METAL SPECIATION: SURVEY OF ENVIRONMENTAL METHODS OF ANALYSIS

Martin H. Mach[1], Babu Nott[2], Judith W. Scott[1], Raymond F. Maddalone[1], Nina T. Whiddon[1],

[1]Chemistry Technology Dept., TRW, 1 Space Park, Redondo Beach, CA 90278, [2]EPRI, Palo Alto, CA 94303

Abstract. As part of a recent task under the EPRI Analytical Methods Qualification Program (RP 1851), TRW has surveyed the methods available for monitoring metal species in typical utility aqueous discharge streams. Methods for determining the individual species of these metals can become important in a regulatory sense as the EPA transitions to assessment of environmental risk based on bioavailability. For example, EPA considers methyl mercury and Cr(VI) much more toxic to the aquatic environment than inorganic mercury or Cr(III). The species of a given element can also differ in their transport and bioaccumulation. Methods for speciation generally include a selective separation step followed by standard metals analysis. Speciation, therefore, is mainly derived from the separation step and not from the method of final quantitation. Examples of separation/analysis include: selective extraction followed by graphite furnace atomic absorption or ICP-MS; separation by GC followed by metals detection; chelation and/or direct separation by LC followed by UV measurement or metals detection; and ion chromatography with conductivity, UV, or metals detection. There are a number of sampling issues associated with metal species such as stabilization (maintaining oxidation state), absorption, and filtration that need to be addressed in order to obtain and maintain a representative sample for analysis.

Key Words. Speciation, Environmental Sampling, Instrumental Methods

1. Introduction

1.1 SCOPE

In 1984, TRW conducted a study of pollutants emanating from steam-electric power plants (EPRI, 1984). Pollutants were selected for further study based on the frequency they were found in the aqueous discharges from power plants, and by comparison with intake water concentrations. Criteria and a methodology for identifying and ranking these pollutants were also developed. Of those pollutants identified, this review will concentrate on arsenic, selenium, chromium, mercury, and lead. While not identified as a power plant water emission, mercury is also discussed as it is a good example of an element that forms a variety of both inorganic and organic derivatives, and for which separation and detection schemes have been developed that are applicable to the other pollutants.

This paper summarizes the result of a survey of Chemical Abstracts and NTIS over the last 4 - 5 years and highlights the most widely used and accepted analytical methods for speciation of selected target metals. This survey was not meant to provide a totally inclusive review but to provide the reader with a feel for the methodology and recent trends.

Water, Air and Soil Pollution **90**: 269-279, 1996.

1.2 SPECIATION.

Speciation in the context of this paper is the analysis of metals to determine their chemical forms. For example, chromium can be present as Cr(III) and Cr(VI), two different oxidation states. Other metals can be present as both inorganic (e.g., mercuric ion) and organic (e.g., dimethyl mercury) forms. Lead can be present as a non-volatile ionic species or a volatile tetraalkyl lead.

The speciation process typically involves collection, sample storage, one or more separation steps, and measurement of the metal in the final extract (the analytical "finish"). Problems can occur at any stage of this process, especially when sampling complex, environmental matrices involving dynamic equilibria between different phases (e.g., partitioning between the liquid phase and particulates), adsorption on sampling containers, inadvertent changes in oxidation state, and the effect of high concentrations of dissolved species on the analytical finish. Thus, the challenge of speciation is to separate the different forms and accurately quantitate each species in the particular matrix under study.

2. Analytical Methods

2.1 ARSENIC

2.1.1 Species

Arsenic exists in either its elemental form or the As(III) or As(V) valence states. The (III) and (V) forms can be either inorganic (e.g., As_2O_3) or contain organic groups (e.g., methyl arsine). Commonly reported organic forms include monomethyl arsonic acid (MMAA) and dimethylarsinic acid (DMAA). Monomethyl arsonous acid (MMAA-As(III)) and dimethyl arsonous acid (DMAA-As(III)), formed by the action of hydrogen sulfide on MMAA and DMAA, have also been reported (Hasegawa, 1994). Bioincorporated forms include arsenobetaine (AB, present in marine organisms and used as an indicator of arsenic uptake), and arsenocholine (AC). Certain researchers have determined that the toxicity of arsenic is dependent on its species. The inorganic arsenics are more toxic than the organoarsenicals, and the trivalent forms more toxic than the pentavalents (Fowler, 1983). Therefore much effort has been devoted to methods that will identify the particular molecule in terms of its bonded groups and oxidation state. Reviews of arsenic toxicity, collection, and analysis methods have been published by Clifford (1993) and McLaren (1992).

2.1.2 Sampling and Collection.

Care must be taken to prevent speciation changes during sample collection and storage. Plastic containers should be acid washed with 5% HCl, and traces of oxidizing and reducing agents avoided to preserve the oxidation state and avoid oxidation of organometallic compounds. Freezing samples to -80C in liquid nitrogen has been recommended (Crecelius, 1986). In addition, the trivalent methyl arsenicals are more subject to oxidation than their inorganic As(III) counterparts (Cullen, 1966).

2.1.3 Analytical Methods.

EPA Method 1632 describes the determination of total inorganic As in water: Inorganic arsenic (As(III) + As(V)) is reduced to arsine (AsH_3), which is purged and trapped on a cooled adsorbent trap. The trapped arsine is thermally desorbed and detected by flame atomic absorption spectrometry (FAAS). This method quantitates total arsenic, and can also separately quantitate the inorganic arsines (as AsH_3) and organic arsines (as higher boiling, volatile arsines) via their boiling points during the thermal desorption step. Method 1632 is reported to have a method detection limit (MDL[1]) of 0.002 µg/L. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, EPA Method 200.8), stabilized temperature graphite furnace atomic absorption spectrometry (ST/GFAAS, EPA Method 200.9), and ICP - atomic emission spectrometry (ICP/AES, EPA Method 200.15) have also been used for the measurement step, with somewhat higher MDLs of 0.1, 0.5, and 3 µg/L, respectively. For the recent literature methods reported below, detection levels[2] (as quoted in the referenced documents) typically fall in the low to sub- µg/L range using the above-cited analytical finishes.

As(III) can be selectively reduced in the presence of As(V) using $NaBH_4$ buffered at pH 6 (Watras, 1992). This allows differentiation between the inorganic As(III) and As(V). In a research setting, laboratories may be able to achieve detection levels for environmental water samples in the low ng/L range.

For samples containing MMAA and DMAA, a hydride/separation scheme has been reported in which MMAA and DMAA are converted to the hydrides and quantitated by fractional distillation with AAS detection after the inorganic As(III)/(V) is separated and independently quantitated via a carbamate precipitate chelation process (van Elteren, 1994). The authors report detection levels for MMAA and DMAA of 0.2 and 0.5 ng, respectively. This process was applied to sediment interstitial water containing arsenic species at low µg/L levels. Another chelation method using carbamate-based separation followed by hydride generation/heated quartz cell AAS has been applied to the speciation of inorganic and organoarsenicals in natural waters, with reported detection levels of around 0.01 µg/L (Hasegawa, 1994).

Other methods obviate the need for the hydride generation step. Micellar liquid chromatography using surfactants coupled with ICP-MS has been applied to the analysis of arsenic species in biological samples without the need for extensive sample cleanup and deproteinization steps (Ding, 1995). This method was used on urine samples with a reported detection level of 0.9 µg/L for DMAA and 3 µg/L for As(III), As (V), and MMAA. One feature of this method is its freedom from chlorine interfere in the ICP-MS, where the $^{40}Ar^{35}Cl$ ion at mass 75 can interfere with the ^{75}As ion. This increases the applicability of this method for the analysis of seawaters. Capillary zone electrophoresis with on-column preconcentration/field amplified injection can achieve sample enrichment factors of around 150, compensating for the method's small sample size (ca. nanoliters). It has been applied to

[1] Method Detection Limit as defined by 40 CFR Part 136, Appendix B, and published in the referenced EPA method. However, MDLs are sample dependent, and may vary as the sample matrix varies.

[2] The detection levels referred to throughout this paper may only be achievable by certain high quality research laboratories, and are not likely to be routinely achieved by commercial laboratories.

the detection of As(V) in tap water (Li, 1995), with a detection level of 25 μg/L; As(III) could not be quantitated by the current separation scheme as it overlaps with a peak arising from an unidentified matrix ion (or ions) in the sample.

2.2 SELENIUM

2.2.1 Species.

Detailed speciation of selenium is complicated by its four possible oxidation states, viz., -II (selenide), 0 (elemental), +IV (selenite) and +VI (selenate), and their selective complexation and/or bonding. Volatile species include dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe). In addition to oxidation state, selenium in water samples is divided into 2 classes: dissolved Se that passes through a 0.45mM filter, and particulate Se (>0.45mM).

Particulate selenium is associated with sediments and other suspended solids. In sediments, selenium may be associated with organic material, iron and manganese oxides, carbonates, or other mineral phases, either adsorbed to or coprecipitated with these phases. Se(II) can be covalently bound to the organic portion of the sediment and other materials to give organoselenides. Two recent reviews of selenium analysis and speciation have been published (Cappon, 1994; Dauchy, 1994).

2.2.2 Sampling and Collection.

Selenium loss by adsorption on the container can be minimized by acidifying to pH 2 with a non-oxidizing acid such as HCl and using 1 liter or larger high density polyethylene or borosilicate glass containers. Se(IV) and Se(VI) in natural waters can be preserved at the 1 μg/L level in pyrex or polyethylene bottles at pH 1.5 (H_2SO_4); acidification with HNO_3 can interfere with the hydride generation process. Determinations should be performed immediately after collection, because organic selenium compounds such as dimethyl selenide are lost within 24 hours. Conversely, organoselenium compounds have been found to increase in concentration due to biological activity; refrigeration can mitigate this process, as well as prevent loss of volatile species.

2.2.3 Analytical Methods.

The basic analytical method for total selenium is generation of the volatile hydride (H_2Se) from Se(IV) using $NaBH_4$, followed by graphite furnace AAS (GFAAS, e.g., EPA Method 200.9, MDL 0.6 μg/L). Watras (1992) describes a scheme for quantitating the different valence states using a differential reduction method followed by a GFAAS finish.

A review of analytical techniques for the speciation of selenium (Olivas, 1994) lists a number of methods for the speciation of different forms of selenium (primarily Se(IV) and Se(VI)), along with the matrices examined and detection levels. Matrices include Milli-Q deionized water, natural waters, ground waters, sediments, and biological materials, with detection levels in the low to sub-μg/L range. Methods include differential pulsed cathodic scanning voltammetry (DPCSV, for selenium in water, 0.04 μg/L), ion chromatography-liquid chromatography (IC-LC) with conductometric detection (in soil extracts, ca. 100 μg/L), molecular fluorescence spectrometry and isotope dilution MS (in natural waters, 5 - 10 ng/L), and liquid chromatography-ICP-AES (in Milli-Q deionized water, 14 - 54 ng/L). A schematic

diagram outlining the preferred analytical separation and analysis methods for selenium speciation is also presented in the above reference.

2.3 CHROMIUM

2.3.1.Species.

There are significant differences in the toxicities of Cr(III) and Cr(VI), with Cr(VI) classified by EPA as a human carcinogen based on studies showing an increase in lung cancer. The adverse health effects of chromium compounds have been reviewed (Cohen, 1993). Cr(III) is considered to be essential for the maintenance of lipid, protein, and glucose metabolism, but Cr(VI) is reported to be toxic due to its facile penetration of biological membranes and its oxidizing potential.

2.3.2 Sampling and Collection.

A number of methods have been used to avoid alteration of the oxidation state during sampling and storage. These include separation of the two forms by solvent extraction or by ion exchange and separate analysis of the fractions, or by coprecipitation techniques. As with other polyvalent species, the use of oxidizing acids or oxidizing/reducing agents in the treatment of collection vessels, etc., is to be avoided.

2.3.3 Analytical Methods

EPA Method 1636 for Cr(VI) consists of isolation of Cr(VI) by ion chromatography, post-column derivatization with diphenylcarbazide, and detection of the colored complex at 530nm, with a claimed MDL of <1 μg/L. Total chromium can be analyzed by EPA Methods 200.8 (ICP-MS, MDL 0.08 μg/L), 200.9 (ST/GFAAS, MDL 0.1 μg/L), and 200.15 (ICP-AES, MDL 2 μg/L).

An automated high performance liquid chromatography (HPLC) method has been reported (Posta, 1993) in which Cr(III) and Cr(VI) are separated by ion pair chromatography followed by AAS detection with high pressure nebulization. This method has been applied to chromium speciation in drinking water, waste water, and soil extracts, with a detection level of 20 - 30 μg/L.

Cr(III) has been detected at the low μg/L levels in estuarine and sea waters via preconcentration on iminodiacetate resin prior to determination by flame AAS (Pasullean, 1995). Concentration on cellulose adsorbents followed by flame AAS detection has been used to speciate Cr (III) and Cr(VI) in tap and surface waters at 0.8 and 1.4 μg/L, respectively (Naghmush, 1994).

Ion chromatography has been used to separate Cr(III) from Cr(VI) using a post-column derivatization method based on the catalytic oxidation of luminol (Beere, 1994), with detection levels of 0.05 μg/L (Cr(III)) and 0.1 μg/L (Cr(VI)) in a simulated fresh water standard reference material. Direct methods that bypass the pre-separation step include fluorimetry of Cr(VI) in the presence of Cr(III) after complexation with a crystal violet-iodine reagent (Hayashi, 1993), and electrochemical techniques. These methods typically allow for detection in the low ppb range for laboratory (i.e., analytical) samples.

2.4 MERCURY

2.4.1 Species

Common forms include inorganic mercuric (II), methyl mercury cation (MeHgX), and dimethyl mercury (Me_2Hg). Humic matter can methylate mercury (Weber, 1993), reduce Hg(II) to Hg^o, and form complexes that EPA considers to be of greater toxicity than the inorganic starting form. Approximately 50 to 90% of total mercury in coastal waters and estuaries is bound to humic matter (Weber, 1988). Because methyl mercury appears to bioaccumulate in organisms, it is of greater concern than other forms of this metal. Several reviews have been published in recent years covering sampling and collection methods (Baeyens, 1992), analytical methods (Puk, 1994), and human health risks (Galli, 1993).

2.4.2 Sampling and Collection

Samples collected for total Hg analysis are usually acidified to a 0.1% HCl concentration to complex Hg and prevent loss through volatilization. The integrity of samples for organomercury speciation can be preserved by freezing without the addition of HCl (Watras, 1992). EPA Method 1631 specifies 125 ml to 1L Fluoropolymer bottles deactivated by a multi-step cleaning process with HCl. After cleaning, the bottles are tightly capped (with a wrench) and double-bagged in new, polyethylene zip-lock bags.

2.4.3 Analytical Methods

EPA claims its Methods 200.8 (ICP-MS) and 200.15 (ICP-AES) have MDLs for mercury of 0.2 and 3 ppb, respectively. EPA Method 1631, using cold vapor atomic fluorescence spectrometry (CVAFS) in combination with stricter contamination control protocols, claims an MDL of <0.0002 μg/L. Again, these MDLs provide only a rough indication of instrumental sensitivity. A typical scheme for the species separation and quantitation of four different mercury fractions has been reported by Watras (1992). Volatile mercury species (Hg^o, Me_2Hg) are determined by purging an untreated water sample through stacked Carbotrap and Au-coated sand. The volatile organomercurials are trapped on the Carbotrap for subsequent analysis of individual compounds by GC and CVAFS detection. Hg^o is trapped on the gold, with quantitation by thermal desorption CVAFS. Total mercury is analyzed by oxidation of all species to Hg(II) by BrCl, reduction to Hg^o by $SnCl_2$, and the resulting Hg^o quantitated by Au adsorption followed by thermal desorption and CVAFS. Methylmercury and Hg(II) are ethylated, the compounds trapped on Carbotrap, and the Hg(II) (as diethyl mercury) and methylmercury (as methylethyl mercury) separated by GC and quantitated by CVAFS.

Hydride generation methods have also been applied to mercury speciation. Hg(II), monomethyl mercury cation (MeHg), dimethyl- and diethyl mercury were determined at levels of from 50 to 110 pg in estuarine marsh grass samples by hydride generation/volatilization, trapping and separation on a GC column, and detection by quartz furnace AAS (Puk, 1994a)

Another scheme for the separation of mercury compounds present in soil and sediments into five different classes has been proposed (Miller, 1995) in which the sample is first divided into toluene- and water soluble fractions, plus insoluble residues. The insoluble fraction is further differentiated into dilute HNO_3 soluble (e.g., HgO), HNO_3 soluble (Hg^o), and

HNO_3/HCl soluble (e.g., HgS) fractions. Mercury-containing fractions in soil were quantitated by ICP-MS at the ppm level.

Inorganic, methyl- and ethylmercury have been analyzed in natural waters (Emteborg, 1993) and biological fluids (Bulska, 1992) at low and sub ng/L levels via preconcentration on a dithiocarbamate resin, followed by extraction, butlylation, and detection by GC-AES.

Speciation of inorganic and methyl mercury in seawater at 0.1 - 0.2 μg/L has been accomplished using HPLC-CVAFS (Aizpun, 1994). Determination of total mercury requires conversion of all forms to Hg(II), and this may involve decomplexation from organic ligands and alkylated forms. Sn(II) or $NaBH_4$ is then used to reduce Hg(II) to Hg^o which can be quantitated by GC/electron capture (Rubi, 1994), or atomic fluorescence (Ritsema, 1994). Speciation of MeHg-X as the hydride (MeHgH) has been accomplished by an acidification/extraction scheme followed by reduction with cysteine (Westwoo, 1967).

2.5 LEAD

2.5.1 Species

The most important organic forms are the tetraalkyl leads (TALs). Researchers have found that these compounds can be readily absorbed by the lungs and also penetrate the skin and biological membranes. They therefore are considered more harmful than inorganic lead. TALs are degraded by sunlight and ozone to trialkyl lead compounds, which are further degraded to inorganic leads via a dialkyllead intermediate.

2.5.2 Sampling and Collection

Adsorption on sample bottles can be avoided by using containers of Teflon or polyethylene that have been acid treated and thoroughly rinsed. In some cases, acid treatment may activate surface sites and lead to adsorption of lead species. Taking these factors into consideration, lead samples should be stored in suitably conditioned containers and analyzed as soon as possible after collection. Samples themselves should not be acidified prior to speciation, as this might change the distribution of lead species.

In addition to the sample containers, another issue is whether or not to filter the samples prior to analysis. Adsorption on particulates is a dynamic process and the distribution between dissolved and adsorbed lead may change with time after the sample is collected. Filtration itself may be problematical, as filtration efficiency for colloidal particles changes depending on the filter load. On the other hand, inhomogeneity of unfiltered samples may lead to errors if care is not taken to assure a uniform sample.

While acidification of samples can lead to speciation changes, samples containing low levels of alkyllead species should be acidified to minimize wall adsorption (Blaszkewicz, 1987). TALs can be extracted from water using organic solvents, with extraction efficiencies significantly higher if the sample does not contain suspended solids. This problem is more severe with filtered samples, since some of the TALs remain on the filter residue.

2.5.3 Analytical Methods

EPA Method 1640 preconcentrates acid-soluble lead using an iminodiacetate functionalized chelating resin to achieve a reported MDL of 0.0081 μg/L. The complex is eluted from the resin using an ammonium acetate buffer at pH 5.5, and determined using on-line ICP-MS. EPA Methods 200.8 (ICP-MS, 0.02 μg/L), 200.9 (ST/GFAAS, 0.7 μg/L), and 200.15 (ICP-AES, 4 μg/L), do not involve preconcentration, and have somewhat higher reported MDLs. The EPA methods are applicable to acid-soluble lead species, and are not suitable for the direct determination of volatile TALs and other acid-insoluble species.

Trapping and concentrating lead species on adsorbent columns allows for its detection at lower levels than if the samples were run directly. Speciation of lead in fresh waters has been accomplished by trapping on three different adsorbents: Chelex-100 (for labile complexes), Sep-Pak C-18 (for non-polar organics) and Fractogel DEAE (for ion exchangeable materials), followed by ICP-MS. Detection levels are in the low ng/L range, while the lead concentration range in fresh waters is 100 - 950 ng/L (Haraldsson, 1993).

A review of the speciation of organolead compound analysis (Lobinski, 1994) details current separation and analysis methods. Ionic organolead compounds in environmental water samples have been extracted as diethyldithiocarbamate complexes into an organic solvent, butylated with a Grignard reagent, and the volatile products detected by GC-quartz furnace AAS or GC-AES . Detection levels of 15 ng/g have been reported for river sediments, and 0.6 - 10 ng/g for soils.

Volatile alkyl lead compounds can be concentrated directly on Porapak and Tenax cartridges and analyzed by GC/MS with selective ion monitoring (Nerin, 1994). Lead-containing particles (Wonders, 1994) have been analyzed for total lead by differential pulsed anodic scanning voltammetry (DPASV), X-ray fluorescence, graphite furnace AAS, and laser microprobe mass analysis.

3. Detection Limits

In Table 1, we have summarized the MDLs stated for EPA's 200 Series and the new 1600-Series methods, plus detection levels for representative methods cited in the literature. The numbers indicate that at least for determining the total metals in a sample, the 1600-series of methods appear at or below the current water quality criteria (WQC) standards. However, it must be emphasized that these new methods have been tested in only 1 to 3 laboratories and may not provide the same low detection levels or reliable results for actual environmental samples with complex matrices. As the EPA transitions toward bioaccumulation risk models which are based on the bioavailability of a particular metal species, these detection levels will require validation as part of a complete metal speciation approach which includes the species-specific separation step.

The literature contains new methods and separation/detection schemes that are being investigated for specific substrates and matrices. While many methods are reported, it is not always possible to meaningfully compare the detection levels for the different analytical techniques because of the different ways detection levels are defined and the different sample matrices examined, e.g., acidic solutions, uncharacterized "natural waters", tapwater,

Table 1
Representative EPA and Literature Cited Analytical Methods

	As	Se	Cr(III)/(VI)	Hg	Pb
EPA WQC[1] (µg/L)	**0.018**	**5.0**	**57/10.5**	**0.012**	**0.14**
EPA "200-Series"					
MDL (µg/L)	**0.1**	**0.5**	**0.08/0.08**	**0.2**	**0.02**
Method No. [2]	200.8	200.8	200.8	200.8	200.8
MDL (µg/L)	**0.5**	**0.6**	**0.1/0.1**	**n/a**	**0.7**
Method No. [3]	200.9	200.9	200.9	200.9	200.9
MDL (µg/L)	**3**	**5**	**2/2**	**3**	**4**
Method No. [4]	200.15	200.15	200.15	200.15	200.15
EPA "1600-Series"					
Technique	Hyd/FAAS[5]	ST-GFAAS	ST-GFAAS /IC	CVAFS	ICP/MS
MDL (µg/L)	**0.002**	**0.83**	**0.10/0.23**	**0.0002**	**0.0081**
Method No.	1632	1639	1639/1636	1631	1640
Literature-Cited Methods					
Technique	Hydride/ AAS	Molec Fluor.	Flame AAS	Hydride/At. fluorescence	Trap/GC-MS
Matrix	Nat'l waters	Nat'l waters	Seawater	Seawater	Air
DL (µg/L)[6]	**0.005**	**0.005**	**5**	**0.001**	**0.7 - 2.6 pg** (TALs)
Reference	Watras	Olivas	Pasullean	Ritsema	Nerin
Technique	Carbamate/ hydride	CZE	Adsorp/ Flame AAS	Adsorp/ GC-ICP-AES	Adsorp/ ICP-MS
Matrix	Nat'l. waters	Tap, spring water	Tap/surface water	Natural. waters	Fresh water
DL (µg/L)	**0.01**	**2**	**1**	**0.001**	**0.005**
Reference	Hasegawa	Li	Naghmush	Emteborg	Haraldsson
Technique	LC/ ICP-MS		IC/Luminol	HPLC/ CVAFS	Extract/ GC-QFAAS
Matrix	Seawater		Fresh water	Seawater	Environ. water
DL (µg/L)	**1**		**0.1**	**0.1**	**1**
Reference	Ding		Beere	Aizpun	Lobinski

[1] Lowest of the freshwater, marine, and human health WQC [Water Quality Criteria] promulgated by EPA for 14 states at 40 CFR Part 131 (57 FR 60848), with hardness-dependent freshwater aquatic life criteria adjusted in accordance with 57 FR 60848 to reflect the worst case hardness of 25 mg/L $CaCO_3$ and all aquatic life criteria adjusted in accordance with the Oct 1, 1993 Office of Water guidance to reflect dissolved metals criteria.
[2] Inductively coupled plasma mass spectrometry in the selective ion monitoring mode
[3] Stabilized temperature graphite furnace atomic absorption spectrometry
[4] Inductively coupled plasma - atomic emission spectrometry
[5] Hydride/flame atomic absorption spectrometry
[6] Detection Level from the reference cited

seawater, biological samples, etc. In addition, some authors report sensitivity in absolute amounts rather than concentrations, making comparative data more difficult to interpret.

4. Conclusions

The EPA has proposed a variety of unvalidated (i.e., no interlaboratory confirmation) analytical methods for total metals that reportedly have detection at or below the current EPA Water Quality Criteria (WQC) levels. However, it is recognized that the biotoxicities of all metal species are not the same, and that future WQC requirements may require speciation in addition to total metals. The literature cites a variety of separation steps combined with different detection techniques to speciate metals at low concentrations. At present, neither the EPA nor the literature methods have been validated in different matrices of environmental concern or in interlaboratory tests, so their performance in real-world matrices is unknown. Factors that must be taken into account in a validation program include sampling, sample preservation, general laboratory cleanliness, specificity, detection levels, ease of use, potential interfering compounds or substances, and cost effectiveness. The candidate methods should be evaluated by a single laboratory using typical utility matrices to screen out those methods not robust enough for the utility environment. A formal procedure can then be proposed for the selected method(s), followed by validation by multiple laboratories using several utility matrices.

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