

CHEMICAL SPECIATION IN THE ENVIRONMENT

Edited by
A. M. Ure and
C. M. Davidson



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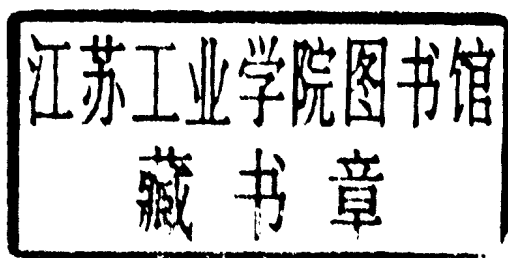
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A.M. URE and C.M. DAVIDSON

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Chemical Speciation in the Environment

Preface

Considerable recent research has focused on the topic of chemical speciation in the environment. It is increasingly realised that the distribution, mobility and biological availability of chemical elements depend not simply on their concentrations but, critically, on the forms in which they occur in natural systems. Continuing developments in analytical chemistry, in particular in hybrid techniques and in the rationalisation and harmonisation of sample extraction procedures, often have made speciation practicable even where analytes are present at trace levels (as is often the case with natural samples).

In this book, we have sought to bring together the expertise of scientists involved in chemical speciation in various fields, with the aim of providing an overview of the current status of speciation science and indications of how the field may develop in the future. The book is broadly divided into two parts, the first dealing with methodology, including the use of mathematical modelling, and the second outlining speciation in various components of the environment. There is also a chapter which deals specifically with the speciation of environmentally important radionuclides.

The book should be of use to scientists from a variety of disciplines with an interest in the environment, but is of particularly relevance to chemists, bioscientists, physicists, water and soil scientists and mathematical modellers involved in the study of environmental pollution.

It would be inappropriate to conclude this preface without expressing our sincere gratitude to all contributing authors who have eased considerably our task of editing the manuscript by submitting work of high quality. Thank you all for your efforts.

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1 Introduction to speciation

A.M. URE and C.M. DAVIDSON

1.1 The need for speciation

Considerable recent research effort in the fields of biological and environmental science has focused on the subject of chemical speciation. It is increasingly realised that the distribution, mobility and biological availability of chemical elements depends not simply on their concentrations but, critically, on the chemical and physical associations which they undergo in natural systems. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Some of the more important controlling factors include pH, redox potential and availability of 'reactive species' such as complexing ligands (both organic and inorganic), particle surfaces for adsorption, and colloidal matter.

Thus, for example, a decrease in the pH of rainwater resulting from the burning of sulfur-rich fossil fuels can increase the leachability of aluminium from aluminosilicate minerals in soils, resulting in detrimental effects including, in extreme cases, fish-kills in receiving waters. Uranium is conservative (and hence mobile) as uranyl-carbonate complexes in oxygenated waters, but may be converted to more particle-reactive uranium (IV) species under anoxic conditions. Arsenic is extremely toxic in its inorganic forms but relatively innocuous as arsenobetaine (a common form in fish), whilst organo-tin compounds, of which perhaps the best known is the antifouling agent tributyltin, are generally more toxic than inorganic tin species.

In order to comprehend the environmental chemistry of an element it would be necessary to characterise in full the proportions and chemistries of all its various forms under the diverse range of conditions possible in natural systems. Whilst this is clearly impracticable, speciation science seeks to characterise, at least some of, the most important forms of an element, in order to understand the transformations between forms which can occur, and to infer from such information the likely environmental consequences. As such, it is a discipline which is of relevance to scientists with many different backgrounds: chemists, biologists, soil and sediment scientists, physicists and specialists in various aspects of nutrition and medicine; all require this type of information.

Although interest in the topic of speciation has increased recently, perhaps as a result of the increased availability of sophisticated analytical equipment with both the sensitivity and selectivity to make speciation studies practicable, it is not a new research area. To give but one example, for many years soil scientists have carried out a type of speciation in which specific reagents are used to extract from soil that portion of an element known, from empirical observations, to correlate with plant availability. A host of methodological approaches to speciation is now available and the literature on the subject is expanding rapidly.

1.2 Aims and structure of the book

This book aims to give a comprehensive review of the current science of speciation, covering relevant methodological, analytical and modelling aspects as well as giving an overview of recent work on speciation within various spheres. It is divided into two parts, the first dealing with the more methodological aspects and the second with specific compartments of the environment and with the speciation of radionuclides.

In part I, general strategies for speciation are reviewed and more detailed descriptions are given both of direct, non-destructive analytical methods such as infrared and nuclear magnetic resonance spectrometries and of indirect methods which, although subject to many potential errors and interferences, have the advantage of being applicable at the trace levels generally encountered in natural systems. Chapter 5 is devoted to speciation modelling since it is an implicit assumption that increased knowledge of chemical speciation will lead to increased activity and accuracy in the computer-based modelling of environmental systems. Modelling also has a role in predicting the kinds and amounts of the different species present in a material or system in circumstances where the species concentrations are too low for observation or measurement.

The second half of the book deals with specific compartments of the environment, i.e. the atmosphere, soils, sediments and natural waters, and with particular aspects of the speciation of environmentally important radionuclides. In each chapter, the current 'state of the art' of speciation in that area is discussed, important examples and specific methodological aspects are presented, and indications are given of areas where further work is most urgently required. An overview of trends and recent developments in speciation science is given in a concluding chapter.

1.3 Definition of speciation

There is no generally accepted definition of 'speciation', and various meanings have been attributed to the term by various workers. For the

purposes of this book, the broad definition put forward (Ure, 1990) and evolved under the auspices of the Commission of the European Communities, Community Bureau of Reference, BCR (Ure *et al.*, 1993a, b) is used.

In this context, speciation may be defined as either (a) the process of identifying and quantifying the different, defined species, forms or phases present in a material; or (b) the description of the amounts and kinds of these species, forms or phases present. Whichever approach is taken, the species, forms or phases are defined (i) functionally, (ii) operationally, or (iii) as specific chemical compounds or oxidation states.

Functionally defined speciation is exemplified by the 'plant available' species, mentioned in section 1.1. Other examples of this type of speciation include the use of terms such as 'biologically active' or 'mobile' forms.

In operationally defined speciation, the physical or chemical fractionation process applied to the sample defines the fraction obtained. For example, sequential extraction procedures are commonly used to isolate, separately, metals associated with the 'water/acid soluble', 'exchangeable', 'reducible', 'oxidisable', and 'residual' (amongst others) fractions of a sediment. The reducible, oxidisable and residual fractions are often equated with iron/manganese oxides, organic matter/sulfides and silicates, respectively. However, it must be emphasised that this association is nominal and may be misleading in some cases. Physical procedures such as the division of a solid sample into particle size fractions or the isolation of soil solution or sediment porewater by filtration, centrifugation or dialysis are also examples of operational speciation. Indeed, even the distinction between soluble and insoluble species in aquatic systems may be considered a crude form of operational speciation since it is based on the ability of a substance to pass through a 0.45 μm filter rather than on whether or not the species is actually in solution.

The third form of speciation, that in which the precise chemical form of an element is measured or defined, is the hardest to achieve since analytical methodology of great selectivity and, generally, sensitivity is required. Some success has been achieved in the analysis of waters where, by judicious choice of absorbent and/or reagents, specific oxidation states of elements (for example, chromium (III) and chromium (VI) (Isshiki *et al.*, 1989), or antimony (III) and antimony (IV) (Mohammad *et al.*, 1990)) may be distinguished and quantified, but for solid samples this narrowly defined type of speciation is seldom possible since specific extraction procedures tend to change the speciation and direct, non-destructive methods (see chapter 3; are, in general, only sensitive enough for major element constituents. Direct methods may be able to identify the speciation but are generally unable to quantify it without resort to associated separation procedures.

With all studies of speciation, extreme care must be taken not to disturb the system during sampling, pretreatment (where necessary) and

measurement. As is pointed out later in the book, it is just those environmental systems that are intrinsically unstable, i.e. liable to change speciation when subjected to stress, where speciation studies are most important and where changes during sampling and processing are most likely. It seems highly probable that variability between sampling regimes and subsequent sample handling protocols has contributed to some of the seemingly contradictory results reported in the literature.

1.4 Quality control

The need for quality control in speciation studies is important not only for the 'absolute' reasons of scientific precision and accuracy but also to assist in achieving analytical methodologies that are robust enough to be used in different laboratories with comparable results. Universally applicable, validated methodologies make it possible for results from different scientists and different laboratories to be compared and provide the basis for the establishment of international databases on the occurrence and distribution of element species in the environment. Within Europe such reliable analyses also provide the legal bases for monitoring and policing the environmental directives of the Commission of the European Communities.

Quality control in speciation science is difficult because few suitable reference materials exist for validation of new or existing analytical methodology. The preparation of reference materials certified for the contents of element species is, however, a difficult task. This is because, firstly, the fractionation of the total content of an element in a material into its different species means that the species concentrations are low, with all the consequential requirements for higher analytical sensitivity and greater care in avoiding contamination. Secondly, the species concentrations in the reference material must be preserved in such a way that they remain constant over the several year's life of a reference material.

Considerable efforts have been made by the BCR, now designated The Measurement and Testing Programme (BCR), of the Commission of the European Communities, to improve the quality of analysis in this field. These have taken the form of interlaboratory studies in several fields of speciation by chemical analysis. These interlaboratory studies aimed to (i) minimise errors in sampling, sample treatment and analysis, (ii) identify the most appropriate analytical procedures, and (iii) harmonise the total analytical procedure into an agreed analytical procedural protocol that could be used for the preparation of reference materials certified for species contents. The process of evolving, over a period of more than 3 years, such reference materials for the validation of the speciation of heavy metals in soils, by selective extraction, and in sediments by sequential extraction is discussed in Ure *et al.* (1993a, b). In these studies, under the auspices of

BCR, some 30 expert European laboratories took part and developed the selective extraction protocols and the simplified three-stage selective extraction procedure used. The final stage of this work, the certification of two contaminated soils is now in process and the two certified soil reference materials (CRM) should be available commercially in mid-1994 from BCR. This should be followed shortly thereafter by a sediment reference material certified for heavy metal species by the above sequential extraction procedure.

The small number of commercially available CRM, certified for species, include the polluted harbour sediment PACS-1, produced by the Natural Research Council of Canada, with certified contents of mono-, di- and tributyl tin and CRM 462, a coastal sediment, certified for di- and tributyl tin, prepared by BCR. A few reference materials for species defined operationally are available, from BCR for example, and include CRM B1-28 certified for the contents of As, Co, Cu, Fe, Mn, Na, Pb and Zn in the $<10\ \mu\text{m}$ fraction of a fly ash, CRM BO-38, and a series of reference soils, B1-41, B1-42, B1-43 and sewage sludges, B1-44, B1-45, B1-46 which have well established, but not certified, *aqua regia* extractable heavy metal contents. The need for reference materials certified for species contents is now well recognised and a number are in preparation by a number of different bodies.

Finally, the authors of this chapter, in their editorial role, would like to acknowledge the dedication and cooperation of our company of distinguished authors who have made this book possible.

References

- Isshiki, K., Sohrin, Y., Karatani, H. and Nakayama, K. (1989) Preconcentration of chromium (III) and chromium (VI) in sea water by complexation with quinolin-8-ol and adsorption on macroporous resin. *Anal. Chim. Acta*, **224**, 55–64.
- Mohammad, B., Ure, A.M., Reglinski, J. and Littlejohn, D. (1990) Speciation of antimony in natural waters: the determination of Sb(III) and Sb(V) by continuous flow hydride generation – atomic absorption spectrometry. *Chem. Spec. Bioavail.*, **3**, 117–122.
- Ure, A.M. (1990) Methods of analysis for heavy metals in soils. In *Heavy Metals in Soils* (ed. Alloway, B.J.). Blackie, Glasgow, pp. 40–80.
- Ure, A.M., Quevauviller, Ph., Muntau, H. and Griepink, B. (1993a) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonisation of extraction techniques under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.*, **51**, 135–151.
- Ure, A.M., Quevauviller, Ph., Muntau, H. and Griepink, B. (1993b) *Improvements in the Determination of Extractable Contents of Trace Metals in Soil and Sediment Prior to Certification* (EUR Report 14763 EN). Commission of the European Communities, Luxembourg.