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Analytical methodologies for Aluminium Speciation in Environmental Samples – a Review

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Abstract. In this paper the briefly overview on analytical methodologies for Al speciation in environmental samples are given. The advances of the different methods for quantitative determination of Al species during last decade are emphasized. Hyphenated techniques (coupling of HPLC/ FPLC with ICP MS/ ETAAS/ ICP AES, etc.) are currently the primary tool for species-selective analysis of Al. The advantages and limitations of the most used methods and the state of the art are pointed. The principal problem connected with Al speciation in environmental samples is absence of suitable certified reference materials for validation of used methods and procedures.

Key words: aluminium species, chemical and physical speciation, fractionation, hybrid techniques

Introduction

Aluminium toxicity is recognized as a serious global problem. Numerous research papers are published every year on the environmental effects of this element. Al is the third most abundant metal in the earth´ s crust, which comprises approximately 8% Al by weight. Because of its low solubility in solution under neutral conditions, Al was regarded as a non-toxic element. During the last two decades, however, it has been found that acid deposition leads to considerable increases of dissolved Al concentrations in acidified soil and surface waters. Elevated concentrations of Al can result in forest decline, reduction of agricultural productivity, and the death of aquatic organisms and fishes. Uptake of Al by man via different routes (food, tap water, water in Al utensils and dialysate) might cause serious neurotic diseases, e.g. Alzheimer´s disease, Parkinson´s disease, dialysis encephalopathy, osteomalacia, and anaemia. All of these make the determination of Al important.

Determination of total dissolved Al has a little environmental and biological relevance because the different Al species differ greatly in toxicity. It has been indicated by laboratory bioassay that monomeric inorganic Al^{3+}, $AlOH^{2+}$, $Al(OH)^{2+}$ and probably $AlSO_4^+$ are the most toxic forms, whereas Al-F and Al-Org can reduce or diminish toxicity. It is well known that free Al^{3+} occurs mainly below pH 4, labile complexed Al, e.g. $AlOH^{2+}$, $Al(OH)_2^+$, AlF^{2+}, AlF_2^+, and $AlSO_4^+$ are dominant in the narow pH range between 4 and 5, the amount of $Al(OH)_4^-$ increases rapidly from pH 5 to 8 (Sposito, 1996). The purpose of this paper is to review advances in analytical methodologies for Al speciation in environmental samples.

Analytical methods for the determination of aluminium species

The existing methods can be classified e.g. according to the principles used:

1. Methods based on size exclusion

Filtration, ultrafiltration and dialysis can be used to physically separate soluble aluminium from fine colloidal polymeric aluminium and aluminium bound to the macromolecular structures of humic and fulvic acids. Dialysis membranes commonly have pore diameters of 1 to 55 nm, ultrafiltration membranes have pore diameters ranging from1 to 15 nm, filtration from 0.1 to 0.45 µm. Speciation using dialysis and ultrafiltration must be done very carefully to avoid the potential problems which are connected with possible contamination from material of membranes, potential problem of changes in pH value during dialysis or reduction the quantity of dialyzed Al from solution of high organic matter content.

2. Application of single and sequential extraction

The utilization a number of single extractants (e.g. KCl, $CaCl_2$, EDTA, $K_4P_2P_7$, $CuCl_2$, $LaCl_3$) for determination of different forms of Al e.g. in agriculture, soil science etc., is known many years (Beckett, 1989).

Sequential extraction procedures are widely applied to soils and aquatic sediments to characterize their chemical phase associations but a little is known their application for Al. Determination of Al and other elements in certified reference materials using the optimized BCR sequential extraction procedure is publicated in Sutherland et al., 2002 and Kubova et al., 2003.

3. Methods based on kinetic or binding strength discrimination

One of the most frequently used strategies for Al fractionation is based on the different reaction kinetics of Al species with selective complexing agents, such as 8-hydroxyquinoline, pyrocatechol violet, aluminon, ferron, etc. (Clarke et al., 1996). By using short reaction times we can discriminate between „free“ and complexed

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aluminium. The chelants react more rapidly with toxic Al species as Al^{3+}, and $Al(OH)^{2+}$ than with other species as labile Al complexed by weak inorganic and/ or organic ligands and non-labile Al complexed by strong organic ligands. Reactive Al species in acidic soils from localities Nálepkovo and Banská Štiavnica (Slovakia) by kinetic discrimination were determined using „oxin" reaction with subsequent MIBK extraction (Dlapa et al., 2002).

Separation of different Al species can be realized by re-equilibration in the presence of chelants where the reaction time or contact time between chelants and Al is not deliberately controlled. This method is denoted the thermodynamic method. It is widely applied to the differentiation of Al species because many chelants are available and the equilibrium constants of the reaction between chelants and Al^{3+} are readily obtained by potentiometric titration (Clarke et al., 1996). The disadvantages of these methods are that the all these chelants can complex with many cations e.g. the coexistence of those cations (especially Fe^{3+}) with Al can also lead to an overestimation of toxic Al.

During the last decade increasing attention has been devoted to kinetic and thermodynamic differentiation of Al species by flow-injection analysis, which has distinct advantages, e. g. high reproducibility and accurate reaction-time control, can be coupled with many used detectors. Its very great importance is a reduced human participation in time –consuming operation such as sample conditioning, reagent manipulation and calibration of measuring system (Pyrzynska et al., 2000)

4. Methods based on ion-exchange

Reactive Al species can be separated from less reactive species by using cation-exchange or chelating resins. This can be accomplished either by short-term batch reaction with a resin or by using column techniques. The batch technique determines reactive monomeric Al by difference in solution aluminium before and after reaction with the resin. This technique was applied for chemical partitioning of Al in soils contaminated by mining activity – Šobov, Slovakia (Matúš et al., 2003). The column techniques can be separated into two types. The earliest and most commonly used method was developed by Driscoll in 1984. With this method a small column of commercialy available, strong acid cation-exchange resin is used to remove reactive monomeric aluminium which is subsequent determined as a difference between Al concentrations in the influent sample and in the effluent solution.

5. Ion chromatographic separations

Ion chromatography with low capacity columns can be used directly to determine Al^{3+} plus hydroxy and sulphato monomers. Ion chromatography coupled with post column reaction with either tiron, pyrocatechol violet or 8-hydroxyquinoline-5-sulphonate, and fluorescence detection for very low Al concentrations and UV detection to higher ones is used (Willet, 1989). The ion-pair chromatography with a stationary phase of unpolar polystyrene-divinylbenzene resin and a mobile phase of lipophilic ions can be used to determination of Al complexes with fluoride and several organic ligands (Michalas et al., 1992).

Among the advantages of ion chromatography it is worth mentioning the very small sample volumes used, the speed of analysis and the possibility of making a direct measurements of individual monomeric forms of Al. It also be possible to determine some fluoride complexes separately, which is difficult with most other methods.

6. Methods based on ion mobility in an electric field

The differential mobility of ions in an electric field as a basis for separation has been used for many decades, primarily for the separation of macromolecules. The first to use it for fractionation of Al were Schmidt et al., 1989. They used isotachophoresis for separation and specific measurement of $[Al(H_2O)_6]^{3+}$ with conductometric detection. The capillary zone electrophoresis was used for separations of AlF^{2+} and AlF_2^+ from „free" Al from its oxalate complex (Wu et al., 1993)

Compared with other methods, electrochemical approaches are more sensitive, easy to perform, less time-consuming and require cheaper instrumentation but it can be realized by regulating the pH of the solutions investigated and using highly selective organic chelants targeting each Al fraction. The utilization of these properties for choice of optimum experimental conditions means that different laboratories in which different chelants have been used in adsorption complexing voltammetry for Al speciation in a variety of real samples give the reliable results (Bi et al., 2001)

7. ^{27}Al nuclear magnetic resonance (^{27}Al NMR)

Aluminium –27 is a nucleus with high intrinsic NMR sensitivity. Its natural abundance is 100% and it has a small quadrupole moment and a high resonance frequency. As a rapid, direct, and non-destructive analytical tool, Al NMR has been widely used to investigate the hydrolysis of Al in the presence and absence of organic and inorganic ligands, to study the structure and reactivity of Al^{3+} complexes with environmentally important ligands, and for quantitative determination of different Al^{3+} species present in environmental samples (Kot et al., 2000; Miyazaki et al., 1999).

The main disadvantage of ^{27}Al NMR in practical analysis is its limited sensitivity. Most studies have been conducted on total Al concentrations in the mmol L^{-1} range. These concentrations are far beyond the concentration range found in natural soils and aqueous systems (total $Al^{3+} \leq 10 \mu mol\ L^{-1}$).

8. Hybrid techniques

Coupled techniques have played an important role in Al speciaton analysis during the last five years (Kot et al., 2000). The combination of techniques of chromatographic separation, e. g. high-performance liquid chromatography (HPLC), or fast protein liquid chromatography (FPLC) coupled with a specific element detection technique such as ET AAS, ICP MS, ICP AES forms an extremely powerful analytical system for the direct speciation of Al. These techniques have several distinct advantages: very low detection limits for Al, rapid separation procedures, closed instrumental system effectively minimizes trace contamination and losses of analyte .

9. Computer simulation

Computer simulation models based on chemical equilibrium calculations are very useful tools for investigation of metal speciation in the environment. Development and application of a variety of computer models for predicting Al speciation in practice under different conditions have been reported, for example general implications of Al speciation-dependent kinetic dissolution rate law in water-rock modeling, speciation and solubility relationships of Al in solutions associated with sulphuric acid leached mine waste rock, etc. These have been essential in increasing our understanding of the interactions between hydrological and geochemical processes. Many models have been developed on the speciation of Al, for example MINEQL, GEOCHEM, WHAM, ALCHEMI, ALSCM (Bi et al., 2001)

Conclusion

The state of the art and the applicability of the different methodologies for quantitative determination of Al species are limited by three problems:

1. unsatisfactory detection limits for practical use in environmental samples,
2. operational definition of Al fractions causes problematic application to real samples and difficult comparisons among different laboratories,
3. absence of suitable certified reference materials which do not permit the procedures to be validated.

Hyphenated techniques (coupling of HPLC/ FPLC with ICP MS/ ETAAS/ ICP AES, etc.) are currently the primary tool for species-selective analysis of Al. Simplification, reduction in cost, and increasing the robustness of the techniques are , however, still necessary.

The advantages of ^{27}Al NMR are its speed, its response to different kinds of coexisting species, no alteration of the sample, and provision of both quantitative and structural information. The application of this method to natural samples is still scarce, because of its limited sensitivity.

On the basis of the thermodynamic and kinetic characteristics of complexing chelants reacting with Al, the toxic forms of Al and total monomeric Al can be satisfactorily determined by FIA and electrochemical analysis. The distinct advantage of these methods are higher sensitivity, high speed, no separation step, and cheaper instrumentation.

Al speciation by computer models plays an important role in evaluating Al species in environment and assessing its ecological risk.

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