination.

The derivatization methods belong to the indirect methods category. They consist in converting the determined substance (after its separation in the analytical column) into its derivatives, which can be then detected with the UV/Vis detector.

The third category encompasses the hyphenated techniques such as IC-ICP-MS and IC-MS. These systems are characterized by very high detection and precision of the determinations, but due to their high price they have not been routinely used in laboratories hitherto.

Tables 1 and 2 demonstrate examples of IC-ICP-MS and IC-MS hyphenated technique applications for selected halide (mainly water disinfection by-products) analysis with consideration for the analytical column and the eluent types, obtained detection limits, and the analyzed matrix type.

METAL AND METALLOID IONS DETERMINATION WITH IC-ICP-MS

The simultaneous separation and determination of metals ions and metalloids at different oxidation states belongs to another important area of ion chromatography applications in speciation analytics.

The most popular instrumental metal determination methods such as AAS (atomic absorption spectrometry) and ICP-MS (inductively coupled plasma-mass spectrometry) are sensitive but do not allow the simultaneous determination of different ions of the same element.

A major breakthrough in respect of ion chromatography applications for metal ion/metalloid speciation analytics was

TABLE 1

The application of IC-ICP-MS for the speciation analytics of selected chlorine, bromine, and iodide species

Analytes	Analytical column	Eluent	Limits of detection [μg/dm^3]	Matrix	References
Br^-, BrO_3^-	Laboratory-prepared column	75 mM NH_4NO_3	0.06	Drinking water	Seubert et al., 2000
IO_3^-, I^-	Agilent G3154A/102	20 mM NH_4NO_3	1.5	Surface water, ground water, drinking water	Chen et al., 2007a
Cl^-, ClO_2^-, ClO_3^-, ClO_4^-, BrO_3^-, Br^-, IO_3^-, I^-	Waters C-Pak A	KNO_3+ HNO_3	Cl^-: 500, ClO_2^-, ClO_3^-: 5, ClO_4^-, BrO_3^-: 1, Br^-: 1, IO_3^-: 0.1, I^-: 0.2	Surface water, drinking water	Pantsar-Kallio et al., 1998
IO_3^-, I^-	Dionex IonPac AS 11	NaOH	0.3	Surface water, ground water, drinking water	Yamaguchi et al., 2006
BrO_3^-, Br^-, IO_3^-, I^-, monobromoacetic acid, monoiodoacetic acid, bromochloroacetic acid, dibromoacetic acid, chloroiodoacetic acid, bromoiodoacetic acid, diiodoacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, tribromoacetic acid	Dionex IonPac AS11-HC	NH_4NO_3	BrO_3^-: 0.7, Br^-: 0.5, IO_3^-, I^-: 0.1, monobromoacetic acid: 0.7, monoiodoacetic acid: 0.1, bromochloroacetic acid: 1.0 dibromoacetic acid: 0.7 chloroiodoacetic acid: 0.2 bromoiodoacetic acid: 0.3 diiodoacetic acid: 0.2 bromodichloroacetic acid: 2.5, dibromochloroacetic acid: 2.0, tribromoacetic acid: 1.0	Drinking water, mineral water	Shia and Adams, 2009
BrO_3^- Br^- IO_3^-, I^-	Laboratory-prepared column on the basis of PS-DVB and latex	NaOH, KOH, Na_2CO_3+ $NaHCO_3$	BrO_3^-: 0.088 Br^-: 0.124 IO_3^-: 0.064 I^-: 0.182	Surface water, ground water, drinking water	Eickhorst and Seubert, 2004
BrO_3^-, Br^-, IO_3^-, I^-	Yokogawa Analytical Systems, Excelpak ICS-A23	5 mM Na_2CO_3+ 3 mM $NaHCO_3$	BrO_3^-/Br^-: 0.42 IO_3^-/I^-: 0.051	Surface water, ground water, drinking water	Yamanaka et al., 1997
IO_3^-, I^-	Dionex IonPac AS9-HC, or IonPac AS16	0.8 mM Na_2CO_3/2 mM $NaHCO_3$, or 30 mM Na_2CO_3/5 mM $NaHCO_3$ or NaOH	IO_3^-: 0.48 I^-: 0.77	Seawater	Sacher et al., 2005

(Continued on next page)

BrO_3^-, Br^-	Dionex IonPac AS12A	11 mM $(NH_4)_2CO_3$	BrO_3^-: 0.47 Br^-: 0.42	Drinking water	Divjak et al., 1999
monobromoacetic acid, monoiodoacetic acid, bromochloroacetic acid, dibromoacetic acid, chloroiodoacetic acid, bromoiodoacetic acid, diiodoacetic acid, bromodichloroacetic acid, tribromoacetic acid	Dionex IonPac AS16	NaOH	monobromoacetic acid: 21.2, monoiodoacetic acid: 0.45, bromochloroacetic acid: 0.34, dibromoacetic acid: 15.6, chloroiodoacetic acid: 0.34, bromoiodoacetic acid: 23.6, diiodoacetic acid: 0.99, bromodichloroacetic acid: 0.58, tribromoacetic acid: 0.42	Surface water, ground water, drinking water	Liu et al., 2004
BrO_3^-	Laboratory-prepared column on the basis of PS-DVB and latex	NH_4NO_3	0.17	Surface water, ground water, drinking water	Nowak and Seubert, 1998
BrO_3^-	Dionex IonPac AS12	NaOH	0.1	Surface water, ground water, drinking water	Creed et al., 1996

TABLE 2
The application of IC-MS for the speciation analytics of chlorine, bromine, and iodide species

Analytes	Analytical column	Eluent	Limits of detection [μg/dm^3]	Matrix	References
ClO_4^-	Dionex IC-Pak Anion HR	100 mM CH_3COONH_4+ water : acetonitryle (50:50 v/v)	1–3	Fruits, vegetables, infant food	Krynitsky et al., 2006
ClO_4^-	Metrohm MetroSep A Supp-5	30 mM NaOH + 30% methanol	< 0.5	Surface water, ground water, drinking water	Gandhi and Hedrick, 2005
ClO_4^-, BrO_3^- monobromoacetic acid, bromochloroacetic acid, dibromoacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, tribromoacetic acid	Dionex IonPac AS9-HC	9 mM Na_2CO_3	0.2–1	Surface water, ground water, drinking water	Roehl et al., 2002
ClO_4^-	Dionex IonPac AS20, IonPac AS16	KOH	0.04–1.7	Surface water, ground water, biological samples, food	Slingsby et al., 2006
ClO_4^-, I^-	Dionex IonPac AS16	KOH	0.03–2	Biological samples	Dyke et al., 2009
ClO_4^-,I^-	Dionex IonPac AS16	NaOH	ClO_4^-: 0.06 I^-: 0.44	Seawater	Martinelango et al., 2006
ClO_4^-, I^-	Dionex IonPac AS20	50 mM KOH	ClO_4^-: 0.05 I^-: 0.33	Urine	Valentin-Blasini et al., 2007
ClO_4^-, BrO_3^-, ClO_3^-	Phenomenex Synergi Max-RP C12	A: 0.1% formic acid (v/v), B: 100% methanol	ClO_4^-: 0.05 BrO_3^-: 0.20 ClO_3^-: 0.70	Hypochlorite solutions	Pisarenko et al., 2010
ClO_4^-	Dionex IonPac AS16	NaOH	3	Milk	Dyke et al., 2006
ClO_4^-, I^-	Dionex IonPac AS20	50 mM NaOH	ClO_4^-: 0.02 I^-: 0.57	Physiological solutions	Blount and Valentin-Blasini, 2006
monobromoacetic acid, monoiodoacetic acid, bromochloroacetic acid, dibromoacetic acid, chloroiodoacetic acid, bromoiodoacetic acid, diiodoacetic acid, bromodichloroacetic acid, tribromoacetic acid	Dionex IonPac AS16	NaOH	0.018–4.85	Drinking water, Water extracts	Barron and Paull, 2006

achieved when new highly selective stationary phases for analytical columns appeared on the market and new methods of preparing samples for analysis were developed. They enabled simultaneous separation of the same element ions and their sensitive detection with proper detection methods.

The simultaneous determination of various ions of the same metal/metalloid with the ion chromatography method can be classified into three types:

1. Forming the anionic complex and separating various forms in the anion exchange column simultaneously or converting all the ions into their cationic form and separating them in the cation exchange column.
2. Using the system of cation exchange and anion exchange columns connected in series, facilitating the separation of metal ions that occur in the cationic and anionic forms.
3. Using columns with mixed anionic-cationic stationary phase, which permits simultaneous separation of both cationic and anionic forms.

Chromium is the metal most often subjected to speciation examination hitherto (Das et al., 2001). This is related to the fact that chromium compounds with oxidation states of +3 and +6 commonly occur in nature, but they differ significantly in terms of their toxicological properties. The rapidly growing interest in elemental speciation brought about the development of a new generation of analytical techniques enabling discrimination among different forms of a metal or metalloid present in a sample. Coupling ion chromatography with IC-ICP-MS is a powerful tool to determine unambiguously different organic and inorganic compounds in one single run.

IC-ICP-MS is a suitable technique for complex speciation since the conditions of the mobile phase can be manipulated accordingly to provide optimal separation. Liquid sample introduction is a standard in ICP-MS. Therefore, the simplest form of liquid chromatography and ICP-MS coupling is the connection of the column outlet with the nebulizer of the sample introduction system via transfer tubing. It should come as no surprise that the hyphenated system resulting from the coupling of liquid chromatography and ICP-MS is the system most often used for speciation analysis related to ICP-MS detection. About one-third of all publications on speciation analytics related to ICP-MS describe the use of IC-ICP-MS.

Despite its advantages, this hyphenated technique, like other methods, has some drawbacks. One of the major limitations of As or Cr speciation with ICP-MS is the formation of ^{75}As or ^{52}Cr isotopically equivalent species such as $^{40}Ar^{35}Cl^+$ and $^{40}Ar^{12}C^+$ in the plasma, due to the presence of chlorides or carbon in the matrix, which interfere with the accurate determination of As at m/z 75 or Cr at m/z 52. There are two main approaches to address this problem. The first approach is to use ion chromatography to separate interferences, such as chloride, from arsenic before the introduction of the sample into the plasma. It can be usually accomplished during IC by a simple manipulation of the mobile phase.

The other approach developed in parallel to the IC solution is the reduction or elimination of the $^{40}Ar^{35}Cl^+$, $^{40}Ar^{12}C^+$ interferences after the sample introduction into the plasma by using collision reaction cell techniques (RC-ICP-MS) (Chen et al., 2007b). Some instruments use a collision mechanism to dissociate polyatomic interferences, whereas others use gas phase reaction chemistry to specifically induce dissociation or formation of a secondary species that can be rejected by the mass analyzer.

A potential interference for chromium determination by ICP-MS is ArC^+. Using 2% methanol in the mobile phase amplifies this interference, which would limit the ability to observe low levels of chromium. To solve this problem ammonia or methane can be used as a reaction gas in the dynamic reaction cell (DRC). Those gases react with ArC^+ and eliminate it, thus leaving $^{52}Cr^+$ free from interferences.

The isobaric overlaps are generally not an issue when using a double-focusing sector field instrument that offers the higher resolution that may be required for the interference-free determination of sulfur, arsenic, or chromium. However, an increase in resolution inevitably leads to a dramatic decrease in sensitivity. It should also be noted that the sensitivity of the latest generation quadrupole instruments is only two or three factors lower than that of high-resolution ICP-MS operated in the low resolution mode. A good tradeoff between sensitivity, freedom from isobaric interferences, and price is offered by ICP-MS instruments equipped with a collision cell (Ellis and Roberts, 1997).

Literature examples of applying IC-ICP-MS systems for the ion examination of selected metals and metalloid forms with consideration for the employed analytical column, the eluent type and concentration, the detector type, and the analyzed matrix are given in Table 3.

SUMMARY

Due to strong environmental impact, metal/metalloid and selected halide ion determination and speciation have received significant attention in the past few years. Ion chromatography has become one of the main powerful analytical tools for the analysis of complex matrices and speciation studies in that field of analysis.

The hyphenated techniques such as IC-ICP-MS and IC-MS create completely new and immense possibilities in speciation analysis. The main advantages of those techniques comprise extremely low detection and quantification limits, insignificant interference influence, and high precision and repeatability of the determinations.

Like all other methods, the hyphenated techniques have their shortcomings. Limitations include issues such as the high price of the apparatus and its complexity, which causes their practical limited availability and usage in laboratories. Employing hyphenated techniques requires in-depth understanding of the analytical methodologies and knowing the apparatus in minute detail. The discussed systems are expensive, and, for this reason,

TABLE 3
Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA)	Hamilton PRP-X100, Dionex AS7, AG7	75 mM Na_3PO_4, 2.5–50 mM HNO_3	ICP-MS	Surface water, Grodnu wtaer	Bednar et al., 2004
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine, arsenocholine	Waters IC-Pak CM/D, Waters Guard-Pak CM/D	$NaHCO_3$+ Na_2CO_3, HNO_3	ICP-MS	Waters	Pantsar-Kallio et al., 1996a
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine, Se^{4+}, Se^{6+},	Hamilton PRP-X100	10–200 mM $NH_4H_2PO_4$	ICP-DRC-MS	Sediments	Iserte et al., 2004
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA)	Hamilton PRP-X100	30 mM $NH_4H_2PO_4$	ICP-MS	Soils	Rahman et al., 2009
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine	Hamilton PRP-X100	20 mM $NH_4H_2PO_4$	ICP-DRC-MS	Waters, brines	Chen et al., 2007b
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine	Dionex AG-11, AS-11	NaOH, HNO_3	ICP-MS	Urine	Xie et al., 2006
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine, arsenocholine	Hamilton PRP-X100	0.3% HNO_3+ 10% methanol	ICP-MS	Fish sauces	Rodriguez et al., 2009
AsO_4^{3-}, AsO_3^{3-}	Hamilton IC PRP X-100	Na_2CO_3	ICP-MS	Surface water	Roig-Navarro et al., 2001
As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA)	Dionex IonPac AS7	HNO_3	ICP-MS	Waters, rice extracts	James et al., 2008
AsO_4^{3-}, AsO_3^{3-}	Dionex IonPac AS9	NaOH, Na_2CO_3+ $NaHCO_3$	ICP-MS	Soils	Koellensprenger et al., 2002
AsO_4^{3-}, AsO_3^{3-}	IC Wescan Anion-S C18	EDTA	ICP-MS	River waters, wastewaters	Gettar et al., 2000
AsO_4^{3-}, AsO_3^{3-}, SeO_4^{2-}, SeO_3^{2-}	IC Biosil 125 SEC	CH_3COONH_4	ICP-MS	Fish tissues	Jackson and Miller, 1999
Cr^{3+}, CrO_4^{2-}, AsO_4^{3-}, AsO_3^{3-}	Waters IC-Pak A HC	NaOH + KNO_3	ICP-MS	Drinking water, wastewaters	Pantsar-Kallio et al., 1997
Sb^{3+}, Sb^{5+}	Hamilton PRP-X100	15 mM HNO_3	ICP-MS	Plants	Ulrich et al., 2000

(Continued on next page)

TABLE 3
Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids *(Continued)*

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
Sb^{3+}, Sb^{5+}	Hamilton PRP-X100	Phtalic acid, tartaric acid, 4-hydroksybenzoesic acid, citric acid	ICP-MS	Surface water, soils extracts	Ulrich, 1998
Sb^{3+}, Sb^{5+}	Hamilton PRP-X100	Phtalic acid, citric acid	ID-ICP-MS	Soils	Amereih et al., 2005
Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}, monomethyloarsenine (MMA), dimethyloarsenine (DMA), arsenobetaine, arsenocholine	Develosil C30-UG-5, Chemcosorb 7SAX	Malonic acid, 1-butylosulphatic natrium, ammonium citrate, methanol	ICP-MS	Biological and environmental samples	Morita et al., 2007
Se^{4+}, Se^{6+}, selenomethionine, trimethyloselenine	Dionex IonPac CS5	10 mM oxalic acid, 20 mM K_2SO_4, 2% methanol	ICP-MS	Urine	Gammelgaard et al., 2000
Se^{4+}, Se^{6+}, selenomethionine, methyloselenocysteine, Te^{4+}, Te^{6+}	Hamilton PRP-X100	0.5 mM ammonium citrate + 2% methanol	ICP-DRC-MS	Urine, powdered milk, rice flour	Kuo and Jiang, 2008
Cr^{3+}, Cr^{6+},Se^{4+}, Se^{6+}	Dionex AS11	20 Mm NaOH	ICP-DRC-MS	Surface water, Grodnu water	Bednar et al., 2009
Cr^{3+}, Cr^{6+}	Waters Guard-Pak CM/D, Waters IC-Pak A	0.4–40 mM HNO_3	ICP-DRC-MS	Wastewaters	Pantsar-Kallio et al., 1996b
Cr^{3+}, Cr^{6+}	Waters IC-Pak CM/D, Waters Guard-Pak CM/D	0.4–40 mM HNO_3	ICP-DRC-MS	Waters	Pantsar-Kallio et al., 1996c
Cr^{3+}, Cr^{6+}	G3145A/101, G3145A/102	30 mM $NH_4H_2PO_4$	ICP-MS	Wastewaters	Chen et al., 2007c
Cr^{3+}, Cr^{6+}	G3145A/101, G3145A/102	20 mM NH_4NO_3	ICP-DRC-MS	Brines	Chen et al., 2007d
Cr^{3+}, Cr^{6+}	Shodex RS-pak NN-814 4DP	90 mM $(NH_4)_2SO_4$, 10 mM NH_4NO_3	ICP-DRC-MS	Cement, homeopathic medicines	Hagendorfer et al., 2008
Cr^{3+}, CrO_4^{2-}	Laboratory-prepared	0.70 M HNO_3	ICP-MS	Seawater	Hirata et al., 2000
Cr$^{3+,}$ CrO_4^{2-}	Dionex IonPac CS5	2 mM PDCA + 2 mM $NaHPO_4$+ 1 mM NaI + 5 mM CH_3COONH_4	ICP-MS	Drinking water	Sikovec et al., 1995
Cr^{3+}, CrO_4^{2-}	Excelpak ICS-A23	1 mM EDTA-$2NH_4$+ 10 mM $H_2C_2O_4$	ICP-MS	Drinking water, wastewaters	Paquet et al., 1998

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TABLE 3
Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids *(Continued)*

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
Cr^{3+}, CrO_4^2-	Dionex IonPac CS5	PDCA + $(NH_4)_2HPO_4$+ CH_3COONH_4+ NH_4OH + NH_4I	ICP-MS	Waters	Williams et al., 1989
Cr^{3+}, CrO_4^{2-}	Dionex IonPac CS5A	40 mM $MgSO_4$+ 30 mM $HClO_4$	ICP-MS	Drinking water, wastewaters	Michalski, 2005b
Hg^{2+}, metyl-Hg^+, phenyl-Hg^+	Discovery C18	35% methanol + 40% acetonitryle + 25% water + 0.1 Mm DCTA	ICP-MS	Biological samples, seawater, tap water, human hair	Chen et al., 2009a
Hg^{2+}, metyl-Hg^+	Shodex MS-pak SP-80 4B	250 mM NaCl, 100 mM GSH	ICP-MS	Urine	Chen et al., 2009b
N-phosphomethyloglicyne, aminomethylophosphonic acid (AMPA)	Laboratory-prepared	10 mM KCl, 10 mM HCL	ICP-DRC-MS	River water, herbicide	Popp et al., 2008
N-phosphomethyloglicyne, aminomethylophosphonic acid (AMPA)	Zorbax SB-C8	50 mM CH_3COONH_4, 5 mM CH_3COOH	ICP-DRC-MS	Herbicides	Sadi et al., 2004
$[Pb(NTA)]^-$, $[Pb(HEDTA)]^-$, $[Pb(EDTA)]^{-2}$	G3145A/101	30 mM $(NH_4)_2HPO4$	ICP-MS	Water soils extracts	Chen et al., 2007e
U^{4+},U^{6+}, Np^{5+}, Pu^{3+}, Am^{3+}	IonPac CG10, IonPac CS10	H_2SO_4	ICP-MS	Nuclear fuel	Rollin and Eklund, 2000
U^{4+}, Np^{4+}, Pu^{4+}, Np^{5+}, Pu^{3+}, Am^{3+}	Laboratory-prepared	25 mM DPA in 0.5 M HNO_3	SF-ICP-MS	Environmental and biological samples	Truscott et al., 2001a
Th^{4+}, U^{4+}, Np^{5+}, Pu^{3+}, Am^{3+}	Laboratory-prepared	0.1 M $(COONH_4)_2$	ICP-MS	Environmental samples	Truscott et al., 2001b
La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+},Th^{4+}, U^{4+}, Np^{5+}, Pu^{3+}, Am^{3+}	IonPac CG10, IonPac CS10	0.04–0.26 mM α-HIBA	ICP-MS	Nuclear fuel	Rollin et al., 1996
La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}	Met-Pak CC-1, CS5A, TMC-1	NH_4OH + $(COOH)_2$+ PDCA	ICP-MS	Seawater	Haley and Klinkhammer, 2003
Sc^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}	ShimPack CLC-ODS	0.7 M butyric acid	ICP-SF-MS	Ultrapure neodyme oxides	Pedreira et al., 2003
Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Tb^{3+}, Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}, Gd^{3+}, Dy^{3+}	Supelcosil C18, Dionex IonPac CS5A	$\alpha-$HIBA	ICP-MS	Geochemical reference materials	Santoyo et al., 2006

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TABLE 3
Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids *(Continued)*

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Tb^{3+}, Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}	Dionex Ion Pac CS3	α−HIBA		Rocks	Dybczynski and Kulisa, 2005
La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}	Dionex Ion Pac CS5A	Oxalic acid + $NaNO_3$	ICP-MS	Fuels	Perna et al., 2002
Lu^{3+}, Er^{3+}, Gd^{3+}, Eu^{3+}, Nd^{3+}, Ce^{3+}, Yb^{3+}, Tm^{3+}, Ho^{3+}, Sm^{3+}	Silica-based C18 column	α−HIBA	ICP-MS	Waters	Gautier et al., 1997
La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}	Dionex IonPac CS5	Oxalic acid, LiOH	ICP-MS	Synthetic samples	Bruzzoniti et al., 1996
La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}	Supelco LC-SCX, Supelco LC-18, Dionex IonPac CS5	α−HIBA	ICP-MS	Magnesium alloys	Al-Shawi and Dahl, 1996
Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}	Dionex IonPac CS5A	PDCA	ICP-MS	Human tissues	Błażewicz et al., 2010
Zr^{4+}, Ru^{4+}, Mo^{4+}, Tc^{7+}, Rh^{3+}, Pd^{2+}, Sb^{3+}, Te^{4+}	Dionex IonPac CS5	1.5–2 M HCl	ICP-MS	Environmental samples	Betti et al., 2000
Sb^{3+}, Sb^{5+}	Hamilton PRP-X100	KOH, ammonium tartate	ICP-MS	Vulcanic rocks	Miravet et al., 2007
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine, arsenocholine, TMAO, TMAP	Exekpak ICS-45	5 Mm HNO_3	ICP-MS	Urine	Inoue et al., 1996
As^{3+}, As^{5+}, MMA, DMA	G3154A/101	2 mM EDTA, 2 mM NaH_2PO_4, 5 mM $(NH_4)_2CO_3$, 5 mM $HCOONH_4$, 5 mM $NH_4H_2PO_4$, 5 mM $(NH_4)_2HPO_4$,	ICP-MS	Soils	Chen et al., 2006
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Selfmade Agilent 65001, 65002	1.6 mM 2 mM NaH_2PO_4, 0.16 mM Na_2EDTA	ICP-MS	Urine	Heitland and Köster, 2009
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Hamilton PRP-X100	10 mM PO_4^{3-}	ICP-MS	Biological samples	Pizarro et al., 2003
As^{3+}, As^{5+}, MMA , DMA,	Hamilton PRP-X100	30 mM phosphate buffer pH = 6	ICP-MS	Wool	Raab et al., 2002
As^{3+}, As^{5+}, MMA , DMA,	Dionex IonPac AS7	TFA in 99% methanol	DRC-ICP-MS, INNA	Rice flour	James et al., 2008

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TABLE 3
Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids *(Continued)*

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Hamilton PRP-X100	4 mM $(NH_4)_2SO_4$, 4 mM $(NH_4)_3PO_4$, 4 mM NH_4HCO_3	ICP-MS	Blood, urine	Todorov et al., 2005
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Hamilton PRP-X100	10 mM $HPO_4^-/H_2PO_4^{2-}$ in 2% MeOH	ICP-MS	Rice, straw, soil, hair, nails	Sanz et al., 2007
As^{3+}, As^{5+}, MMA , DMA,	Hamilton PRP-X100, SCX-100	20 mM $NH_4H_2PO_4$, 25 mM pyridine	DF-ICP-MS	Cucumber sap	Mihucz et al., 2005
As^{3+}, As^{5+}, MMA , DMA,	Hamilton PRP-X100 Supelcosil LC-SCX	25 mM pyridine buffer pH = 3 15 mM carbonate buffer pH = 8	ICP-MS	Hairs, nails	Raab and Feldman, 2005
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine, arsenocholine, TMAO,	Hamilton PRP-X100 Zorbax 300-SCX	$NH_4H_2PO_4$	ICP-MS	Waters, sediments, plants	Zheng et al., 2003
As^{3+}, As^{5+}, MMA , DMA	Dionex IonPac AS14	50 mM NaOH, 10 mM NaH_2PO_4	ICP-MS	Poultry wastes	Jackson and Bertsch, 2001
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine, arsenocholine, TMAO, TMAP	Dionex IonPac AS7	From 0.5 mM HNO_3 to 50 mM HNO_3 in 1% MeOH	ICP-MS	Seafood	Dufailly et al., 2008
As^{3+}, As^{5+}	Hamilton PRP-X100	50 mM CH_3COOH, 40 mM NH_4NO_3, 500 ppm EDTA, pH = 4.7	ICP-MS	Drinking water	Creed et al., 2005
As^{3+}, As^{5+}, MMA, DMA	Hamilton PRP-X100	30 mM $NH_4H_2PO_4$ in 3% MeOH	ICP-MS	Peanut butter	Hovanec, 2004
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine, arsenocholine, TMAO	Hamilton PRP-X100, Dionex IonPac CS10	20 mM $(NH_4)_2HPO_4$, 20 mM NH_4HCO_3, 20 mM pyridine	ICP-MS ES-MS	Seaweeds	Van Hulle et al., 2002
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Dionex IonPac AS7	$NH_4H_2PO_4$, NH_4OH	ICP-MS	Waters	Ronkart et al., 2007
As^{3+}, As^{5+}, MMA, DMA, arsenobetaine	Shodex Asahipak ES-5023N 7C	15 mM citric acid monohydrate, pH = 2.0	ICP-MS	Biological samples	Mandal et al., 2004
As^{3+}, As^{5+}, MMA, DMA, Se^{4+}, Se^{6+}, Sb^{5+}, Te^{4+}	Hamilton PRP-X100	12.5 mM $(NH_4)_2HPO_4$ in 3% MeOH	ICP-MS	Waters	Guerin et al., 1997
GluMetCys, MeIn, MeCys, GluAlCys, AlIn, AlCys, Met, Cys_2, SeMet, MeSeCys, GluMeSeCys.	Shodex Asahipak GS - 320 HQ	50 mM CH_3COOH, pH = 6.5	ICP-MS ES-MS-MS	Selenized odorless garlic, shallot	Ogra et al., 2005
Se^{4+}, Se^{6+}, $SeMet^+$, $MeSeCys^+$	Chrompak Ionspher 5C, Hamilton PRP-X100	2 mM pyrydinium formate 10 mM $NH_4H_2PO_4$ in 1% MeOH	ICP-MS	Green onions	Kapolna and Fodor, 2006

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TABLE 3

Application of IC-ICP-MS for the speciation analysis of selected metals and metalloids *(Continued)*

Analytes	Analytical column	Eluent	Detection mode	Matrix	References
Se^{4+}, Se^{6+}, $SeMet^{+}$, $MeSeCys^{+}$	Hamilton PRP-X100	Ammonium hydrogen citritate in 2% MeOH	ICP-MS ESI-MS	Wheat-based food	Warburton and Goenaga-Infante, 2007
SeMet, MeSeCys, SeCya, Se^{4+}, Se^{6+}, $Se(Cys)_2$	Xterrs MS C_{18}	0.01–0.05% TEACl in 2% MeOH	ICP-MS ESI-MS	Digested *Saccharomyces cerevisiae*	Dumont et al., 2004
SeMet, MeSeCys, Se^{4+}, Se^{6+}, TMSe	Asahipak GS-220, GS-320, GC-520HQ	10 mM CH_3COONH_4	ICP-MS ESI-MS	Mushrooms	Ogra et al., 2004
23 Selenium species	Waters RP-8	0.1% HFBA + 0.1% TFA in MeOH	ICP-MS	Garlic, onion, ramp	Kotrebai et al., 2000
Organoselenium species	Hypersil BDS C18	OPTIMA water + 2% CH_3COOH, 80% methanol + 20% 2-propanol	ICP-MS MS-MS	Human urine	Cao et al., 2001
Pt^{2+}, Pt^{4+}	Dionex IonPac AS11	75 mM $NaClO_3$	ICP-MS	Road dust	Nischwitz et al., 2003
Cisplatin, mono and diaquacisplatin	ThermoHypersk Hypercarb	1 mM NaoH	ICP-MS	Water and human urine	Hann et al., 2003
Cisplatin, mono and diaquacisplatin, carboplatin, oxiplatin	Discovery HS 5	20 mM ammonium formate	ICP-MS	Waste waters	Hann et al., 2005
V^{3+}, V^{5+}	Self-made – G3154A101 G3154A102	5 mM CH_3COONH_4	ICP-MS ESI-MS	Environmental samples	Chen et al., 2007f
Sb^{3+}, Sb^{5+}, $TMSbCl_2$	Hamilton PRP-X100 Dionex IonPac AS14	20 mM EDTA	ICP-MS	Urine	Krachler and Emons, 2001
Sb^{3+}, Sb^{5+}	Hamilton PRP-X100	Phtalic acid, EDTA	ID-ICP-MS	Soil	Amereih et al., 2005
Ga monocyclic chelates	ZIC-HILIC SeQuant	20 mM CH_3COONH_4 in 60% acotonitrile	ICP-MS	Contrast agents	Raju et al., 2010
Cr^{3+}, CrO_4^{2-}	Self-made – Brownlee C8	0.6 mM EDTA, 0.2 mM TBAH	ICP-MS	Sea sediments	Graham et al., 2009
Heme and none-heme Fe fractions	Hypersil ODS guard TSK Gel G2000SW	Tris(hydrohymethyl)-aminomethane hydrochloride	ICP-MS SF-ICP-MS	Raw and cooked beefstreak	Harrington et al., 2001
Al complexes	Dionex IonPac CG2	0.2 M ammonium formate	ICP-MS	Environmental samples	Tsunoda et al., 2001
Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}	Bio-Res 50W-X8 Dionex IonPac AS11	50 mM NH_4NO_3, NH_4OH	ICP-MS	Environmental water	Ammann, 2002
MeHg, Hg^{2+}	Self-made – Hypersil ODC	0.5 mM CH_3COONH_4	ICP-MS	Environmental samples	Wilken and Falter, 1998

so far they are used in scientific research rather than in routine analyses. Nevertheless, development of the hyphenated techniques is becoming more and more important and the growing number of works concerning this subject seems to corroborate this (Szpunar and Lobiński, 2003).

ABBREVIATIONS

AMPA	Aminomethylophosphonic acid
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photochemical ionization
ASA	Atomic absorption spectrometry
DCTA	1,2-Diaminocyclohexanetetraacetic acid
DMA	Dimethyloarsenine
DPA	Diaminopropionic acid
DRC	Dynamic reaction cell
EDTA	Ethylenediaminetetraacetic acid
ESI	Electrospray ionization
GC-AAS	Gas chromatography-atomic absorption spectrometry
GC-AES	Gas chromatography-emission atomic spectrometry
GC-ICP-MS-TOF	Gas chromatography-inductively coupled plasma-time of flight mass spectrometry
GC-MS	Gas chromatography-mass spectrometry
GSH	Glutathione
HEDTA	Hydroxyethylethylenediaminetriacetic acid
HIBA	Hydroxyisobutyric acid
HPLC-ICP-MS	High performance liquid chromatography-inductively coupled plasma-mass spectrometry
HPLC-MS	High performance liquid chromatography-mass spectrometry
IARC	International Agency for Research Cancer
IC-ICP-MS	Ion chromatography-inductively coupled plasma-mass spectrometry
IC-MS	Ion chromatography-mass spectrometry
ICP-DRC-MS	Inductively coupled plasma mass spectrometry with dynamic reaction cell
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-SF-MS	Inductively coupled plasma-sector field-mass spectrometry
ID-ICP-MS	Isotope dilution-inductively coupled plasma-mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
MMA	Monomethyloarsenine
NTA	Nitrilotriacetic acid
PDCA	2,6-Pyrridine dicarboxylic acid
PS-DVB	Styrene-divinylbenzene
RC-ICP-MS	Reaction cell-inductively coupled plasma-mass spectrometry
SIM	Selected ion monitoring
SM	Scan mode
TMAO	Trimethyl arsine oxide
TMAP	Trimethyl arsine phosphate
U.S.EPA	United States Environmental Protection Agency
WHO	World Health Organization

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