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Journal of Chromatography A, 774 (1997) 3–19

JOURNAL OF CHROMATOGRAPHY A

Review

Chromatographic and hyphenated methods for elemental speciation analysis in environmental media

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Abstract

This review discusses chromatographic techniques that permit the analysis of speciated metals in the environment using conventional detectors, such as UV, and element-specific detectors, such as flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry. The importance of determining precise elemental forms in hazardous waste-contaminated soil, water and biota in terms of toxicity is outlined. Previous reviews on this subject are described and recent research on this subject is discussed. Most of the work cited has been performed in the 1990s and a table summarizing the chromatographic method and the detector system used, including brief comments on the work, is included to enable quick reference. © 1997 Elsevier Science B.V.

Keywords: Reviews; Metal speciation; Hyphenated techniques; Water analysis; Environmental analysis; Detection, LC; Detection, GC; Soil; Metals; Organotin compounds; Metallothioneins

Contents

1. Introduction

Definitions of hazardous waste vary considerably and often include many exceptions, omissions and qualifications, necessary to satisfy the legal requirements of a particular country. In this review, hazardous waste will be defined in general terms as waste that is likely to cause harm to the environment, regarding effects on health, surface water, soil and biota. Tests capable of assessing effects of a particular chemical on health and the environment have been developed by the US Environmental Protection Agency (EPA) and consider the following four

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0021-9673/97/$17.00
PII S0021-9673(97)00325-7

characteristics: Ignitability, corrosivity, reactivity and toxicity [1].

Hazardous waste is highly variable in composition and is dependent on its source, but major categories are as follows: Inorganic aqueous waste, organic aqueous waste, organic liquids, oils, inorganic sludges/solids, organic sludges/solids and radioactive waste. The problems of disposing of this material arise because of it's inherent toxicity and the vast quantities produced every year, for example, in 1990, countries involved in the Organisation for Economic Co-operation and Development (OECD) produced $1.5 \cdot 10^9$ tons of industrial waste, which includes $300 \cdot 10^6$ tons of hazardous waste.

Hazardous waste can be disposed of, or treated, in a number of ways, depending on its composition and economic aspects. Incineration is very effective at destroying toxic organic fractions but can result in contamination of surrounding land with metal pollution from deposition of the plume. Incineration is also often economically unfavourable and results in an ash which requires disposal. Composting is another option and has the added advantage that the end product can be sold. If the waste contains a high metal content, the uses for the compost can, however, be severely restricted. Recycling is also being used to treat some wastes on an increasing scale and is environmentally and often economically favourable. The main method of disposal or containment of hazardous waste at present is landfill. In the European Union (EU), 70% of municipal waste is disposed of by this method and it is the analysis of metal contaminants arising from such sites that will be covered in this review. Such sites, if not properly managed, pose significant risks to the surrounding environment. The soil used to cap landfill sites readily becomes contaminated and wind blow of this soil can occur, polluting nearby areas. Acid rain or water made acidic by simply passing through the landfill can leach a cocktail of pollutants, including dissolved metals and organometallics, which can pollute streams and surrounding land. Metals in the run-off can become associated with soils via ion exchange and adsorption processes. Plants growing in such soils can take up organometallic elements both passively and actively and these, in turn, can poison local animal populations. Metals that are organically bound, such as methylmercury, have the potential to bio-accumulate and the EU classifies compounds with a bioaccumulation factor (BCF) greater than 100 as having the potential to bioaccumulate and to be 'dangerous to the environment' [2]. Although pollutant concentrations close to a hazardous waste site can be significantly elevated compared with unpolluted sites, the problems associated with analysis are essentially those relevant to trace analysis of soil, run-off and biota in general. From the literature search that has been carried out, it was found that very few references concern the analysis of speciated forms of metals at hazardous waste sites, but are, instead, largely concerned with analysis of the environmental compartment that may have been contaminated, i.e. soil, water, biota. Therefore, in this review, techniques will be discussed that have been used to determine speciated metal concentrations in such compartments. Literature that is specifically concerned with hazardous waste sites is primarily concerned with management and engineering aspects. This has not been included in this review due to the nature of the journal, but, if such aspects are of interest, a very good book has been written by LaGrega et al., entitled Hazardous Waste Management [3]. Reclamation and treatment of contaminated land has been covered by Smith [4]. Information regarding the testing of industrial solid waste can be found in Quality Control in Remedial Site Investigation [5] and Hazardous and Industrial Solid Waste Testing [6], however, although these are useful for many survey problems, they contain very little information on elemental speciation.

Determination of the total concentration of an element in an environmental compartment is important. For example, water quality guidelines set maximum permissible levels for individual elements. Techniques such as flame atomic absorption spectrometry (FAAS) [7,8], electrothermal atomic absorption spectrometry (ETAAS) [9,10] and inductively coupled plasma mass spectrometry ICP-MS [11,12] are all capable of performing this task in conjunction with total sample dissolution. It is, however, often desirable to determine the precise form the element is in, as this can effect its mobility, bio-availability and toxicity. Metals in the environment can become inorganically bound, especially if the pH is high; reducing their bio-availability and their toxicity. Metals may pose the greatest threat to

health when they are organically bound, as these forms have greater bio-availability and often greater residence times in the organism. Metals can be discharged directly to the environment in an organic form, e.g. tetrabutyllead and -tin and methylmercury, or they can become methylated naturally by the action of bacteria. In a landfill site, mercury compounds may become methylated to mono- or dimethylmercury, particularly if the pH is low. The half life of methylmercury compounds in the human body is approximately 70 days [13], which is longer than that of the inorganic salt, enabling higher levels to accumulate in the body. Other elements that may become methylated in the environment are Co, Se, Te, As and Pb. There is some evidence of biomethylation of tin, but organic forms of this element can be found at landfill sites, as dialkyltin^{4+}, used as a stabiliser in polyvinyl chloride, and trialkyltin^{4+} compounds, which are used as biocides. It is also important to determine the inorganic form of an element, as this can also effect toxicity. For example, Cr^{6+} is more toxic than Cr^{3+} and As^{5+} is more toxic than As^{3+}, as it is retained in the body longer because it becomes bound to sulphydryl groups. For these reasons, it is important to determine the form in which the element is present. As conventional atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) techniques etc. cannot identify the form, when used on its own, hyphenated techniques have been developed that combine chromatographic separations with element-specific detectors. It is these techniques that will be emphasised in this review, although a number of chromatographic methods that employ more traditional detectors are also included.

2. Problems of coupling techniques

Combining chromatographic techniques with atomic detectors produces very powerful instruments for performing speciation analysis. These combinations of equipment, that were never designed to be coupled, are, however, not without their problems. It appears from the literature that most hyphenated techniques for inorganic determination rely on liquid chromatography for the separation stage. The main reason for this is that many of the organometallic complexes are non-volatile and, therefore, have to be derivatised prior to gas chromatographic determination [4,15]. With all such procedures, there is a risk that contamination can be introduced. The samples that are to be analysed must also be thermally stable and not break down at oven temperatures. The transfer lines linking the two instruments will also need to be heated in order to prevent condensation of the analyte. Care must also be taken to ensure that there is no dead volume or cold areas in these lines. Gas chromatography (GC) has, however, been used for a limited number of determinations and can offer some advantages over liquid chromatography. FAAS or ICP instruments generate atoms using what are essentially gases (flames or plasmas). The gas stream emerging from the GC can be readily introduced, as it is itself a heated gas. Combination of a GC with a FAAS can overcome some of the problems associated with the comparative insensitivity of the flame system. The nebuliser of a FAAS system is only around 10% efficient and, if the gas emerging from the GC can be introduced by-passing the nebuliser, an increase in sensitivity can be achieved. FAAS will not, however, be as sensitive as ETAAS because of the shorter residence times of the atoms in the flame. GC is also well suited for combination with ICP-MS [6], as this also uses a nebuliser uptake. Gains in sensitivity can be achieved, although this is not so important a consideration with ICP-MS, as it has inherently very high sensitivities. Combination of a GC method with ETAAS is more problematic due to its non-continuous mode of action. The most common way of overcoming this problem is to introduce the sample into the graphite cuvette, which is held at the atomisation temperature for the entire time of analysis. Although this is effective, it significantly reduces the lifetime of the graphite cuvette. An alternative, but less straightforward, technique is to condense the gas before transferring it to the cuvette. The literature shows that coupling liquid chromatographic (LC) techniques to AAS instruments is a far more popular technique than the use of GC. Combining LC and AAS does, however, present more of a challenge than GC–AAS. Directly coupling the outlet from the LC column to a FAAS system will result in reduced sensitivity because it is unlikely that the output from the LC system will match the

uptake rate of the FAAS system. In addition, dilution of the analyte in the mobile phase of the LC system will also reduce sensitivity, as will any band broadening during transport to the FAAS system. Ebdon et al. [17], in a review paper, discussed ways in which LC systems could be connected to FAAS, ETAAS, flame atomic fluorescence spectrometry (FAFS) and optical emission spectrometry (OES). These problems of reduction in sensitivity apply equally to ICP techniques, although this is a less important consideration in ICP-MS due to its very low detection limits. This has also been extensively covered in a review by Hill et al. [18]. The eluent from the LC instrument may be rich in organic constituents and these can cause further problems when connected to a plasma instrument. Organic solvents can adversely effect the stability of the plasma, deposit soot on the faces of the sampler and on the skimmer of a MS instrument, resulting in increased noise and varying responses. Organic solvents can also produce high reflected powers that can result in generator cut-off. The nebuliser can also become blocked if the solvents contain high concentrations of salt. This can be overcome by nebulising solutions of HNO_3 after each run, if required. The problem of organic solvents entering the plasma can be overcome by reducing the quantity of solvent reaching the plasma by employing micro LC separations [18] or by increasing the amount of O_2 in the plasma gases, although this significantly reduces the lifetime of the skimmers and of the sampler.

3. Previous reviews

There have been a number of recent reviews regarding the analysis of speciated metals by chromatographic methods. These contained varying amounts of detail on the application of techniques to environmental systems but are nevertheless useful in that they contain critical discussions on the use of various techniques, which may then be applied, when they are used for real samples. These reviews tend to fall into two main categories; those that discuss the analysis of a specific element by a particular technique and those that discuss techniques that are used to analyse a range of metals.

A useful review for information regarding the determination of organotin species in water and sediment was compiled by Dirkx et al. [19]. This work discusses the use of GC with optical spectrometric detection, i.e., AES, flame photometric detection and includes a critical discussion of various extraction methods that are in use. Fairman et al. [20] have compared various methods for the determination of labile aluminium species in natural waters. The inter-laboratory comparison concluded that the standard Driscoll PCV [21] method was effective at determining labile aluminium species and recommended that ETAAS detection should be used. They also recommend that high density polyethylene containers should be used for long-term storage and that the pH should be kept low to avoid losses by precipitation of volatile aluminium hydroxy species. A comprehensive review on the speciation of metals and organometallics in environmental samples using ethylation derivatisation by sodium tetraethylborate (STEB) has been written by Rapsomanikis [22]. A number of references are included that demonstrate the applicability of GC–AAS and GC–MS. It is, however, the ethylation step that is covered in most detail. It was concluded that STEB was an effective derivatisation agent for Pb, Hg, Cd, and that ethylation of Sn using STEB may be preferable to hydride generation because it does not suffer from foaming and critical interferences. A useful review for speciation analysis with atomic spectrometry techniques has been written by Sanz-Medel [23]. It contains a discussion of the pros and cons of connecting chromatographic equipment to atomic detectors. The review does, however, lack detail on the application of these techniques to environmental systems and concentrates mainly on human serum. Vela and Caruso [24] have assessed the potential of coupling liquid chromatographic equipment to ICP-MS. The chromatographic techniques discussed are reversed-phase liquid chromatography (RPLC), ion-pair chromatography (IPC), micellar LC, site-exclusion chromatography (SEC) and supercritical fluid chromatography (SFC). Van Loon and Barefoot [25] have presented an 'Overview of analytical methods for environmental analysis' covering 1986–1990. Analysis for individual metals are discussed in turn. This review also contains a useful discussion on various interface devices that are required to couple chromatographic and atomic detectors. Another review

that contains a discussion of interface designs is that by Chau [26]. In addition, various coupled techniques are discussed and their detection limits quoted. In two less recent papers by Ebdon et al. [17,27], the coupling of high-performance liquid chromatography (HPLC) and GC, respectively, to atomic instruments for metal speciation have been covered. These are included due to their exhaustive list of references on these techniques to that date. For information on chromatographic determination of metals prior to these reviews, it is worth examining a publication by Nickless [28] that contains almost 250 references.

As a consequence of the very large number of techniques and combination of techniques available to determine speciated forms of heavy metals in the environment, each of the techniques will not be discussed in turn. Instead, the review will be divided up into the determination of speciated metals in soil, leachate and biological material. As a result of this, identical techniques may be discussed in each section, although an attempt will be made to keep this to a minimum. A table is also included that describes analytes that have been studied, together with the chromatography system and detector used, and this is intended to enable quick reference. The table includes all of the references that have been discussed in the text (except for review articles) and additional references to work that may not have been applied to environmental samples but which is potentially applicable to environmental speciation problems (see Table 1 Table 2 Table 3 Table 4).

3.1. Water

Urasa et al. [29] demonstrated how an ion chromatograph could be used in conjunction with a d.c. ICP-AES instrument to study the solution chemistry of Fe, Mn, P and Pt. They found that ICP-AES was an ideal multielement detector that suffered few interference effects. Ion chromatography (IC) coupled to AES was also used by de Beer and Coetzee [30] to examine V speciation. The IC method involved using a carbonate buffered 1,2-cyclohexylenedinitrilo tetraacetic acid eluent. V^{4+} was separated from V^{5+} by anion-exchange chromatography. Detection limits were estimated to be 145 and 70 ng ml^{-1} for V^{4+} and V^{5+}, respectively. Vanadium speciation, together with Ni and Cr, has also been investigated by Tomlinson et al. [31] using (IC)–ICP-MS. They found that the system worked well for Cr and Ni, but the exact structures of V^{4+} and V^{5+} could only be identified by electron paramagnetic resonance or X-ray diffraction due to its complicated solution chemistry. Research regarding Cr speciation in water was reported by Inoue et al. [32], who used IC coupled to ICP-MS.

Ethylenediaminetetraacetic acid (EDTA) was used to chelate Cr^{3+} and Cr^{6+}, which were then separated using IC. Excelpak ICS-A23 was used, which is a hydrophilic polymer-based anion-exchange resin and EDTA ioxalic acid was used as the mobile phase.

Separation was complete within 8 min and detection limits were $8.1 \cdot 10^{-5}$ and $8.8 \cdot 10^{-5}$ ppm, respectively, with a quoted R.S.D. of 2.5. Detection limits of 4.5 and 1.5 mg ml^{-1} for Cr^{3+} and Cr^{6+}, respectively, were reported by Pobozy et al. [33] who used IC separation together with post column reaction of the Cr species with diphenylcarbizide. Although the method performed well, it was admitted that the sensitivity is not as good as that achievable with chemiluminescence [34,35] or ICP-AES/MS [36,37]. Interference problems were also encountered with 20 ppm Mg and 50 ppm Ca. Arsenite and arsenate were analysed by IC with electrochemical detection for As^{3+} and with spectrophotometry for As^{5+} by Li et al. [38]. Colour development was achieved using the reaction between heteropolymolybdoarsenic and bismuth in the presence of Triton X-100. The detection limits were found to be 2.9 μg l^{-1} for As^{3+} and 13 μg l^{-1} for As^{5+}. Spiked waste water samples were examined and recoveries ranged from 93 to 104%. In the papers on ion-exchange techniques described so far, very little has been said regarding possible interference effects. Recently, Vasconcelos and Gomes [39] examined the effect on recovery that various chelating agents likely to be present in an environmental sample may have on metal ions. The chromatographic system used consisted of an Ion-PAC CS5 column with 2,6-pyridinedicarboxylic acid (PDCA) on column derivatisation. Post-column colour development was accomplished with 4-(2-pyridylazo)resorcinol (PAR). The chelating agents examined were citrate, nitrilotriacetic acid (NTA), EDTA, cyclohexylenediaminetetraacetic acid

Table 1
References related to water analysis

Analyte	Chromatography	Detector	Comments	Reference
Se species	GC	ICP-ID-MS	Detection limit of 0.02 ng ml^{-1} for selenite	[16]
Species of Fe, Mn, P and Pt	IC	ICP-AES	ICP-AES was found to suffer very few interferences	[29]
V speciation	IC, carbonate buffered 1,2-cyclohexylenedinitrilo tetraacetic acid eluent	AES	Detection limits of 145 and 70 ng ml^{-1} for V(IV) and V(V), respectively	[30]
V^{4+}, V^{5+}, NI^{2+} Cr^{3+}, Cr^{6+}	Dionex HPLC-CS5 column with lithium hydroxide–2,6-pyridine dicarboxylic acid as the eluent	ICP-MS	Effect of varying pH, mobile phase and ionic strength was examined	[31]
Cr^{3+} and Cr^{6+}	IC, Excelpak ICS-A23 column. EDTA–oxalic acid used as the mobile phase	ICP-MS	Detection limits of $8.1 \cdot 10^{-5}$ and $8.8 \cdot 10^{-5}$ ppm, respectively	[32]
Cr^{3+} and Cr^{6+}	Anion exchange with phthalate as the mobile phase	PC reaction with diphenylcarbizide	Sensitivity not as great as with chemiluminescence or ICP-AES/MS detection	[33]
As^{3+} and As^{5+}	IC	Electrochemical and spectrophotometric detection. Reaction between heteropolymolybdoarsenic and bismuth	Detection limits of 2.9 and 13 $\mu l\ l^{-1}$, respectively	[38]
Cu^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+}	Ion-PAC CS5 column with PDCA derivatisation	PC reaction with PAR	Examined the interference effect of chelating agents on recovery	[39]
Species of Cu and Pb	Silica and C_{18}-bonded columns	ETAAS	A heated microcolumn manifold was employed	[41]
Species of Cu, Cd, Pb and Mn.	C_{18} RP, Dowex anion-exchange and Chelamine columns used	ETAAS	The system showed very good reproducibility, even in complex media.	[42]
Heavy metal complexes	HPLC	ICP-ID-MS	A reliable, sensitive technique that is free form organic interference	[43]
Pb speciation	Cellex 100, Spheron oxin, Amberlite XAD-2, C_{18} and cellulose sorbents modified with phosphoric acid and carboxymethyl groups	FAAS	Cellulose sorbents were found to have the best retention characteristics	[44]

Table 1 (*continued*)

Analyte	Chromatography	Detector	Comments	Reference
Sb^{3+}, Sb^{5+}	HPLC, Hamilton PRP-X100 with phthalic acid as the mobile phase	HGAAS–ICP-MS	Very efficient sample transfer to the plasma. Largely free from interferences, the method was applied to waste water samples	[46]
Organotin and organo-germanium	On-column cGC	FPD	Detection limits ranged from 0.2–2.3 pg for ethylated, butyl- and phenyltin and 50–100 pg for germanium complexes	[47]
Tributyltin	On-column cGC	FPD	TBT recovery of 90% for aquatic matrices	[48]
As^{3+} and As^{5+}.	Extraction chromatography	FAAS and ETAAS	Waste waters from a metallurgical plant were studied	[49]

(CDTA) and the elements studied were Cu^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+}. They achieved 100% recovery for all metals in the presence of citrate and NTA, and for Cu, Zn and Mn with EDTA. Only 68% recovery was achieved with EDTA present and <20% recovery was obtained with CDTA. The reduction in recovery was thought to be due to kinetic factors. This work has obvious implications for metal determination using IC for environmental samples when naturally occurring chelates are likely to be present. Korte and Fernando [40] have discussed how As^{3+} determination reported in the literature may be inaccurate because of incorrect preservation and storage and how, as a result, quoted As^{3+} concentrations may be systematically underestimated. Levels of Cu and Pb species in the ppb range have been determined by Atallah et al. [41] who used silica and C_{18}-bonded columns together with ETAAS detection. A micro-column manifold system is also described that allows automatic delivery of the eluent to a heated graphite atomiser. A three-column system consisting of a C_{18} RP, a Dowex anion-exchange resin and Chelamine chelating resin is described by Groschner and Appriou [42] for the speciation of Cu, Cd, Pb and Mn. The detector was an ETAAS fitted with an auto-sampler with which, presumably, the fractions were collected. The system showed very good reproducibility even in complex media. A reliable method for speciation analysis and sensitivity in the pg ml^{-1} region has been proposed by Heumann et al. [43]. This involved the coupling of a HPLC system with ICP-isotope dilution mass spectrometry (ID-MS). It was found that the ID technique effectively eliminated interference effects from organic matter. Gallus and Heumann [16] have also developed a GC–ICP-ID-MS instrument that enables accurate determination of volatile element species. They initially used the instrument for the analysis of Se. In their method, selenite is converted to volatile piazselenol. Selenate is determined after conversion to selenite. A 62%-enriched ^{82}Se spike solution was used for the isotope dilution step and the ratios of ^{77}Se–^{82}Se and of ^{78}Se–^{82}Se were used for quantification. Using this method, selenite was determined in water and the detection limit was found to be 0.02 ng ml^{-1}. In this paper, ID-MS is described as the internationally accepted definitive method for speciation analysis. Naghmush et al. [44] have studied lead speciation using a flow injection technique and a FAAS detector. The chelation columns examined were chelex 100, spheron oxin 1000, amberlite XAD-2 modified with pyrocatechol violet, C_{18} sorbent non-modified and modified with pyrocatechol violet or 8-quinolinol and cellulose sorbents with phosphoric acid and carboxymethyl groups. The functionalised cellulose sorbents were found to have the best

Table 2
References related to soil and leachate analysis

Analyte	Chromatography	Detector	Comments	Reference
Al speciation	IC	Fluorescence detection. PC reagent was 8-hydroxyquinoline-5-sulphonic acid–cetyltrimethylammonium bromide	Al species detectable at 5 n*M* and the method was applied to soil extracts	[52]
Cr^{3+} and Cr^{6+}	Chelation ion exchange and IC	Photometry	The reliability and reproducibility of results for a number of techniques was examined	[53]
Cr^{3+} and Cr^{6+}	Chelation IE	ETAAS	Clay, peat and sandy soils contaminated with tannery waste were tested	[54]
Cu and Cr fulvic acid complexes	GPC	IR speciation	Complexation capacities and stability constants were calculated	[55]
Al, Mn and Fe complexes	SEC, Fractogel TSK HW-40(S)	UV and ICP-AES	Al, Fe and Mn were found complexed to organic ligands	[56]
Hg species	HPLC	AFD	Area of contaminated land studied	[57]
Al and hydroxy forms	Chelation ion-exchange chromatography	ICP-AES and 8-hydroxyquinoline method	The two detection systems were compared	[59]
Metallo–cyanide complexes	IC, C_{18} column	UV (214 nm)	Cyano complexes of Cu, Ag, Fe and Au were determined	[60]

retention characteristics. Cellex P performed the best and elution with fractions of nitric acid and ethanol allowed differentiation between tetraalkyl and inorganic lead.

Information in the literature regarding determination of the various redox states of antimony is quite scarce, but quantification of the different valency states is important as trivalent Sb is up to ten times more toxic than pentavalent complexes of Sb. In addition, inorganic species are more toxic than organic species [45]. Usually when such determinations are performed, total antimony is determined and Sb^{5+} is calculated by difference. A method has, however, been proposed by Smichowski et al. [46] that enables the direct determination of Sb^{3+} and Sb^{5+}. The researchers investigated the coupling of HPLC using a Hamilton PRP-X100 anion-exchange column with phthalic acid as the mobile phase to a hydride generation atomic absorption spectrometer (HGAAS), ICP-MS and, finally, combined all three, i.e. HPLC–HGAAS–ICP-MS. This three-stage instrument was found to have the advantage of almost 100% efficient sample transport to the plasma, with a corresponding increase in sensitivity. The interference study showed the determination to be free from interferences from the hydride-forming elements As, Se, Bi and from Hg, Ca, Fe and Ni, all of which were present at 5 ppm. This was attributed to the

Table 3
References related to the analysis of biological material

Analyte	Chromatography	Detector	Comments	Reference
Tributyl- and triphenyltin	GC with Grignard derivatisation	FPD	Method was successful for TBT, but analysis of triphenyltin was more problematic	[65]
Pb^{2+}	GC	ID-MS	Methods applicability to biological samples is discussed	[66]
Cd–metallothionein	HPLC, elution with linear gradient of Tris buffer	AAS	Detection limit of 5 μg g^{-1} was achieved	[67]
Zn^{2+} and Cd–metallothionein	HPLC	FAAS	New design of thermospray nebuliser was assessed	[68]
Species of Co, Cu, Ni, Fe^{2+} and Fe^{3+}	High-speed counter-current chromatography	DCP–AES	Each element was well resolved at high partition efficiencies	[69]
Protein bound Al and Fe	HPLC	ETAAS	Method was sensitive and accurate	[70]
Se–metallothionein	HPLC	ICP-MS	No difference was observed in the uptake of selenate and selenite	[71]
Species of Al and Si	Polymeric anion exchange, Protein-Pak DEAE-5PW	ETAAS	Speciation in human serum was examined	[72]
Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+}	Ion-exchange chromatography	Co used as the internal standard	Detection limits of around 1 μg g^{-1} for each element	[73]
Se	SEC	ICP-MS	Body distribution of Se was examined	[74]
Cu^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} chelates	RPLC, C_{18} column with acetonitrile–sodium acetate as the mobile phase	Electrochemical detection	Waste water and biological samples were analysed	[75]
Se speciation	HPLC	UV/DCP	Plants, shellfish and food supplements were determined	[76]
Zn and Cd speciation	GPC	ETAAS	Speciation in cytosols was studied	[77]
Cd–Zn complexes	GFC and HPLC	–	Concluded that phytochelatin sequestration of Cd, Zn does occur in Cd- or Zn-contaminated crops	[78]

Table 4
General references on analysis of speciated forms

Analyte	Chromatography	Detector	Comments	Reference
Butyltin species	GC, derivatisation with sodium tetraethylborate	ETAAS	River sediment was examined. Detection limits of 0.08, 0.34, 0.11 ng of tin for mono-, di and trbutyltin, respectively	[14]
Cr^{3+}, Cr^{6+}	GC, derivatisation with trifluroacetylacetone	ETAAS	Precision was found to vary from 3.8–1.4% for 2.5–25 $\mu g\ l^{-1}$ of Cr(VI), respectively	[15]
SeO_3^{-2}, SeO_4^{2}	Affinity chromatography (AC) and SEC	ICP-MS	Detection limit of 0.5–3 pg	[79]
Mn^{2+}, Co^{2+},Ni^{2+} Cu^{2+} and Zn^{2+}	Anion exchange, cetylpyridinium chloride on RP	UV–Vis is at 520 nm with PAR	Investigated metal oxolate complexes	[80]
Complexes of As, Pd, Ga, Se, Fe	CE, CZE, isotachophoresis, isoelectric focusing	UV	General discussion on the chromatographic techniques and their applicability to ecological media	[81]
AsO_3^{2-}, SeO_3^{2-}, AsO_4^{3-}, VO^{3-}, Se_4^{2-}, WO_4^{2-} CrO_4^{2-}	Non-suppressed IC, potassium phosphate as the eluent	UV (205 nm)	Accuracy of results compared to AAS techniques. River water was examined	[82]
Metallothionein bound Cd, Cu, Zn	SEC, Progel-TSK 3000PW eluted with trishydroxymethyl methylamine buffer	AAS	Supercritical fluid extraction with CO_2 was used. Analytes isolated from rabbit liver	[83]
Se^{4+}, Se^{6+} plus a variety of other elements	CE	ICP-MS	A direct injection nebuliser enabled ppt-to-ppb sensitivity	[84]
Metallothionein and ferritin bound Cd and Fe	CE, ATI Unicam Crystal 300	ICP-MS	Detection limits: Fe, 57184 fg and Cd, 4.0 fg	[85]
Cr^{3+}, Cr^{6+}	HPLC microbore column	ICP-MS	Detection limit was 3 pg for both species	[86]
Trimethyl and triethyllead	LC, C_8, CH_3COOH^- CH_3COONH_4 in methanol mobile phase	HG–ICP-MS	Sensitivity, reproducibility was better than those of a LC–ICP-MS system	[87]
Organically bound Al, Fe and Cu	SEC, mobile phase ammonium acetate	UV–ICP-MS	Metal organic association in soil leachates was studied	[88]

Table 4 (*continued*)

Analyte	Chromatography	Detector	Comments	Reference
V^{4+}, V^{5+}	Chelating functional group, immobilized silica gel	ICP-AES	Recovery was better than 98%. V speciation studied in natural waters	[89]
Methyl and inorganic Hg	CGC, non-polar column	Microwave induced plasma (MIP)–AES	Mercury concentrations in whole blood examined	[90]
Fe and Cu species	Flow injection analysis	Double beam spectrophotometer	Sample throughput: 30 samples h^{-1}	[91]
Species of Al, Cd, Co, Cu, Fe Pb, Mn, Mo, Ni and Zn	Chelex 100, Sep-Pak C_{18}, Fractogel DEAE.	ICP-MS	Method distinguishes between labile complexes, non-polar organic absorbable matter and ion-exchangeable substances	[92]
Organotin	Cryogenic trapping GC	AAS	Interferences were found to be a problem and the reasons why are discussed	[93]
Fe^{2+}, Fe^{3+}	Flow injection (FI), uses a C_{18}-modified silica column	FAAS	Fe^{3+} passes straight to detector, whereas Fe^{2+} is trapped as Fe^{2+}–ferrozine and then eluted with methanol	[94]
Cu^{2+}, Cd^{2+}, Pb^{2+} and Mn^{2+}	C_{18} RP, Dowex anion exchange, Chelamine	ETAAS	The analysis can be performed without pre-treatment, thus equilibria are unaltered	[95]
Al species	Flow injection analysis, reaction of Al with oxine	ETAAS	Sample throughput was 10 h^{-1}. Fe interference was masked	[96]
As, Pb species, inorganic elements	CE	Proton-induced X-ray emission	The potential for lowering the detection limits is discussed	[97]
Sr^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}, Fe^{3+}	CE	–	Investigation into metal aquatic fulvic acid complex behaviour	[98]
Seven As species	IC–HPLC	FAAS	Entrained Ar–H flame was used, together with a slotted tube atom trap. Polluted soil samples were analysed	[99]

(*continued on p. 14*)

Table 4 (*continued*)

Analyte	Chromatography	Detector	Comments	Reference
Cr^{3+}, Cr^{6+}	FI, microcolumn packed with acid alumina	FAAS	Recovery of 90–106% for natural waters	[100]
Se^{4+}, Se^{6+}	IC, KHP saturated with Ni(OH) as the mobile phase	FAAS/GFAAS	Detection limits of 0.6 ng for selenate and 1 ng for selenite with FAAS detection	[101]
Organic As complexes	RP-anion exchange with benzenesulphonates as ion-pair agents	FAAS	Arsenite and methylarsonic acid could not be separated	[102]
Zn, Pb, Cr	Affinity and gel filtration chromatography	ETAAS	The design of an ultrasonic nebuliser for interfacing LC and ETAAS is discussed	[103]
As and As^{3+}	HPLC, C_{18} column	ETAAS	Results agreed well with certified reference material	[104]
Alkylselenides	GC	ETAAS	The method was applied to organic vapour-phase selenium in soil	[105]
As species	Generation of arsine in FI system by the Fleitmann reaction	ETAAS	Detection limit was 10 pg of arsine. Various water samples were analysed	[106]
Se species	Anion-exchange ammonium citrate as the eluent	ETAAS	Detection limits of 1.67, 1.27 and 0.76 for trimethylselenium, selenite and selenate, respectively	[107]
As species	IC, $NH_4H_2PO_4$ mobile phase	ETAAS	The As species were trapped on a palladium-coated tube	[108]
Organotin complexes	Hydride generation GC	ETAAS	Detection limits ranged from 30–130 pg, depending on the species	[109]
Organically bound Al	SEC, a sucrose column and acetate as the mobile phase	ETAAS, UV post column reaction with pyrocatechol violet polymeric form	Results indicated that inorganic Al was present in a polymeric form	[110]

ability of the HPLC stage to effectively separate Sb from the matrix. The method was employed on various water samples, including industrial and municipal wastewaters. Jiang et al. [47] have analysed water and sediments for organotin and organogermanium compounds using on-column capillary GC (cGC) with flame photometric detection. Detection limits ranged from 0.7–2.3 pg for ethylated butyl- and phenyltin compounds and from 50–100 pg for pentylated dimethyl-, trimethyl- and

tetrabutylgermanium compounds. A comparison of butyltin determination was made with GC–AAS for water. The method proved to be 'simple, highly sensitive and reproducible'. Tributyltin (TBT) speciation in aquatic matrices has also been studied by Tolosa et al. [48]. In this method, TBT was extracted as the chloride using HCl followed by liquid extraction. Grignard derivatisation was then performed and the organotin fraction was isolated from the derivatised fraction by column chromatography. The TBT was then determined by on-column cGC with flame photometric detection. MS was used to confirm the results. TBT recovery was found to be around 90% for water samples. Arsenic^{3+} and arsenic^{5+} were analysed by Russeva et al. [49] in waste waters from a metallurgical plant and potable water from the same region. Recoveries were in the range of 85–115% and the method used was extraction chromatography followed by AAS detection using FAAS and ETAAS. In this method, the sample was adjusted to pH 3.5 and passed through a chromatographic column that was filled with support material modified with $(C_8H_{17})_2SnCl_2$. Arsenate is quantitatively retained whilst arsenite is not. Arsenate can then be removed from the column by HCl and both fractions quantified by AAS.

3.2. Soil and leachate

A useful article for those interested in determining speciated metals in soils and sediment has been written by Tack and Verloo [50]. Techniques covered include chemical extractions, ion exchange/gel chromatography, filtration, centrifugation and selective solvent extraction. The article also includes a discussion on the value and limitations of speciation and fractionation techniques. Another useful review has been written by Das et al. [51], who discussed metal speciation in solid matrices. The various pretreatment methods required for analysing solid materials have been highlighted. Instrumental techniques for characterising the various species have been outlined and are reported in terms of detection limits, precision and accuracy. The determination and speciation of aluminium in soils has been studied by Gibson and Willett [52], who used fluorescence detection and ion chromatography. The post-column fluorescence reagent was a mixture of $4 \cdot 10^{-3}$ *M* 8-hydroxyquinoline-5-sulphonic acid and $2 \cdot 10^{-3}$ *M* cetyltrimethylammonium bromide in a 1-*M* acetate buffer, pH 4.4. Aluminium species were said to be detectable at 35 n*M* and the method was applicable to soil solutions and extracts. The interference effects of nine metals were evaluated and only Zn^{2+} and Cd^{2+} were found to give responses. The technique was also said to be more sensitive than existing colorimetric methods. Various methods for analysing Cr^{3+} and Cr^{6+} in blue shavings were evaluated by Milacic et al. [53]. Blue shavings have a protein base matrix with a high Cr^{3+} and organic polymer content. This work was undertaken to ensure that the blue shavings did not have a high content of Cr^{6+}, which could pose a hazardous waste problem. Ion-pair reversed-phase HPLC with FAAS or ETAAS detection was found to be severely effected by matrix effects arising from the organic polymers and high salt content of the buffers and extractants. Chelation ion-exchange and IC overestimated the Cr^{6+} concentration because of incomplete retention of Cr^{3+}. Finally, reliable and reproducible results were achieved by spectrophotometry with the addition of diphenylcarbazide, which gave a detection limit of 2 ng ml^{-3}, while extraction of the Cr^{6+} into methyl isobutyl ketone (MIBK) gave a poorer detection limit of 15 ng ml^{-3}. Cr^{3+} and Cr^{6+} was also determined by Kozuh et al. [54], who used chelation ion-exchange with ETAAS detection. The main aim of this work, however, was to assess the parameters affecting extraction efficiencies of the chromium complexes from clay, peat and sandy soils. Water and KH_2PO_4 were used as extractants and soil samples contaminated by tannery waste were analysed. Krajnc et al. [55] have characterised the complexes formed in soil between copper, chromium and fulvic acids (FAs). Gel permeation chromatography with infrared spectroscopic detection was used. Complexation capacities (CC) and stability constants (*K*-st) of the FAs were determined by a method based on ion exchange. Significant differences were found between the IR spectra, *K*-st and CC between Cu and Cr complexes of the same FA, as well as between the same metal complexed with different FAs. The Cr complexes proved to have high *K*-st and larger CC values than Cu complexes and the IR spectra showed that Cu is predominantly bound to COO^-

groups. The higher *K*-st and CC values of Cr complexes suggest that Cu is more readily taken up from contaminated soils than Cr. In a paper by Kerven et al. [56], chromatographic techniques for the separation and identification of Al complexes are discussed. The chromatographic performance of a Fractogel TSK HW-40 (S) column was assessed. The eluent was passed through an ultraviolet (UV) detector to an ICP-AES system for multi-element determination. The SEC–ICP-AES system was used to analyse soil samples and it was found that Al, Fe and Mn were present as complexes with organic ligands. An area of contaminated land in Germany was investigated by Hempel et al. [57] for mercury and its speciated forms. Extraction of organomercurials from soil and percolating water was accomplished using dithizone. Separation of the complexes was performed by HPLC and atomic fluorescence detection (AFD) was used. Gaseous organic mercury and gaseous elemental mercury were detected by adsorption on Carbotrap and gold filters, followed by thermal desorption and detection by AFS. The behaviour of eight organomercurials was investigated using a new design of lysimeter. Very little movement of mercury species was observed when the soil was treated with percolating synthetic rain. The use of IC has been reviewed by Otu et al. [58] for the determination of metal cyanide complexes. IC provides information on all free and complexed cyanide species and information on different oxidation states. Kozuh et al. [59] have compared column chelation ion exchange–ICP-AES and the 8-hydroxyquinoline spectrophotometric method. In this method, Al^{3+} and hydroxy complexes were retained on the column and eluted with HCl. Positively charged labile monomeric aluminium species in the eluent were determined by ICP-AES, using Y as an internal standard. The method produced similar results when compared to the 8-hydroxyquinoline method, although the detection limit was higher, at 650 ng g^{-1} compared to 200 ng g^{-1} for the spectroscopic method. Metallo-cyanide complexes arising from cyanidation of gold from its ores have also been determined by Fagan and Haddad [60]. The sample is separated by ion-interaction chromatography using a C_{18} column with low-UV paired ion chromatography (PIC) as the mobile phase. A UV detector operating at 214 nm was used to elucidate cyano complexes of Cu^{+}, Fe^{2+}, Ag^{+}, Fe^{3+} and Au^{+}.

3.3. Biological material

If analysis of biological materials is to be performed using a hyphenated technique, sample pretreatment may have to be modified depending on the detector that is going to be used. This is discussed in a useful review by Subramanian [61]. Detectors that are covered include ETAAS, FAAS, ICP-AES, ICP-MS and X-ray fluorescence (XRF). The capabilities of ICP-MS for trace-element analysis and speciation analysis in body fluids and tissue has been reviewed by Vanhoe [62]. A review has also been written by D'Haese et al. [63], covering HPLC–AAS. Hybrid techniques for studying the speciation of trace metals in biological fluids have been covered by Das et al. [64]. The combination of ICP-MS and chromatographic techniques is also discussed. Fish tissue spiked with TBT and triphenyltin was analysed by Okamoto [65] by GC with flame photometric detection (FPD). HCl and ethylacetate were used as the extractants and the resulting solutions were cleaned using anion- and cation-exchange columns. Derivatisation was performed using a Grignard reagent. The method proved very sensitive and selective for organotin analysis. Problems were encountered, however, in the analysis of TPT. Pb^{2+} was determined by GC–ID-MS by Feldman et al. [66]. Detection was performed by single-ion monitoring and the detection limit quoted was 0.3 ng g^{-1} for a 2-ml sample. Although this work is largely concerned with aqueous samples, the technique's application to biological samples is discussed. A rapid reproducible method of analysing metallothionein in mouse and rabbit liver has been developed by Pan et al. [67] using HPLC and AAS as an element-specific detector. Separation was achieved using anion-exchange columns and elution with a linear gradient of Tris buffer. A detection limit of 5 μg g^{-1} liver was reported. The ratio at which Zn^{2+} will displace Cd^{2+} from metallothionein has been determined by Chang and Robinson [68]. HPLC was used, coupled to a FAAS system, and the performance of a new design of thermospray nebuliser was assessed. High speed counter-current chromatography was used by

Kitazume et al. [69] to separate species of Co, Cu, Ni, Fe^{2+} and Fe^{3+}. Two solvent systems were used, consisting of bis(2-ethylhexyl)phosphoric acid as the stationary phase and citric acid as the mobile phase. Direct current plasma (DCP)–AES was used for continuous detection of the elements. HPLC and ETAAS have been combined by Van Landeghem et al. [70] to study the protein binding and speciation of aluminium and iron. The method was found to be sensitive and accurate. HPLC–ICP-MS was used by Takatera et al. [71] to study the incorporation of selenium species by zinc-induced metallothionein. No difference was observed regarding the uptake and incorporation of selenate and selenite. Aluminium and silicon speciation in human serum was also examined by Wrobel et al. [72], using ion-exchange HPLC–ETAAS. A polymeric anion-exchange column was used and results showed that transferrin bound almost 90% of the total serum aluminum. Sturaro et al. [73] investigated the concentration of Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Pb^{2+} in human hair after extraction with nitric/perchlorate acids. Ion-exchange chromatography was used and the detection limits were in the region of 1 $\mu g\ g^{-1}$ for each of the metals, using Co as the internal standard. Suzuki et al. [74] utilized SEC and ICP-MS to investigate the body distribution of Se. Results indicated that urine, liver and kidneys contained higher concentrations of Se than plasma and red blood cells. Butylxanthate was used by Nagaosa and Mizuyiiki [75] for the separation of Cu^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} chelates using a C_{18} column with RPLC and an acetonitrile–sodium acetate mobile phase. Electrochemical detection with a glassy carbon electrode was used and the method showed sensitivity when applied to wastewater and biological samples. Se speciation was studied by Childress et al. [76] using HPLC–UV–DCP. Various samples were analysed, such as plants, shellfish and food supplements. Gunther and Waldner [77] studied zinc and cadmium speciation in cytosols of vegetables such as spinach and leek using gel permeation chromatography (GPC) and ETAAS. It was found that in the case of Zn, between 80 and 99% was found in the cystols as low-molecular-mass complexes. Cd–Zn complexes have been identified in lettuce leaves by McKenna and Chaney [78] using gel filtration chromatography and HPLC. It was concluded that sequestration of Cd or Zn by phytochelatin does not occur in crops contaminated by Cd or Zn.

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