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Modern methods for the determination of physicochemical states of microelements in natural waters

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Abstract. The state-of-the-art in studies on the determination of ion – molecular and colloidal forms of microelements in aqueous solutions is analysed. Instrumental and hyphenated methods for the determination of such forms of microelements as aqua-ions, complexes, true and adsorption colloids are considered. The bibliography includes 153 references.

I. Introduction

The methods used to monitor the concentrations of microelements in aqueous media, determine the sources from which they enter the hydrosphere and predict the dynamics of migration of separate physicochemical forms of microelements in the hydrosphere are of importance for studies in environment protection.[1–5] A survey of publications on this subject over the past 10 – 15 years revealed considerable changes in the instrumentation and theoretical generalisation of methods used to determine the physicochemical state of microelements in aqueous media. We intend to analyse these changes in the present review.

The role of microelements in environmental objects is estimated by determining their concentrations in samples. If the content is low, concentration and separation methods based on distribution of microelements between phases, *viz*., ion exchange, sorption, extraction, precipitation and coprecipitation, flotation, electroprecipitation, filtration, distillation, sublimation, dialysis, *etc*. are used, depending on the analysis scheme. Each of the methods listed above involves trans-phase interaction of separate chemical forms of a microelement; therefore, knowledge of the physicochemical state of a microelement in a sample is required in order to maximise its concentration and/or separation from admixtures. In the laboratory, this is achieved by converting the existing form of a microelement to a chemical form convenient for concentrating. Under field conditions, correction of the state of a microelement is often impossible or inefficient; therefore, the selection of a chemical analytical method for the determination requires independent information about both the chemical and phase compositions of all the forms of the extracted microelement in the medium of interest.[5]

This problem has been studied insufficiently, so difficulties of a methodological nature exist. First, the physicochemical processes involving microelements and occurring in industrial and natural aqueous systems are complex indeed. Second, the development of the interphase distribution-based theory of reactivity in interrelated systems of ionic, molecular, colloidal and suspended forms of microelements in solution is in its infancy. Third, for field conditions (unlike laboratory conditions), there is a lack of approved methods for the determination of the chemical and phase compositions of microelements in natural aqueous media; approved test procedures and standard samples of their separate chemical forms are also unavailable.[6–10] Fourth, it is necessary to consider the factors affecting the violation of equilibrium and/or steady states of microelements in a sample when it is transferred from a natural medium to a laboratory.[1–9,11]

Not only analytical chemists, but also heads of enterprises and bodies involved in environmental monitoring, are interested in development and perfection of methods for analysis of the physicochemical state of microelements in the hydrosphere.[12] The most promising methods result from combinations of column chromatography with high-performance spectrometric detection of separate elements. Analyses can be made less expensive by using combined methods of selective oxidation – reduction, coprecipitation, membrane extraction, dialysis and stripping voltammetry.[12–18]

The relationships between the transport properties of microelements in the aqueous phase and the content of specific organic and inorganic components of soils or bottom sediments are studied using selective dissolution of groups of compounds, anion-exchange and distribution chromatography and ultrafiltration.[1,7,9,19] A sample can contain coexisting microelements as suspensions and colloids along with truly dissolved forms, including molecular, cationic and anionic complexes with inorganic and organic ligands.[1,19] Colloidal forms of microelements can be detected by sequential filtration of a liquid sample through membranes with pore sizes from 0.5 μm to 1 nm. Ionic compositions are determined by electrophoresis and ion-exchange chromatography after separation of the suspended fraction.[20,21]

In the early 1990s, the interest of researchers in the forms in which inorganic compounds exist in solutions increased due to the aggravation of global environmental problems (Fig. 1). As a result, new instrumental and combined physicochemical methods appeared; these methods made it possible to monitor not only the analytical concentrations of microelements in aqueous solutions, but also their chemical and phase compositions.

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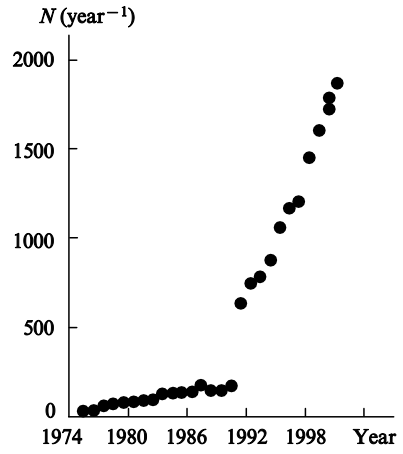


Figure 1. Data from the Institute of Scientific Information (USA) on the worldwide statistics of publications dealing with studies on the chemical state of inorganic compounds in solutions.
N is the number of papers on the subject.

II. Instrumental methods

1. Time resolved laser fluorescence spectroscopy

Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is a popular modern instrumental method used to determine the state of microelements in solutions.[22–26] Neodymium lasers with a pulse energy of 2.5–2.7 mJ and adjustable frequency are the main elements of setups that implement this method. For example, the wavelength of 266 nm was selected to excite the fluorescence of UO_2^{2+} ions; pulse excitation is followed by a decay of the fluorescence signal in the wavelength range from 407.0 to 634.0 nm. This is measured by scanning at discrete times in the range from 0.1 to 15 μs. Each spectrum in this time range is obtained by averaging the results from 100 laser-induced excitations.[22] This method was used to determine the interaction between uranium(VI) ions and silicic acid in model solutions of sodium perchlorate. Analysis showed[22] that the red shift in the fluorescence spectrum is caused by chemical reaction of UO_2^{2+} with $Si(OH)_4$.

According to the theory of fluorescence signal formation, the overall amplitude (A_0) and the amplitudes of signals from various complexes (A_i) are related by the following expression:

$$A_0 = \sum_{i=1}^{n} A_i e^{-t/\tau_i}, \quad (1)$$

where t is the signal relaxation time and τ_i is the characteristic time of fluorescence decay. It was shown[22] that uranyl silicate complexes comprise species of a single type with the ratio $UO_2 : UO_2Si(OH)_3^+ = 1 : 0.95$. By decomposing the fluorescence spectrum into components, one can determine the stability constants of complexes directly in solution (without concentrating). By combining TRLFS and thermodynamic simulation methods, it is possible to use characteristic fluorescence spectra and τ_i values in order to identify uranium complexes (Fig. 2), including $Ca_2UO_2(CO_3)_3(aq)$ in mine waters,[23] and determine the compositions and stability of complexes of trivalent actinides with natural analogues of fulvic and humic acids in model solutions[24,25] and in hot brines.[26] The theory and potential of the TRLFS method are described in detail elsewhere.[27]

2. Laser induced breakdown spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS)[28–30] is among the most promising instrumental methods for the study of the state of inorganic compounds in solutions. The method is based on controlled excitation of characteristic emission spectra. Plasma

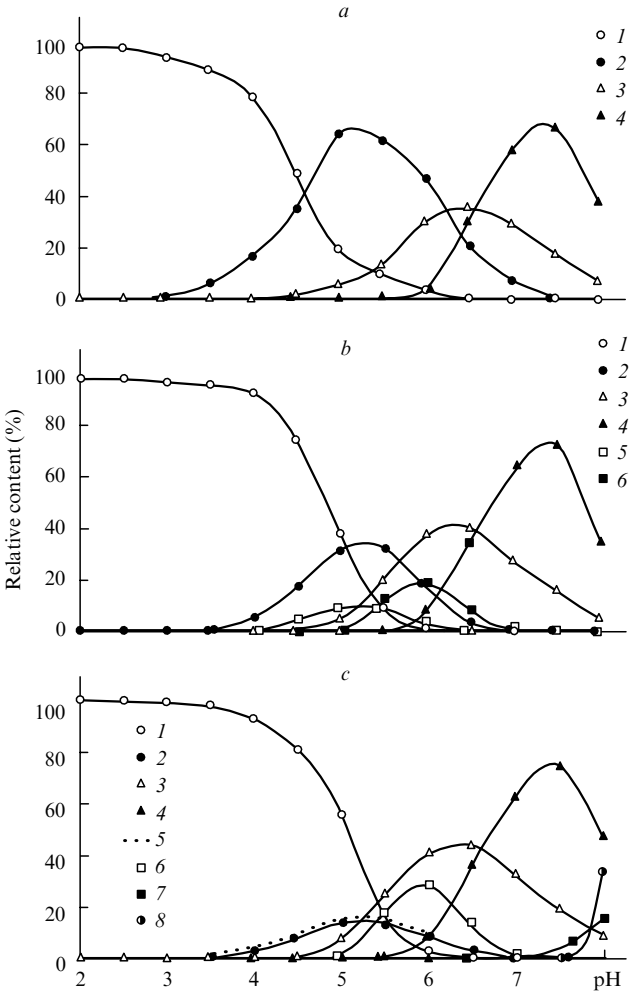


Figure 2. Results of TRLFS determination of the compositions of uranium complexes (a–c);[22]
(*1*) UO_2^{2+}, (*2*) $UO_2OSi(OH)_3^+$, (*3*) $UO_2(OH)_2(aq)$, (*4*) $(UO_2)_2CO_3(OH)_3^-$, (*5*) UO_2OH^+, (*6*) $(UO_2)_3(OH)_5^+$, (*7*) $(UO_2)_2CO_3^{2-}$, (*8*) $UO_2(CO_3)_3^{4-}$.

with a temperature of 2500–25 000 K is formed by focusing a pulsed laser beam on the solution studied; the beam has a power density of 10^{15} W cm^{-2} and creates an electrostatic field of up to 10^{11} V cm^{-1} in the focal plane.[28] As the plasma temperature is lowered and the intensity of the continuous spectrum from the microsample within the sample decreases, characteristic lines of elements appear in the emission spectrum; they are analysed using a special detector.

The LIBS method is used to perform elemental analyses of solid samples (alloys, soils, minerals, microelectronic devices), liquids (milk) and gases (air, aerosol particles). The application of this method to analysis of liquids opens up new prospects in chemical analytical studies.[28,30] Transformation of an aqueous solution or droplet-sized samples to plasma by a laser beam with a wavelength of $\sim$ 500 nm with beam focusing makes it possible to obtain signals from microelements that exist as colloidal phases or adsorption colloids (in this case, the intensity of emission lines is 10^3 times higher than that from ionic and molecular forms of the same element).

The use of the method under consideration in studies of uranium, americium and plutonium migration with ground waters makes it possible to determine the amounts of colloidal fractions of these elements in complex natural objects. By varying the power of the laser beam, it is possible to determine the phase compositions and sizes of colloid particles of hydroxycarbonates of certain transuranium elements [*e.g.*, $Am(OH)CO_3$] at their

solution concentrations of $10^{-5}-10^{-6}$ mol litre^{-1}. The LIBS method is most sensitive to low concentrations of colloid particles typical of natural waters. In the case of high concentrations of such particles (*e.g.*, in aqueous carbonate solutions of uranium and plutonium), the intensity of emission lines of an element decreases due to secondary oxidation of metal atoms in hot plasma and due to multiple scattering effects. To determine the phase composition and size distribution of colloid particles, it is recommended that the LIBS method be combined with other colloid fractionation methods.[28,29]

3. Laser photo-acoustic spectroscopy

The potential of a new highly sensitive method for the determination of the state of ionic and colloidal forms of microelements in solutions, *viz.*, laser photo-acoustic spectroscopy (LPAS), is based on the absorbing ability of species being studied and on the power of the available pulse laser with adjustable wavelength:[31] the intensity of the photo-acoustic signal in this method is proportional to the power density absorbed by particles. The method is based on the determination of characteristic changes in the volume of molecules of a compound of interest (that are in contact with solvent molecules) caused by emission of thermal energy upon transition from an excited state to a ground state following selective absorption of laser irradiation quanta.

The selectivity of LPAS is determined, first, by the high conversion efficiency of absorbed energy of monochromatic irradiation into thermal energy; second, the possibility of recording (using high-precision piezoelectric sensors and detection circuits with high time resolution) a sound wave that appears due to changes in the volumes of molecules upon their deactivation.[31–38] In addition to a laser, the main elements of a photo-acoustic registration system comprise a cell for the solution being studied, a transducer of ultrasonic waves to voltage pulses, and an electronic system for starting the registration scheme, digitising and storing of data that arrive from the ultrasonic transducer. The construction of miniaturised photo-acoustic cells allows one to study microsamples (down to 10^{-7} dm^3) in real-time mode.[32,33]

The LPAS method can be used to determine a microelement concentration down to 5×10^{-6} mol litre^{-1} and to monitor its variations in time, both in homogeneous and heterogeneous samples. The LPAS method has the advantage that it allows one to determine the physicochemical state of elements in aqueous solutions simultaneously containing molecular forms as well as true and adsorption colloids of microelements.[31,35–38] This method was used to study the state and sorption behaviour of Cr(VI) microquantities on hematite under competitive sorption of phosphate ions,[35,39] to determine the concentration and sizes of Tc(IV) colloid particles[36,38] and to reveal the physicochemical state and nature of Np(IV) colloids.[37]

4. X-Ray absorption spectroscopy

X-Ray spectroscopic absorption methods with the use of synchrotron radiation are widely used to study the nearest environment of atoms of a microelement in aqueous and heterogeneous electrolyte–solid systems.[40–67] Data on the structure and short-range order of microelement compounds in a suspended adsorbed state can be obtained by EXAFS (Extended X-Ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge Structure) methods.[41]

The EXAFS method provides extended data on the local environment of an absorbing atom, namely, the type and number of its nearest neighbours, interatomic distances in a sphere with a radius of 5–6 Å; furthermore, information on bond angles can be obtained based on multiple diffusion of photoelectrons and on data for near-edge absorption of several different elements in a compound studied. The EXAFS oscillation structure originating from diffusion of photoelectrons on atoms of the local environment is usually observed in the range of 100–1000 eV above the absorption edge.

The XANES method is used to study the electronic structures of compounds. Using this method, one can obtain information, *e.g.*, about the oxidation state of the absorbing atom and on the symmetry of its coordination sphere. An XANES structure occupies the range from $\sim$ 50 eV before the absorption edge to 100–150 eV after the edge. The resonance bands generated by electron transitions from the core level to vacant levels up to removal of the electron from the atom (photoionisation) are comparatively narrow; the bands after the absorption edge, which correspond to electron transitions to quasi-bound states, are broader.

Both methods are used to study the state of elements in bulk samples and in surface phases that are formed due to sorption processes involving microelements and surface sorbents, *i.e.*, soils and colloid particles.

If traditional instrumental methods are used to study the state of microelements in a liquid phase (*e.g.*, UV and IR spectroscopies), distinguishing individual signals corresponding to a compound of interest from those corresponding to the support without their chemical separation is the main difficulty.[41] After chemical separation, it is incorrect to apply data on the composition of chemical forms of a microelement to the original natural solution or heterogeneous system.

The EXAFS method is devoid of such restrictions, because, as noted above, the spectra contain information about the chemical environment, interatomic distances and the number of the closest neighbours of a microelement atom.[41] In fact, it was noted in an EXAFS study on the identification of the state of hardly soluble lead compounds in soil that it was possible to decrease the detection limit of chemical compounds (below 10^{-3} mass%) at a relative measurement error of 5%.[41]

By combining the EXAFS method with free boundary electrophoresis, it is possible to reach sensitivity of 10^{-5}–10^{-8} mol litre^{-1}. It was shown using these methods that the sorption of uranium by hematite at pH 4.5 is caused by partial binding of carbonate (hydrogencarbonate) anions with uranyl cations in monomeric carbonate uranium complexes. However, it is dimeric complexes that are responsible for the sorption of uranium on the surface around pH 6.5. Based on this fact, it was concluded that the mobility of U(VI) tricarbonate complexes in ground water is low.[43]

Studies on the state and sorption behaviour of actinides with different oxidation states showed that their mobilities were considerably affected by the redox potential of the solution. Foster *et al.*[35] and Antonio *et al.*[44] developed a procedure to determine the formal redox potentials of neptunium in soil and ground waters for the Np(IV)/Np(V) and Np(IV)/Np(III) pairs and formulated the objectives for subsequent EXAFS studies on the sorption behaviour of neptunium complexes in natural waters. This method was used to study the coordination environment of Cd(II) sorbed by goethite in the presence of sulfate, oxalate and citrate ions and anions of humic acids; it was shown that cadmium atoms are surrounded by six oxygen atoms in the first coordination sphere and by two iron atoms in the second sphere.[45] In oxalate and citrate solutions, precipitation of a sparingly soluble cadmium compound on goethite facets occurs. A drawback of the latter study[45] is that the results obtained for cadmium concentrations of $10^{-3}-10^{-4}$ mol litre^{-1} in solution were extrapolated to the region of microconcentrations typical of soil and ground waters.

The EXAFS method was used to obtain structural information on the composition of cadmium, zinc and copper complexes with organic ligands in non-aqueous solutions;[46] data on the composition and structure of chloride Cu(II) complexes at ordinary and elevated temperatures in solutions simulating sodium chloride thermal water by matrix elements are reported by Collings *et al.*[47] It was shown that copper chloride complexes are not formed in the temperature range of 25–75 °C at sodium chloride concentrations in the range of 0.2–2.2 mol litre^{-1}; under hydrothermal conditions, the $CuCl^+$ and $CuCl_2^0$ species

start to predominate as the temperature is increased from 125 to 175 °C; at chloride concentrations up to 5 mol litre^{-1} in the temperature range of 25–75 °C, the $CuCl_3^-$ and $CuCl_4^{2-}$ species predominate, but the $CuCl^+$ and $CuCl_2^0$ species start to predominate again at 175 °C (due to the formation of Na–Cl ion pairs).

The EXAFS method was used to study the state of $AuCl_3$ in chloride solutions.[48] Sherman *et al.*[49] analysed the state of different-valent tin chloride complexes in 0.5–2.5 mol litre^{-1} sodium chloride solutions in the temperature range of 25–250 °C. Data on the coordination of copper, zinc and arsenic ions in sodium hydrogensulfide solutions were reported.[50,51] Seward *et al.*[52–54] used EXAFS to determine the state of $AgNO_3$, $CdCl_2$, $AgClO_4$ and $SrCl_2$ in aqueous solutions. Mosselmans *et al.*[55] studied the coordination of molybdenum, cobalt and cadmium aqua-complexes; the state of antimony and yttrium in chloride solutions was studied in a number of works.[47,48,56,57] The compositions of metal complexes (in particular divalent and tetravalent tin complexes) found by EXAFS sometimes noticeably differ from the compositions obtained by thermodynamic simulation:[49] in the chloride concentration range 0.5–2.5 mol litre^{-1} and the temperature range of 25–350 °C, an increase in chloride concentration increases the numerical value of factor n in the formula $SnCl_n^{2-n}$ from 3.4 to 3.9, which suggests that the $SnCl_3^-$ and $SnCl_4^{2-}$ complexes predominate. If the temperature has been increased from 250 to 350 °C, the $SnCl_4^{2-}$ complexes are mainly present. The $SnCl_6^{2-}$ complex predominates in oxidising media; this implies higher solubility of SnO_2 (in comparison with that obtained by thermodynamic calculation) in this medium and the possibility of efficient transport of di- and tetravalent tin in hydrothermal processes.

It is particularly efficient to use EXAFS spectroscopy in combination with molecular dynamics methods in studies on the polymerisation of aqua complexes in solutions, because it is possible to register changes in the inner coordination sphere (metal–ligand–metal) directly. In this way, the polymerisation of $SrCl_2$ in concentrated chloride solutions was confirmed directly.[52]

This method is efficient in studies on ion–molecular and other forms of elements in solutions. However, its use in ecological studies of natural waters that have complex microelement compositions is presently limited by the low sensitivity and selectivity, as well as by the necessity of preliminary withdrawal and conservation of samples.

The XANES method, which is being intensely developed at present, is much more sensitive.[58–67] Using this method, one can analyse the chemical bonds between atoms, oxidation states and chemical compositions of compounds formed by microelements at their solution concentrations of about 10^{-6} mol litre^{-1}. The theory of the method has been described in a number of publications.[65–67] The XANES method was used to obtain data on the sorption behaviour of lead in soils,[62,63] the physicochemical state of arsenic in bottom sediments,[59,60] the mechanism of Cr(VI) reduction in natural solutions[61] and also to study the state and sorption behaviour of separate valent forms of plutonium in the water–soil system.[64]

5. Mass spectrometric methods

The Laser Microprobe Mass Spectrometry (LMMS) and especially the Static Secondary Ion Mass Spectrometry (SSIMS) methods are used as direct instrumental methods for determination of the physicochemical state of microelements that predominantly exist in the adsorbed state. The characteristic mass spectra of simple ions and ion clusters serve as the main source of data on the chemical composition of compounds being studied.[68]

The use of LMMS mass spectrometers with Fourier transform of the signal provides a mass resolution of 10^5 with a sensitivity of about 1 ppm for separate ions.[68]

The instrumental potential of Secondary Ion Mass Spectrometry (SIMS) for chemical analysis of microquantities of inorganic compounds is more versatile, since the signal results from bombardment of the surface of a sample of interest by a primary ion beam (*e.g.*, Ar^+, O^-) with an energy of several kiloelectronvolts. This increases considerably the intensity of the secondary beam of ions (both positive and negative) from the sample and the overall sensitivity of the method. The static version of this method, *viz.*, SSIMS, employs a low-intensity beam of primary particles, thus making it possible to study compositions of compounds with extremely high mass numbers. The sensitivity of the SSIMS method can range within 10^{21}–10^{15} atoms cm^{-2}. Time of Flight Static Secondary Ion Mass Spectrometry (TOF SSIMS) makes it possible to identify the molecular composition of a compound of interest based on the set of secondary ion clusters, which is unique for each compound.[68,69] Therefore, when analysing biological and natural solid samples, compounds can be identified by matching the sample composition with the secondary ion spectrum.[68]

Mass spectrometric methods are used in high-precision studies on the molecular composition of microcomponents with concentrations below 10^{-6} mol litre^{-1}. These methods are primarily used to assess the state of adsorbed compounds. A mass spectrum obtained by SSIMS is a superposition of spectra corresponding to original molecular states of microelements and to their reaction products with stable ions in the gas phase. In the LMMS method, the possibility of obtaining mass spectra of molecules of interest is based on the specific features of the signal formation. An advantage of the LMMS method is that it provides a relatively high spatial resolution on the sample surface (0.1–10 μm); the SSIMS method makes it possible to perform sequential in-depth analysis of a sample at molecular resolution. Owing to the high signal-to-noise ratio, the LMMS method provides direct (that is, without the use of composition standards) data on the molecular composition of samples. To obtain such data by SSIMS, one has to compare the mass spectra of a sample in question with the mass spectra of samples with standard compositions. Evidently, the two methods complement each other. They can be modified in order to study the chemical composition of microelements in solution, provided that the relationship between the composition of the solid sample being analysed and the composition of the original sample is established when the solution is being prepared for analysis.

The problem of sample preparation for mass spectrometric studies on the composition of complex compounds of microelements in solutions is solved, to a considerable extent, by using Electrospray Mass Spectrometry (ESMS).[70] It is used for quantitative determinations of metal ions in inorganic, organometallic and complex compounds and is based on a genuine way of generating ionic clusters.

The experimental value of the ESMS method is that electrospraying of a sample transfers ions and molecules existing in the original solution to be studied to the gas phase. This occurs due to two main processes, *viz.*, creation of charged micro-droplets of the solution and transfer of ions of elements from the micro-droplets to the gas phase. The original information on the chemical composition and oxidation state of an element is preserved in these processes. Charged micro-droplets are formed on passing a solution of interest through a conductive capillary with an inner diameter of $\sim$ 100 μm kept under a 2–4 kV voltage relative to the counter-electrode, as a rule, the mass spectrometer sampler (the tool for introducing a sample into the mass spectrometer). Under an electric field gradient, separation of charges occurs in the surface layer of electrolyte micro-droplets; as a result, it acquires an excess positive charge leading to intense carryover of positive ions from the surfaces of micro-droplets and evaporation of the surface layer of the liquid meniscus in the capillary (Taylor's cone).[71] Owing to the electrophoretic motion of the liquid in the near-surface region, the charged surface layer stretches as a thin (1–10 μm) fibre towards the sampler of the mass spectrometer, breaks into positively charged micro-droplets and forms a cone in a stable electrospraying mode.[72]

The field of application of ESMS includes studies on molecular reactions in the gas phase and formation of bioorganic and organometallic complexes in non-aqueous solvents.[70] The drawbacks of the method include the complexity of sample preparation from natural objects and the necessity of maintaining reproducible instrumental conditions when mass spectra are recorded. An advantage of the method is that information on the oxidation states of metals (microelements) in aqueous solutions and on the presence of mono- and polyatomic anions (nitrates, thiocyanates, chromates, permanganates, oxohalides, various sulfur anions, *etc*.) and transition metal complexes with inorganic and organic ligands can be obtained. The limitations of the quantitative version of this method include the dependence of the reproducibility and sensitivity in the determination of clusters of microelements on the solution electrical conductivity and the narrow signal range (3–4 orders of concentration). These limitations can be eliminated by simultaneous spraying of an additional background electrolyte solution. This will make it possible to determine the chemical composition of microelements at concentrations $\sim 10^{-8}$ mol litre^{-1} (see Ref. 70).

Determination of the state of microelements by ESMS in real natural solutions is complicated by the noise that appears in the mass spectra. Preliminary separation of elements and their chemical forms, *e.g*., by high-performance liquid chromatography and other methods, is used to increase the signal-to-noise ratio.[70, 73]

6. Voltammetry methods

Electrochemical methods are among the most convenient instrumental methods for the study and determination of the ion–molecular state of microelements in natural aqueous solutions; of these, Stripping Voltammetry (SV) is worth special attention.[74] The main advantage of this method in studies of natural waters is its selectivity with respect to separate chemical forms of microelements and low detection limits of microelements. The relatively low cost of analysis, the possibility of its automation and the small size of the instruments make it possible to use the stripping voltammetry under field conditions, in particular, in prolonged continuous analyses and when composing distribution maps of separate forms of microelements in seawater and fresh water as part of above-water and underwater experiments.[74] After preliminary concentration of a microelement from the aqueous phase, the SV method can be combined with subsequent cathodic or anodic dissolution of the analyte accumulated on the working electrode.

The multi-element version of the accumulation method makes it possible to reach detection limits of microelements in seawater as low as 10^{-10}–10^{-12} mol litre^{-1} (Ref. 74). Up-to-date polarographs are three-electrode systems (working electrode, auxiliary electrode and reference electrode); a dropping mercury electrode, a hanging mercury drop electrode or a thin rotating film mercury electrode is used as the working electrode. In the former case, measurements are carried out on a continuously renewed surface of the working electrode; this is advantageous as high analysis reproducibility is ensured. The second version is usually implemented by electrodeposition of mercury on surfaces of glassy carbon, graphite, metallic conductors (gold, iridium), graphite fibre; this enhances the sensitivity owing to high ratios of the working electrode surface to the solution volume.

In recent years, mercury (deposited on carbon fibre or iridium wire) and gold microelectrodes with sizes < 10 μm have become more and more popular. They are characterised by a much weaker effect of capacitance current and an increased signal-to-noise ratio; these electrodes allow microelement concentrations $< 10^{-10}$ mol litre^{-1} to be determined owing to an improved efficiency of deposition on the working electrode and the suppression of diffusion effects.

Stripping voltammetry with anodic polarisation (Anodic Stripping Voltammetry, ASV) is used successfully to analyse relatively high (due to adverse effects of overlapping of signals from interfering elements) concentrations of copper, cadmium, lead, zinc and thallium in seawater.[74] It is recommended to increase the negative potential in the metal deposition stage so as to make it 0.3–0.4 V higher than the reduction potential. After accumulation of a microelement of interest as an amalgam in the reduction stage, subsequent anodic polarisation of the working microelectrode results in oxidation of the reduced form of the microelement, thus providing both quantitative and qualitative information (as the oxidation potential is a specific characteristic of an element) about the metal on the electrode. The method requires additional analytical operations, *viz*., calibration and standardisation of measurements.

The SV version with cathodic polarisation and adsorption of the sample (Adsorptive Cathodic Stripping Voltammetry, AdCSV) is a more sensitive method used as an alternative to traditional inversion voltammetry. The sensitivity is increased by introducing a specific ligand into a solution. The role of the ligand is to form a relatively stable complex ion with the microelement being determined which can be adsorbed on the working electrode surface at constant potential and then be involved in the reduction process. The reduction is generally carried out with linear sweep of the signal amplitude; if the discharge electrochemical stage is reversible, a square high-frequency AC component is applied. This suppresses the interfering capacitance currents, slows down the competing step of adsorbed oxygen reduction and shortens the analysis duration. The techniques described above create conditions for reaching very low detection limits of metals (10^{-12} mol litre^{-1} for cobalt, platinum, titanium) in seawater.[74]

The high sensitivity for trace amounts of compounds makes SV a convenient method to study forms of existence of microelements in aqueous solutions. For example, the concentrations of many transition metals (cobalt, copper, iron, zinc) in natural water (river, lake, seawater) are generally extremely low but they can considerably affect biochemical processes involving hydrobionts.[75–77] Simple aqua ions are the most bioactive and toxic forms as they easily penetrate cell membranes of phytoplankton and algae. Complexes with organic ligands (humic and fulvic acids, ethylenediaminetetraacetic acid, *etc*.) are devoid of this ability, and the susceptibility of micro-organisms to these metals decreases if such ligands are present in aqueous solutions.

In studies on exchange processes, the SV method is one of the few instrumental methods that make it possible to determine the valence of microelements in solutions, as well as the fractions of separate microelements in the free form and as organic complexes at concentrations around 10^{-9} mol litre^{-1} in natural water (see Refs 78–92). For example, it was shown using the AdCSV method that the natural state of Cr(VI) in Mediterranean Sea water matches the data from thermodynamic calculations of the concentration of the most stable form of chromium, CrO_4^{2-}, in an oxygen-saturated solution. However, determination of the overall chromium content in seawater after decomposing its organic complexes by UV irradiation and sorption separation of Cr(III) showed that it contains tri- and hexavalent chromium ions (Fig. 3). The presence of trivalent chromium is explained by the photochemical reduction of the CrO_4^{2-} ions in the seawater surface layer.[79]

The ratio of free metal forms to those bound in complexes can be found using the ASV and AdCSV methods. The equilibrium concentrations of an aqua ion and its labile complexes with inorganic and organic ligands are determined using the ASV method. The AdCSV method is used to establish the chemical nature of organic ligands. To do so, it is necessary to provide conditions for competitive complexation of an added ligand (with a known complexation scheme) and natural ligands in a solution of interest. Based on results of concentration measurements for the free and bound forms of a microelement, the concentration complexation constant with natural ligands is calculated. The true compositions of organic (primarily bioorganic) complexes of the majority of microelements in seawater and fresh water are unknown; algae and products of phytoplankton biodegradation are believed to be the main sources of organic ligands.[74] For example, it was found by means of SV that over 99% of dissolved

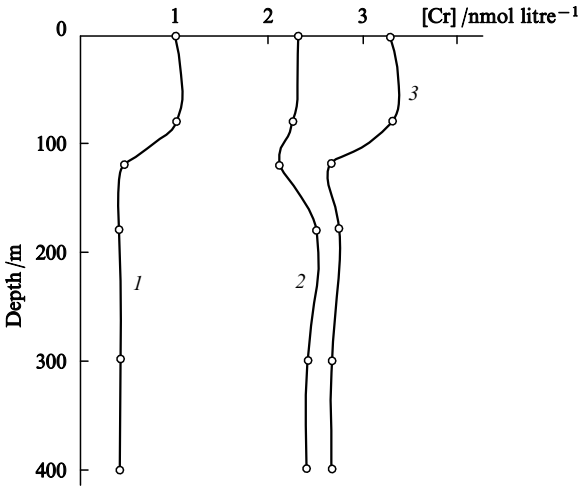


Figure 3. Concentration profiles of Cr(III) (*1*), Cr(VI) (*2*) and total chromium (*3*) at different depths of the western part of the Mediterranean Sea determined by AdCSV.[55]

iron is bound with organic ligands and is characterised by an arbitrary complexation constant of $\sim 10^{18}$. Using SV combined with direct determination of microelement concentrations and preliminary filtration-based fractionation, it is possible to determine the ratio of ion–molecular and colloidal forms of a metal of interest.

III. Hyphenated methods

At present, studies on the physicochemical state of microelements in solutions combining techniques for separation of individual microelement forms with high-sensitivity instrumental methods for detection of separated microelements have become one of the leading directions.[7,9,93–102] In favour of this is the appearance of high-sensitivity instruments for electrochemical, emission and mass spectrometric analyses.

1. Chromatographic methods

Numerous procedures have been developed based on chromatographic methods including a procedure for the determination of hexavalent chromium and tungsten by extractive isolation of their ternary complexes with rutin (quercetin-3β-rutinoside) in the presence of cetyltrimethylammonium and procedures for determination of the valence and chemical composition of molecular and cationic complexes of tri- and pentavalent arsenic (mono- and dimethylarsonium, arsenobetaine and some other arsenic compounds), organic and inorganic derivatives of tetra- and hexavalent selenium, divalent lead and mercury, di- and tetravalent tin, tri- and hexavalent chromium.[103] The multistage separation and independent determination of the forms of state of these microelements in aqueous media are carried out by automated control of the chromatographic process, using standard samples of the states and compositions of microcomponents in the medium of interest or in some other similar medium. The sensitivity of hyphenated methods with respect to separate chemical forms can reach 10.0–0.01 μg litre^{-1} for media in which the chemical compositions of the complexes to be analysed are known beforehand.

In their review, Vanhaecke and Moens[94] analysed works published in the past decade and dealing with chromatographic methods with mass spectrometric detection for the determination of the chemical composition of microelements in natural objects. Of these, column separation with reversed phases, ion-exchange sorption, ion pair sorption and gel filtration are the most popular methods. The latter method can be used to determine simultaneously the behaviour and degree of complexation of metal ions in natural waters in the presence of dissolved organic compounds. This is achieved by combining gel filtration and mass spectrometry with simultaneous determination of the total carbon content (*e.g.*, by UV spectroscopy) in the fractions eluted from a chromatographic column.[94]

Today, the analytical instrumentation market offers transportable toolkits for the analysis of the chemical state of separate microelements. A toolkit comprises a microcolumn of specific type for high-performance liquid chromatography (HPLC) combined with a mass spectrometer; this allows one to determine the concentration of separate valence forms of such microelements as chromium, selenium and arsenic.

Hyphenated methods based on chromatography are beginning to compete with traditional radiochemical methods for the analysis of the isotopic and elemental composition conventionally used in technologies of processing and burial of spent nuclear fuel. Using the methods considered here, one can determine the forms of migration of both radionuclides corresponding to the middle of the Periodic System (s-, p-, d- and f-elements) and trans-actinide elements.[104–110] The possibility of using inductively coupled plasma mass spectrometry and thermal-ionisation mass spectrometry was shown: preliminary HPLC separation of ionic complexes of uranium, americium, and curium is followed by determination of the $^{241}Am/^{238}U$ and $^{244}Cm/^{238}U$ isotope ratios in separate chemically pure fractions with the use of the double isotope dilution method.[111] The chemical separation of uranium and plutonium was performed in an anion-exchange column; that of americium and curium, by HPLC (stationary phase, Nucleosil SA; 0.14 M 2-hydroxy-2-methylbutyric acid, pH 4.1 as the eluent). The use of the hyphenated method provides a relative determination error of 2.5% in the isotope ratio range from 1 to 0.001.

Hyphenated methods are generally used with standard samples of states of the microelements studied (*e.g.*, alkyl derivatives of tin, mercury and arsenic). Their kinetic inertness makes it possible to neglect the effects of foreign components, that is, potential ligands and competing complexing agents, when an aliquot of the standard is added to the solution under study.[112]

An example of the use of hyphenated methods for determining the states of labile organic and inorganic metal complexes is given by Pesavento *et al.*[113] who studied the formation of manganese, nickel, cadmium, and copper complexes with ligands of unknown composition. The Chelex-100 chelating resin with iminodiacetate groups was used as a selective ion exchanger. The state of ions of these elements in seawater (samples from Ligurian Sea, Italy) was determined by ion-exchange titration of the solution with a selective ion-exchange resin under static conditions. Based on the results of titration, the content of the elements sorbed by the ion-exchange resin was determined from the ratio of the volumes of the solution and the resin. The total concentrations of an element in a system with standard composition and in a natural system being studied, as well as the coefficient of side reactions were found from experimental data using the Schubert method. The agreement between the results of measurements served as a criterion that the degree of complexing of a microelement with ligands of unknown nature in seawater was determined correctly. Seawater was initially purified from suspended matter and (partially) from colloidal particles. Therefore, one can characterise the ratios of simple and complex ions of manganese, nickel, cadmium and copper in seawater, but not the composition and nature of these complexes, based on information obtained. Pesavento *et al.*[114] also studied the physicochemical state of aluminium in potable water by ion exchange titration and found that very stable aluminium complexes with complicated composition were present at pH 6–7 in addition to aquahydroxo complexes.

The application of chromatography-based hyphenated methods makes it possible to carry out detailed studies on the state of microelements, identify their oxidation states and determine their environment in both simulated and natural aqueous systems.[114–117]

2. Electrophoresis

Methods for the determination of the state of stable and radioactive microelements based on the analysis of electrophoretic mobilities of ions and colloidal particles in a free electrolyte and in a porous medium have been used for a long time. Both theoretical and methodical approaches have been developed for these methods.[7,9,95,96] The application of such methods has broadened considerably over the past decade. Instruments based on the principle of capillary electrophoresis are now commercially available.[118–121] These instruments are successfully used in radiochemistry and in ecological and biochemical studies in order to determine the charges of individual ions, oxoanions, as well as inorganic and organic metal complexes.[119–121]

Separation by capillary electrophoresis is based on differences in the migration of ions of microelements along a capillary filled with a solution of an electrolyte. The capillary diameter is close to the thickness of the dense part of the double electric layer at the capillary walls; therefore, the resulting mobility of ions in the capillary is concurrently affected by the electrophoretic and electroosmotic flows of the electrolyte.

Two versions of capillary electrophoresis are used, *viz*., zone electrophoresis in free electrolyte and electrokinetic micellar chromatography. The first version is used to separate individual chemical forms of a microelement in ordinary solutions. In this case, separation depends primarily on the ratio of the charge of a solvated ion to the size of its solvate shell. The second variant is intended for separation of microelements in micellar (colloidal) solutions; its efficiency is mainly determined by the micelle charge and the mechanisms of distribution of the molecular forms of the microelement between the electrolyte and micelles.[120] Capillary electrophoresis is particularly efficient if the element being determined is present as both charged complexes and colloidal particles. As in the case of free boundary electrophoresis, the efficiency of separation of individual microelement forms is strongly affected by kinetic factors of the reaction of the complex-forming ion with the ligands.[112,119,120]

A number of publications are available [119–122] on the results of separations and determinations of metals in various oxidation states by combined methods based on capillary electrophoresis on quartz glass microcolumns. For example, the following elements were separated and determined: selenium, arsenic, tin, mercury, chromium, iron, platinum and vanadium; trivalent iridium, europium, cadmium and tetravalent rhodium, $Al^{3+}-F^{-}$ complexes, divalent zinc, di- and trivalent cobalt and a number of their alkyl derivatives, amino, cyano, chloro, and acetate complexes, both in artificial solutions and in river water, seawater and rainwater, as well as in soil extracts, liquid radioactive waste and biological environments. The following issues were noted: insufficient sensitivity of detecting instruments, necessity of using spectral detection methods, improvement of sampling methods and methods for preparation of media for sampling, improvement of procedures for checking the quality of analytical data obtained, and creating a base of standard samples of particular microelements and media in various states.

3. Filtration methods

In the past decade, there has been an increasing number of studies on the role of the colloid-dispersed state of microelements in their migration in water.[123–153] The usual method of studying the colloidal state of microelements employs the principle of ultrafiltration. Chemically inert filtering materials with pore size from a few nanometres to tens of nanometres have been developed. Filtrating devices using both ordinary frontal filtration and cross-flow filtration (CFF) are now commercially available. Owing to the more favourable flow dynamics, the latter variant provides considerable advantages in studies on the size of colloidal particles, their charge and chemical nature.[130–140]

The CFF principle involves the separation of colloidal particles with a volume concentration c_B on a membrane filter surface.[138] The movement of the incoming colloidal solution occurs laterally with respect to the porous membrane surface, while the filtration occurs tangentially with respect to the wall due to the hydrostatic pressure gradient, which appears in the near-the-wall liquid film because of the concentration polarisation, and a change in the penetrating filtration flow (J). The J value depends on the concentration parameters of a colloid solution by the relationship

$$J = k\ln\left(\frac{c_w - c_p}{c_B - c_p}\right), \quad (2)$$

where k is the mass-transfer coefficient determined experimentally or from empirical hydrodynamic relationships; c_w is the concentration of colloidal particles near the wall; and c_p is the concentration in the flow that has passed through the membrane. The initial flow of a liquid being analysed is divided into two flows during cross-flow filtration: the penetrated and delayed flows. It is the ratio of concentrations in these flows that carries information about the content of the colloid fraction, for which the rejected particle size is equivalent to the membrane pore diameter, in the original flow.[138]

A comparison of cellulose- (Millipore Pre-scale CFF) and polysulfone-based (Amicon CFF) commercial filters in the cross-flow filtration mode [139] showed their similar efficiencies: both filter types retain up to 91% of colloidal particles with rejected sizes shown in the filter passports. The major fraction of standard colloidal dextrin solution with a nominal molecular mass of 3000 is removed from water by filters with a rejecting mass of 1 kDa; up to 30% of colloidal dextrin particles are lost in the case of polysulfone-based membranes owing to the sorption in the filter material. Losses of protein colloids (in particular, lactalbumin) are considerable on both filters. The content of colloidal particles of organic carbon introduced in seawater as a standard is determined without a systematic error. However, when seawater is analysed using cross-flow filtration, 'breakthrough' of some fractions of both low- and high-molecular fractions is observed.[140,141]

For example, in a study of organo-inorganic colloids of ^{230}Th and ^{234}Th in seawater by ultrafiltration it was found that physical separation of the ionic and colloidal fractions of thorium on membrane filters with rejecting mass < 10 kDa is accompanied by adsorption of micro-quantities of thorium and mechanical interaction with the membrane material (polysulfone, polypropylene, *etc*.).[140] The adsorption losses increase with a decrease in the organic carbon concentration; they cannot be suppressed by acid treatment of the membranes. In total, the changes in the fraction of the colloidal fraction of ^{234}Th coincide with the changes in the concentration of the colloidal fraction of organic carbon with molecular masses > 10 kDa.

Using frontal or cross-ultrafiltration in combination with monitoring the sizes and charges of particles by dynamic light scattering methods (laser photon-correlation spectroscopy) and Doppler electrophoresis, it is possible to determine not only the usual characteristics of colloids but also their acid–base properties. These methods were employed [130] to show the possibility of transferring natural colloidal particles from an estuary (river–sea hydrochemical border) to an electrolyte solution followed by determination of the acid–base properties of the colloids that have been concentrated. Furthermore, a conclusion about the nature of an organic colloidal compound in river water was drawn, and the range of organic colloid sizes (2–3000 nm) in the electrolyte solution after filtration concentrating was determined. It was found that the particle size increases with time and decreases with an increase in pH of the electrolyte. The acid–base properties of freshly prepared concentrates of a natural organic colloid differ from the acid–base properties of humic acids. This fact was explained [130] by possible formation of organo-mineral colloids involving large particles of colloidal iron hydroxide.

Sorption of humic acids on the surface of boehmite (γ-AlOOH) particles involves a similar interaction mechanism of

colloidal particles: anion exchange of ligands occurs in the initial stage; after that, the organic acid undergoes condensation on the hydroxide surface as its concentration increases.[142] The ion-exchange mechanism of interaction of organic and inorganic colloids is considered as a complex variety of the metal–ligand coordination interaction[143] characteristic of microcomponents with high hydrolysis constants (in particular, for high-charged ions of transition metals and actinides).[131, 144, 145] In radiochemistry, such interaction occurs during the heteronucleation of colloids present in trace amounts.[9]

The real picture of stepwise colloidal interactions in natural aqueous systems is complicated by the fact that colloids of inorganic hydroxides of the majority of transition metals present in trace amounts are nano-sized particles,[107–114] migration of which in natural waters increases considerably in the presence of humic acids. The migration of microelements mainly occurs by this mechanism.[123, 124, 131, 146]

The discreteness of fractional analysis of the colloidal state of microelements in frontal and cross-ultrafiltration methods does not allow the size distribution of colloid particles to be estimated and hence prevents a comprehensive explanation of the effects of size on the physicochemical state and migration. The drawbacks of filtration methods also include poor resolution of particles according to size and frequent fouling of filter pores.

These drawbacks are eliminated in a hyphenated method uniting sedimentation separation of colloids in a centrifugal field with mass spectrometric detection of the elemental compositions of separate colloidal fractions in the stream (Sedimentation Field-Flow Fractionation, SdFFF).[128, 147–153] According to this method, the capillary with the colloid solution of interest is simultaneously affected by a tangential centrifugal field and a longitudinal axiosymmetrical pressure field. The effect of these fields on the flow results in separation of particles into fractions, which are successively eluted from the capillary. The concentration of colloidal particles in the eluate is determined by inductively coupled plasma mass spectrometry or by UV spectroscopy. The method makes it possible to concentrate colloidal fractions. The eluate fractions can be passed for a more thorough study of the composition of colloidal particles by scanning tunnelling microscopy, X-ray diffraction analysis and X-ray fluorescence spectroscopy.[128, 148–153] Based on SdFFF data, one can plot a differential curve of distribution of colloidal particles against eluate fractions (volumes) or elution time, and then according to the diameters of spherically similar particles with concentrations < 100 μg litre^{-1}. By comparing distribution curves for organic carbon and separate elements, particles are identified as true colloids or pseudo-colloids (of organic or mineral nature). This method is particularly efficient in studies of the state of colloidal forms of microelements.

* * *

By now, studies of physicochemical states of microelements in aqueous media have become an independent scientific direction of interdisciplinary type that combines problems and methods of analytical and physical chemistry of ultra-dilute solutions, radiochemical and geochemical analysis of the ion–molecular and phase analysis of compounds. It is obvious that the instrumental base is growing rapidly, and ample new information is therefore appearing about the chemical, phase and dispersion composition and reactivity of separate forms of stable microelements both in natural systems and their geochemical combinations.

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References

1. B F Myasoedov, A P Novikov, F I Pavlotskaya *Zh. Anal. Khim.* **51** 124 (1996)[a]
2. R W Buddemeier, J R Hunt *Preprint UCRL-98204* (Livermore, CA: Lawrence Livermore National Laboratory, 1988)
3. A F B Tompson, C J Bruton, D E Bourcier, A B Kersting, D K Smith, S F Carle, G A Pawloski, J A Rard, in *Proceedings of 7th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere. MIGRATION'99, Hyatt Regency Incline Village, 1999* C4-03
4. R Finch, E Buck, J Fortner, C Mertz, S Wolf, P Finn, W Ebert, J Cunnane, in *Proceedings of 7th International Conference on the Chemistry and Migration Behaviour of Actintdes and Fission Products in the Geosphere. MIGRATION'99, Hyatt Regency Incline Village, 1999* A-04
5. B F Myasoedov *Ros. Khim. Zh.* **37** 13 (1993)[b]
6. V I Zemlyanukhin, I S Serebryakov, V V Shatalov, in *Radiokhimiya-2000 (Tez. Dokl. Tret'ei Ros. Konf. po Radiokhimii), Sankt Peterburg, 2000* [Radiochemistry-2000 (Abstracts of Reports of the Third Russian Conference on Radiochemistry), St Petersburg, 2000] p. 193
7. I E Starik *Osnovy Radiokhimii* (Foundations of Radiochemistry) (Leningrad: Nauka, 1969)
8. Yu V Egorov *Statika Sorbtsii Mikrokomponentov Oksigidratami* (Statics of Sorption of Microcomponents by Oxyhydrates) (Moscow: Atomizdat, 1975)
9. P Benes, V Majer *Trace Chemistry of Aqueous Solutions* (Prague: Academia, 1980)
10. T Berg, E H Larsen *Fresenius J. Anal. Chem.* **363** 431 (1999)
11. *Modelling and Study of the Mechanisms of the Transfer of Radioactive Materials from Terrestrial Ecosystems to and in Water Bodies Around Chernobyl. Experimental Collaboration Projects No. 1–5 (Final Reports) EUR. 16527-16531, 1996*
12. B Walz *Spectrochim. Acta, Part B* **53** 169 (1998)
13. J A Jonsson, L Mathiasson *Trends Anal. Chem.* **18** 318 (1999)
14. H B Xue, L Sigg *Anal. Chim. Acta* **363** 249 (1998)
15. K Novotný, A Turzíková, J Komárek *Fresenius J. Anal. Chem.* **366** 209 (2000)
16. E J M Temminghoff, A C C Plette, R Van Eck, W H Van Riemsdijk *Anal. Chim. Acta* **417** 149 (2000)
17. A Pleßow, H Heinrichs *Aquatic Geochem.* **6** 347 (2000)
18. A M Carro, M C Mejuto *J. Chromatogr., A* **882** 283 (2000)
19. H Amano, T Matsunaga, S Nagao, Y Hanzawa, M Watanabe, T Ueno, Y Onuma *Org. Geochem.* **30** 437 (1999)
20. A P Novikov, F I Pavlotskaya, T A Goryachenkova, A I Smagina, I E Kazanskaya, V V Emel'yanov, E V Kuzovkina, K B Barsukova, E A Lavrinovich, P A Korovaikov, E G Drozhko, S I Rovnyi, A K Posokhov, B F Myasoedov *Radiokhimiya* **40** 453 (1998)[c]
21. F I Pavlotskaya, A P Novikov, T A Goryachenkova, I E Kazanskaya, V V Emel'yanov, E V Kuzovkina, K B Barsukova, E A Lavrinovich, P A Korovaikov, B F Myasoedov *Radiokhimiya* **40** 463 (1998)[c]
22. H Moll, G Geipel, V Brendler, G Bernhard, H Nitsche *J. Alloys Compd.* **271–273** 765 (1998)
23. G Bernhard, G Geipel, V Brendler, H Nitsche *J. Alloys Compd.* **271–273** 201 (1998)
24. C-D Tiseanu, M U Kumke, F H Frimmel, R Klenze, J I Kim *J. Photochem. Photobiol., A* **117** 175 (1998)
25. R Klenze, J I Kim, P A Panak *J. Alloys Compd.* **271–273** 746 (1998)
26. D Th Fanghanel, J-I Kim *J. Alloys Compd.* **271–273** 728 (1998)
27. A Molski, J Hofkens, T Gensch, N Boens, F De Schryver *Chem. Phys. Lett.* **318** 325 (2000)
28. R Knopp, F J Scherbaum, J I Kim *Fresenius J. Anal. Chem.* **355** 16 (1996)
29. A Brachmann, S Mihardja, D A Wruck, C E A Palmer *Preprint UCRL-JC-135555* (Livermore, CA: Lawrence Livermore National Laboratory, 1999)
30. R J Harrach *Preprint UCRL-52389* (Livermore, CA: Lawrence Livermore National Laboratory, 1977)
31. N S Foster-Mills, J E Amonette, T Autrey, J R Small, Y Chen, E Small *EMSL. Environmental Dynamics and Simulation. Laser Photoacoustic Spectroscopy: Basic and Applied Research* http://lancair.emsl.pnl.gov:2080/docs/eds/annual_report1999/1627b-4a.html

32. T Autrey, N S Foster, K Klepzig, J E Amonette, J L Daschbach *Rev. Sci. Instrum.* **69** 2246 (1998)
33. T Autrey, N S Foster, K Klepzig *J. Photochem. Photobiol., A* **125** 13 (1998)
34. N S Foster, T Autrey, J E Amonette, J R Small, E W Small *Am. Lab.* **31** 96S (1999)
35. N S Foster, J E Amonette, S T Autrey *Appl. Spectrosc.* **53** 735 (1999)
36. T Sekine, S Naito, Y Kino, H Kudo *Radiochim. Acta* **82** 135 (1998)
37. V Neck, J I Kim, B S Seidel, C M Marquardt, K Dardenne, M P Jensen, W Hauser *Radiochim. Acta* **89** 439 (2001)
38. T Fujita, T Sekine, H Hiraga, K Yoshihara, A Mutalib, R Alberto, J I Kim *Radiochim. Acta* **63** 45 (1993)
39. N S Foster-Mills, J E Amonette, B K Williams, A E Taylor *Environmental Dynamics and Simulation. Laser Photoacoustic Spectroscopy: Basic and Applied Research* http://lancair.emsl.pnl.gov:2080/docs/eds/annual_report 1999/1627b-3b.html
40. M V Kuznetsov, E V Shalaeva, N I Medvedeva, A L Ivanovskii *Khimiya Poverkhnosti Razdela Titan–Gaz. Eksperiment i Teoriya* (The Chemistry of Titanium–Gas the Interface. Experiment and Theory) (Ekaterinburg: Urals Branch of the Russian Academy of Sciences, 1999)
41. E Welter, W Calmano, S Mangold, L Treger *Fresenius J. Anal. Chem.* **364** 238 (1999)
42. Ya V Zubavichus, Yu L Slovokhotov *Usp. Khim.* **70** 429 (2001) [*Russ. Chem. Rev.* **70** 373 (2001)]
43. J R Bargar, R Reitmeyer, J J Lenhart, J A Davis *Geochim. Cosmochim. Acta* **64** 2737 (2000)
44. M R Antonio, L Soderholm, W Clayton in *Proceedings of the 7th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere. MIGRATION'99* (Livermore, CA: Lawrence Livermore National Laboratory 1999) PA3-01
45. C R Collins, K V Ragnarsdottir, D M Sherman *Geochim. Cosmochim. Acta* **63** 2989 (1999)
46. S B Erenburg, N V Bausk, S M Zemskova, L N Mazalov *Nucl. Instrum. Methods Phys. Res., Sect. A* **448** 345 (2000)
47. M D Collings, D M Sherman, K V Ragnarsdottir *Chem. Geol.* **167** 65 (2000)
48. F Farges, J A Sharps, G E Brown *Geochim. Cosmochim. Acta* **57** 1243 (1993)
49. D M Sherman, K V Ragnarsdottir, E H Oelkers, C R Collins *Chem. Geol.* **167** 169 (2000)
50. G R Helz, J M Charnock, D J Vaughan, C D Garner *Geochim. Cosmochim. Acta* **57** 15 (1993)
51. G R Helz, J A Tossell, J M Charnock, R A D Pattrick, D J Vaughan, C D Garner *Geochim. Cosmochim. Acta* **59** 4591 (1995)
52. T M Seward, C M Henderson, J M Charnock, B R Dobson, in *Proceedings of the 4th International Symposium on Hydrothermal Reactions* (Nancy: Institute Lorrais des Geosciences, 1993) p. 231
53. T M Seward, C M Henderson, J M Charnock, B R Dobson, in *Water and Rock Interaction-9* (Rotterdam: Balkema, 1995) p. 43
54. T M Seward, C M Henderson, J M Charnock, B R Dobson *Geochim. Cosmochim. Acta* **60** 2273 (1996)
55. J F W Mosselmans, P F Schofield, J M Charnock, C D Garner, R A D Pattrick, D J Vaughan *Chem. Geol.* **127** 339 (1996)
56. E H Oelkers, D M Sherman, K V Ragnarsdottir, C R Collins *Chem. Geol.* **151** 21 (1998)
57. K V Ragnarsdottir, E H Oelkers, D M Sherman, C R Collins *Chem. Geol.* **151** 29 (1998)
58. E Welter, W Calmano, S Mangold, L Tröger *Fresenius J. Anal. Chem.* **364** 238 (1999)
59. S P Schwenzer, C E Tommaseo, M K T Kirnbauer *Fresenius J. Anal. Chem.* **371** 927 (2001)
60. B A Manning, S E Fendorf, S Goldenberg *Environ. Sci. Technol.* **32** 2383 (1998)
61. R R Patterson, S Fendorf, M Fendorf *Environ. Sci. Technol.* **31** 2039 (1997)
62. Y Izumi, F Kiyotaki, T Minato, Y Seida *Anal. Chem.* **74** 3819 (2002)
63. J Rose, I Moulin, J-L Hazemann, A Massion, P M Bertsch, J-Y Bottero, F Mosnier, C Haehnel *Langmuir* **16** 9900 (2000)
64. M S Duff, D B Hunter, I R Triay, P M Bertsch, D T Reed, S R Sutton, G Shea-McCarthy, J Kitten, P End, S J Chipera, D T Vaniman *Environ. Sci. Technol.* **33** 2163 (1999)
65. L A Bugaev, P Ildefonse, A M Flank, A P Sokolenko, H V Dmitrienko *J. Phys.: Condens. Matter* **12** 1119 (2000)
66. S D Longa, A Soldatov, M Pompa, A Bianconi *Comput. Mater. Sci.* **4** 199 (1995)
67. F de Groot *Chem. Rev.* **101** 1779 (2001)
68. L Van Vaeck, A Adriaens, F Adams *Spectrochim. Acta, Part B* **53** 367 (1998)
69. D Briggs, A Brown *Handbook of Static Secondary Ion Mass Spectrometry* (Chichester: Wiley, 1989)
70. I I Stewart *Spectrochim. Acta, Part B* **54** 1649 (1999)
71. G I Taylor *Proc. R. Soc. London, Ser. A* **280** 383 (1964)
72. M Dole, L L Mack, R L Hines, R C Mobley, L D Ferguson, M B Alice *J. Chem. Phys.* **49** 2240 (1968)
73. J J Corr, E H Larsen *J. Anal. At. Spectrom.* **11** 1215 (1996)
74. E R Achterberg, Ch Braungardt *Anal. Chim. Acta* **400** 381 (1999)
75. D M Anderson, F M Morel *Limnol. Oceanogr.* **23** 283 (1978)
76. P G C Campbell, in *Metal Speciation and Bioavailability in Aquatic Systems* (Chichester: Wiley, 1995) p. 4
77. M Gledhill, M Nimmo, S J Hill, M T Brown *J. Phycol.* **33** 2 (1997)
78. C M G Van den Berg, S H Khan, P J Daly, J P Riley, D R Turner *Estuar. Coast. Shelf Sci.* **33** 309 (1991)
79. E P Achterberg, C M G Van den Berg *Deep-Sea Res. II, Top. Stud. Oceanogr.* **44** 693 (1997)
80. C M G Van den Berg, A G A Merks, E K Duursma *Estuar. Coast. Shelf Sci.* **24** 785 (1987)
81. O Abollini, E Mentasti, C Sarzanini, V Porta, C M G Van den Berg *Anal. Proc.* **28** 72 (1991)
82. G Capodaglio, G Scarponi, P Cescon *Anal. Proc.* **28** 76 (1991)
83. E Deaver, J H Rodgers *Environ. Toxicol. Chem.* **15** 1925 (1996)
84. L J A Gerringa, T C W Poortvliet, H Hummel *Estuar. Coast. Shelf Sci.* **42** 629 (1996)
85. P B Kozelka, S S Wilhelmy, A R Flegal, K W Bruland *Estuar. Coast. Shelf Sci.* **44** 649 (1997)
86. F L L Muller *Mar. Chem.* **52** 245 (1996)
87. E L Rue, K W Bruland *Mar. Chem.* **50** 117 (1995)
88. H B Xue, W G Sunda *Environ. Sci. Technol.* **31** 1902 (1997)
89. H Zhang, C M G Van den Berg, R Wollast *Mar. Chem.* **28** 285 (1990)
90. P B Kozelka, K W Bruland *Mar. Chem.* **60** 267 (1998)
91. M L Wells, P B Kozelka, K W Bruland *Mar. Chem.* **62** 203 (1998)
92. L A Miller, K W Bruland *Anal. Chim. Acta* **343** 161 (1997)
93. Yu P Davydov *Sostoyanie Radionuklidov v Rastvorakh* (State of Radionuclids in Solutions) (Minsk: Nauka i Tekhnika, 1978)
94. F Vanhaecke, L Moens *Fresenius J. Anal. Chem.* **364** 440 (1999)
95. V P Shvedov (Ed.) *Elektromigratsionnye Metody v Fiziko-khimicheskikh i Radiokhimicheskikh Issledovaniyakh* (Electromigration Methods in Physicochemical Investigations) (Moscow: Atomizdat, 1971)
96. B Gorski, Z Z Pkhar *Preprint R12-87-146* (Dubna: Joint Institute for Nuclear Research, 1987)
97. M P Volynets *Tonkosloinaya Khromatografiya v Neorganicheskom Analize* (Thin-Layer Chromatography in Inorganic Analysis) (Moscow: Nauka, 1974)
98. Yu A Zolotov, N M Kuz'min *Kontsentrirovanie Mikroelementov* (Preconcentration of Microelements) (Moscow: Khimiya, 1982)
99. T R Roberts *Radiochromatography. The Chromatography and Electrophoresis of Radioactive Compounds* (New York: Elsevier, 1978)
100. A Zlatkis, R E Kaiser (Eds) *HPTLC. High Performance Thin-Layer Chromatography* (New York: Elsevier, 1977)
101. L N Moskvin, M F Gumerov, A A Efimov V M Krasnoperov, G G Leont'ev, V A Mel'nikov *Metody Khimicheskogo i Radiokhimicheskogo Kontrolya v Yadernoi Energetike* (The Methods of Chemical and Radiochemical Control in Nuclear Power Engineering) (Moscow: Energoatomizdat, 1989)

102. B F Myasoedov, A V Davydov (Ed.) *Sovremennye Metody Razdeleniya i Opredeleniya Radioaktivnykh Elementov* (Modern Methods of Separation and Determination of Radioactive Elements) (Moscow: Nauka, 1989)
103. S Sarzanini, E Mentasti *J. Chromatogr., A* **789** 301 (1997)
104. W F Kinard, N E Bibler, C J Coleman, S B Wyrick *Radiochim. Acta* **66 – 67** 259 (1994)
105. C K Kim, S Morita, R Seki, Y Takaku, N Ikeda, D J Assinder *J. Radioanal. Nucl. Chem.* **156** 201 (1992)
106. R Chiappini, J M Taillade, S Brebion *J. Anal. At. Spectrom.* **11** 497 (1996)
107. J I Garcia Alonso *Anal. Chim. Acta* **312** 57 (1995)
108. J I Garcia Alonso, F Sena, P Arbore, M Betti, L Koch *J. Anal. At. Spectrom.* **10** 381 (1995)
109. S Rëllin, Z Kopatjtic, B Wernli, B Magyar *J. Chromatogr., A* **739** 139 (1996)
110. J I Garcia Alonso, D Thoby-Schultzendorff, B Giovanonne, J P Glatz, G Pagliosa, L Koch *J. Anal. At. Spectrom.* **9** 1209 (1994)
111. F Chartier, M Aubert, M Pilier *Fresenius J. Anal. Chem.* **364** 320 (1999)
112. S J Hill, J Les, L J Pitts, S Andy, A S Fisher *Trends Anal. Chem.* **19** 120 (2000)
113. M Pesavento, R Biesuz, F Baffi, C Gnecco *Anal. Chim. Acta* **401** 265 (1999)
114. M Pesavento, G Alberti, R Biesuz *Anal. Chim. Acta* **367** 215 (1998)
115. D Nachtigall, S Artelt, G Wünsch *J. Chromatogr., A* **775** 197 (1997)
116. N Ulrich *Fresenius J. Anal. Chem.* **360** 797 (1998)
117. P Smichowski, Y Madrid *Fresenius J. Anal. Chem.* **360** 623 (1998)
118. N A Priemyshev, G D Bonchar, G A Bozhikov, D V Filosofov, P I Ivanov, O D Maslov, S N Dmitriev, M V Milanov, in *Radiokhimiya-2000 (Tez. Dokl. Tret'ei Ros. Konf. po Radiokhimii), Sankt-Peterburg, 2000* [Radiochemistry-2000 (Abstracts of Reports of the Third Russian Conference on Radiochemistry), St Petersburg, 2000] p. 87
119. A R Timerbaev *Talanta* **52** 573 (2000)
120. E Dabek-Zlotorzynska, E P C Lai, R Andrei, A R Timerbaev *Anal. Chim. Acta* **359** 1 (1998)
121. J W Olsik, J A Kinzer, E J Grunwald, K T Kurt, S V Olesik *Spectrochim. Acta, Part B* **53** 239 (1998)
122. O P Semenova, A R Timerbaev, R Gagstaedter, G K Bonn *J. High Resolut. Chromatogr.* **19** 177 (1996)
123. A B Kersting, J L Thompson *Preprint UCRL-JC-127977* (Livermore, CA: Lawrence Livermore National Laboratory, 1996)
124. A B Kersting, D W Efurd, D L Finnegan, D J Rokop, D K Smith, J L Thompson *Nature (London)* **397** 56 (1999)
125. L E Schemel, B A Kimball, K E Bencala *Appl. Geochem.* **15** 1003 (2000)
126. B Dupre, J Viers, J-L Dandurand, M Polve, P Benezeth, P Vervier, J-J Braun *Chem. Geol.* **160** 63 (1990)
127. L Gou, P H Santschi *Mar. Chem.* **59** 1 (1997)
128. G B Douglas, B T Hart, R Beckett, C M Gray, R L Oliver *Aquatic Geochem.* **5** 167 (1999)
129. S L Wen, P Santschi, G Gill, Ch Paternostro *Mar. Chem.* **63** 185 (1999)
130. F L L Muller *Anal. Chim. Acta* **331** 1 (1996)
131. L-S Wen, P H Santschi, D Tang *Geochim. Cosmochim. Acta* **61** 2867 (1997)
132. J R Lead, J Hamilton-Taylor, W Davison, M Harper *Geochim. Cosmochim. Acta* **63** 1661 (1999)
133. F L L Muller *Estuar. Coast. Shelf Sci.* **46** 419 (1998)
134. S Mounier, R Braucher, J Y Benakhim *Water Res.* **33** 2363 (1999)
135. I H Huisman, Ch Tragargh *Chem. Eng. Sci.* **54** 271 (1999)
136. I H Huisman, Ch Tragargh *Chem. Eng. Sci.* **54** 281 (1999)
137. S R Bellara, Zh Cui *Chem. Eng. Sci.* **53** 2153 (1998)
138. H Carre're, F Rene *Exp. Fluids* **25** 243 (1998)
139. M Dai, K O Buesseler, P Ripple, J Andrews, R A Belastock, O Gustafsson, S B Moran *Mar. Chem.* **62** 117 (1998)
140. J Ingri, A Widerlund, M Land, O Gustafsson, P Andersson, B Ohlander *Chem. Geol.* **166** 23 (2000)
141. L Guo, L-S Wen, D Tang, P H Santschi *Mar. Chem.* **69** 75 (2000)
142. E Tombacz, A V Dobos, M Szekeres, H D Narres, E Klumpp, I Dekany *Colloid Polym. Sci.* **278** 337 (2000)
143. C H Langford, in *Coordination Chemistry* Ch. 33 (Washington, DC: American Chemical Society, 1994) p. 406
144. B Jung, N M Edelstain, G T Seaborg, in *Coordination Chemistry* Ch. 30 (Washington, DC: American Chemical Society, 1994) p. 361
145. P Zhao, S A Steward *Preprint UCRL-ID-126039* (Livermore, CA: Lawrence Livermore National Laboratory, 1997)
146. R Kretzshmar, W P Robarge, A Amoozegar *Water Resour. Res.* **31** 435 (1995)
147. J Van Berkel, R Beckett *J. Chromatogr., A* **733** 105 (1996)
148. R Beckett *At. Spectrosc.* **12** 228 (1991)
149. R Beckett, G Nicholson, D Hotchin, B Hart *Hydrobiologia* **235 – 236** 697 (1992)
150. R Beckett, G Nicholson, B T Hart, M Hansen, J C Giddings *Water Res.* **22** 1535 (1988)
151. R Beckett, J C Bigelow, J Jhang, J C Giddings *Environ. Sci. Technol.* **21** 289 (1988)
152. Y Ran, J M Fu, G Y Sheng, R Beckett, B T Hart *Chemosphere* **41** 33 (2000)
153. J F Ranville, D J Chittleborough, F Shanks, J S Richard, R J S Morrison, T Harris, F Doss, R Beckett *Anal. Chim. Acta* **381** 315 (1999)

[a] — *J. Anal. Chem. (Engl. Transl.)*
[b] — *Mendeleev Chem. J. (Engl. Transl.)*
[c] — *Radiochemistry (Engl. Transl.)*