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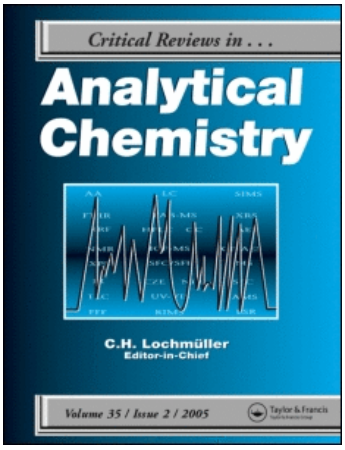

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The Speciation of Aluminum in Environmental Samples

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There are many sources of heavy metals in the environment. They can get there from the atmosphere as a result of intensive rain or snowfall, or they can be eroded out of the bedrock or soil. Larger amounts, often exceeding permitted concentrations, are most frequently due to emissions/discharges from industrial areas. The great variety of sources and physico-chemical conditions means that an element can occur in many different forms. That is why any assessment of the degree of contamination of the environment should be carried out not only from the point of view of the total amount of a metal found in environmental samples; it is also very important to know the contents of stable species of metals, constituting a potential reserve in the biocirculation. Moreover, the forms of occurrence of aluminum determine its toxicity or the synergistic relationships it enters into with other substances, which in turn determine its uptake and absorption by living organisms.

Keywords Aluminum, speciation, environmental samples

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INTRODUCTION

Aluminum, which does not occur in the native state, is the third most common element in the earth's crust. Its naturally occurring compounds include the aluminosilicates orthoclase $K[A1Si_3O_8]$, albite $Na[AISi_3O_8]$, anorthite $Ca[AI_2Si_2O_8]$, leucite $K[AISi_2O_6]$, nepheline $Na[AISiO_4]$, silimanite Al_2SiO_5, and kaolinite $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$. Bauxite AlO(OH) and cryolite Na_3AlF_6 are technically important ores. Pure Al_2O_3 occurs as corundum, but when colored with minimal amounts of oxides of other metals, it forms precious stones like red rubies or blue sapphires (1,2). Aluminum salts are widely applied in the dyeing, paper, and tanning industries, and also in water and sewage treatment, where aluminum sulfate $Al_2(SO_4)_3{\cdot}18H_2O$ is used as a coagulant.

The natural content of aluminum in the earth's crust (7.8% of the total mass of the earth), as well as its susceptibility to external agents and the numerous reactions it undergoes in the environment, are reflected in the forms of its occurrence, which govern the degree of its bioavailability and mobility in aquatic ecosystems (3). Normal aluminum concentrations in surface waters range from 60 to 300 $\mu g/dm^3$, while the average amount of aluminum in river waters is 64 $\mu g/dm^3$. Al levels are low in aquatic ecosystems where temperature, pH, and redox potential are constant, and levels of organic and inorganic contaminants in the water are stable (4). Varying environmental conditions can cause sorption-desorption and water-sediment equilibria to shift; in consequence, the amounts of dissolved (i.e., bioavailable) forms may increase (5). Al therefore occurs in a variety of chemical compounds which in the material objects under investigation (e.g., ecosystems) can be present in different physical forms.

Very little aluminum dissolves as a result of weathering processes, but at low or high pH it becomes soluble. In the pH range of 5.0–9.0, characteristic of most natural waters, this element is insoluble. The fulvic and humic substances present in the environment can form quite large conglomerates, on the surface of which aluminum can adsorb (6). In the simplest case we can identify three types of aluminum: soluble Al^{3+}, prevalent under acidic conditions; insoluble aluminum hydroxide $Al(OH)_3$, which occurs in a neutral environment; and $Al(OH)_4^-$, which is dominant where conditions are alkaline. But if we take into account the partial dissociation products of $Al(OH)_3$ and the formation of aluminum complexes with organic substances, the number of Al species in surface waters becomes much greater (5).

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In the aquatic environment, aluminum invariably occurs as a hydrated cation, e.g., $[Al(H_2O)_6]^{3+}$. During hydrolysis various macromolecular complexes of a colloidal nature come into existence, which are in equilibrium with one another: $Al^{3+} \leftrightarrow AlOH^{2+} \leftrightarrow Al_2(OH)_2^{4+} \leftrightarrow Al_3(OH)_4^{5+} \leftrightarrow Al_8(OH)_{20}^{4+} \leftrightarrow Al_{13}O_4(OH)_{24}^{7+} \leftrightarrow Al(OH)_3$ (7). Moreover, aluminum is an amphoteric element, so in a strongly acidic environment (pH < 4) hydrated cations are prevalent $[Al(H_2O)_6]^{3+}$ (6), whereas under alkaline conditions $[Al(OH_4)(H_2O)_2]^{2-}$ ions are the rule. At pH 4.5–5.5, the $[Al(H_2O)_6]^{3+}$ ion can form mixed complexes with the ligands present in the water—organic and inorganic contaminants, e.g., humic acids and fluorides. At pH $\sim$ 6.0, $Al(OH)_3$ becomes slightly soluble and from pH = 6.2 aluminum forms a series of intermediate species like $[Al(OH)_2(H_2O)_4]^+$ and $[Al(OH)(H_2O)_5]^{2+}$, whereas in alkaline media we find $[Al(OH)_4(H_2O)_2]^-$ and $[A1(OH)_5(H_2O)]^{2-}$ ions (8). As a consequence, aluminum can occur at levels exceeding permissible concentrations that are toxic to living organisms.

Aluminum, therefore, occurs in natural waters as hydroxide, sulfate, fluoride, and fluoraluminate complexes, as well as hydrated forms, which hydrolyze to produce a multitude of macromolecular complexes, e.g., $[Al_2(OH)_2]^{4+}$ $[Al_3(OH)_4]^{5+}$, $[Al_6(OH)_{15}]^{3+}$, $[Al_8(OH)_{20}]^{4+}$, $[Al(OH)_2(H_2O)_4]^+$, $[Al(OH)(H_2O)_5]^{2+}$, and $[Al_{13}O_4(OH)_{24}]^{7+}$, which are in equilibrium with each other (7, 8). As mentioned above, Al has amphoteric properties; depending on the pH; therefore, it can form complexes both cationic and anionic, organic and inorganic, with a tendency towards polymerization (5, 9). At pH 5–8 the poorly soluble aluminum(III) hydroxide $Al(OH)_3(H_2O)_3$ forms, which then precipitates into the bottom sediment. The numerous organic and inorganic ligands present in the environment compete with Al; as a result of these reactions, the proportions of Al complexes and general monomeric Al can vary. In the aquatic environment, organic species of monomeric Al are present alongside the inorganic ones (10, 11).

Apart from pH, the factors determining the type of complex that forms include the temperature, ligand concentration, and ionic strength of the solution. In a highly acidic environment, sulfate is the principal anion co-present with the dissolved inorganic forms of aluminum, forming complexes with them (3). The dominance of aluminum sulfate complexes depends on the sulfate concentration in the water: when this is low, the $AlSO_4^+$ form prevails, but when it is higher, $Al(SO_4)_2^-$ ions dominate (1, 3, 9). $AlSO_4^+$ complexes are the principal ones only at high sulfate concentrations and low pH (<4.5); they are not as stable as Al-F complexes (12), e.g., AlF_2^+, $(AlF)^{2+}$, and AlF_6^{3-} (13, 14).

The change in solubility due to the large diversity of Al concentrations gives rise to different chemical species (15). Aluminum is most soluble in strongly acidic environments, e.g., in volcanic areas, sulfide ore oxidation zones, and in strongly alkaline ones, e.g., alkaline lakes, dissolution zones of low-pressure products, or the thermal metamorphism of carbonate rocks (15).

A change in pH from neutral to very acidic can more than double the amount of dissolved aluminum and quadruple the concentration of its exchangeable forms. Increasing bottom sediment acidity may cause mobile Al (dissolved in water and exchangeable) and organic-bound Al to accumulate in the eluvial horizon. The granulometric composition (lithology) and the humus content have a greater influence than pH on the content of strongly organic-bound Al, amorphous Al, and free Al (16, 17). From the hydrochemical standpoint, the percentage of dissolved forms in the total transport is given by the transport index—aluminum is a metal with a small transport index and migration coefficient.

Despite the relatively small content of total general aluminum in waters, it is the quantitative and qualitative definition of its species, especially inorganic monomeric species, containing toxic forms of aluminum, that will enable the actual threat to a riverine ecosystem to be evaluated. The term "inorganic monomeric aluminum" includes its complexes with fluorides, phosphates, and sulfates (18–20).

Depending on the nature of the complex bonding, the Al species formed may have different toxic effects on living organisms (21–23). Inorganic, monomeric aluminum bound to fluoride or sulfate is a toxic form of the element (24–26). Conditions for Al adsorption are the best at pH $\sim$ 4.0, when $[A1(H_2O)_6]^{3+}$ ions and the toxic hydrolysis products $[A1(OH)]^{2+}$ and $[A1(OH)_2]^+$ are present in the water (7).

Present in all plants, aluminum enters animal organisms via the food chain. For a long time it was thought that aluminum was not toxic. Studies on plants demonstrated, however, that in excess, Al could wring changes in the morphology of the root system. The consequences are a considerable retardation of root development, smaller increments in plant biomass, and, in extreme cases, the complete disappearance of the species in question (27–29). The harmful action of aluminum is also manifested by the disruption of nutrient uptake and transport in plants and the imbalance between cations and anions during ion exchange processes. Al^{3+} ions prevent the uptake of Ca^{2+} ions by plant cell walls; they can also form insoluble complexes with phosphate ions obtained from the soil, thereby giving rise to a deficit of assimilable phosphorus. Aluminum also adversely affects cell membranes, cell division, and DNA synthesis, and also disrupts the mechanisms regulating ATP-driven ion transport (30).

In the case of fish, the toxic species of aluminum, $Al(OH)^{2+}$ and $Al(OH)_2^+$, can enter the organism through the gills, where they accumulate in very large quantities. These species readily cross cell membranes, in which they reduce the activity of numerous enzymes; following polymerization, they are deposited on the gills, where they prevent ion exchange and impair respiration in fish (31).

Aluminum can enter the human body through the digestive and respiratory systems, and in dialyzed persons also via the blood circulation (6). This element interferes with numerous essential metals and metalloids in the human organism by

altering their bioavailability. In the body, aluminum ions compete in reactions with metal ions such as zinc, iron, chromium and calcium; the lower concentration of Ca is one of the reasons why Al is deposited in the organism. Al ions replace phosphates in the lysosomes of the brain, kidneys and liver, calcium in bones, and magnesium in the heterochromatin of cell nuclei. In the plasma, like the Fe^{3+} ion, Al ions form compounds with transferrin (32–34).

This action of aluminum is thought to be responsible for neurotoxic diseases, such as encephalopathy, senile dementia (Alzheimer's disease), and osteomalacia (6, 35, 36). The effect of chronic toxicity due to the absorption of Al-containing smokes and dusts is a disease known as bronchopneumopathy, which occurs in the form of a chronic, unspecific respiratory syndrome, pulmonary parenchymal fibrosis and pneumothorax (6, 36, 37).

It should be emphasized that the toxicity of aluminum depends on the form in which it occurs, and the mechanisms of its action depend on the range of tolerance of an organism to the Al concentration (38). Thus, speciation is of crucial significance as regards the problems caused by environmental pollution and the interaction of Al with living organisms.

Investigations into the toxicity, bioavailability, and circulation of metal ions in nature must take into account their occurrence in diverse chemical forms. Since the activity of such an ion is often due to the presence of a particular species, analytical methods capable of determining them separately take on considerable significance. To this end, speciation analysis is applied—this enables the individual species to be determined.

Speciation analysis can be carried out with the aid of a variety of techniques, not only at the determination stage, but also during the preparation of the analyte, when the sample is suitably concentrated. A methodology (sample preparation and measurement) is chosen to match the purpose of the analysis (one species, several species, total content) and the range of concentrations to be analyzed.

According to the definition of the speciation analysis of environmental samples, we can distinguish the following types of speciation:

- functional—determination of the compounds of elements of known chemical or biological activity;
- operational—determination of the labile or inert species of an element;
- classical—determination of an element occurring in several chemical forms (in different oxidation states, bound to different ligands, etc.) in the study material (39).

A different classification (40) in speciation analysis differentiates between physical and chemical speciation. The former discovers, separates, and determines the various physical forms of the same analyte, the latter determines the various chemical forms containing the element of interest. With respect to the diverse forms of occurrence of species in the environment and the analytical objective, chemical speciation can be divided into the following types:

- group—joint determination of groups of analytes;
- individual—determination of all the species of a given element;
- screening—the search for one particular analyte;
- distributional—determination of the concentration of the same analyte in different parts of a sample;
- chiral—separation and determination of enantiomeric compounds (40).

Each of these procedures comprises many different analytical schemes, due to the physical and chemical diversity of the matrices and the material to be analyzed. These schemes cover data collecting in the field, the choice of sampling site and method of sampling, and the preparation of the sample for analysis. Which procedure is adopted depends on the objective of the analysis, the type and complexity of the matrix, and the possibility of applying detection techniques appropriate to the expected analyte concentrations.

PREPARATION OF ENVIRONMENTAL SAMPLES FOR ANALYSIS

The diversity of environmental samples, due to their different physical states, sampling sites, matrix composition, as well as the types of analytes and their concentrations, means that acquiring all the desired information is an exceedingly difficult process. Sample preparation involves a whole range of different operations (40). The first step is to carry out a preliminary reconnaissance of the geographical area from which the samples are to be taken. Once physiographical, geological, and geobotanical factors have been taken into consideration, the geochemical processes unfolding at the sampling site can be tracked. Also at this stage a general assessment of the current state of the environment is made, and decisions are taken regarding the selection of sampling method and apparatus.

Determining the content of metals in a solid sample, such as bottom sediment, requires an appropriate procedure in order to obtain reliable information about the presence of a particular species in the environment. A wrongly chosen procedure can produce considerable errors during the sample preparation step; these in turn can lead both to losses of the elements to be determined, e.g., through their adsorption on organic residues and to contamination of the sample by compounds derived from the air, laboratory glassware, or the use of reagents of insufficient purity (41, 42).

The preparation of environmental samples for analysis is a complicated and time-consuming process, the reason for this very often being the complexity of the sample matrix. The basic operations and processes to be carried out during the preparation of environmental samples are:

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- Preliminary field studies—location and assessment of the study area, mapping the sampling sites, selection of sampling method, and equipment;
- Detailed field studies—a sketch-map and data card of the terrain, its GPS coordinates, analysis of environmental parameters, phytosociological records and profiles;
- Collection, storage, and transport of samples—field analysis of samples, measurement of physicochemical variables like Eh and pH, selection of samples for analysis, collection of representative samples, screening bottom sediments/soils, prevention of decomposition, and contamination of samples;
- Preparation of samples for analysis—filtration, acidification, dessication, grinding, screening, weighing, dissolution/enrichment, purification, and reduction of sample/extract volume, separation, release of bound analytes, derivatization;
- Laboratory analysis of samples—chemical, mineralogical, microbiological;
- Interpretation of analytical results—verification of results, selection of statistical method, parameter analysis;
- Validation of measurement and analytical procedures (43).

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The sampling technique and the container for storing samples are therefore important aspects. It should be made a rule to use a sampling technique enabling representative material to be obtained from the undisturbed surface layer of a bottom sediment or soil. It is also recommended that duplicate samples (one for every ten samples) be taken, so that the analysis can be monitored (44). Multicomponent determinations (trace elements) are frequently carried out on the same samples; hence, tools and sieves should be made from stainless steel, and bags and bottles from polyethylene (6, 41, 45).

In order to find out in which phase the largest proportion of an element is contained and what effect its mobility has on its leachability, sequential extraction is applied (46). Sequential extraction from solid or liquid environmental samples is carried out in various ways using classical laboratory techniques, i.e., several consecutive extractions to isolate one of the forms in which the element of interest is present in the sample. Every technique used in trace element analysis must be performed in compliance with the requirements of this type of analysis to ensure that:

- the decomposition of the sample is quantitative and that inorganic components are dissolved;
- the operation is simple, quick, and inexpensive;
- automation of the process is possible;
- the new matrix forming after decomposition does not hinder or prevent the determination using a particular analytical method or technique (47).

It should be remembered that the choice of techniques for separating and isolating analytes depends not only on the type and characteristics of the matrix and the physicochemical properties of the species to be determined, but also on the available methods of detection.

SPECIATION OF ALUMINUM IN THE AQUATIC ENVIRONMENT

Like other heavy metals, aluminum occurs in the form of free hydrated ions to only a small degree. A considerable proportion of it is bound to organic substances like amino acids, amines, sugars, and organic acids, as well as polymolecular compounds of incompletely known structures like humic and fulvic acids, as well as many others often containing atoms of nitrogen or sulfur.

In order to distinguish the different forms of Al, various speciation schemes have been postulated. In the literature on the speciation of aluminum(III) compounds in the aquatic environment, especially their operational speciation, the forms of occurrence of this element are frequently divided into groups. The reason for this is the need, especially in studies of the chemistry and toxicology of aluminum, to treat inorganic low-molecular weight compounds of aluminum separately from high-molecular weight compounds (colloidal particles with a molecular mass $> 10^4$ daltons) (10).

Lydersen et al. (10) took the principal criteria for distinguishing aluminum species to be the molecular weight and the polymeric or monomeric nature of the particles (Fig. 1). They also treated inorganic and organic forms of monomeric aluminum separately.

Water samples of pH 5–6 containing small quantities of labile aluminum and large amounts of organic matter should be processed as soon as possible after sampling. This is because of the sensitivity of this system during storage, even at low temperatures, to microbiological processes, which are capable of causing changes in the organic matter, and thus a conversion of one form of aluminum into another (4, 6). Such changes in form are particularly frequent when the storage temperature differs markedly from the sampling temperature. In contrast, samples of water mains and lake water can be stored in polyethylene containers for up to 30 days (6).

Preparing samples for the analysis of their aluminum content involves a variety of acidification and filtration techniques, as well as solid-phase extraction (SPE), considered to be a good means of defining the reactivity/lability of soluble fractions. To separate aluminum bound to organic matter, water samples are first passed through 0.45 μm mesh filters; only then are the soluble forms of Al separated and analyzed. Depending on the purpose of the assay, filtration can also be carried out with polycarbonate membranes or with ultrafiltration (e.g. $<$ 200 kDa), when the "truly soluble" forms of aluminum are sought. To separate the forms of aluminum bound to different biological materials, filters with a larger mesh, e.g., 2, 5, 20, 55, or 210 μm, can be used (45).

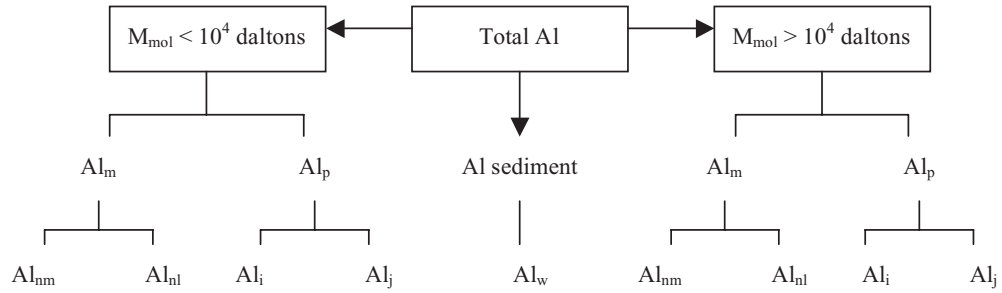

FIG. 1. Classification of aluminum species in the aquatic environment: Al_m—total monomeric aluminum; Al_{nm}—inorganic monomeric aluminum represented mainly by Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^{2+}$ ions; Al_{nl}—non-labile monomeric aluminum, Al_p—total non-monomeric aluminum (represented mainly by polymeric colloidal species); Al_i—strongly positively charged colloidal particles, colloids with strongly positive domains (in corners and domains with a disrupted structure), strongly polarized complexes; Al_j—weakly positively or negatively charged colloids, neutral and slightly polarized complexes; and Al_w—complexes of aluminum(III) precipitated from solution (bottom sediment) (10).

The usual method of separating and then determining the different forms of aluminum is the one developed by Driscoll (48). It involves the separation of inorganic monomeric Al from organic complexes by cationic exchange. In this way the following three fractions can be isolated:

1) acid-reactive aluminum (Al_r);
2) total monomeric aluminum analyzed in a separate stage without dissolution in acid (Al_{tm});
3) non-labile monomeric aluminum (Al_{nl}), determined after the sample has been passed through a column containing Amberlite IRA-120.

The content of labile, inorganic monomeric aluminum, that is, the most toxic fraction containing aluminum(III) in the form of hydroxides, sulfates, fluorides, and silicates, is calculated from the difference $Al_{tm} - Al_{nl}$. It is also possible to determine the acid-reactive fraction of aluminum by subtracting Al_r (total) from Al_{tm} (total monomeric). It should be borne in mind that organic complexes of Al may be released during ion exchange in the column—the inorganic monomeric fraction is then overestimated, especially when variable quantities of organic carbon are present (49, 50). This situation can be avoided, however, by conditioning the resin with NaCl, which has exactly the same conductivity as the water to be analyzed.

Driscoll's method has undergone numerous modifications, thus enabling errors to be reduced (51–58). One of them is based on determining the following fractions:

- Al_r in the sample acidified to pH = 1 by reaction with PVC;
- Al_{tm} reacted with PVC without acidification;
- Al_{nl} in the sample without acidification and after being passed through an ion-exchange column (Amberlite IRA-120)—this is treated as the reference method (51).

The methods of separating and analyzing the different fractions of aluminum provide the opportunity to obtain complete information on the state and quality of waters. However, there is no one specific, direct method of determining the aluminum fractions present in aquatic ecosystems (Table 1).

In the presence of contaminants in natural waters, aluminum speciation is impaired because of the constantly changing physico-chemical parameters. Interesting empirical studies and theoretical calculations of aluminum speciation in the presence of fluoride ions (AlF^{2+}, AlF_2^+ besides Al^{3+}) were carried out by Motellier and Pitsch (73): the conclusion from these results is that the proportion of the AlF_2^+ fraction increases in waters of pH = 5.

An additional difficulty is the analysis of toxic forms of aluminum, i.e., $Al(H_2O)_6^{3+}$, $Al(OH)_2^+$, and $Al(OH)^{2+}$, which are more reactive and present a greater danger to living organisms than the polymeric and organic compounds of the metal. Mitrovič et al. (13) attempted to distinguish these toxic fractions. In order to assess the impact of aluminum on an ecosystem, it is sufficient to know the concentration of the one fraction evaluated as toxic, that is, the fraction containing aluminum in the form of the labile complexes $Al(H_2O)_6^{3+}$, $Al(OH)_2^+$, and $Al(OH)^{2+}$. This fraction, i.e., inorganic monomeric aluminum, is quickly analyzed by spectrophotometry. Even so, various elaborate analytical procedures (fractionation) are still applied, which can distinguish a large group of aqua-ions. In all of these procedures, however, the fraction defined by the separation methodology is measured, which impairs or even prevents comparison of results obtained by different methods.

All forms of Al can be identified by spectrophotometric techniques (24, 57, 101–104), e.g., determining aluminum in the form of ion pairs (three-component complexes) using pyrogallol red and bromopyrogallol red in the presence of cetyltrimethylammonium bromide, cetyldimethylbenzylammonium chloride, or t-octylphenoxypolyethoxyethanol (Triton X-100) (105, 106). The method using these reagents is sensitive and reproducible, but the pH range within which the complex is formed is very narrow. For spectrophotometric determinations, other authors (107, 108) applied pyrocatechol violet and

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TABLE 1
Determinations of some aluminum fractions in the aquatic environment using different analytical techniques—a selection of examples

Methodology	Technique(s) of final determinations	References
Retention of monomeric Al on a Diovex CG2 column; elution with 0.1 M K_2SO_4 at pH = 3.0; post-column chelation with 8-HQS (8-hydroxyquinoline-5-s ulfonic acid)	FIA, HPLC with fluorescence detection	(51)
Al^{3+} (in the form of monomeric hydroxycomplexes, sulfates, carbonates, silicates) at a given pH reacts with 8-hydroxyquinoline (oxine) or with 2,2′-dihydroxy-3,3′-dicarboxy-1,1′-dinaphthylmetane	Spectrophotometry (λ = 390 – 420 nm) or AAS	(59–61)
Compounds yielding colored complexes with aluminum: 8-hydroxyquinoline (8-quinolinol), eriochromocyanin, Chromazural-S, Alizarin-S, pyrocatechol violet, ferron	Absorption spectrophotometry	(62–64)
Aluminium in natural water with Eriochrome Cyanine R and cationic surfactants	Flow injection spectrophotometric	(65)
Simultaneous determination of positively-charged Al^{3+}, Al-fluoro, Al-oxalate complexes distinguishes non-complexed Al from fluorides such as AlF_2^+	Capillary electrophoresis	(66)
Al in the form of fluorides, oxalates, citrates etc. reacts with butane sulfonic acid to form ion pairs; 3 peaks are determined: the species with charge +1 (organically bound Al), species with charge +2 (AlF^{2+} and other organic complexes), species with charge +3 (dissolved forms of Al after hydrolysis), which enables fluorides to be separated from other monomeric species of Al	HPLC	(67)
The use of Chelex-100 resin with iminodiacetate groups enables Al to be separated into labile (exchangeable) and non-labile (non-exchangeable) forms		(58, 68–70)
Ion exchange chromatography with chelating reagents, determination of the sum of positively charged aqua- and hydroxy monomers at pH $\leq$ 7		(58, 71, 72)
CS 2 (Dionex) cation exchange column, mobile phase 0.5 M NH_4Cl – 0.01 M HCl, post-column reagent Tiran $8x10^{-4}$ M in 3.0 M CH_3COONH_4, eluent pH 6.7, UV detection		(73)
Determination of the inorganic forms AlF^{2+}, AlF_2^+ and Al^{3+} by separation on IonPac CS5A and IonPac CG5A columns (Dionex), mobile phase NH_4Cl at pH ~3, retention time 8 min during a single analysis	HPLC-FAAS	(14)
Distinguishes positively charged $AlSO_4^+$ and AlF_2^+ complexes from negative oxalates and citrates co-eluted with $Al(OH)_2^+$; AlF^{2+} and $Al(OH)^{2+}$ are co-eluted	FPLC-ICP-AES, MCC-ETAAS	(13, 74, 75)
Filtered and unfiltered, synthetic sample of variable pH, distinguishes Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(SO_4)^+$, AlF_2^+, negatively charged oxalates, tartrates co-eluted with $Al(OH)_2^-$, and AlF^{2+} with $Al(OH)^{2+}$	HPLC-ICP-AAS	(13, 75)
Ion exchange chromatography with a Chelex-100 microcolumn; eluent 1.0 M HCl (determination of labile monomeric Al); for analyses in biological liquids	HPLC-ET AAS	(76–78)
An increasingly common method—combining ion chromatography with post-column derivatization in the fluorescence version, distinguishes AlF^{2+}, AlF_2^+, hydro-Al, sulfate-Al, separation of aqua– and hydroxy-Al from Al contained in citrates, silicates, acetates, and fluorides	HPLC, fluorescence detection	(6, 67, 79)
The isolation of the Al fraction with 8-hydroxyquinoline (pH 5.0); complex is sorbent-extracted from the sample stream onto mini-columns containing Amberlite XAD-2 non-ionic resin	ICP-MS	(80)

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TABLE 1
Determinations of some aluminum fractions in the aquatic environment using different analytical techniques—a selection of examples (*Continue*)

Methodology	Technique(s) of final determinations	References
Three types of aluminum species (Al^{+2}, Al^{2+}, Al^{3+}) were separated from one lake water sample; the comparison of the system with an established CE-HPLC with fluorimetric detection using 5-sulfo-8-quinolinol (CE-HPLC/FL) was described	ICP-MS	(81)
Cyanex 921 at pH 4.5 – 5.5, neutral extractant TOPO (tri-*n*-octylphosphoric oxide)	Selective extraction	(82)
Extraction using oxine in $CHCl_3$ at pH 13; used in Ga separation from Al in a strongly alkaline solution		(83)
HDEHP (di-ethylhexylphosphoric acid) in toluene and in xylene from weakly acidic solutions		(82, 84)
Cyanex 302 (bis(2,4,4-trimethylphenyl)monothiophosphoric acid) in various solvents, e.g., $CHCl_3$, CCl_4, hexane, toluene and xylene, concentration range 0.5 – 3.5 $\mu g \cdot cm^{-3}$; samples were muilticomponent mixtures		(85)
Used to determine aluminum in all waters except seawaters (their high salinity precludes this method)	AAS with an electrothermal atomizer	(86)
LOD 0.05 $\mu g \cdot dm^3$; only F^- ions interfere; levels of 100 $\mu g \cdot dm^3$ detectable in acidic waters	Fluorescence	(87)
Aluminium in waters with N-(3-Hydroxy-2-pyridyl)salicylaldimine as a reagent	Fluorimetric	(88)
Detection to within 15 ppb following concentration with calmagite; recommended for analysis of drinking water and in commercial 4% acetic acid	Adsorptive stripping voltammetry	(89–91)
Chelex-100 column, 69% HNO_3, and 25% NH_4OH; PVC membrane, *o*-nitrophenyloctyl ether (NPOE), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB); bis(5-phenylazo-salicylaldehyde)2,3-naphatene diimine as the ionophore for Al	FIA	(92)
PCV reagent consisting of 0.3 mM PCV, buffering and iron masking reagent using a solution of 1.5 M hydroxylamine hydrochloride, 1 M ethanolamine and 7 mM 1,10-phenanthroline; FIA-LAB II Flow Analyzer (MLE Dresden GmbH) (optical detector, 10 mm optical path, 590 nm interference filter)		(20)
Chelex-100 ion exchange resin under various conditions, e.g., static conditions with a long contact time	SPE	(24, 68, 93–95)
Al speciation in the presence of humic acids and on a RP-18HCD column; eluent–acetonitrile-water mixture (58–15% v/v)	GF-AAS	(96)
Preconcentration of trace aluminum by a cloud point extraction (CPE); complex of Al(III) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), and then entrapped in non-ionic surfactant Triton X-114; the detection limit for Al(III) is 0.09 $ng \cdot mL^1$, the relative standard deviation 4.7% at 10 $ng \cdot mL^1$ Al(III) Level (n = 7)		(97)
determination of Al^{3+} in drinking, river and sea water, sample filtration (0.45 μm), Chelex-100 column [CAS 68954-42-7 (Bio-Rad Laboratories)]		(98)
Drinking water analyzed for the presence of monomeric and labile Al	FI	(99)
Two types of aluminum species (Al^{3+} and AlF^{2+}) were separated with 8-hydroxyquinoline-5-sulfonic acid from natural water samples; problems with the detection method for Al-speciation analysis such as ion interferences and salt concentration of the mobile phase	HPLC-ICP-MS	(100)

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tetradecyldimethylbenzylammonium chloride in the extraction version (109). In a later paper Wyganowski suggested a very simple and quick method based on bromopyrogallol red and n-tetradecyltrimethylammonium bromide for determining aluminum in river waters (105).

Most reactions taking place in the aquatic environment do so at the solid phase-solution interface. Suspended particulate matter (SPM), a major constituent of surface waters, therefore plays an important role in the transport of metal pollutants (110–112), including that of aluminum. The solid phase of SPM consists mainly of inorganic colloids like the aluminates, oxides, hydroxides, and carbonates of metals. Two fractions can be distinguished in the SPM phase in aquatic systems: 1) particles of diameter > 1 μm, which are deposited quite rapidly, and 2) particle of diameter < 1 μm, which remain in suspension and participate in the transport of adsorbed substances over long distances. Nonetheless, the quantities of metals adsorbed on the surface of SPM vary: they depend, among other things, on land use, the geological substrate (bedrock), climate, and even season. Given such a situation, it is difficult to carry out a sequential extraction process of several steps because, to mention just two reasons, of the required sample size (1 g) and the possibility that the extracted metal will be readsorbed on post-extraction residues. Instead, a single-stage process has been suggested for extracting metals adsorbed on SPM (including Al) using ethylenediaminetetraacetic acid (EDTA) as a ligand to complex the metals of interest. The scheme of this procedure is as follows:

- weighing 15–150 mg SPM in clean polystyrene containers;
- addition of 30 mL of a mixture of extractants: 0.05 M EDTA or 0.005M, 1 M HCl, 1 M NH_4OAc or 25% (v/v) $CH_3COOHAc$;
- agitation for a stipulated period of time;
- centrifugation at 3000 rpm for 10 minutes;
- transfer of solutions to clean polyester containers;
- analysis by ICP-MS using a VG Elemental PQ2 Turbo instrument.

The optimum time for the formation of Al-EDTA is 72 hours at a concentration of 0.05 M ligand and an extractant:SPM ratio of 200:1 (v:w) (113).

For the speciation of aluminum in waters containing little organic matter, a very common method is ion chromatography (IC). In such waters, the principal ions complexing Al, apart from OH^-, are F^- and SO_4^{2-}. Based on the slow kinetics of complex decomposition, IC distinguishes the individual species of the metal. Many IC methodologies require cation-exchange columns for separating the various forms of aluminum, followed by post-column reaction to detect them. Other chromatographic techniques are also used to analyze compounds of Al with organic substances; for example, HPLC is used to determine Al citrate compounds.

For determining Al oxalates, Al citrates, and Al-EDTA a methodology based on FLC-ICP-AES (114, 115) was developed, where in fast protein liquid chromatography (FPLC) a Mono QHR 5/5 anion-exchange column packed with hydrophilic polyester resin containing quaternary amine groups was used. One use of this methodology was to analyze Al citrates in serum, which is an extremely important chelating agent.

SPECIATION OF ALUMINUM IN BOTTOM SEDIMENTS AND SOIL

Bottom sediments should be treated as an integral part of every aquatic ecosystem. The composition and properties of bottom sediments depend on the numerous physico-chemical parameters characterizing the water, like temperature, pH, salt content (salinity, mineralization), redox potential, oxygen concentration, and the presence of organic substances. Directly or indirectly, these parameters affect the solubility of metal compounds. Moreover, the transport of dissolved and undissolved contaminants also affects the content of metals in bottom sediments, whereby a certain amount of transported pollutants is precipitated. From the geochemical viewpoint, the proportion of precipitated contaminants is quantitatively described by the migration coefficient, defined as (2):

$$k_x = m_x \cdot 100 / n_x \cdot a \qquad [1]$$

where m_x is content of "x" in the aqueous phase, n_x is the content of "x" in the bedrock, and a is the mineralization of water.

From the hydrochemical point of view, however, the percentage of dissolved forms in the total transport is defined by the transport index (116). Aluminum is a metal with a small transport index and migration coefficient.

Knowledge of metal levels in waters and bottom sediments can be used to acquire a full chemical picture of the aquatic environment; it can also be an indicator of the geochemical situation in a watershed and of the spread of contaminants. Bottom sediments are the chief link in the circulation of elements: they are the focus of the accumulation, chemical transformations, and decomposition of toxic compounds entering natural waters. The properties of bottom sediments are a fairly representative indicator of long-term changes in the contaminants of water bodies and can be used as biological and chemical indices of the changes taking place in them. Exchange reactions are continually taking place between the bottom sediments and the water, redox and sorption processes playing a particularly important part (42).

From the chemical point of view, metals in sediments can take the form of carbonates, hydroxides, silicates, sulfides, phosphates, and compounds with organic ligands in various stages of crystallization with different stoichiometries and water contents (117). Moreover, some of these compounds can be adsorbed on larger particles. What is physically or chemically adsorbed can easily pass into the water—all that is needed is a change in salinity or an increase in the concentration of Cl^- complexing

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metals. Metals bound to organic matter are released following its degradation, but those in silicate crystal lattices practically do not get into the water.

With such a diversity of forms of occurrence of metals in sediments, analysis of the total content of a given metal is insufficient to evaluate its effect on the environment. Such a result provides no information on the potential mobility of a metal and its possible removal from the sediment following a change in conditions, e.g., in pH or salinity, or the presence of complexing ligands. A change in conditions causes a change in the chemical species in which a metal occurs, and consequently its bioavailability. Hence the analysis of metals in bottom sediments should supply an answer to the question: "As what chemical species is this metal present?" Analysis of bottom sediments involves operational speciation based on the isolation of a selected fraction defined by the procedure of its isolation.

In order to differentiate reactivities and types of bonding of metals in solid samples of soil, sediments, or wastes, the following techniques, among others, have been suggested:

- single extraction (leaching) with a solution simulating the natural conditions under which components pass from sediments and soils to waters and plants;
- sequential extraction using consecutive extractions with solutions of increasing aggressivity (118, 119).

The use of sequential extraction, although a longer process, yields more complete information on the mobility of metals under different environmental conditions (acidity, alkalization, oxidation, activity of chelating agents). The reliability of this method is affected by such factors as the chemical properties of the extractants used, the order in which they are applied, the effect of the matrix given the presence of other contaminants and possible re-adsorption, association in the solid fraction, and yield (efficiency).

The following extraction reagents are used:

- neutral electrolytes—$CaCl_2$, $MgCl_2$;
- buffers or weak acids—acetic, oxalic;
- chelating agents—EDTA, DTPA;
- reducing agents—NH_2OH, strong acids HCl, HNO_3, HF, or bases NaOH (Na_2CO_3 has also been used).

The ability of different extractants to remove metals depends on the association of the latter with the various fractions of soil or other solid sample. Extractants like electrolytes, weak acids, and chelates release metals from the coordination sphere, whereas strong acids and redox agents release metals by decomposing the matrix. Sequential extraction supplies information on the mobility of metals in different environmental conditions, e.g., to identify Al species in soil (120) combined with sequential extraction with HPLC and ET AAS. To obtain information on some specific component or form a single extraction run may suffice – for soil-bound aluminum it is recommended to use extraction with $CaCl_2$, then with KCl, after which the species are separated using ion chromatography (79).

In practice, speciation analysis uses sequential extraction for the stepwise separation of the species in which metals are present in soils or bottom sediments. The first methodology of this type was developed by Tessier et al (121), who distinguished five fractions: exchangeable metals, metals bound to carbonates, metals bound to the hydrated oxides of iron and manganese, metals bound to an organic matrix of sulfides, and other metals (mainly silicates) (Table 2).

TABLE 2
Conditions for extracting metals from soils or bottom sediments according to Tessier (116, 121)

Fraction	Extractant	pH	Extraction time	Temperature	Stirring
I—exchangeable metals	1.0 M aq $MgCl_2$ or 1.0 M aq CH_3COONa	7.0 8.2	1 h	Room	Continuous
II—metals bound to carbonates	1.0 M aq CH_3COONa acidified with CH_3COOH	5.0	Determined experimentally	Room	Continuous
III—metals bound to hydrated oxides of iron and manganese	0.3 M aq $Na_2S_2O_4$+ 0.175 M aq sodium citrate + 0.025 M aq citric acid or 0.04 M aq $NH_2OH{\cdot}HCl$ + 25% aq (v/v) CH_3COOH		Determined experimentally	$96 \pm 3^{\circ}C$	Intermittent
IV—metals bound to an organic matrix or sulfides	0.02 M aq HNO_3+ 30% aq H_2O_2 (acidified with HNO_3 to pH 2), flushing with 3.2 M aq CH_3COONH_4 in 20% aq (v/v) HNO_3		5 h	$85 \pm 2^{\circ}C$	Intermittent
V—other metals (mainly silicates)	Mineralization with HF + $HClO_4$ acids				

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TABLE 3
BCR sequential extraction procedure (129–131)

Extraction step	Extractant	Extracted form of metals
I	0.11 M aq CH_3COOH	Exchangeable, soluble in water and acids
II	0.1 M aq $NH_2OH{\cdot}HCl$, pH 2	Reducible, bound to Fe/Mn hydroxides
III	8.8 M aq H_2O_2, flushing with 1.0 M aq CH_3COONH_4, pH 2	Oxidizable, bound to organic matter and sulfides

Tessier's original method has been modified many times: the separation into fractions, extraction conditions, leaching agents, and leaching parameters have all been changed. Separation of the first fraction into three subfractions took account of different adsorption mechanisms (121). Reagents like $BaCl_2$, $MgCl_2$, $CaCl_2$, NH_4Cl, and a mixture of CH_3COONH_4 and $(CH_3COO)_2Mg$ were used to separate the subfractions on the basis of the degree of affinity of the cation for the active centers of exchange occupied by heavy metals and the influence of the complexing properties of chlorides. The third fraction was also divided into two subfractions—very easily reducible and fairly easily reducible metals (122, 123). From the ecological point of view this division seems important, because the reduction conditions (solution of hydroxylamine hydrochloride acidified with 0.01 M HNO_3) simulate conditions in natural ecosystems. Likewise, a wide range of reagents for separating metals bound to organic matter from those bound to sulfides have been tried. Subfractions of metals bound to humic and fulvic acids were separated by extraction with 0.1 M aq NaOH, a typical extractant of these acids (123).

The benefits of sequential extraction procedures are as follows:

- they simulate the conditions occurring in the environment;
- they supply information on the potential remobilization of metals when environmental conditions change;
- they are a basic tool in the evaluation of element speciation in natural samples (124).

Further elaboration of sequential extraction schemes did not always bring about the desired effects, however. The number of necessary laboratory activities was multiplied, as a result of which lower concentrations of metals were extracted into the different fractions, and this led to greater error in determining their contents. Hence, simplified extraction schemes began to appear in the literature, the best known being the suggestion to combine Tessier's fractions I and II, and III and IV to give a total of three fractions (118, 125). These simplified procedures were validated in interlaboratory comparisons (126, 127) and in attempts at unification; as a result of this work, a unified procedure was worked out (118, 128) (Table 3).

The unified sequential extraction procedure recommended by BCR was also used to determine the aluminum content in marine bottom sediments (130–132) and in river sediments. Table 4 lists examples of Al determination in marine samples.

Sequential extraction was used to determine the contents of the various aluminum fractions in the bottom sediments of two watersheds with different rates of deposition of sulfur and nitrogen compounds (133) and in marine sediments (134). It was found that most Al occurred in the form of the third fraction. In this latter case the total Al content in the sediment obtained by the mineralization of the sediment with aqua regia was compared with the total Al content in the sediment obtained during analysis of the several fractions following sequential extraction. The first method gave better results than the second. Earlier, Bernard et al. (136) had obtained similar results; these authors explained the difference by the weak attack of the extraction reagents on the aluminosilicates in the sample. Scanning microscopy analysis (SEM-EDX) of the surface of the sediment samples revealed that part of the mineral fraction, which should have dissolved in the extractant, remained in the solid phase. Baffi et al. (134) suggested optimizing sequential extraction by applying an appropriate selection of extractants and extraction conditions, and verification using scanning microscopy.

Other authors also noted the lack of reproducibility in the results of BCR extraction of Al (130). As a consequence, it was suggested that the sample mass be increased from 1 to 5 g: this would make it more representative and would guarantee a constant volume ratio of sample to extractant. Attention was

TABLE 4
Sequential extraction conditions for Al determination in solid samples of marine origin

Sample	Sequential extraction conditions	Reference
Soils from areas with a low (high) intensity of Si and N deposition	1.0 M KCl 2H, 0.5 M $CuCl_2$ 18 h; 0.2 M $(NH_4)C_2O_4$, 4 h	(133)
Suspended particulate matter in sea water	Unfiltered samples, detection by AAS or ICP-AES	(134)
Bottom sediments from the coastal zone	1.0 M KCl, 0.1 M $Na_2P_2O_7$, 0.012 M $(NH_4)_2C_2O_4$	(135)

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also drawn to the numerous parameters affecting the course of extraction, e.g., the pH in the second sequential extraction stage, and the means of desiccating the sample (air-dried samples gave better reproducibility).

Because of the above difficulties in the sequential analysis of aluminum, modifications of the BCR procedure were introduced; for example, for the analysis of sediments from Lake Balaton (Hungary), an additional, fourth fraction was suggested: acid-soluble aluminum, which was separated from the residue of the third fraction by treatment with a mixture of concentration $HClO_4$ and conc. HNO_3 at 100°C for 2 hours. The proportion of this fraction was the largest, since under these experimental conditions the aluminosilicates in the solid phase could be attacked (137).

The speciation analysis of aluminum in sediments, a characteristic site of its deposition, has in the case of particular watersheds been combined with analyses of Al species in soils in the close vicinity of water. This type of study required the use of reagents enabling the bonding of Al to the soil to be elucidated. Hence, 1.0 M KCl was used to isolate exchangeable Al, together with 0.5 M $CuCl_2$ and 0.2 M $(NH_4)_2C_2O_4$ to separate aluminum bound amorphously with oxyhydroxides (138, 139).

To determine the content of selected Al species in river bottom sediments and in soils located close to the river, a two-stage procedure was adopted. Soil samples were stirred with 0.05 M EDTA (pH = 7) at room temperature for 1 hour, after which the Al concentration in the solution was measured by FAAS. Bottom sediment samples were treated with 0.5 M HCl, stirred for 1 hour, filtered and determined by ICP-AES. Both soil and sediment residues were extracted with 10 % HCl, then determined by ICP-AES. A mixture of HNO_3, $HClO_4$, and HF was then used to determine total Al in these samples. This procedure enabled the soluble species of Al to be defined and their concentrations to be compared with the total Al in different matrices (140).

Aluminum was also analyzed in aqueous extracts of sediments and soils in accordance with procedures normally applied to waters (72); labile monomeric aluminum, i.e., the fraction regarded as toxic, could thus be isolated (141). In this last case, aluminum was leached with aq $CaCl_2$, then determined using ion chromatography (79). Cation exchange and size exclusion HPLC methods with postcolumn fluorescence detection using 5-sulfo-8-quinolinol were applied to the chemical speciation of aluminum in soil-extract samples, too. The addition of an appropriate amount of F^- to the postcolumn reagent solution makes it possible to eliminate the interference of F^- in a sample with Al^{3+} detection. The reliability of this method was evaluated by a computer-assisted equilibrium calculation for aluminum species and ICP-AES. Considerable parts of water-soluble Al^{3+} (the Al^{3+} fraction extracted into distilled water) in both sedimentary and granitoid soil samples were found to be complexed with organic substances. On the other hand, exchangeable Al^{3+} (the Al^{3+} fraction extracted into 1 mol/dm^3 KCl) in granitoid soil samples was mostly free Al^{3+} (142).

Note that single leaching separates one selected fraction, whereas sequential extraction yields information on the mobility of aluminum. At the same time, however, the stages in sequential extraction are all very time-consuming—they require tens of hours to carry out. Microwave sequential extraction, a relatively new approach, has enabled the time to analyze metals contained in geological samples to be shortened quite considerably (143, 144).

To evaluate aluminum speciation, soil water analysis was used (145) and also soil extracts in doubly distilled water using an ion exchange column containing 8-hydroxyquinoline or Chelex-100, with which the labile monomeric aluminum fraction was isolated (72). For this purpose, other authors used $CaCl_2$ (146), KCl (147), NaCl (148), and NH_4Cl (149). But with these approaches, reliable results in the speciation analysis of aluminum using sequential extraction are very hard to obtain. This methodology requires a large number of operations to be carried out; samples are not representative, there are problems with reference materials, not to mention the considerable time outlay—not a very promising prospect.

Dissolving samples in the traditional way takes a very long time, sometimes several days. Applying microwave energy to decompose the organic and inorganic matrices at the stage of leaching the several fractions can solve this problem. Microwaves have been used as a source of heat in the laboratory for dissolving samples since 1975 (150). Later, they were used to dissolve samples under pressure in the Teflon bomb technique (151). The combination of temperature (microwave energy) and pressure is the most efficient method of decomposing organic and inorganic substances in samples (152). Microwave-assisted extraction has been used for the speciation of metals in biological samples (144) and in river bottom sediments (16, 42).

Aluminum was analyzed in bottom sediments of the Silnica and Sufraganiec Rivers (E. Poland) using microwave-assisted sequential extraction; the results were compared with those obtained using the extraction methods of Tessier and also of Perez-Cid et al. (16). This comparison (Table 5) shows that with $MgCl_2$ as the extracting reagent in Step I of Perez-Cid's method, the Al content is lower than that achieved by means of Tessier's method. The solution of $MgCl_2$ extracts only part of the aluminum from the first fraction. In Steps II and II, the

TABLE 5
Al content in bottom sediment samples from the Silnica River (Poland), in the individual sequential extraction fractions for the measuring point at Dąbrowa ($n \geq 3$) (16)

	m_{Al} [mg/100 g d.w.]		
Method	Step I	Step II	Step III
After Tessier et al.	1.86	0.12	0.80
After Perez-Cid et al.	0.70	1.45	5.45
Suggested methodology	1.70	1.60	5.60

TABLE 6
Determinations of some Al fractions in soils samples using different combined techniques—some examples

Methodology	Final determination techniques	References
Sample filtration (pore Ø 0.45 μm), Superdex HR75 10/30 column, elution 0.15 M NaCl in 0.025 M TRIS-HCl buffer, pH = 5.5; determination of Al dissolved in water and Al bound to humic and fulvic acids	ICP-AES-UV	(154)
Sample filtration (pore Ø 0.45 μm), Mono S HR 5/5 cation exchange column, eluent 8 M NH_4NO_3, 0.05 M potassium hydrogen phthalate buffer, pH = 4.0–6.0; determination of Al dissolved in water and Al bound to humic acids	FPLC-ET-AAS	(74, 154)
Sample filtration (pore Ø 0.45 μm), IonPac CS5A ion exchange column (Dionex) with an IonPac CG5A column (Dionex), NH_4Cl as mobile phase, pH $\sim$ 3; determination of Al forms of the general formula $AlF_n^{(3-n)+}$ (AlF_2^+, AlF^{2+}) and Al^{3+}	HPLC-FAAS	(14)
Flushing with 0.5 M KCl, pH = 5.8, sample-to-solution ratio = 1:10 (5 g: 50 ml), agitation for 24 h, centrifugation and filtration, Cation/R SN IC1 818 cation column (Altech), mobile phase 0.1 M Na_2SO_4 in 7.5 mM H_2SO_4, pH $\sim$ 2.4, exchangeable Al forms	HPLC-IC-UV-Vis	(30)

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results with microwave-assisted mineralization are decidedly better than with Tessier's traditional method. Since the same reagents were used in the corresponding steps of all three methods, i.e., hydroxylamine hydrochloride in Step II, and hydrogen peroxide and ammonium acetate in Step III, it is highly likely that Al extraction with microwave-assisted mineralization is more complete than with the traditional method.

It was also found that aluminum was bound to the solid matrix so strongly that the extraction conditions provided by traditional sequential extraction techniques (121, 153) were insufficient to remove it, which led to the results being underestimated. The difference in the results of the analysis of the residues following Tessier extraction and those remaining after microwave–assisted extraction merely confirms this supposition: elevated temperatures and pressures ensure better Al extraction. Electron micrographs of the sediments and residues from each sequential mineralization step (Tessier) and the microwave methods proposed by the present authors provide further evidence in support of these observations. The results achieved with microwave-assisted mineralization are as good as and often better than those obtained with traditional methods. Moreover, the mineralization time is shorter, and the use of closed systems reduces losses and quantities of reagents; with the traditional method this is not possible.

Combined techniques, based mostly on chromatography (Table 6), provide many opportunities for isolating aluminum species from solid samples.

The application of chromatographic techniques to isolate aluminum species does require, however, the solid environmental sample to be prepared in the appropriate way, which is not easy. Special attention must be paid to the pH of the systems in which extraction and then isolation are to be carried out, since one species of Al can convert into another; also, attention must be paid to the solutions used for buffering the medium and the available means of detection.

SPECIATION OF ALUMINUM IN BIOLOGICAL MATERIAL

For samples with a high organic content, like forest understory material, plant matter, or organic sediment, digestion with HNO_3 can be replaced by microwave-assisted digestion with HF. Once the EPA recommended microwave-assisted digestion with HNO_3, this procedure became standard for the examination of soil, bottom sediment, and mud samples (155). Nevertheless, the efficiency of microwave mineralization depends on a number of factors, among them, the combination of reagents, heating power and duration, sample size, and the water content in the sample.

In biotoxicology, speciation still presents a considerable challenge owing to the very low concentrations of analytes, their (usually) poor stability, and the complex matrix (numerous interferences) (156). In this respect, particular attention should be paid to:

- identification of species;
- understanding the role species play in the physiology and pathology of the physiological process;
- assuring analytical methods of an acceptable quality;
- the practical and ethical aspects of sampling.

Speciation analysis, in which both toxicology and environmental medicine have an interest, can be carried out in two ways:

- speciation analysis in environmental matrices, especially in air and water, yields information on the sources of discharge/emission (quantity, quality, chemical form), release mechanisms, and the extent of interaction with the different components of the environment;
- analysis carried out directly in biological matrices supplies information on the absorption of an environmen-

tal toxin, its degradation in the organism, its reactivity, bioavailability toxicity, and excretion (157).

The information obtained in the second way is more complete, hence the increasing numbers of speciation analyses of particular elements carried out within biological matrices. Elements, especially metals, play various parts in tissues, and so several definitions and schemes of speciation, based on different criteria, have been formulated. One such scheme, in which metal ions are classified according to their biological activity (158), covers the following groups:

- organometallic compounds of relatively small molecular weight which undergo no changes in the organism, e.g., alkyl compounds of zinc;
- metal-bioureas, which do undergo transformation in the organism, e.g., arsenic metabolized to acids;
- biologically active metallic elements able to exist in different oxidation states, e.g., chromium, zinc in enzymes;
- metals forming complex compounds with organic ligands, e.g., aluminum citrates.

Another classification is based on the criterion of the stability and lability of metallic compounds in tissues (159). Here, the following compounds are distinguished:

- thermodynamically stable but kinetically inert, e.g., tributyl tin;
- thermodynamically stable but kinetically labile, e.g., compounds containing a metal-heteroatom bond such as aluminum-transferase;
- thermodynamically not very stable and kinetically labile, e.g., all the toxic forms of aluminum: Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$.

A third classification based on the type of compound in which a metal occurs in an organism (160) distinguishes inorganic compounds, organic compounds, organometallic compounds, and macromolecules as species. According to this criterion, the compound between aluminum and transferase is an organic one.

Many schemes are now known for the speciation analysis of metals, including aluminum, in biological matrices. A variety of analytical methods can be used to analyze the content of a particular species of a metal that plays a definite role in the organism. In the case of Al determinations, speciation analysis should cover such forms as:

- the simple ion Al^{3+} and its hydrolysis products, taking account of mixed complexes, found under physiological conditions by Martin (161) and Harris et al. (162), among other authors;
- organic chelate forms such as Al complexes with citrates, oxalates, transferrin, and phosphates (this last form is regarded as the principal blood protein binding aluminum—transferrin binds 80–85% of aluminum present in the blood, citrates only 15–20%) (163).

In healthy people the level of Al in the serum does not normally exceed 2 $\mu g/dm^3$, but in patients with chronic kidney diseases it can rise to 100–200 $\mu g/dm^3$. It was demonstrated that proteins complex micromolecular complexes of Al such as Al citrates and Al oxalates. The protein present in human serum (transferrin) binds about 90% Al, where 10% of this is in citrate form (164). In humans, absorption rises in the presence of citrates and Al is accumulated in the stomach (165). In plants, by contrast, citrates act as detoxifiers (generally, the presence of organic acids raises the tolerance of plants to Al) (156, 166).

The problems peculiar to the analysis of aluminum in tissues include the very low levels of the metal and the complexity of the matrix; this means that the analyte has to be first isolated and then enriched before it can be analyzed. These conditions impose the need for the careful selection of analytical and preliminary sample processing techniques. Usually, Al is analyzed in blood serum, a heterogeneous mixture of lipoproteins (e.g., albumin, immunoglobulin, transferrin) together with small molecules and ions. The inhomogeneity and complexity of this matrix requires the fraction containing the analytes to be isolated. One of the ways of doing this is to use membrane techniques and ultraflotation to isolate the low-molecular-weight fraction in which, for example, chelate compounds of Al will be present (164). Chen et al. (167) used cellulose membranes to divide a homogenized sample into subcellular fractions and then determined the Al content in each of them by neutron activation analysis. The researches of the inside distribution explain what role aluminum plays in the different parts of the cell. With capillary electrophoresis aluminum complexes can be separated, depending on their means of coordination (168).

Chromatographic methods offer a wide range of possibilities for isolating analytes from biological material. The usual method is liquid chromatography, following which the separated species are analyzed by ET-AAS or ICP-AES, ICP-MS (168–170). HPLC was used to separate Al complexes with transferrin and citrates (34, 169, 171, 172), and FPLC with a Mono Q (HR 5/5) anion exchange column was used to separate high-molecular-weight proteins from aluminum complexes with citrates or transferrin (169, 170). Lopez-Garcia (173) suggested using an additional column (Celex-100 on silica gel impregnated with C_{18}) to remove other forms of Al, incorporating it in an *on-line* system in combination with a Mono Q (HR 5/5) column. The LOD of this method was 2.5 $\mu g/dm^3$, making it suitable for analyzing Al species in blood serum. HPLC combined with ET-AAS was used to analyze Al in the form of citrates and complexes with desferrioxamine (DFO) in urine, thus enabling the metabolism of drugs to be tracked (169, 172).

Because of their great sensitivity, electrochemical methods can also be used to analyze trace amounts of aluminum. Lo Balbo et al. (174) applied inversion voltamperometry to analyze

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trace amounts of Al^{3+} in liquids for dialysis. But because of their strongly negative reduction potential, voltamperometric methods are not applied directly: indirect methods are used, like adsorptive inversion voltamperometry, in which the Al^{3+} ion is complexed with Solochrome violet RS (90), with 1,2-dihydroxyanthraquinone-3-sulfonic acid (175), or cupferron (176). Square wave adsorptive cathodic stripping voltammetry (SWAdCSV) with a hanging mercury drop electrode (HMDE) and an auxiliary platinum electrode, in an atmosphere of nitrogen, enabled Al traces in the form of the $Al(PR)_3 \cdot 9TBATFB$ complex to be detected in urine (177). A stripping voltammetric method for the determination of aluminum as a ontaminant in dialysis concentrates to be detected in dialysis, too. It is based on the adsorptive deposition of the complex Al-1,2-dihydroxyanthraquinone-3-sulfonic acid (DASA) at the HMDE at -0.9 V (versus Ag/AgCl) and its cathodic stripping during the potential scan (178).

The HMDE can be replaced by an electrode with a thin mercury film on a solid carrier. The use of such an electrode and complexation of Al(III) with eriochrome black T lowered the LOD of Al in liquids for dialysis to 0.5 $\mu g/dm^3$ (174).

The literature also mentions the use of X-ray fluorescence spectroscopy to analyze aluminum in tissues (179, 180). According to these authors, an undoubted advantage of this method was that it did not destroy the sample and that any sample, regardless of its state of matter, could be analyzed; a possible drawback, however, was that with trace concentrations in the region of 10^{-7}–10^{-12} g/g^1, the analyte might become contaminated by the container in which it was stored.

The use of the highly sensitive technique of secondary ion mass spectrometry (SI-MS) was also considered (181); its application to biological materials, however, appeared to be encumbered with a very large error, owing to the possible interference of aluminum isotopes (^{26}Al, ^{27}Al), ^{26}Mg, or polyatomic ions like $^{13}C^{14}N^-$ and $^{12}C^{15}N$, present in tissues (182).

In clinical studies to confirm the correlations between the Al content in liquids for dialysis and that in serum on the one hand, and the hemoglobin concentration on the other, AAS was used to determine the overall content of Al in serum (183). The same technique was used to determine the Al level in bones: this is a reflection of the effect of long-term exposure to this element (184). Hongve et al. (185) found that AAS could be successfully applied to analyze Al deposited in bones or soft tissues like the liver. Sample preparation involved a number of different procedures: ashing, wet mineralization, and extraction of Al with chelating agents dissolved in tetramethylammonium hydroxide (185, 186). Hongve demonstrated that ashing at 550°C for 20 hours enabled Al to be determined in bones at levels of 0.6–0.7 mg/kg d.w. The use of graphite cuvettes, obviating the need for long-term ashing or acid dissolution of the sample, led to a further reduction in the LOD (187–189).

A graphite cuvette was also used to determine the total Al content in food products, e.g., powdered egg, powdered milk, and corn. In the opinion of Motkosky and Krotochwil (190), however, ET eliminates the effect of the matrix. Apart from AAS, AES was also used to analyze Al in bones (191). Later years witnessed modifications to the ICP version (192); of all the possible analytical lines, that of length 308 nm was chosen for analyses of biological material (193). Hu et al. (194) expressed the opinion that with this method, the LOD for the total Al content in biological material could be reduced to 5 pg. Hu et al. (194) found that electrothermal vaporization and inductively coupled plasma atomic emission spectrometry with polytetrafluoroethylene (PTEE) as a chemical modifier to improve the vaporization of aluminium, could be successfully applied to analyze Al in biological materials. The absolute detection limit of aluminium is 5.0 pg and the R.S.D. is 2.2% at an aluminium concentration of 0.2 $\mu g/mL^1$ ($n = 9$).

A point worth stressing is that both the development of new procedures for separating the forms of an analyte and the choice of new, more sensitive methods come up against the lack of appropriate reference materials, which means that these procedures cannot be validated. The problem of standardization with regard to analyses of biological material, the matrices of which are quantitatively and qualitatively diverse, is of crucial importance. Lovell et al. (195) found that the commonly applied metal standards, containing metals dissolved in acids, cannot be applied to analyses in tissue samples because the matrix is different. A standard matrix for solutions of metals should contain, among other things, phosphate ions, organic bases, and alkali metal ions—in other words, the components present in tissues.

SUMMARY

Aluminum is very widespread in the environment. With its amphoteric properties, it can form a whole range of compounds depending on the pH. It also occurs as monomeric aluminum (mainly Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^{2+}$ ions), nonlabile monomeric Al, and non-monomeric Al (mostly polymeric colloidal forms). We also find strongly positively charged colloidal particles, colloids with strongly positive domains, strongly polarized complexes, weakly positively or negatively charged colloids, as well as neutral and slightly polarized complexes, such as those of aluminum(III) precipitated from solution (bottom sediment). Thus we have both organic and inorganic compounds, with diverse activities with respect to living organisms. Depending on the mobility, nature, and condition of an organism, aluminum may not only disturb its correct functioning, but also cause serious disease. It is for these reasons that speciation analysis is a major tool in determining the state of the environment and the threats to living organisms.

The concentrations of the various aluminum species, their different stability in relation to factors like pH, Eh, temperature, and the presence of micro-organisms, as well as matrix complexity, require increasingly precise methods to be applied both to the preparation of environmental samples for analysis and to the detection process. Where solid samples (soil or bottom sediment) are concerned, sequential extraction is of fundamental

importance. In the case of liquid samples, however, chromatography is playing a greater role as a basic technique for separating and isolating different species of aluminum: in combination with such methods as ICP-AAS, ICP-AES, and MCC-ETAAS, it enables a broad spectrum of Al species or groups of Al compounds to be determined.

REFERENCES

1. D. K. Nordstrom, The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. *Geochimica et Cosmochimica Acta* 46(4) (1982):681–892.
2. A. Kabata-Pendias and H. Pendias, *Trace Elements in Soils and Plants* (CRC Press LLC, Boca Raton, FL 2000).
3. P. Matúš and J. Kubová, Complexation of labile aluminium species by chelating resins Iontosorb—A new method for Al environmental risk assessment. *Journal of Inorganic Biochemistry* 99 (2006):1769–1778.
4. D. M. McKnight and K. E. Bencala, The chemistry of iron, aluminum, and dissolved organic material in three acidic, metal-enriched, mountain streams, as controlled by watershed and in-stream processes. *Water Resources Research* 26(12) (1990):3087–3100.
5. H. Habs, B. Simon, K. U. Thiedemann, and P. Howe, *Aluminium, Environmental Health Criteria 194* (World Health Organization, WHO Library Cataloguing in Publication Data, Geneva, 1997).
6. N. Clarke, L.-G. Danielsson, and A. Sparén, Analytical methodology for the determination of aluminium fractions in natural fresh waters (Technical Report). *Pure and Applied Chemistry* 68(8) (1996):1597–1638.
7. J. Burgess, Kinetic aspects of chemical speciation. *Analyst* 117 (1992):605–611.
8. N. B. Milić, Z. D. Bugarčić, and P. T. Djurdjević, Hydrolysis of aluminum(III) ion in sodium nitrate medium. *Canadian Journal of Chemistry* 69 (1991):28–32.
9. A. Zioła and T. Sobczyñski, The effect of water ionic composition on liberation of aluminium from bottom sediment. *Polish Journal of Environmental Studies* 14 (2005):101–104.
10. E. Lydersen, B. Salbu, A. B. S. Poleo, and I. P. Muniz, The influences of temperature on aqueous aluminium chemistry. *Water, Air, and Soil Pollution* 51 (1990):203–215.
11. E. Lydersen, N. W. A. Rukke, J. G. B. Jensen, B. M. Kjelsberg, B. Tornsjø, R. D. Vogt, L. A. Vøllestad, and A. B. S. Poléo, Seasonal variation in mortality of brown trout (*Salmo trutta*) in an acidic aluminium-rich lake. *Journal of Limnology* 61(1) (2002):61–68.
12. C. T. Driscoll and K. M. Postek, The chemistry of aluminum in surface waters, in *The Environmental Chemistry of Aluminum* ed. G. Sposito (Lewis Publishers, Chelsea, MI, 1995), 363–418.
13. B. Mitrovič, R. Milačič, and B. Pihlar, Speciation of aluminium in soil extracts by employing cation-exchange fast protein liquid chromatography-inductively coupled plasma atomic emission spectrometry. *Analyst* 121 (1996):627–634.
14. A. Zioła-Frankowska, M. Frankowski, and J. Siepak, Development of a new analytical method for online simultaneous qualitative determination of aluminium (free aluminium ion, aluminium-fluoride complexes) by HPLC-FAAS. *Talanta* 78 (2009):623–630.
15. R. B. Martin, Aluminium: A neurotoxic product of acid rain. *Ace. Chem*. Rex. 27 (1994):204–210.
16. E. Bezak-Mazur and A. Rabajczyk, Speciation analysis of aluminium in solid environmental samples, In *Micropollution in the Human Environment* Czêstochowa University of Technology Publishing House, Poland, 48 (2002):55–63. (In Polish).
17. M. C. Arbestain, M. E. Barreal, C. Mourenza, E. Álvarez, P. Kidd, and F. Macías, Rhizosphere chemistry in acid forest soils that differ in their degree of Al-saturation of organic matter. *Soil Science* 168(4) (2003):267–279.
18. J. P. Boudot, T. Becquer, D. Merlet, and J. Rouiller, Aluminium toxicity in declining forests: A general overview with a seasonal assessment in a silver fir forest in the Vosges mountains (France). *Annales of Forest Science* 51 (1994):27–51.
19. J. P. Boudot, O. Maitat, D. Merlet, and J. Rouiller, Evidence for the redissolution of soil spodic horizons under the influence of acid deposition in the Vosges mountains (north-eastern France). *Science of the Total Environment* 184 (1996):211–214.
20. G. Wauer, H.-J. Heckemann, and R. Koschel, Analysis of toxic aluminium species in natural waters. *Microchimica Acta* 146 (2004):149–154.
21. S. P. Bi, X. D. Yang, F. P. Zhang, X. L. Wang, and G. W. Zou, Analytical methodologies for aluminium speciation in environmental and biological review. *Analytical Chemistry* 370 (2001):984–996.
22. G. Berthon, Aluminium speciation in relation to aluminium bioavailability, metabolism and toxicity. *Coordination Chemistry Reviews* 228 (2002):319–341.
23. G. Guibaud and C. Gauthier, Study of aluminium concentration and speciation of surface water in four catchments in the Limousin region (France). *Journal of Inorganic Biochemistry* 97 (2003):16–25.
24. C. T. Driscoll, A procedure for the fractionation of aqueous aluminium in diluted acid waters. *International Journal of Environmental Analytical Chemistry* 16(4) (1984):267–273.
25. C. T. Driscoll and W. D. Schecher, The chemistry of aluminium in the environment. *Environmental Geochemistry and Health* 12 (1990):28–49.
26. G. Guibaud and C. Gauthier, Aluminium speciation in the Vienne river on its upstream catchment (Limousin region, France). *Journal of Inorganic Biochemistry* 99 (2005):1817–1821.
27. M. Andersson, Toxicity and tolerance of aluminium in vascular plants. *Water, Air, and Soil Pollution* 39(3–4) (1988): 439–462.
28. D. Berggren and G. Fisksjö, Aluminium toxicity *and* speciation in soil liquids-experiment with *Allium cepa. L*. *Environ*. *Toxicology and Chemistry* 6 (1987):771–779.
29. É. Darkó, H. Ambrus, É. Stefanovits-Bányai, J. Fodor, F. Bakos, and B. Barnabás, Aluminium toxicity, Al tolerance and oxidative stress in an Al-sensitive wheat genotype and in Al-tolerant lines developed by in vitro microspore selection. *Plant Science* 166 (2004):583–591.
30. O. Drabek, L. Borucka, L. Mladkova, and M. Kocarek, Possible method of aluminium speciation in forest soils. *Journal of Inorganic Biochemistry* 97 (2003):8–15.
31. H. Klöppel, A. Fliedner, and W. Kördel, Behaviour and ecotoxicology of aluminium in soil and water—review of the scientific literature. *Chemosphere* 35 (1997):353–363.
32. U.S. EPA. Health effects assessment document for aluminum. prepared for the office of solid waste and emergency response

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by the environmental criteria and assessment office, U.S. EPA document (ECAO-CIN-H114, Cincinnati, OH, 1987).
33. P. O. Ganrot, Metabolism and possible health effects of aluminum. *Environmental Health Perspectives* 65 (1986):363–441.
34. M. H. Nagaoka and T. Maitani, Speciation of aluminium in human serum investigated by HPLC/High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS): Effects of sialic acid residues of the carbohydrate chain on the binding affinity of aluminium for transferring. *Journal of Health Science* 55(2) (2009):161–168.
35. V. B. Gupta, S. Anitha, M. L. Hegde, L. Zecca, R. M. Garruto, R. Ravid, S. K. Shankar, R. Stein, P. Shanmugavelu, and K. S. Jagannatha Rao, Aluminium in Alzheimer's disease: Are we still at a crossroads? *Cellular and Molecural Life Sciences* 62 (2005):143–158.
36. R. A. Yokel and R. L. Florence, Aluminum bioavailability from the approved food additive leavening agent acidic sodium aluminum phosphate, incorporated into a baked good, is lower than from water. *Toxicology* 227 (2006):86–93.
37. B. Platt, A. J. Drysdale, C. Nday, E. Linstow Roloff, B. D. Drever, and A. Salifoglou, Differential toxicity of novel aluminium compounds in hippocampal culture. *NeuroToxicology* 28 (2007):576–586.
38. E. Gauthier, I. Fortier, F. Courchesne, P. Pepin, J. Mortimer, and D. Gauvreau, Aluminum forms in drinking water and risk of alzheimer's disease. *Environmental Research* 84(3) (2000):234–246.
39. A. M. Ure, Trace elements in soil: Their determination and speciation. *Fresenius' Journal of Analytical Chemistry* 337 (1990):577–581.
40. J. Namieśnik, Trends in environmental analytics and monitoring, in *New Horizons and Challenges in Environmental Analysis and Monitoring* eds. J. Namieśnik, W. Chrzanowski, and P. Szpinek (Centre of Excellence in Environmental Analysis and Monitoring, Gdańsk, 2003), Ch. 14, 260–283.
41. M. Hoenig, Preparation steps in environmental trace element analysis—facts and traps. *Talanta* 54 (2001):1021–1038.
42. A. Rabajczyk, Sediment sample preparation for speciation of heavy metals. *Ecological Chemistry and Engineering* 15 (2008): 123–137.
43. J. Namieśnik and P. Szefer, Preparing samples for analysis—the key to analytical success. *Ecological Chemistry and Engineering* 15 (2008):167–244.
44. W. H. Ficklin and E. L. Mosier, Field methods for sampling and analysis of environmental samples for unstable and selected stable constituents, in *The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health*, eds. G. S. Plumlee, and M. J. Logsdon (Issues: Society of Economic Geologists Reviews in Economic Geology, Littleton, CO, 1999), Vol. 6A, 249–264.
45. J. Tria, E. C. V. Butler, P. R. Haddad, and A. R. Bowie. Determination of aluminium in natural water samples. *Analytica Chimica Acta* 588 (2007):153–165.
46. A. Sahuquillo, A. Rigol, and G. Rauret, Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *Trends in Analytical Chemistry* 22(3) (2003):152–159.
47. J. Namieśnik, Z. Jamrógiewicz, M. Pilarczyk, and L. Torres, *Preparation of Environmental Samples for Analysis* (WNT, Warsaw, 2000). (in Polish)
48. C. T. Driscoll, *Geological Aspects of Acid Deposition in Acid Precipitation* (Butterworth, London, 1989).
49. C. A. Backes and E. Tipping, An evaluation of the use of cation-exchange resin for the determination of organically-complexed Al in natural acid waters. *International Journal of Environmental Analytical Chemistry* 30(1) (1987):135–143.
50. D. Berggren, Speciation of aluminium, cadmium, copper, and lead in humic soil solutions—A comparison of the ion exchange column procedure and equilibrium dialysis. *International Journal of Environmental Analytical Chemistry* 35 (1989):1–15.
51. B. Fairman and A. Sanz-Medel, Improved determination of aluminium species in waters using fia separation/fluorimetric detection techniques. *International Journal of Environmental Analytical Chemistry* 50(3) (1993):161–171.
52. P. Canizares and M. D. Luque de Castro, Fluorimetric flow-through sensor for aluminium speciation. *Analytica Chimica Acta* 295 (1994):59–65.
53. X. Goenaga and D. J. A. Williams, Aluminum speciation in surface waters from a Welsh upland area. *Environmental Pollution* 52 (1988):131–149.
54. N. Christophersen, C. Neal, R. Vogt, J. M. Esser, and S. Anderesen, Aluminium mobilization in soil and stream waters at three Norwegian catchments with different acid deposition and site characteristics. *Science of the Total Environment* 96(1–2) (1990):175–188.
55. E. Alvarez, A. Perez, and R. Calvo, Aluminium speciation in surface waters and soil solutions in areas of sulphide mineralization in Galicia (N.W. Spain). *Science of the Total Environment* 133(1–2) (1993):17–37.
56. K. R. Bull and J. R. Hall, Aluminium in the Rivers Esk and Duddon, Cumbria and their tributaries. *Environmental Pollution* Ser. B 12 (1988):165–193.
57. M. Achilli, G. Ciceri, R. Ferraroli, G. Culivicchi, and S. Pieri, Aluminium speciation in aqueous solution. *Water, Air, and Soil Pollution* 57–58 (1991):139–148.
58. J. R. Miller and J. B. Andelman, Speciation of aluminum in an acidic mountain stream. *Water Research* 21 (1987):999–1005.
59. B. D. LaZerte, Forms of aqueous aluminum in acidified catchments of central Ontario: A methodological analysis. *Canadian Journal of Fisheries and Aquatic Sciences* 41 (1984):766–776.
60. E. Casassas, A. Izquierdo-Ridorsa, L. Garcia-Puignou, and J. Dunach, Spectrophotofluorimetric determination of trace amouts of aluminium with 2,2′-dihydroxy-3,3′-dicarboxy-1,1′-dinaphthylmetane (Pamoic Acid). *Analytical Letters* 18(A18) (1985):2239–2258.
61. L. G. Danielsson, A. Sparén, and A. W. Glynn, Aluminium fractionation in a simulated rat stomach: An in vitro study. *Analyst* 120(3) (1995):713–720.
62. J. M. Samaritan, J. D. Wehr, A. Buccafuri, and M. Sahn, Automated measurement of aqueous aluminum by the pyrocatechol violet method. *International Journal of Environmental Analytical Chemistry* 50(3) (1993):173–182.
63. P. M. Jardine and L. W. Zelazny, Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with

ferron. *Soil Science Society of American Journal* 50 (1986):895–900.
64. A. Shokrollahi, M. Ghaedi, M. S. Niband, and H. R. Rajabi, Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium Ion. *Journal of Hazardous Materials* 151(2–3) (2008):642–648.
65. O. Royset, Flow injection spectrophotometric determination of aluminium in natural water using eriochrome cyanine r and cationic surfactants. *Analytical Chemistry* 59 (1987):899–903.
66. N. Wu, W. J. Horvath, P. Sun, and C. W. Huie, Speciation of Al using capillary zone electrophoresis with indirect UV detection. *Journal of Chromatography A* 635 (1993):307–312.
67. S. H. Sutheimer and S. E. Cabaniss, Acqueous Al (III) speciation by high-performance cation exchange chroniatography with fluorescence detection of the ahimtnum-luimogaHion complex. *Analytical Chemistry* 67, 1995: 2342–2349.
68. P. G. C. Campbell, M. Bisson, R. Bougie, A. Tessier, and J. P. Villeneuve, Speciation of aluminum in acidic fresh waters. *Analytical Chemistry* 55 (1983):2246–2255.
69. C. L. Chakrabarti, Y. Lu, J. Cheng, M. H. Back, and W. H. Schroeder, Studies on metal speciation in the natural environment. *Analytica Chimica Acta* 267 (1993):47–64.
70. Y. Lu, C. L. Chakrabarti, M. H. Back, D. C. Grégoire, and W. H. Schroeder, Kinetic studies of aluminum and zinc speciation in river water and snow. *Analytica Chimica Acta* 293(1–2) (1994): 95–108.
71. E. Courtijn, C. Vandecasteele, and R. Dams, Speciation of aluminium in surface water. *Science of the Total Environment* 90 (1990):191–202.
72. N. Kožuh, R. Milacic, and B. Gorenc, Comparison of two methods for speciation of aluminium in soil extracts. *Annali di Chimica* 86(3–4) (1996):99–113.
73. S. Motellier and H. Pitsch, Determination of aluminium and its fluoro complexes in natural waters by ion chromatography. *Journal of Chromatography A* 660(1–2) (1994):211–217.
74. B. Mitrovič, R. Milačič, B. Pihlar, and P. Simončič, Speciation of trace amounts of aluminium in environmental samples by cation-exchange FPLC–ETAAS. *Analusis* 26 (1998):381–388.
75. R. Milačič, N. Kožuh, and B. Mitrovič, Combination of three analytical techniques for speciation of Al in environmental samples. *Mikrochimica Acta* 129(1–2) (1998):139–145.
76. N. Kožuh, R. Miločič, B. Gorenc, O. Aballino, C. Sarzanini, Speciation of aluminium in environmental water samples employing microcolumn chelating ion-exchange chromatography—ETAAS. *International Journal of Environmental Analytical Chemistry* 67(1–4) (1997):27–40.
77. F. Y. Leung, A. E. Niblock, C. Bradley, and A. R. Henderson, Speciation studies of serum aluminum/citrate complex by liquid chromatography-furnace AAS. *Science of Total Environment* 71(1) (1988):49–56.
78. A. K. Datta, P. J. Wedlund, and R. A. Yokel, Investigating aluminium citrate speciation by high performance liquid chromatography. *Journal of Trace Elements and Electrolytes in Health and Disease* 4(2) (1990):107–114.
79. J. A. E. Gibson and I. R. Willett, The application of fluorescence detection to the determination and speciation of aluminium in soil solutions by ion chromatography. *Communications in Soil Science and Plant Analysis* 22(13) (1991):1303–1313.
80. B. Fairman, A. Sanz-Medel, and P. Jones, Field sampling technique for the "ast reactive" aluminium fraction in waters using a flow injection mini-column system with inductively coupled plasma atomic emission spectrometric and inductively coupled plasma mass spectrometric detection. *Journal of Analytical Atomic Spectrometry* 10 (1995):281–285.
81. K-I. Tsunoda, T. Umemura, K. Ohshima, S.-I. Aizawa, E. Yoshimura, and K-I. Satake, determination and speciation of aluminum in environmental samples by cation exchange high-performance liquid chromatography with high resolution ICP-MS detection. *Water, Air, and Soil Pollution* 130(1–4) (2001):1589–1596.
82. B. Y. Mishra and P. M. Dhadke, Solvent extraction separation of beryllium(ll) from aluminum(lll) by cyanex 921 (TOPO). *Separation Science and Technology* 33(11) (1998):1681 – 1692.
83. H. Filik and R. Apak, A chelating ion exchanger for gallium recovery from alkaline solution using 5-palmitoyl-8-hydroxyquinoline immobilized on a nonpolar adsorbent. *Separation Science and Technology* 33(8) (1998):1123–1134.
84. P. N. Phalke, A. V. Sherikar, and P. M. Dhadke, Separation of beryllium (II) and aluminium (III) by solvent extraction using Bis-2 ethylhexyl phosphoric acid [HDEHP]. *Separations Technology* 6(4) (1996):247–251.
85. H. S. Ajgaonkar and P. M. Dhadke, Solvent extraction separation of iron(III) and aluminium(III) from other elements with Cyanex 302. *Talanta* 44(4) (1997):563–570.
86. A. Cedergren and W. French, Determination of aluminium in biological materials by graphite furnace atomic absorption spectrometry (GFAAS). *Pure and Applied Chemistry*, 59 (1987): 221–228.
87. D. J. Hydes and P. S. Liss, Fluorimetric method for the determination of low concentrations of dissolved aluminium in natural waters. *Analyst* 101 (1976): 922–931.
88. F. Sanchez Rojas, A. Garcia de Torres, C. Bosh Ojeda, and J. M. Cano Pavon, N-(3-Hydroxy-2-pyridyl)salicylaldimine as a reagent fot the selective fluorimetric determination of aluminium in waters. *Analyst* 113 (1988):1287–1290.
89. E. Stryjewska and S. Rubel, Adsortive stripping voltammetry for the determination of trace amounts of aluminiun with calmagite. *Elektroanalysis* 3(9) (1991):995–998.
90. J. Wang, P. A. M. Farias, and J. S. Mahmoud, Stripping measurements of aluminum based on the adsorptive accumulation of its solochrome violet rs complex at the static mercury drop electrode. *Analytica Chimica Acta* 172 (1985): 57–64.
91. J. Wang, P. Tuzhi, and T. Martinez, Trace metal speciation using adsorptive stripping voltammetry of metal chelates of dihydroxyzao dyes. *Analytica Chimica Acta* 201 (1987):43–50.
92. M. I. S. Veríssimo and M. T. S. R. Gomes, The quality of our drinking water: Aluminium determination with an acoustic wave sensor. *Analytica Chimica Acta* 617 (2008):162–166.
93. J. E. Van Benschaten and J. K. Edzwald, Aluminum measurements during water treatment: methodology and applications. *Journal AWWA* 82(5) (1990):71–78.
94. D. Bérubé, and D. G. Brûlé, Influence of the addition of organic wastes on the metal contents of a soil. *Fresenius' Journal of Analytical Chemistry* 363(5–6) (1999):558–561.
95. S. C. Hodges, Aluminum Speciation: A comparison of five methods. *Soil Science Society of American Journal* 51 (1987):57–64.

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96. J. Szpunar-Łobińska, C. Witte, R. Łobiński, and F. C. Adams, Separation techniques in speciation analysis for organometallic species. *Fresenius' Journal of Analytical Chemistry*, 351(4–5) (1995):351–377.
97. H. Sang, P. Liang, and D. Du, Determination of trace aluminum in biological and water samples by cloud point extraction preconcentration and graphite furnace atomic absorption spectrometry detection. *Journal of Hazardous Materials* 154(1–3), (2008): 1127–1132.
98. G. Alberti, G. D'Agostino, G. Palazzo, R. Biesuz, and M. Pesavento, Aluminium speciation in natural water by sorption on a complexing resin. *Journal of Inorganic Biochemistry* 99 (2005):1779–1787.
99. Ch.W. K. Chowa, S. D. Thomas, D. E. Davey, D. E. Mulcahy, and M. Drikas, Development of an on-line electrochemical analyser for trace level aluminium. *Analytica Chimica Acta* 499 (2003):173–181.
100. B. Fairman, A. Sanz-Medel, P. Jones, and E. H. Evans, Comparison of fluorimetric and inductively coupled plasma mass spectrometry detection systems for the determination of aluminium species in waters by high-performance liquid chromatography. *Analyst* 123 (1998):699–703.
101. B. R. James, C. J. Clark, and S. J. Riha, An 8-hydroxyquinoline method for labile and total aluminum in soil extracts. *Soil Science Society of American Journal* 47 (1983):893–897.
102. J. Luster, A. Yang, and G. Sposito, On the interpretation of labile aluminum as determined by reaction with 8-hydroxyquinoline. *Soil Science Society of American Journal* 57, (1993):976–980.
103. N. Clarke, L.-G. Danielsson, and A. Sparén, The determination of quickly reacting aluminium in natural waters by kinetic discrimination in a flow system. *International Journal of Environmental Analytical Chemistry* 48 (1992):77–100.
104. G. M. Morrison, Relevance of the reaction of aluminium with pyrocatechol violet to speciation and complexation capacity analysis. *Analyst* 115 (1990):1371–1373.
105. C. Wyganowski, S. Motomizu, and K. Tôei, Spectrophotometric determination of aluminium with bromopyrogallol red and a quaternary ammonium salt: Determination of aluminium in river water. *Microchimica Acta* 79(1–2) (1983):55–64.
106. C. Wyganowski, Effect of quaternary ammonium salts on spectrophotometric characteristic of pyrogallol ref and bromopyrogallol red. *Microchemical Journal* 29 (1984):318–325.
107. T. Korenaga, S. Motomizu, and K. Tôei, Modified extraction procedure for the spectrophotometric determination of trace amounts of aluminium in sea water with pyrocatechol violet and removal of excess of reagent. *Analyst* 105 (1980):328–332.
108. T. Korenaga, S. Motomizu, and K. Tôei, Extraction-spectrophotometric determination of aluminium in river water with pyrocatechol violet and a quaternary ammonium salt. *Talanta* 27(1) (1980):33–38.
109. G. Wauer, H. J. Heckemann, and R. Koschel, Analysis of toxic aluminium species in natural waters. *Microchimica Acta* 146 (2004):149–154.
110. Y. Ding, R. Dresnack, and P. C. Chan, Internal Report-Assessment of High-Rate Sedimentation Processes: Microcarrier Weighted Coagulation Jar Tests (U.S. EPA, Edison, NJ, 1999, EPA/600/X-99/033).
111. G. Blo, C. Contado, C. Conato, and F. Dondi, Separation and elemental characterization of water born particles, in *New Horizons and Challenges in Environmental Analysis and Monitoring* eds. J. Namieśnik, W. Chrzanowski, and P. Szpinek (Centre of Excellence in Environmental Analysis and Monitoring, Gdańsk, 2003), ch. 20a, 433–444.
112. R. M. Cenci and J.-M. Martin, Concentration and fate of trace metals in Mekong River Delta. *Science of the Total Environment* 332 (2004):167–182.
113. D.-J. Whitworth, E. P. Achterberg, V. Herzl, M. Nimmo, M. Gledhill, and P. J. Worsfold, Development of a simple extraction procedure using ligand competition for biogeochemically available metals of estuarine suspended particulate matter. *Analytica Chimica Acta* 392 (1999):3–17.
114. T. Bantan, R. Milačič, and B. Pihlar, Possibilities for speciation of Al-citrate and other negatively charged Al complexes by anion-exchange FPLC-ICP-AES. *Talanta* 46(1) (1998):227–235.
115. T. Bantan, R. Milačič, and B. Pihlar, Quantitative determination of trace amounts of Al-citrate by anion-exchange FPLC-ETAAS. *Talanta* 47(4) (1998):929–941.
116. J. Zerbe, T. Sobczyński, and J. Siepak, The heavy metals in bottom sediments, their speciation on road of sequencial extraction. *Ecology and Technicist* 3 (1995):7–12. [In Polish]
117. M. Sager, R. Pucsko, and R. Belocky, Evaluation of the Speciation of Inorganic Constituents in Sediments of the Reservoir at Altenwörth of the River Danube. *Arch. Hydrobiol. Supplement* 84, (1990): 37–72.
118. U. Fórstner and W. Salomons, Trace metal analysis on polluted sediments. Part II. Evaluation of environmental impast. *Environmental Technology Letters* 1 (1980):506–517.
119. W. Salomons and U. Förstner, *Metals in the Hydrocycle* Springer, (New York: 1984).
120. P. E. Gardiner, R. Schierl, and K. Kreutzer, Aluminium speciation in soil solutions as studied by size exclusion chromatography, *Plant and Soil* 103(1) (1987):151–154.
121. A. Tessier, P. G. Campbell, and M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51(7) (1979):844–851.
122. B. Welte, N. Bless, and A. Montiel, Study of different methods of speciation in sediments. *Environmental Technology Letters* 4 (1983):79–88.
123. F. E. Fernex, D. Span, G. N. Flatan, and D. Renard, Behavior of same metals in surficial sediments of the northwest mediterranean continental shelf, in *Proceedings of the Third International Symposium on Interaction Between Sediments and Water* (Geneva, Switzerland, August 27–31, 1984 Springer-Verlag, London), 27–31.
124. A. V. Hirner, Trace element speciation in soils and sediments using sequential chemical extraction methods. *International Journal of Environmental Analytical Chemistry* 46(1–3) (1992):77–85.
125. U. Fórstner, Metal speciation—general concepts and applications. *International Journal of Environmental Analytical Chemistry* 51 (1993):5–23.
126. W. Salomons, Adoption of common schemes for single and sequential extractions of trace metal in soils and sediments. *Intern. J. Environ. Anal. Chem.* 51 (1993):3–4.

127. P. Quevauviller, G. Rauret, H. Muntau, A. M. Ure, R. Rubio, J. F. López-Sánchez, H. D. Fiedler, and B. Griepink, Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments. *Fresenius' Journal of Analytical Chemistry* 349(12) (1994):808–814.
128. A. M. Ure, P. Quevauviller, H. Muntan, and B. Gniepink, *EUR Report No* 14763, CEC, Brussels, 1992.
129. C. M. Davidson, P. C. S. Ferreina, and A. M. Ure, Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil. *Fresenius' Journal of Analytical Chemistry* 363(5–6) (1999):446–451.
130. C. M. Davidson, R. P. Thomas, S. E. McVey, R. Perala, D. Littejohn, and A. M. Ure, Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. *Analytica Chimica Acta* 291(3) (1994):277–286.
131. A. U. Belazi, C. M. Davidson, G. E. Keating, D. Littlejohn, and M. McCartney, Determination and speciation of heavy metals in sediments from the Cumbrian Coast, NW England, UK. *Journal of Analytical Atomic Spectrometry* 10(3) (1995):233–240.
132. P. Matúš, J. Kubová, M. Bujdoš, V. Streško, and J. Medvd, Chemical partitioning of aluminium in rocks, soils, and sediments acidified by mining activity. *Analytical and Bioanalytical Chemistry* 379 (2004):96–103.
133. A. C. Norrström, Retention and chemistry of aluminium in groundwater discharge areas. *Environmental Pollution* 81 (1993):269–275.
134. F. Baffi, M. C. Ianni, M. Ravena, and E. Magi, Study of the influence of free dissolved amino acids on copper(II) adsorption/remobilization from inorganic fractions of marine sediments using a reversed-phase liquid chromatographic procedure. *Analytica Chimica Acta* 294(2) (1994):127–134.
135. G. C. Schafran and R. V. Ika, The role of near-shore sediments in metal mobilization and the neutralization of acidic groundwaters entering an acidic lake. *Water, Air, and Soil Pollution* 60 (1991):149–180.
136. P. C. Bernard, R. E. Van Grieken, and L. Brügmann, Geochemistry of suspended matter *from the* Baltic Sea. 1. Results of individual particle characterization by automated electron microprobe. *Marine Chemistry* 26 (1989):155–177.
137. I. Bodog, K. Polyak, and J. Hlavay, Determination of heavy metals in lake and river sediments by selective extraction leaching. *International Journal of Environmental Analytical Chemistry* 66 (1996):79–94.
138. C. T. Driscoll, N. Breemen, and J. Mulder, Aluminum Chemistry in a Forested Spodosol. *Soil Science Society of American Journal* 49 (1985):437–444.
139. J. Mulder, M. Pijpers, and N. Christophersen, water flow paths and the spatial distribution of soils and exchangeable cations in an acid rain-impacted and a pristine catchment in Norway. *Water Resources Research* 27(11) (1991):2919–2928.
140. R. A. Sutherland, Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. *Applied Geochemistry* 17 (2002):353–365.
141. C. T. Driscoll, J. P. Baker, J. J. Bisogni, and C. L. Schofield, Effect of aluminum speciation on fish in dilute acidified waters. *Nature* 284 (1980):161–164.
142. K.-I. Tsunoda, T. Yagasaki, S.-I. Aizawa, H. Akaiwa and K-I. Satake, Determination and speciation of aluminum in soil extracts by high-performance liquid chromatography with fluorescence detection using 5-sulfo-8-quinolinol. *Analytical Sciences* 13(5) (1997):757–764.
143. S. Nakashima, R. E. Sturgeon, S. N. Willie, and S. S. Berman, Acid digestion of marine samples for trace element analysis using microwave heating. *Analyst* 113(1) (1988):159–163.
144. M. Bettinelli, M. Baroni, and N. Pastorelli, Microwave oven sample dissolution for the analysis of environmental and biological materials. *Analytica Chimica Acta* 225 (1989):159–174.
145. C. T. Driscoll, B. J. Wyskowski, P. De Staffan, and R. M. Newton, Chemistry and transfer of aluminium in a forested watershed in the Adirondack region of New York, in *Environmental Chemistry and Toxicity of Aluminium* ed. T. E. Lewis (Lewis Publishers: Michigan, USA, 1989), Ch. 5, 83–105.
146. J. O. Reuss, R. W. E. Hopper, P. M. Walthall, and E. C. Roswall, Aluminum solubility, calcium-aluminum exchange, and pH in acid forest soils, *Soil Science Society of American Journal* 54 (1990):374–380.
147. E. Metzner and J. Prenzel, Acid deposition in the German solling area: Effects on soil solution chemistry and Al mobilization. *Water, Air, and Soil Pollutionion* 61(3–4) (1992):221–234.
148. P. B. Hoyt and M. Nyborg, Toxic metals in acid soil: i. estimation of plant-available aluminum. *Soil Science Society of American Journal* 35 (1971):236–240.
149. E. R. Rhodes and W. L. Lindsay, Solubility of aluminium in soils of the humid tropics. *Journal of Soil Science* 29 (1978):324–330.
150. A. Abu-Samra, J. S. Morris, and S. R. Koirtyohann, Wet ashing of some biological samples in a microwave oven. *Analytical Chemistry* 47 (1975):1475–1477.
151. B. D. Zehr and M. A. Fedorchak, Microwave acid digestion of inorganics using a bomb vessel. *American Laboratory* 23 (1991):40–45.
152. H. Matusiewicz, Development of a high pressure/temperature focused microwave heated teflon bomb for sample preparation. *Analytical Chemistry* 66 (1994):751–762.
153. B. Pérez-Cid, I. Lavilla, and C. Bendicho, Application of microwave extraction for partitioning of heavy metals in sewage sludge. *Analytica Chimica Acta* 378 (1999):201–210.
154. B. Mitrovič and R. Milačič, Speciation of aluminium in forest soil extracts by size exlusion chromatography with UV and ICP-AES detection and cation exchange fast protein liquid chromatography with ETAAS detection. *Science of the Total Environment* 258 (2000):183–194.
155. D. Sarkar, R. Datta, and R. Hannigan, *Concept and Applications in Environmental Geochemistry* (Elsevier Ltd., Amsterdam, 2007).
156. G. Sastre, V. Fornes, and A. Corma, On the preferential location of Al and proton siting in zeolites: A computational and infrared study. *Journal of Physical Chemistry B* 106 (2002):701–708.
157. P. Apostoli, The role of element speciation in environmental and occupational medicine. *Fresenius' Journal of Analytical Chemistry* 363(5–6) (1999):499–504.
158. R. Cornelis, Involvement of analytical chemistry in chemical speciation of metals in clinical samples. *Annals of Clinical and Laboratory Science* 26 (1996):252–263.

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159. A. Sanz-Medel, Beyond total element analysis of biological systems with atomic spectrometric techniques. *Analyst* 120 (1995):799–807.
160. D. M. Templeton, Biomedical aspects of trace element speciation. *Fresenius' Journal of Analytical Chemistry* 363 (1999): 505–511.
161. R. B. Martin, The chemistry of aluminum as related to biology and medicine. *Clinical Chemistry* 32 (1986):1797–1806.
162. W. R. Harris, G. Berthon, J. P. Day, C. Exley, T. P. Flaten, W. F. Forbes, T. Kiss, C. Orvig, and P. F. Zatta. Speciation of aluminum in biological systems. *Journal of Toxicology and Environmental Health* 48 (1996):543–568.
163. R. B. Martin, J. Savory, S. Brown, R. L. Bertholf, and M. R. Wills, Transferrin binding of Al^{3+} and Fe^{3+}. *Clinical Chemistry* 33 (1987):405–407.
164. J. Perez Parajon, E. Blanco González, J. B. Cannata, and A. Sanz-Medel, A critical appraisal of the speciation of aluminium in serum by ultrafiltration. *Journal of Trace Elements in Medicine and Biology* 6 (1989):41–46.
165. P. Slanina, Y. Falkeborn, W. French, and A. Cedergren, Aluminum concentrations in the brain and bone of rats fed citric acid, aluminum citrate and aluminum hydroxide. *Food and Chemical Toxicology* 22 (1984):391–397.
166. J. D. Ownby and H. R. Popham, Citrate reverses the inhibition of wheat root growth caused by aluminum. *Journal of Plant Physiology* 135 (1989):588–591.
167. C. Chen, P. Zhang, X. Lu, X. Hou, and Z. Chai, Subcellular distribution of Al, Cu, Mg, Mn and other elements in the human liver. *Fresenius' Journal of Analytical Chemistry* 363(5–6) (1999):512–516.
168. A. Sanz-Medel, The chemical speciation of aluminium and silicon in human serum. *Analusis Magazine* 26(6) (1998):76–80.
169. A. B. Soldado Cabezuelo, M. Montes Bayón, E. Blanco González, J. I. Garcia Alonso, and A. Sanz-Medel, Speciation of basal aluminium in human serum by fast protein liquid chromatography with inductively coupled plasma mass spectrometric detection. *Analyst* 123 (1998):865 – 869.
170. A. B. Soldado Cabezuelo, E. Blanco-González, and A. Sanz-Medel, Quantitative studies of aluminium binding species in human uremic serum by fast protein liquid chromatography coupled with electrothermal atomic absorption spektrometry. *Analyst* 122(6) (1997):573–577.
171. K. Wróbel, E. Blanco-Gonzalez, Kz. Wróbel, and A. Sanz-Medel, Aluminium and silicon speciation in human serum by ion-exchange high-performance liquid chromatography, electrothermal atomic absorption spectrometry and gel electrophoresis. *Analyst* 120 (1995):809–815.
172. A. Sanz-Medel, A. B. Soldado Cabezuelo, R. Milačič, and T. Bantan Polak, The chemical speciation of aluminium in human serum. *Coordination Chemistry Reviews* 228 (2002):373–383.
173. A. López García, E. Blanco González, and A. Sanz-Medel, Determination of trace elements in seawater by electrothermal atomic absorption spectrometry with and without a preconcentration step. *Microchimica Acta* 112(1–4) (1993):19–29.
174. A. Lo Balbo, V. Campo Dall'Orto, S. Sobral, and I. Rezzano, Linear scan stripping voltametry at glassy-carbon based thin mercury film electrodes for determination of trace aluminium in dialysis fluids. *Analytical Letters* 31 (1998):2717–2728.
175. C. M. G. Van der Berg, K. Murphy, and J. Riley, The determination of aluminium in seawater and freshwater by cathodic stripping voltammetry. *Analytica Chimica Acta* 188 (1986): 177–185.
176. J. Wang, J. Lu, and R. Setiadji, Adsorptive stripping measurements of trace aluminum in the presence of cupferron, *Talanta* 40 (1993):351–354.
177. V. Arancibia and C. Muñoz, Determination of aluminium in water samples by adsorptive cathodic stripping voltammetry in the presence of pyrogallol red and a quaternary ammonium salt. *Talanta* 73 (2007):546–552.
178. L. M. de Carvalho, P. C. do Nascimento, D. Bohrer, R. Stefanello, and D. Bertagnolli, Determination of aluminum as contaminant in dialysis concentrates by adsorptive cathodic stripping voltammetry. *Analytica Chimica Acta* 546(1) (2005):79–84.
179. A. J. Downs (Ed.) *Chemistry of Aluminium, Gallium, Indium, and Thallium* (Blackie Academic & Professional, London, 1993).
180. R. Klockenkämper, *Total-Reflection X-Ray Fluorescence Analysis* (Wiley & Sons, New York, 1997).
181. P. Galle, H. Campos, and C. Giudicelli, Ultrastructural localization of aluminum in the parathyroid cells of patients on chronic dialysis. *Comptes rendus des séances de l'Académie des sciences. Série III* 296(12) (1983):545–550.
182. P. Zatta, Microanalysis and analytical imaging of aluminum in biological samples. *J. Trace Microprobe Techniques* 16(3) (1998):395–400.
183. S. Hosokawa, A. Oyamaguchi, and O. Yoshida, Trace elements and complications in patients undergoing chronic hemodialysis. *Nephron* 55 (1990):375–379.
184. J. P. Day, Biochemistry of aluminium in relation to the assessment of aluminium exposure in humans. *Environmental Geochemistry and Health* 12(1–2) (1990):75–76.
185. D. Hongve, S. Johansen, E. Andruchow, E. Bjertness, G. Becher, and J. Alexander, Determination of aluminium in samples from bone and liver of elderly Norwegians. *Journal of Trace Elements in Medicine and Biology* 10 (1996):6–11.
186. J. G. Heaf, J. Pødenphant, and J. R. Andersen, Bone aluminium deposition in maintenance dialysis patients treated with aluminium-free dialysate: Role of aluminium hydroxide consumption. *Nephron* 42(3) (1986):210–216.
187. W. French and D. C. Baxter, Evaluation of the solid sampling technique for the determination of aluminium in biological materials by atomic absorption and atomic emission spectrometry. *Fresenius' Journal of Analytical Chemistry* 328(4–5) (1987):400–404.
188. N. J. Miller-Ihli, Solid analysis by GF AAS. *Analytical Chemistry* 64 (1992):964–968.
189. C. Bendicho and M. De Loos-Vollebregt, Solid sampling in electrothermal atomic absorption spectrometryusing commercial atomizer. *Journal of Analytical Atomic Spectrometry* 6 (1991): 353–367.
190. N. Motkosky and B. Kratochvil, Characterization of trace amounts of aluminium in biological reference materials by electrothermal atomic absorption spektrometry. *Analyst* 118 (1993):1313–1316.
191. A. Uchiumi, A. Takatsu, and Y. Teraki, Sensitive detection of trace aluminium in biological tissues by confocal laser scanning microscopy after staining with lumogallion. *Analyst* 123(4) (1998): 759–762.

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192. S. Recknagel, U. Rösick, and P. Brätter, Determination of aluminium in infusion solutions by inductively coupled plasma atomic emission spectrometry—A critical comparison of different emission lines. *Journal of Analytical Atomic Spectrometry* 9, (1994): 1293–1297.
193. H. Matusiewicz and R. M. Barnes, Determination of aluminum and silicon in biological materials by inductively coupled plasma atomic emission spectrometry with electrothermal vaporization. *Spectrochimmica Acta* Part B 39 (1984):891–899.
194. B. Hu, Z. Jiang, and Y. Zeng, Direct determination of aluminium in biological materials by electrothermal vaporization-inductively coupled plasma atomic emission spectrometry with polytetrafluoroethylene as chemical modifier. *Analytica Chimica Acta* 296(2) (1994):213–218.
195. M. A. Lovell, W. D. Ehmann, W. R. Markesbery, S. Melethil, C. R. Swyt, and P. F. Zatta, Standardization in biological analyses of aluminum: what are the needs? *Journal of Toxicology and Environmental Health* 48(6) (1996):637–648.

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