Review on Toxic Metal Speciation Analysis Based on Coupled Technique HPLC-ICP-MS (Environmental Aspects).

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Summary: Trace elements target humans and animals by different means like, air, drinking water, and from soil. Trace metals like As, Cr, Se, Sb, Hg and Sn may be toxic and speciation of these metals has become an important research area in elemental analysis. The elemental toxicity mainly depends on its available chemical form and its oxidation state. Metal toxicity can occur at a very low level i.e. from trace to ultra-trace levels, so there is a need of highly sensitive detector. In recent years, various methods for the speciation of toxic metals are studied. This article discusses the methods currently used for particular toxic metal ions using HPLC-ICP-MS. About 79 published papers (1978-todate) are reviewed in this document. Results from the previous data reflect that the coupled HPLC technique with ICP-MS detector is widely used method for various toxic metals speciation studies.

Key words: speciation, toxic metals, HPLC-ICP-MS

Introduction

Due to the versatile and ultimate detection power inductively coupled plasma mass spectrometry (ICP/MS) has been developed as one of the foremost influential techniques to analyze the trace elements. This article elaborates the function of coupled high performance liquid chromatography (HPLC) with ICP-MS as the ideal and suitable techniques in environmental sciences. For this review previous two decades scientific literature was screened to cover the analytical technique. Significant procedural features for the combination of ICP-MS with HPLC will be illustrated first. Illustrative applications in environmental sciences along with this improvement will be discussed further to accentuate the importance of the practical developments.

Inductively Coupled Plasma Mass Spectrometry ICP-MS

Among analytical techniques; ICP-MS is considered as the most powerful, and reveals LODs from low level to sub-ng per liter for most of toxic elements. This method more precisely describes by the surveyable spectra, multi-element capabilities, a linear dynamic range and possibility of analyzing large number of samples. A number of instruments have a provision for the availability of mass filters. (QMS) quadruple mass spectrometer uses mass filter followed by time of flight instruments (TOF-MS) and (SFMS) double focusing sector field instruments to prepare first ICP-MS instruments.

For very accurate determinations of isotopic- ratios, multi-collector instruments were designed which have recently introduced in the market although still quadruple based instruments are presenting majority of the instrument manufacturer. To conquer the inadequate resolving power of quadruple based mass filters ICP-MS instrument were upgraded by multipole collision or reaction cells, this made it efficient for a diversity of spectral interferences like ArCl at ^{76}Se and ^{75}As [1].

The peculiar features which are related with ICP-MS instruments presented in detail [2 -4]. Over a number of decades these instruments have become a routine method of analysis to determine trace and ultra-traces of hazardous elements like radionuclide's, metals and metalloids, ICP-MS are frequently used in the environmental studies. Typical ICP-MS applications include estimation of total metals concentrations in industrial waste water samples. For the analysis of matrix rich samples like water, sludges and biological materials the samples needs to be digested prior to the analysis of ICP-MS.

Solid phase extraction procedures are used for the separation of low concentration matrix. Besides the determination of elemental concentration this is also used for measuring isotopic ratio which enables it for the isotopic analysis [2, 5, 8]. Natural and anthropological Fluctuations in Isotopic composition of some metals like Sr and Pb made it possible for the ICP-MS to be used as a tracer [9]. ICP-MS can also employ for collection of data for

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radionuclides in the environment, like U, Pu, and Tc [10, 11]. Operating conditions of ICP-MS (ELAN 9000) are shown in Table-1 [12].

Table 1: ICP- MS operating condition for the ICP-MS (ELAN 9000)

Operations	Conditions
RF Power	1175 W
Nebulizer Gas Flow	0.80 L/min
Argon Gas Pressure	60 psi
Lens Voltage	7.25 V
Analog Stage Voltage	-2078.13 V
Pulse Stage Voltage	1300.00 V
Discriminator Threshold	300.00
AC Rod Offset	-9.50
Detector Mode	Dual
Number of replicates	5
Reading/replicates	1
Sweeps/readings	30
Rinse Delay Time	34 sec
Flush Delay Time	34 sec
Read Delay Time	14 sec

Rationale for Elemental Speciation

Historically environmental accidents like severe intoxication of seafood in Manimata bay of Japan have generated the concept of elemental speciation. This accident happened due the discharge of mercury wastes into the bay by a Japanese company. The Micro-organisms convert this inorganic mercury into methyl mercury which ultimately entered the biological cycle as the part of fish and shellfish, which resulted in intoxication of seafood.[13 – 14]. In view of the fact that, a number of separation coupling techniques have generated like LC, CE and GC with ICP-MS for elemental speciation [15]. Elemental matabolomics and proteomics are the focal areas which made it possible that there is integration between environmental and elemental speciation studies, so these were the new developments in ICP-MS environmental analysis [16, 17, 18]. For the development of method, use of standard procedures like electrospray mass spectrometry is the main requirements for the analysis of elemental speciation through ICP-MS. Besides this advanced quantification strategies for the isotopic analysis requires species specific and species unspecific isotope analysis. Isotopically rich, species specific standards are utilized for of organomatellic compounds estimation like methyl mercury, mono, di and tributyltin, which are very important from environmental point of view [7, 19]. Table-2 gives an overview of the coupled method using HPLC-ICP-MS in speciation environmental analysis.

HPLC-ICP-MS Coupled Technique (Methodology)

HPLC separations have the option of the availability of different types of stationary phases along with the provision of coupling with ICP/MS. Therefore for the estimation of environmental samples ion chromatography is considered as the best technique after coupling with the ICP-MS [20, 21], which is considered as an excellent detector giving low LODs. There are numerous methods have already been reported for the separation based on HPLC and ion chromatography [5, 6, 22, 23].

Moreover a major advantage of the coupling of these two techniques offers a convenient and suitable interface between them. The flow rates of liquids which is necessary for the regular spraying compressed air and the suitable flow applied for the separation through HPLC, must tuned with the column effluent. HPLC separations are not temperature dependent and can occur at room temperature or maximum in the range i.e. (30-40° C), so there is no need for the temperature control of HPLC-ICP-MS interface. Nevertheless, many problems [20, 21, 24] have been reported regarding the introduction of effluent to HPLC-ICP-MS. The mobile phase used for HPLC can contains buffered solution, organic solvents and ion pairing reagents depending on the type of separation. ICP-MS provides lenience for those elements using these mobile phases. Normally diluted buffers are most commonly used for ICP-MS determinations. The concentrations of $\geq$ 0.1 mol L-1 are often necessary for IC solutions. Higher salt contents affect the robustness of the procedure. Signal suppression, nebulizer blockage, the injection system or a sampling cone also affects the method and have already been reported [20]. In some cases, sampling cone and skimmer erosion are reported [20, 24]. HPLC-ICP-MS coupled system for metal speciation is shown in Fig. 1 [25].

In contrast, for RP-HPLC the extensive use of organic solvents ultimately results in lowering the plasma consistency that leads to the lowering of performance of the analytical work. Furthermore, the use of organic solvents may lead to spectral noise like ARC^{+} on $^{52}Cr^{+}$) resulting also the deposition of carbon at the cone and the torch that ultimately creates large noise, along with fluctuations in signal [20.24]. Thus, various strategies [6, 20, and 24] have been evaluated to overcome these issues. To rectify the problem associated to the quantity of solvent used in plasma, spray cooling room and the integration of desolvation units have been considered as the best tool. Plasma stability can be improved by increasing the RF power, although unwanted reflected light energy is observed and ultimately damages the RF generator [6, 26].

Table-2: LC-ICP-MS coupled methods reported for most important metal/metalloid species.

Species	Instrumental method	Detection limit[a]	Matrix
As (III), As (V), MMA, DMA and (P-ASA)	IP-RP-HPLC-ICP-QMS (d-DIHEN)	0.4–5.4 pg (VInj = 50 nL)	Aqueous standards [35]
As (III), MMA, As(V), DMA, AB andTMAO	IC-ICP-MS (cation exchange)	11 ng L^{-1}–27 ng L^{-1}	Landfill leachates [37]
As (III), DMA, MMA, As (V)	IC-ICP-MS (AEC)	0.02–0.10 ugL^{-1}	Industrial waste water [36]
As(III), As(V), MMA, DMA, AB, AC and arsenosugars	RP-HPLC-ICP-MS	0.075–0.15 ugL^{-1}[b]	Natural waters, biological samples [38]
As (III), As (V), MMA, DMA and AB	IC-ICP-SFMS (AEC)	0.049–0.072 ng g^{-1}	Soil solutions, soil water extracts [32]
As(III), As(V), MMA, DMA, AB, AC, TMAO, TeMA, Sb (III), Sb (V)	Ion pairing RP-HPLC-ICP-MS, (C-30 column)	As: 0.2 ugL^{-1}; Sb: 0.5 ugL^{-1}	Hot spring water and a fish sample [39]
Cr (III), Cr (VI)	IC-ICP-MS (AEC)	5–16 ng L^{-1}	water samples [42]
Cr (VI), Se (IV) and Se (VI), As (III), As (V), MMA , DMA	IC-ICP-MS (AEC)	As: 40–60 ng L^{-1} Cr: 130 ng L^{-1}, Se: 1.2–1.4 ugL^{-1}	Surface water [44]
Cr (III) and Cr (VI)	RP-HPLC-ICP-DRC-MS	0.06–0.09 ugL^{-1}	Natural waters, soil leachates,
Cr (III), Cr (VI)	IC-ICP-MS (AEC)	0.2 ugL^{-1}	Waste water [43]
Cr(III), Cr(VI), V(IV), V(VI)	IP-RP-HPLC-ICP-DRC-MS	V: 0.06 ugL^{-1}; Cr: 0.05 ugL^{-1}	Soil and plant material [45]
Hg (II), $MeHg^+$ and $EtHg^+$	DGT and RP-HPLC-ICP-MS	<15 ng L^{-1}	Soil and soil solution [54]
Hg (II) and $MeHg^+$	IC-CV-ICP-MS (CEC)	35–73 ng L^{-1}	Soil [52]
Hg (II) and MeHg+	Online enrichment and RP-HPLC-ICP-MS	0.02–0.07 ng L^{-1}	Seawater samples; suspended solids [55]
Hg (II), $MeHg^+$, $EtHg^+$, $PhHg^+$	RP-HPLC-ICP-MS	8–32 ng L^{-1}	Groundwater, waste water, sea Water [53]
Sb (III), Sb(V)	IC-ICP-MS (AEC)	50–70 ng L^{-1}	Extracts (airborne PM) [56]
Sb(III) Sb(V) and TMSbCl2	IC-USN-ICP-QMS (AEC)	9–14 ng L^{-1}	Water samples (tap water) [57]
Sb(III) , Sb(V)	IC-ICP-MS (AEC)	0.2 ugkg^{-1}	Soil [59]
Sb(III) , Sb(V)	IC-SU-ID-ICP-MS (AEC)	20–65 ng L^{-1}	Soil extracts [58]
Various organotin species	IC-ICP-MS	2.8–16 pg	Harbor water [67]

a Given as methodological detection limit for the investigated element.
b Recalculated from LOQs (10s) as LOD (3s).

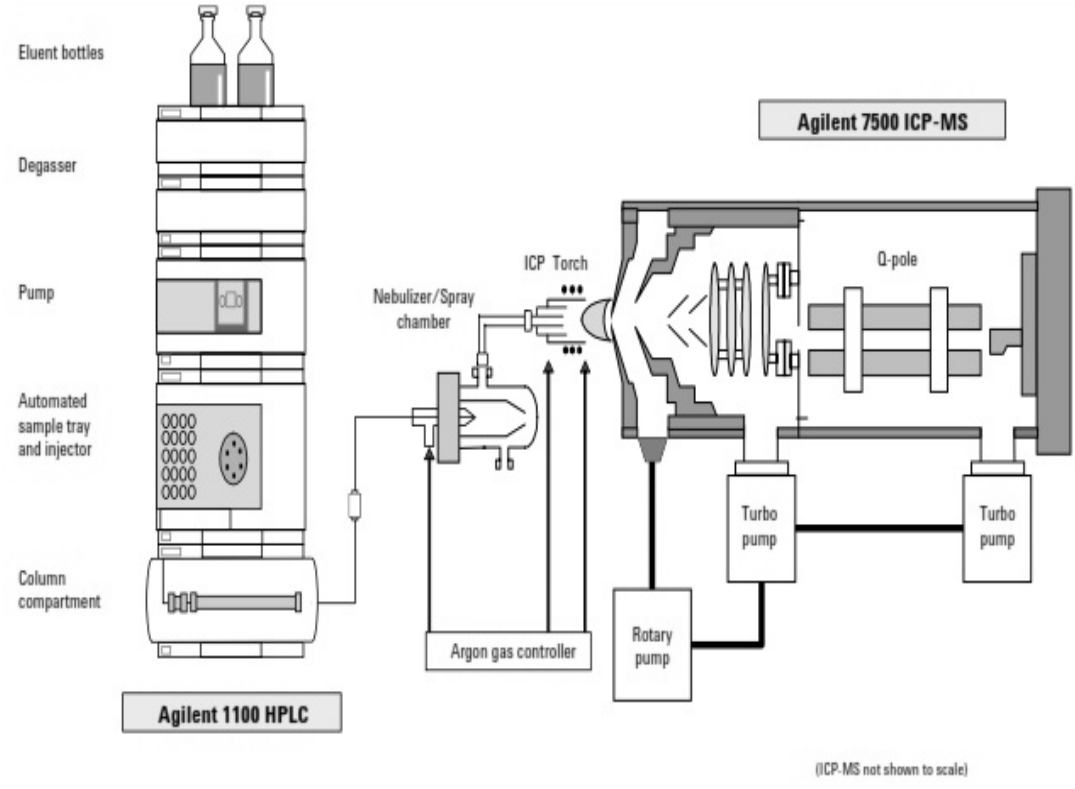

Fig. 1: HPLC-ICP-MS coupled system for metal speciation.

In addition, the problem associated with the deposition of carbon on cone and torch can be rectified by inserting a small amount of oxygen in the system; these conditions may shorten the life span of sample cone [24, 26]. Peltier-cooled spray chamber along with a provision to oxygen incorporation [27] has been reported for the introduction section of ICP, which ultimately gave the advantage of less quantity of organic solvents at plasma.

Column diameter and their respected flow rate are linked to the square function of column diameter for chromatographic separations. The use of capillary column for HPLC gave a suitable provision in system. However, by reducing the diameter of the column ultimately gave positive effect on the stability of the plasma due to the reduced amount of solvent reaches the plasma [28].

Environmental Aspects

In the previous years it has been evident that for the speciation studies of the most important toxic metals like As, Se, Hg, Sn, Sb and Cr, HPLC-ICP-MS has played an important role. Most of the reported literature studies mainly targeted on environmental risk assessment, or to determine the fate of toxic elements in water air or natural soil sediments.

Arsenic (AS)

Arsenic is perhaps the most considered element among all the toxic metals known so far for speciation studies. HPLC-ICP-MS technique has been considered best for the speciation of different arsenic species for various biological and environmental samples. It has been reported that numerous Organoarsenicals, the most importantly, arsenocholine, arsenobetaine, monomethylarsonate and dimethylarsinate, rather than arsenate and arsenite [29].

Variety of procedure are available for separation through HPLC but Ion chromatography have been proposed ideally for the speciation of As. Most recently Hydrophilic interaction chromatography (HILIC) has been assessed with ZIC-HILIC column for speciation studies [30], and verifies that HILIC showed a well matched behavior with ESI-MS or ICP-MS detectors, these proved a better substitute for RP-HPLC methods for upcoming studies of arsenic speciation [31]. Generally for the quantification of As, as it is monoisotopic the polyatomic interference caused by ArCl needs to be compromised this is treated as a drawback for the quantification of As. So during the quantification of arsenic, co-elution of chloride occurred, in samples like sea water and soil solution which are rich in chloride, elaborated with HPLC-ICP-MS based methods. Modified HPLC separations are facilitated for the elution of interference free As. Elaboration of instruments like (SFMS) high resolving sector-field mass spectrometers or quadruple based on collision cell technology has been proposed for interference free arsenic species [32, 33, 34]. Excellent LOD have been reported from 0.04 to 0.08 ng /g for arsenobetain, dimethlylarsinate, Arsenic (V), monomethylarsonate and Arsenic (III) with IC/ICP/SFMS for arsenic speciation in extracts of soil water and solutions [32]. Fig 2 shows the chromatograms of 5ug Arsenic L^{-1} standard solution of all arsenic species and 2ug As L^{-1} spiked soil solution of all arsenic species taken by AEC-ICP-SFMS, which indicates the importance of this approach for speciation, even in complex matrices of the sample.

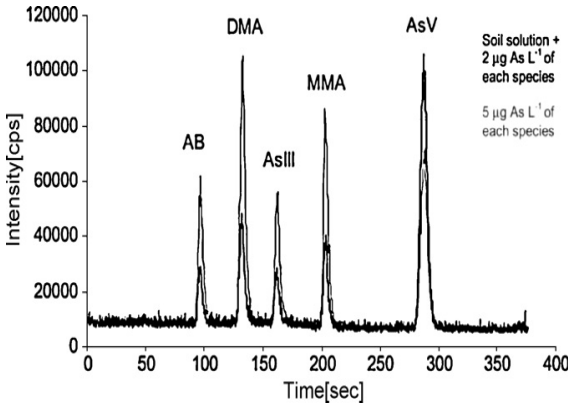

Fig. 2: Chromatogram of standard and spiked soil solution.

The high sensitivity has been obtained by combining nano-HPLC with ICP-MS adopting the (d-DIHEN demountable direct injection high efficiency nebulizer) [35]. Efficient separation of various arsenic species has been done with RP-HPLC with a range of detection of 0.4 picto gram to 5.4 picto grams. Speciation of waste water samples of different arsenic species like DMA, MMA and arsenic (V) and arsenic (III) has been performed by using IC-ICP-MS [36]. Cation exhcange chromatography combined with ICP-MS has been used for the speciation of arsenic species [37]. It was noted that the high variability in concentration levels (from from 0.2 to 250 ug As^{L-1}), due to several factors as the nature of waste, landfill, climatic conditions or differences in degradation phase. Highly variable arsenic recovery of different

leachates resulting from dilution and filtration depicts that still there is a room for methodology enhancement.

River in Japan which is rich in arsenic contents has been taken in to consideration. For this purpose arsenic species separation based on HPLC the inverse Phase separation has been obtained [38]. It was reported that it contains only As (V), where as heavy amounts of inorganic arsenicals and oxo arsenosugar glycerol in water bug extracts. Greater concentrations of oxo-arsenosugar glycerol and oxo arsenosugar phosphate have been reported in algae samples taken from freshwater, where as the fish and crustaceans contained different amounts of AB, DMA, oxo arsenosugar glycerol or phosphate.

Reverse phase HPLC coupled with ICP-MS using C-30 column was used for the estimation of different arsenic and antimony species [39].

Chromium (Cr)

Environmental chromium toxicity can be a function of its chemical form. Chromium (III) has been admitted as a necessary micronutrient, similarly along with Chromium (VI), it has adverse effects e.g. these can cause mutations which may lead to cancer. Chromium (VI) and Chromium (III) can be a constituent of industrial waste water this is because of corrosion inhibitors being used in metallic pipes or as a result of leaching sanitation landfill into ground water [40]. The isotopes of chromium like ^{52} Cr, ^{53} Cr and ^{54} Cr can be detected by ICP-MS. The most common chromium isotopes ^{52} Cr, ^{53} Cr endure from carbon and interference polyatomic based on chlorine (for example, $^{40}Ar\ ^{12}C^{+}$, $^{35}Cl\ ^{16}O\ ^{1}H^{+}$, $^{37}Cl\ ^{16}O^{+}$) may limit the analytical figures of IC-ICP-MS. To overcome this issue an initial stage of the method study IC-ICP-MS was performed to measure accurately Cr (III) and Cr (VI) [41, 42]. Anion exchange chromatography facilitates in combination with ICP-QMS to demonstrate the chromatographic separation with chloride interference. Chromium species were estimated in wastewater samples having a detection limit 0.2 ug/L [43].

Another study reported that shape of the spectrum has been extended for the concurrent estimation of MMA, DMA, Selenium (IV), Selenium (VI) Chromium (VI), Arsenic (III) and Arsenic (V), emphasizing the high sensitivity and advanced multi element by ICP-MS [44]. For the speciation of vanadium or chromium present in the soil or plant material a new procedure using ion-pair reverse phase HPLC-ICP-DRC-MS with a mobile phase of tetra-n-butyl ammonium phosphate has been reported [45], detection limit of 0.06 ug/L for Vanadium and 0.05 ug/L for Cr were obtained. Same method was reported for the speciation of Chromium (III) and Chromium (VI) [46].

Detection of chromium species at very low levels using HPLC/ICP-MS (Fig. 3), with detection limits approaches to 0.06 ng/mL, the adoption of dynamic reaction Cell ICP/MS with ammonia as the reaction gas to remove isobaric interferences from ArC^{+}, $ClOH^{+}$, ClO^{+}, and $ArCH^{+}$ at isotopic masses of ^{52}Cr and ^{53}Cr, thus permitting lower detection limits [47].

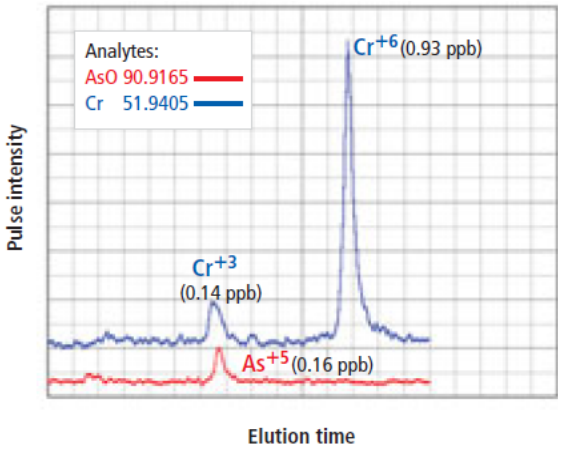

Fig. 3: Separation of Cr (III) and Cr (VI) using ICP-MS.

Mercury (Hg)

Toxicological and environmental fate of mercury and organo mercury species are of more interest. Species of mercury like methyl-mercury, dimethyl mercury and Inorganic mercury are the most critical one. Other species of mercury like alkylated and aromatic have also been reported. The use of HPLC for speciation study of mercury reviewed recently [48]. RP-HPLC is the main method for the separation of mercury until this time; it is based on silicon bond phases which are supported by organic modifiers / chelating agent like pyrrolidine dithiocarbamate, 2-mercapto-ethanol and L-cysteine in restricted pH [49, 50]. Alternative approach for the rapid formation of inorganic mercury and methyl mercury eluted with a low content of organic solvent and adding dodecyldimethyl-ammonium bromide [51]. Polar mercury species through the ion-chromatographic methods for separation have been reported [52, 53]. Ion chromatography combined with (CV) cold vapor

generation ICP-MS was used to determine Hg^0 or Hg (II) and $MeHg^+$ in soil sample, the results obtained for the detection limits of Hg^{2+} as 35 ng L^{-1} and for $MeHg^+$ as 73 ng/L [52]. Gradient elution method for HPLC/ICP/MS is used for the estimation of Hg (II), $MeHg^+$, EtHg at pH 3 combined with micro HPLC column to ICP-MS [54]. This approach was adopted for the direct measurement of the filtrate through 0.22 micro meters after that spike surface water was used by avoiding sample preparation and derivatisation steps. As a result LOD's were observed in the range of 8 ng/L for $EtHg^+$ upto 32 ng/L for $PhHg^+$. A method was developed by combining HPLC-ICP-MS with integrated online enrichment method for mercury estimation in sea water [55]. Improving the detection limit of 0.07 ng/L for Hg^0 or Hg (II) and 0.02 ng/L for $MeHg^+$ has been reported.

Antimony (Sb)

Two different oxidation states of Inorganic antimony are present in environment; the most toxic form is Sb (III). As discussed earlier elements the separation was carried out through the anions exchange chromatography has been a common approach. Quantitative analysis of antimony (III) and antimony (V) has been performed by complexation with citric acid. As a result LOD's were observed 50 ng/L for antimony (III) and 70 ng per litre for antimony (V) [56]. Speiation of antimony (III), antimony (V) and trimethylantimony dichloroethane can be achieved by using anion exchange ICP/MS with the provision of ultrasonic atomization (USN) together with membrane desolvation, with limit of detection of 14 ng/L for antimony (III), 12 ng/L for antimony (V) and 9 ng/L for $TMSbCl_2$ [57].

Analysis of soil samples speciation of antimony carried out by the use of AEC-ICP-MS by non-specific isotope dilution (ID) [58]. This approach was applicable to determine the fate of Sb along two Austrian motorways [59]. It was observed that the concentration of antimony (V) was more as compared to natural background with range 4-10 Sb (V). High levels of Sb arise from various man-made sources, such as abrasions of brake pads and the surface of motor vehicles concluded from the study.

By combing the (SEC) size exclusion chromatography with IC/ICP/MS, similar study on speciation of water extractable Sb (III) and Sb (V) in samples of soil and separation of humic acids from soils along the highway in Massachusetts [60] has been carried out. It has been established that Sb (V) is available at a high concentrations on the top layer of soil. Two soil derived humic acids were obtained examines using incubation experiments form the roadside and it was observed that one of these humic acids was having significant binding with antimony (V).

Tin (Sn)

R_4Sn, R_3SnX, R_2SnX_2 and $RSnX_3$ are classified as the organ tin compounds, where R can be an aryl/alkyl groups whereas X stands for anionic group like -OH, etc., these all are toxic at different levels among all tributyltin and triphenyltin are stated as the most toxic. Tin speciation was performed in water taken from sea with the main concern as matrix [61-67].

Coupling of chromatographic techniques like HPLC [64-67] with ICP-MS [63-67] in water samples for the speciation of tin is reported. Various organ tin species in harbor waters has been separated through GC or HPLC and the online detection through ICP-MS and reported by several authors [63-67]. The LOD's observed 2.8 to 16 picto grams for different organ tin species [67]. Whereas better LOD's obtained by the other procedure ranged 15 to 35 ficto gram tin [63] shows the best detection limits reported previously.

Selenium (Se)

Selenium has been considered a compulsory nutrient for the living things [68-69]. The toxicity; bioavailability and the biological effects of this element are fully based on its chemical forms. This is present in the form of organ selenium compounds like selenium proteins in living system, these proteins are fully involved in metabolic reactions of organisms. Nutritional supplements for selenium are available in different like medicinal plants, clover and yeast for human beings [70-71]. Its speciation is very important from human beneficial point of view [72].

Use of hyphenated separation technique along with ICP-MS has been well recognized [73-74]. The excellent technique for speciation of this element is HPLC [75-79], as it can be combined with ICP/MS. HPLC based on the types of ion exchange has been used for the speciation [80], but in case of biochemical forms of selenium (SEC) size exclusion chromatography has been considered best. For anionic and cationic separation, neutral molecules Ion-pair reversed-phase chromatography (RP)-HPLC is used for further studies of selenium compounds [75, 76, 78].

Conclusion

HPLC-ICP-MS coupled analytical technique attains the level of maturity as for as environmental analysis are concerned. Better know how of the metals/metalloid chemistry in soil, water and air which are considered as the three most important environmental areas is required. The disposal of compounds that contains metal/metalloid in environment by humans needs to be studied through a very sensitive analytical technique for accurate determination in complex matrices. HPLC coupled to ICP-MS based methods will be vital to monitor the particular targeted values. Also in the upcoming years expansion in the environmental monitoring programs with respect to the speciation analysis for highly toxic species (arsenic, chromium, mercury, selenium etc.) is expected. Organ tin compounds have tremendous applications and still there is a room available for the speciation studies.

Elemental speciation analysis can be used on climatic environmental research to forecast and better knowledge on global process, as speciation is an ideal and sensitive approach to reduce toxicity of metal/metalloids in environment.

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