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The Determination of the Physicochemical and Chemical Forms of Trace Elements in Natural Waters

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Published material on methods for determining the physicochemical and chemical forms of trace elements (micro-elements) in natural waters in relation to their presence in definite water fractions (inorganic, organic, colloidal, surface-film, and suspended), magnitude, lability with respect to the analytical technique used, and the natural stability of their chemical compounds and oxidation state has been reviewed. All stages of the analysis, from the selection of the position for the removal of the samples and their preliminary treatment to the instrumental determination of the forms of the trace elements have been examined. The bibliography contains 175 references.

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I. INTRODUCTION

The degree of contamination of inland and coastal waters in many industrially developed countries now exceeds an ecologically safe level. The principal contaminants of natural waters (NW), in addition to pesticides and petroleum, are the trace elements (TE), with concentrations below 1 mg litre^{-1} water (1 p.p.m.), many of which are highly toxic—Hg, Pb, Cd, As, etc. Only in recent years has it been possible to obtain reliable values of the total concentrations of Te in various NW, which have proved to be at the level of several micrograms per litre, or in many cases tenths or hundredths of this figure.

The determination of the total concentration of TE, however, does not give definite information on the toxicity of water, since there is no direct relationship between these parameters. A knowledge of the forms in which TE exist in NW has therefore become of primary importance, since in addition to different biological accessibility[1] they have a significant influence on the geochemical cycles and the transfer of TE in NW, the methods of obtaining domestic water and water for industry, etc.

There are two basic approaches to the study of the forms of TE in NW. The first of these is theoretical, and calculates the equilibrium concentrations of all dissolved forms by means of mathematical models based on the use of the experimentally determined concentrations of TE and ligands, and also the published values of TE–ligand stability constants. Chemical modelling now covers all competing equilibria, and computer programs are used for thermodynamic calculations. The accuracy of computer modelling is lowered considerably, however, by variations in published data on stability constants and activity coefficients. Moreover, the calculation generally does not include many of the parameters influencing the form of TE, since qualitative and quantitative data are not available for many of them: pH, redox potential, the great majority of organic ligands, colloidal particles and adsorption on them, inter-phase reactions of precipitation, solution, and sorption, biological and physical processes, etc. These factors, and also the lack of information on the non-equilibrium conditions existing in many NW, cast doubt on the relation to reality of the results of the calculation of the forms of TE. Chemical modelling has been described in detail elsewhere[2-9].

The second approach to the study of the forms is analytical. It is convenient to divide all experimentally determined forms of any TE in NW into two large groups: 1) the physicochemical forms present in definite fractions of NW (for example, dissolved organic and suspended), which are subdivided either according to size (for example by ultrafiltration and gel filtration) or their lability with respect to the analytical technique used (for example, ion exchange and stripping voltammetry); 2) the chemical forms, characterised either by definite chemical compounds (for example, MeHgCl and Ph_4Sn) or by a definite oxidation state in different classes of TE (for example, inorganic Se^{IV} and Se^{VI}). According to this classification, the chemical forms of TE represent a fraction of their physicochemical forms, which in sum give the total concentration of TE in NW.

At the very low concentrations of TE in NW, the determination of their forms has proved to be an extremely difficult analytical problem, which has not yet been solved. The forms of TE are very sensitive to large variations in salt composition, pH, the concentration of dissolved organic and macromolecular compounds, colloidal and suspended particles, etc., which also depend on the type of NW and the time of year[10]. The equilibrium concentrations of the forms of TE present in NW are unavoidably changed on the removal of samples, as a consequence of their contact with oxygen and with the walls of the sampling equipment, changes in temperature and pressure, and the methods of separation (isolation) and analysis used. The extent of these changes is not known, but it is important to reduce all these effects to a minimum.

The aim of the present work is to summarise methods for determining the physicochemical and chemical forms of TE in NW in the last 5–7 years. The former have been reviewed[2,11,12], and their development followed[7], while the latter have been partly reviewed, but only for sea water[13]; in recent years, however, new experimental results have extended considerably existing views on the physicochemical and chemical behaviour of TE.

Since most errors in the determination of the concentration of TE and their forms in NW due to the introduction of contaminants are made during the removal and preliminary treatment of specimens for analysis, these stages will be examined, and recommendations given for carrying them out correctly. Colloidal particles which pass through a filter with a pore

diameter of 0.45 μm will be assigned to the dissolved fraction, although they introduce some ambiguity into the definition of the colloidal and dissolved forms of the elements.

The analytical methods most frequently used for determining the forms of TE are stripping voltammetry (SV) (its use for NW has been reviewed[14]), atomic-absorption spectrophotometry (AAS), emission spectrometry (ES), gas–liquid chromatography (GLC), neutron-activation analysis (NAA), mass spectrometry (MS), liquid chromatography (LC), and spectrophotometry. The last method will not be considered, however, because of its low selectivity and the consequent impossibility of taking correct account of the interfering influence of many other TE and chemical substances present in NW.

II. THE REMOVAL AND STORAGE OF NATURAL WATER SAMPLES

The reliable determination of the concentration of TE and their forms in NW is possible only when contamination is excluded at all stages of the analysis: in the laboratory on shore when containers are being washed for an expedition, in the removal of samples and their filtration on board the vessel, during their conservation and storage, and also during the measurement using the instrument. All these stages must be checked for the possible introduction of contaminants, since attempts to achieve high purity at any one stage may be nullified by contamination at another stage. It is therefore recommended[15] that specimens be treated both on board the vessel and in the laboratory on shore in so-called "clean" rooms with dust-free air, in which there are no metal surfaces, and the work is carried out in special clothing in an extraction cupboard. It is difficult to observe all these requirements, but an essential condition is the absence of dust, which is achieved by working in a clean extraction cupboard. The preparation of ultrapure water for trace analysis has been described[16].

Experience has shown that the most vulnerable stages of the analysis to the introduction of contaminants are the collection, filtration, and storage of the samples.

a) Sample Collection

The choice of position is important only for surface specimens. The chief danger is possible contamination of the water surface by the vessel. Samples of all types of NW should therefore be taken at a distance from the vessel, either from a ship's boat[15] or from a rubber boat at its moving front in uncontaminated water from the windward side[17]. This method cannot be used, however, when there are waves or when a large number of specimens is required.

The procedure for collecting samples is now well developed[17–20]. Samples are collected using bottles, sampling devices, and suction systems. The best materials for these are Teflon, polycarbonate, polypropylene, and polyethylene. Various types and their characteristics were recently described[15] and compared in the removal of identical samples[16]. Unfortunately, they all show unsatisfactory features. Thus bottles and suction assemblies are suitable only for the collection of relatively shallow specimens, whereas the widely-used Niskin and Go-Flow deep-water sampling devices are open when they pass through the surface layer and are often made of polyvinyl chloride, which is usually contaminated by TE. Sampling device designs free from these unsatisfactory features have now been developed, however[15].

b) Filtration

When the forms of TE have to be determined, it is necessary to filter the specimen as soon as possible after collection, through a membrane filter with a pore size of 0.45 μm, since the distribution of the forms of TE in unfiltered water may change rapidly, mainly as a consequence of bacterial activity and, to a lesser extent, adsorption–desorption processes. If the time required is greater than several hours, the sample must be cooled to ~4 °C before filtration is complete. All phytoplankton and most bacteria remain with the suspended matter on the filter[19]. Filtration is particularly important for fresh water and estuarine water, in which the suspended form makes up a significant fraction of the total concentration of an element. By general agreement[21], the filtrate contains the dissolved fraction of TE, which, however, also contains colloidal particles and a fraction consisting of very fine particles of mineral and biological origin which pass through the filter[22].

Polycarbonate or cellulose acetate Nuclepore, Millipore, Gelman, and Synpore filters are generally used; these must be purified from TE before use by washing thoroughly with mineral acid, distilled water, and the sample[2,19,22,23]. The absence of clean conditions in the determination of TE has been discussed[24]. The separation of the phases is carried out in a vacuum, under pressure, and by centrifuging. Their advantages and disadvantages, and types of filtration apparatus, have been described[19].

c) Storage

It is often impossible to analyse samples for TE immediately after collection and filtration. It then becomes necessary to store them before analysis. Here the main problems are adsorption losses, which depend on the storage time[25], and contamination[19,26,27]. Sorption depends chiefly on the TE concentration, the material of the storage vessel, pH, and salinity[27]. NW samples must be kept in vessels of Pyrex glass, Teflon, or high-density polypropylene or polyethylene. Wash solutions, consisting chiefly of a mineral acid[28], have been proposed for cleaning them, and the treatment conditions are generally different. It is not possible to compare their efficiency for different NW, vessel materials, and storage conditions, however, because of the inadequate experimental conditions. This comparison has been made only for the storage of fresh water in polyethylene vessels at 1 °C;[28] it was found that it is best to clean the vessels by shaking with 10% HNO_3 for 48 h. It has also been suggested that vessels for the storage of all types of NW should be cleaned by shaking with 2 M HCl and then washing with a filtered sample[19], since acid washing removes surface contamination from the walls of the vessels, but at the same time activates adsorption centres capable of removing TE from the sample.

To ensure minimum adsorption losses during the storage of samples in which it is necessary to determine only the total concentration of TE, the samples after filtration are usually acidified with HCl or HNO_3 to pH $\leq$ 2.[19,20,26] In the case of germanium, for example, they can be kept for several years[29]. In the determination of the physicochemical forms of TE, however, acids cannot be added. When filtered samples are stored at natural pH and room temperature, bacterial activity leads to the appearance of suspended particles and a decrease in the concentration of organic substances and hence to either the removal of TE from the solution or a change in their forms[19]. Thus to decrease bacterial activity and hence the loss of TE, it is suggested

that NW samples be kept in a refrigerator at 4 °C [30] for up to 1–3 months[31–33]. For the same purpose, sea water samples are kept in the frozen state between −20 °C and −45 °C, for up to three months without treatment[34], after filtration[22,32], and after filtration and acidification[22,35]. In the case of fresh water, a decrease in the labile form of TE has been observed[33].

The storage of samples for the determination of the total concentration of mercury shows differences, however, related to the characteristic features of its chemical and physical properties. Firstly, they cannot be kept in polyethylene vessels, whose walls are permeable to mercury vapour[36–38], but only in glass vessels. Secondly, Hg^{II} is readily sorbed on the walls and reduced to Hg_2^{II}, followed by disproportionation to Hg^0. In sea water, these processes are suppressed by acidifying with mineral acids[37], and in fresh water and dilute standard solutions by the further addition of oxidising agents, for example $K_2Cr_2O_7$ to a concentration of 0.05%,[36,39,40] or complex-forming agents, for example NaCl to a concentration of 3–4%.[37,41] Under these conditions, specimens and standard solutions can be kept for several months.

There are no general methods, however, for the storage of samples for the subsequent determination of the chemical forms of TE, in contrast to the case of their physicochemical forms. These are usually found empirically. Samples with inorganic forms of As^{III} and As^{V} can be kept for three weeks at room temperature[42], 10 days at ~4 °C,[43] for a long time below −15 °C,[44,45] for several days when acifified to 0.05 M HCl,[46] and for 125 days at pH 1.5.[47] In the case of inorganic forms of Se^{IV} and Se^{VI}, samples can be kept for a long time at 4 °C,[48] in the frozen state[49], or when acidified[49,50], for 125 days at pH 1.5,[48] and for 4.5 months at pH 2.[51] Different storage conditions of pH, concentration, and type and size of storage vessel material have been studied for the storage of As^{III}, As^{V},[36] Se^{IV} and Se^{VI}.[48] Samples containing methylarsinic acid (MAA) and dimethylarsinic acid (DMAA) can be kept indefinitely when acidified to 0.05 M HCl.[44] The vessels must be sealed to exclude atomospheric oxygen.

Very little is known about the storage of samples with chemical forms of other TE. Thus $MeHg^{II}$ can be kept for not more than 10 days at pH 2.5,[38] but it is lost quantitatively on lyophilisation[52], and Ph_2Hg and RHg^{II} (R = Me, Et, Ph) are only slightly converted to Hg^{II} after 30 days in 1% H_2SO_4.[40] It has also been noted that little Cr^{VI} is lost at pH 6–8,[53] but R_4Pb cannot be stored at all[54], since in river water it decomposes to the extent of 60% in 24 h.[55]

III. PHYSICOCHEMICAL FORMS

For most TE determined, stripping voltammetry (SV) has low detection limits, which for the most part coincide with their average concentrations in NW, and does not require preliminary chemical preparation of the samples. Thus combined with various methods of separation and decomposition it has been made the basis of recently developed general schemes for determining the physicochemical forms of trace metals (TM).

In the first of these[2,56,57], the following are measured in the sample after filtration through a membrane filter with a pore size of 0.45 μm: a) SV-labile metal, and b) total metal. The determinations are carried out systematically: 1) before treatment of the sample; 2) after it has passed through a column of Chelex-100 ion exchange resin; 3) after ultraviolet irradiation; and 4) after passage of the photo-oxidised specimen through a column of resin. This makes it possible to separate the physicochemical forms of the TM into the four classes given below, of which the last three are further divided into inorganic and organic forms, so that it is possible to determine seven dissolved forms of each metal: 1) free metal ions and labile complexes (in sea water at natural pH, this form corresponds to simple inorganic complexes such as chlorides and sulphates, and in fresh water to citrate and aminoacid complexes); colloidal metals; 2) SV-active and 3) SV-inactive (these classes in sea water correspond chiefly to metals adsorbed on organic and inorganic colloidal particles, or included in them, since the presence of appreciable concentrations of metal complexes which would not be held by the resin is unlikely; in fresh water the picture may be different, because of the higher concentrations of organic substances, particularly such powerful complex-forming agents as humic and fulvic acids; 4) labile complexes which dissociate on passage through the resin, for example those with cysteine, and also dissolved sulphides and silicates. There are no strict boundaries between these classes, however, and there is some overlap. An important advantage of the scheme is the low reagent background[58]. The dependence of the possible physicochemical forms of metals on their size is given in Table 1.

Table 1. Possible physicochemical forms of TE in NW in relation to their dimensions[2].

Form	Example	Approximate dimensions (μm)
Suspended	remains on a filter with pore diameter 0.45 μm	>0.45
Simple hydrated metal ions	$(H_2O)_6Zn(II)$	0.0008
Simple hydrated complexes	$(H_2O)_5ClZn(II)$	0.001
Simple organic complexes	Cu glycinate	0.001—0.002
Stable inorganic compounds	PbS, $ZnCO_3$	0.001—0.002
Stable organic compounds	Cu fulvate	0.002—0.004
Adsorbed on inorganic colloids	Cd(II)—MnO_2 Cu(II)—Fe_2O_3	0.01—0.50
Adsorbed on organic colloids	Pb(II) -humic acid; Zn(II) -organic detritus	0.01—0.50

Note: In this and subsequent tables M(II) = M^{II}, M(III) = M^{III}, etc.

The use of this scheme has shown that in coastal sea water[32], up to 40–60% Cu, 45–70% Pb, and 15–35% Cd, relative to their total concentrations, are combined with colloidal particles; in fresh water[33], Cu also predominates in these forms, but Pb is present in suspended inorganic form, and Cd exists only in labile ionic forms.

The results obtained using this scheme, however, do not necessarily reflect the true equilibrium concentrations of the forms of TM, because of their decomposition when an acid, the acetate anion, or a mercury salt are added to the sample being analysed[59,60].

Another general scheme for fresh water[61] is based on the fractionation according to the dimensions of the forms bearing the metals by filtering the samples through membrane filters with pore sizes of 12 μm and 1.0 μm, followed by ultrafiltration of the last filtrate through filters with pore sizes of 0.4, 0.08, and 0.015 μm (it is possible to divide the forms into even finer fractions by ultrafiltration through filters with pore sizes of 0.014, ~0.005, and ~0.0012 μm, but it has been found that ultrafilters do not have absolute pore sizes and

show variable adsorption, so that it has not been possible to obtain consistent results). The last six fractions are analysed for the total metal concentration by SV after photo-oxidation (Cd, Pb, and Cu) and by flameless AAS (Fe and Mn). In the series of filtrates, SV-labile metals are found at natural pH before and after ultraviolet irradiation. Particular attention has been paid to the limitations of the different schemes, and it has been shown that photo-oxidation is not suitable for the quantitative estimation of the forms in fresh water.

The continuum of the dimensions of the forms in this scheme makes it possible to avoid an arbitrary distinction between dissolved and suspended metal, and also emphasises the importance of colloidal fractions of the metals. The scheme has been used for fresh water[61,62]. In particular, it has been shown that the difference in the forms of metals in the waters of two rivers is due to a marked difference in the concentration of suspension, and that only a small fraction of the metals is SV- and Chelex-100-labile. The results[61] have also revealed a marked lack of agreement with the physico-chemical model for TM in fresh water[63], due to the inability of the latter to take account of suspended and colloidal forms of the metals.

Another approach to the continuum of dimensions of dissolved form of TM in fresh waters[64] is based on the principle of successive ultracentrifuging[65]. The sample is first filtered through a filter with a pore size of 0.45 μm, and then fractionated successively according to molecular mass through ultrafilters with pore sizes of 100 K, 25 K, 10 K, and 1 K (where K is the molar mass in multiples of 1000); this makes it possible to divide the dissolved organic matter and the forms of TM into definite fractions, depending on their molecular masses. In each of the fractions obtained, the metals are determined by SV and AAS. The highest concentrations of Cd, Pb, and Cu are found in fractions with molecular mass 10^3–10^4, and correlate with the concentration of organic carbon; there are no free or labile forms present. On the other hand, Fe and Mn are often found in fractions with higher molecular mass, and do not correlate with the concentration of dissolved carbon, and Ca and Mg are bound in fractions with lower molecular mass. The same regular features were observed for Cu by ultrafiltration and gel filtration[66].

A combination of a large number of analytical methods[12] can be used to determine the following forms of TM in fresh water: total, suspended, dissolved, free ionic, and combined, and also the distribution of the complexes with respect to molecular (ionic) mass in the range ~500–150000. Its advantages include the possibility of finding the sign of the charge of the free and complexed metal ions and studying complex formation, including its kinetics. Dissolved Mn is present chiefly as anionic complexes with high molecular mass. A serious disadvantage of the scheme is the insufficient attention to colloidal forms.

These general schemes cannot be used in many laboratories, however, because they are relatively complex and laborious. Simplified schemes for determining the physicochemical forms of TM, or individual fragments of general schemes, or details of the latter, have therefore been widely used.

In one simplified scheme[67,68], Cd, Cu, Pb, and Zn are determined in the suspended and dissolved forms, and in the latter the ion-exchangeable (free metal ions and simple inorganic and organic complexes) and combined (mainly a colloidal fraction with molecular mass less than 1000) forms. It has been applied to fresh and estuarine waters[69].

In another scheme[34], the sample is first filtered through a filter with a pore size of 0.22 μm to remove micro-organisms, after which part of the filtrate is passed through a filter with a pore size of ~0.001 μm with a restricted nominal molecular mass of 1000 to separate the forms with high and low molecular masses, that is colloidal and true dissolved forms. The three fractions obtained are analysed for the concentrations of total metal, the SV-labile forms at natural pH, and the SV-acid-labile forms at pH 2.8 (in the last case except the original specimen). This scheme has shown that in sea water, Cd is present exclusively in labile forms of low molecular mass, and Pb chiefly in non-labile forms of low molecular mass, while the distribution of Cu was irregular, with appreciable binding in colloidal and organic forms.

The range of experimentally determined physicochemical forms of TM is not restricted to the above schemes. To improve understanding of the role of TM in NW, it is necessary to have finer sub-divisions within each form or fraction. Thus depending on the time of contact with Ca-Chelex-100 resin, SV makes it possible to define the relative lability of TM as very labile, moderately labile, and inert[70,71]. This kinetically based classification may be useful for estimating the bio-availability of TM. In particular, Cd and Zn exist in forms more labile than Cu and Pb.

Identification of the lability of TM with their bio-availability may lead to serious errors, however, since the measured concentrations of labile metals depend markedly on the analytical conditions and the method used—SV, ion exchange, solvent extraction, absorption, etc. In particular, in SV the labile forms are free metal ions, together with metal complexes, which will dissociate in the diffuse layer, liberating the metal ion. The possibility of a more exact treatment of this term from the viewpoint of the values of the equilibrium and rate constants has been discussed[7]. For example, this method has shown[72] that in sea water, with decrease in pH from 8.1 to 2.0, there is a sharp increase in the proportion of labile Cd, Pb, and Cu detected: 0.17 → 0.45, 0.34 → 1.91, and 0.67 → 2.43 μg litre^{-1} respectively. When they are concentrated on Chelex-100 resin at pH 1 with subsequent determination by the same method, however, the Cd, Pd, and Cu concentrations obtained were 0.31, 0.81, and 2.03 μg litre^{-1} respectively. An increase in the labile fraction of TM when the samples were acidified has been observed by other workers[73]. This can be attributed to the conversion of colloidal, acid-sensitive, and acid-exchangeable forms into labile forms. Labile mercury is defined as that fraction in NW which is reduced by $SnCl_2$.[74–76]

The labile fractions of TM usually make up only a small proportion of their total concentration in NW. Most of the TM are combined with organic, colloidal, and suspended fractions, particularly in fresh, estuarine, and coastal sea water. The first of these fractions may contain an appreciable and even a greater proportion of TM, both in fresh water: Cu,[31,33,77] Cd,[78,79] Al, Cr, Fe, Pb,[80] and Hg;[78,81] and in sea water: Cu,[73,82,83] Zn,[73,83], Pb,[73] and Hg.[74,84]

Organic forms of TM are separated from the sample on anion-exchange resins[77,83], and organic mercury together with inorganic mercury on resin[85] and polyurethane[86] treated with dithiocarbamate, or on silica gel covered with benzothiazole-2-thiol.[87] They can be fractionated according to molecular mass or size by ultrafiltration[78,84,88], centrifuging[79,88], ion-exchange membranes[88], gel chromatography[80], and gel filtration[89,90]. The organic fraction of TM can be found less accurately from the difference between the total and labile metal in the same sample, determined by the same method. For this purpose it is necessary to separate the TM from their organic complexes and compounds, and also their colloidal particles. This is achieved by boiling the sample at pH 0.7 [58] or by ultraviolet irradiation[31,82,91,92]. The last method, involving irradiation by a 550 W mercury

lamp for 4 h, is particularly noteworthy, since it is suitable for all types of NW and gives a low reagent background[92]. In the determination of total Hg, because of the fairly high stability of its organic derivatives, the latter are decomposed by ultraviolet irradiation[91,93], or oxidising agents such as $K_2S_2O_8$, $KMnO_4$, Br_2,[37,39,74,94] or reducing agents such as $NaBH_4$,[95] $SnCl_2$ and $CdCl_2$, after concentrating the Hg on a resin treated with dithiocarbamate[96], or by combustion of the resin with the Hg at 850 °C.[85]

The important role in the binding of TM of colloidal particles of inorganic (hydrated oxides of Fe, Mn, Si, clays, and sulphides) and organic (humic substances, biota residues) origin has been emphasised[2,58]. Metals present in ionic forms and combined with colloidal particles are separated by dialysis, ultrafiltration, centrifuging, ion exchange, and electrophoresis, the methodology of which, together with methods of determining colloidal forms of TM, is given in the above schemes (see also Refs.2, 58, and 82). In particular, the concentration of more than 30 metals in colloids can be determined by NAA after ultrafiltration of the sample through a filter with a pore size of 0.0012 μm.[97] Cation exchange resins apparently do not concentrate colloidal forms of TM at natural pH,[58] which are too large to enter the pores of the resin. An important feature is that it is often difficult to prove unambiguously whether TM are present in the colloidal, particularly organic, fraction or in the dissolved organic fraction, if they are not clearly separated from one another. Thus the extent of the distribution of the TM between them is often only tentatively determined.

Most NW show coordinative unsaturation, revealed by the binding of added ionic TM. It is assumed that this so-called complex-forming power of NW is due to the presence of organic substances of the fulvic acid type. Analytical methods for determining it (amperometric titration, ion-selective electrodes, ion-exchange equilibria, etc.) and the theoretical basis of the concept have been reviewed[98].

Suspended particles play an important role in the distribution of TM in NW. Thus rivers may carry most of them (up to 80–90%) to the ocean in suspended form[83,99]. Mercury may also be present chiefly in this form in estuarine[100] and sea[101] water. The concentration of TM in the suspension may vary considerably, however, depending on the time of year[102].

Usually, suspended fractions of TM are separated from dissolved fractions by three methods—filtration, centrifuging, and precipitation[103]—but most frequently the suspension is removed on membrane filters with a pore size of 0.45 μm. The concentration of TM in the suspension remaining on the filter can be determined by several methods, depending on the availability of methods for treating the suspension and on available analytical methods. A number of the latter (NAA and ES) make it possible to determine many TM simultaneously without any treatment of the suspension[104,105]. Combustion of part of the filtrate with the suspension in an atomiser has been proposed for the determination by flameless AAS of a number of metals having approximately equal volatilities[106].

In most cases, before determination, the TM together with the filters are transferred to solution either with complete solution of the suspension or with extraction using acids without affecting the crystal lattices of the suspension. In the first case, a necessary component of the decomposition mixture is hydrofluoric acid, together with various other mineral acids[107–109]. It can also be achieved by fusing the suspension at 1000 °C with $LiBO_2$ with subsequent solution in HNO_3.[109] The extraction is usually carried out either by heating the suspension with mineral acids under different conditions[109–113] or with their mixtures[101,114], or with acid and 30% H_2O_2,[85] or by combustion of the suspension in a furnace at 450–600 °C followed by solution in HCl.[115,116] The TM in the solutions obtained are most frequently determined by AAS.

Suspended TM are sometimes found from the difference between their concentrations in the unfiltered and filtered samples[100,117]. Dispersion of the suspension in an ultrasonic bath after solution of the filter in $CHCl_3$, with subsequent determination by flameless AAS, has also been described[118].

In addition to the two phase forms of TM, dissolved and suspended, MW also contain a third form, the film (surface micro-layer), which contains the highest concentrations in NW of dissolved and suspended TM, and also organic substances, biogenic elements, etc. Compared with the layer under the water surface, the concentrations of dissolved TM may be several times greater[117], and the concentrations of suspended TM greater by a factor of up to 10, in fresh[117] and sea[114] water. The organic and inorganic forms of TM can be determined in the suspended film fraction[119]. Usually, the surface film of thickness <0.3 mm is removed, by various methods[120], including sampling devices[121].

Of the analytical methods for determining the dissolved physicochemical forms of TM without preliminary separation from the sample, only SV is used, because of its high sensitivity and simplicity of operation, and also the availability of instruments and equipment. Its use to determine the forms of metals has been described in detail[2,122]. The main limitation of SV is that it is applicable to only a small number of TM—Cd, Pb, Cu, and Zn. In recent years, the development of polarographic methods has made it possible to obtain information on the chemical state of a number of other elements—Tl, Cr, Sb, As, Bi, and U.[2,7]

The use of other analytical methods involves the preliminary concentration of the TM, which can be achieved by various methods[123], including filtration of the sample through chelating filters[124]. Methods of concentration have been compared[125,126]. All the stages in the analysis of TM in NW have been described in detail for the following methods: AAS,[20,126–128] NAA,[129] ES,[130] and X-ray fluorescence[131].

IV. CHEMICAL FORMS

Because of the extremely low concentrations of the chemical forms of TE in NW, only a few examples of their determination without concentration have been described. The determination of Cr^{III} by a chemiluminescent method with a detection limit of 0.02 μg litre^{-1} has been proposed[132]. As^{III} can be determined by differential pulse polarography (DPP) with a detection limit of ~10 μg litre^{-1},[46] but As^{V} is found from the difference between As (total inorganic) and As^{III} after reductive evaporation of the sample, with a detection limit of ~1 μg litre^{-1}. Hg^{II}, $MeHg^{II}$, and $PhHg^{II}$ have been determined separately by AAS in an automatic system on the basis of the selective reduction of combinations of these forms by EDTA, $SnCl_2$, and $CdCl_2$. The low detection limit of ~0.001 μg litre^{-1} was obtained as a result of the equilibrium of mercury vapour with a small volume of air at 90 °C.[40]

Because of the insufficient sensitivity of present-day analytical methods, the determination of most chemical forms of TE requires concentration, which can be achieved using liquid extraction, solid extracting agents, and the formation of volatile hydrides.

Methods for determining the chemical forms of TE with concentration by liquid extraction are given in Table 2. Inert compounds, for example R_4Pb, are extracted by

organic solvents such as hexane or benzene. After separation by GLC, the forms are determined by AAS with a detection limit of 0.2–0.5 μg litre^{-1}.[54,55] Most chemically active forms of TE must be concentrated by extraction with organic solvents in the presence of complex-forming agents. For Bu_nSn^{IV} (n = 1–3), tropolone is used. The forms in the extracts are alkylated by Grignard reagents to the corresponding methyl[133] and pentyl[134] derivatives of tin, and the latter are analysed. $MeHg^{II}$ and $PhHg^{II}$ are concentrated using dithizone, and RA makes it possible to determine them with a detection limit of 0.01 μg litre^{-1}.[135] Se^{IV} can be determined with detection limits of 0.0008 μg litre^{-1} and 0.002 μg litre^{-1} using 4-nitro-o-phenylenediamine[51] and 1,2-diamino-3,5-dibromobenzene[137] respectively. By oxidising $Se^{-II,0}$ with bromine and reducing Se^{VI} with a mixture of bromine and bromide to Se^{IV} with the last ligand, it is possible to determine all these forms separately. Their distributions in river and sea water have been given[138].

Table 2. Methods for determining the chemical forms of TE with concentration by liquid extraction.

Chemical form of TE	Extraction	Method of determination	Refs.
R_4Pb (R=Me, Et)	hexane	GLC-AAS	[55]
Me_nEt_mPb (n=m=0–4)	ditto	ditto	[54]
Bu_nSn(IV) (n=1–3)	tropolone	GLC-MS	[133]
ditto	ditto	GLC	[134]
MeHg(II), PhHg(II)	dithizone	RA*	[135]
Hg(II)	mixture of amines	GLC	[136]
MeHgCl	4-nitro-o-phenylenediamine	ditto	[51]
Se(IV)	1,2-diamino-3,5-dibromobenzene	»	[137]
ditto	ditto	»	[138]
Se(—II; 0)	ammonium salt and thiocyanate	AAC	[53]
Se(IV), Se(VI)	dithiocarbamate	AAS	[139]
Cr (III), Cr (VI)	ditto	RA	[140]
ditto		AAS	[141]
»	»	ditto	[142]
As (III), As (V)			
Sb (III), Sb (V)			
Se(IV), Se(VI)			
Sb (III), Sb (V)	»	»	[143]
Se (IV), Se (VI)	»	»	[144]
Te (IV), Te (VI)	»	»	[145]
Cr (III), Cr (VI)	»	»	[146]
Cr (VI)	»	»	[147]

*RA = radioanalytically.

In a similar method, As^{III} is first determined using dithiophosphate (detection limit 0.006 μg litre^{-1}), and then As^{V} is determined after reducing to As^{III} using sulphite[139].

Pyrrolidine- and diethyldithiocarbamates are used particularly frequently as complex-forming reagents. They have been used for the selective extraction of As^{III},[140–142] Sb^{III},[142,143] Se^{IV},[142,144] Te^{IV},[145] Cr^{VI}.[146,147] The interfering influence of many metal ions is masked by adding EDTA.[141,143–145] The total concentration of these elements is then found by using KI [140,141] with acidification[143], heating[146], or boiling[144,145] with acids to convert all the inorganic forms of these elements into the above forms, and, from the difference between them, the forms As^{V}, Sb^{V}, Se^{VI}, Te^{VI}, and Cr^{III}. The detection limit is 0.2 to 0.4 μg litre^{-1} [140,141,143–145] or 0.02 μg litre^{-1}.[147] In NW, the highly oxidised forms of these elements predominate.

The use of GLC to determine organomercury compounds and inorganic mercury compounds by converting them into organic compounds has been reviewed[148]. LC has been used for the quantitative separation of RHg^{II} (R = Me, Et, Ph), R_3Pb^{IV} (R = Me, Et), and $MePh_3Sb^{V}$,[149] organic derivatives of Hg, Sn, Pb, and As,[150] and metal ions[151].

Methods for determining the chemical forms of TE with concentration on solid extracting agents are summarised in Table 3. Cr^{III} is coprecipitated quantitatively at pH 8 with $Fe(OH)_3$, and Cr^{VI} is either coprecipitated with cobalt pyrrolidinedithiocarbamate (CPDC) [154] or found from the difference between the total dissolved Cr, concentrated by coprecipitation on $Fe(OH)_2$ [111] or on $Bi(OH)_3$,[152,153] and Cr^{III}. Cr(inorganic) amounting to up to 60% of all dissolved forms of chromium has been detected for the first time in sea water[152,153]. This may be of considerable importance for other TE in NW, whose organic forms have not been studied.

Table 3. Methods for determining the chemical forms of TE by concentration on solid extracting agents*.

Chemical form of TE	Solid extracting agent	Method of determination	Refs.
Cr (III), Cr (VI)	$Fe(OH)_3$ and $Fe(OH)_2$	AAS	[111]
ditto	$Fe(OH)_3$ and $Bi(OH)_3$	ditto	[152, 153]
»	$Fe(OH)_3$ and CPDC	F	[154]
»	electrodeposition	AAS	[155]
Se (IV), Se (VI)	carbon	F	[50]
Hg(0)	Ag(0)	AAS	[156]
Me_2Hg			
As (III), As (V) , MAA	ion exchange resin	ditto	[157]
As (III), As (V) , MAA	ion exchange resin	AAS	[158]
ditto	ditto	DPP	[159]
Se (IV)	»	F	[160]
Se (VI)			
Cr (VI)	»	CL	[161]
V (IV), V (V)	»	NAA	[162]
Cr (III), Cr (VI)	»	ditto	[163]
ditto	»	AAS	[164]

*CDTC = cobalt pyrrolidinedithiocarbamate, F = fluorescent, CL = chemiluminescent.

Promising methods for concentrating other TE are the adsorption of Se^0 on active carbon after selective reduction of Se^{IV} by l-ascorbic acid[50] and the electrodeposition of Cr^{III}.[155] These methods detect down to 0.05 μg litre^{-1}. Volatile mercury compounds are blown from the sample, Hg^0 is amalgamated on a column of silver wool, and Me_2Hg after thermal decomposition at 900 °C. The detection limit is 0.001 μg litre^{-1}.[156]

Cation- and anion-exchange resins are used both to concentrate and to separate the chemical forms of TE. In the case of Se^{IV}, dithiocarbamate is added to the specimen before concentration on the resin[160]. The detection limit is 2 μg litre^{-1} [158] or 10 μg litre^{-1} [157] for the forms of As^{V}, 0.005 μg litre^{-1} for Cr^{VI},[161] and 0.01 μg litre^{-1} for the forms of V.[162]

Because of the appreciable stability in water and relative simplicity of the preparation of the hydrides of a number of TE, considerable use has recently been made of methods for determining the chemical forms of TE, in which, depending on the pH of the sample, the forms of TE are selectively reduced by $NaBH_4$ to the corresponding hydrides, which are then concentrated by blowing out in a stream of helium into cryogenic traps cooled with liquid nitrogen. The

hydrides, after separation by GLC or successive evaporation, are determined by various analytical methods (Table 4). The detection limit may reach thousandths of a microgram per litre[49,165,166,169,171] or less[44,168,170]. The interfering action of various cations and anions in the reduction by $NaBH_4$ has been studied, and it has been shown that the actual concentrations in most NW do not interfere in the determination of the forms of the TE.[165,168–170]. The use of EDTA as a masking agent has been proposed[167]. The distribution in NW has been determined for the forms of As,[44,165–167] Sb,[168] Se,[49] Ge,[169] and Sn.[170,171]

Table 4. Methods for determining the chemical forms of TE with hydride formation.

Chemical form of TE	Method of concentration	Method of determination	Refs.
As (III) + As (V), MAA DMAA	cryogenic trap	ES	[165]
As (III), As (V), MAA, DMAA	ditto	AAS	[166]
ditto	»	AAS-GLC	[44]
»	»	AAS	[167]
Sb (III), Sb (V), MSA*, DMSA	»	ditto	[168]
Ge (IV), MeGe (IV), Me_2Ge (IV)	cryogenic trap	ES	[169]
Se (IV)	ditto	AAS	[49]
Se (VI)			
Me_nSn(IV) (n=0–3)	»	ES	[170]
R_nSn (IV) (R = Me, n-Bu, n=1–3; R=Ph, n=1; R=Et, n=2, 3)	»	AAS	[171]
Sn (IV)			
Se (IV)	$Fe(OH)_3$	ditto	[172]
Ph_nSn (IV) (n=1–4)	hexane	GLC	[173]

*MSA = methylstibonic acid, DMSA = dimethylstibinic acid.

Se^{IV}, Se^{VI}, Te^{IV}, and Te^{VI} are determined by AAS without the separation and concentration of the hydrides[174], but serious difficulties may be encountered in the interpretation of the results when this method is used for the determination of As^{III}, As^{V},[174,175] Sb^{III}, and Sb^{V},[174] in particular because of the influence of the oxidation state of the TE hydride on the magnitude of its AAS signal[174].

The reduction of the forms of TE can be carried out, however, not in the sample but after their concentration by precipitation with $Fe(OH)_3$ [172] or by extraction with hexane[173]. The detection limits are <1 μg litre^{-1} and <10 μg litre^{-1} respectively.

* * *

The methods for determining the physicochemical forms of TE in NW are only beginning to be developed. The main difficulties are the insufficient sensitivity of the analytical methods and the consequent need to concentrate the forms for the determination; this generally leads to breakdown of their natural equilibrium and to uncertainty in the relationship between the measured and actual forms present in water. The question of the bio-availability of the forms of TE and related analytical problems are poorly understood and have been little studied. Greatest attention should therefore be paid to these problems in the future.

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