Chemical Speciation in the Environment

Second Edition

Edited by
A.M. URE and C.M. DAVIDSON
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow

Blackwell
Science

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Contents

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 have made speciation practicable even where analytes are present at trace levels (as is often the case in 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.

Interest in speciation has grown greatly since the publication of the first edition and, with this expansion, there has developed a range of new techniques for identifying and quantifying species in a variety of materials. The result is a growing number of publications dealing with the methods for speciation in the natural environment. It was felt that it was appropriate to prepare a second edition of *Chemical Speciation in the Environment* to provide an update of the information given in the first edition, together with some additional chapters to make the treatment of speciation more comprehensive.

As before, the book is broadly divided into two parts, the first dealing with methodology, including the use of quality control, and the second outlining speciation in various compartments of the environment. The final chapter summarises recent developments and trends.

This second edition will be even more relevant to the work of scientists with an interest in the environment, including chemists, biochemists, physicists, geochemists, and water and soil scientists. It should also serve as a source book for statutory authorities and legislators charged with monitoring, protecting or remediating polluted compartments of the environment.

We once again thank authors, old and new, for the quality of their work that has made this second edition possible.

1 Introduction

A.M. URE and C.M. DAVIDSON

1.1 The need for speciation

The continued rapid growth in interest in speciation, since the first edition of this book was published, is evidenced by the holding of the '1st International Conference on Trace Element Speciation in Biomedical, Nutritional and Environmental Sciences' in Neuherberg, Germany, in 1998 (Michalke and Schramel, 1999a) and, for example, by the formation, in 1997, of an 'EU-network on trace element speciation: preparing for the 21st century' (Cornelis *et al.*, 1999) under the auspices of the Standards Measurement and Testing Programme.

It is now generally accepted that the distribution, mobility, biological availability and toxicity of chemical elements depend not simply on their concentrations but, critically, on their forms. These determine the physical and chemical associations that 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 the 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 can be immobilised by conversion to more particle-reactive uranium (IV) species in anoxic waters. Arsenic is extremely toxic in its inorganic forms but relatively innocuous as arsenobetaine (a common form in fish), whilst organotin compounds, of which the best known is the antifouling agent tributyltin, are generally more toxic than inorganic tin species.

To comprehend fully the environmental chemistry of an element it would be necessary to characterise in detail 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 that are likely to occur, and to infer from such information the probable environmental consequences. Speciation science is, therefore, a discipline which is of relevance to scientists with many different backgrounds: chemists, geochemists, biologists, soil and sediment scientists, physicists and specialists in various aspects of nutrition and medicine. In addition, legislators in the field of environmental protection should be aware of the importance of basing legislation on a knowledge of the speciation of an element and not simply on an assessment of an element's concentration in some compartment of the environment.

Although the topic of speciation is now a major focus of research and application it is not a new one. To give but one example, soil scientists have, for many decades, carried out a type of speciation in which specific selective reagents have been used to extract from soil that portion of an element known from field experiments to correlate with plant availability. A host of methodological approaches to speciation is now available and this edition attempts to provide an up-to-date documentation of the state-of-the-art as we enter the new millennium.

1.2 Aims and structure of the book

This second edition retains the structure of the first edition. It aims to provide 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 in 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, with the speciation of radionuclides, and presents a review of current trends and developments.

In general the book has been substantially updated and many chapters have been extensively rewritten to take account of developments in this rapidly changing field.

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 spectrometry 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 an important role in predicting the kinds and amounts of different species present in a material or system in circumstances where the species concentrations are too low for observation or measurement.

An important and entirely new chapter, Chapter 6, *Quality Control in Speciation Studies for Environmental Monitoring* by the international authority on the topic, Ph. Quevauviller of the Standards Measurement and Testing Programme of the European Commission, has been added.

Part II considers speciation in specific compartments of the environment viz. the atmosphere, biological systems, soils, sediments and natural waters, and with particular aspects of the speciation of environmentally important radionuclides. Two new chapters have been added to make the coverage even more comprehensive. These new chapters are Chapter 10, *Chemical Speciation in Soils and Related Materials by Selective Chemical Extraction* by the editors, and Chapter 12, *Speciation in Seawater* by R.H. Byrne of the University of South Florida.

In each chapter of Part II, the current state-of-the-art of speciation in the subject area is discussed, important examples and particular methodological aspects are presented, and the needs for further development or research are indicated. A final chapter gives an overview of trends and recent developments in speciation science.

Some changes in chapter authorship have occurred since the first edition for a variety of reasons. Chapter 2, *General Strategies for Speciation* has been left unchanged following the much regretted death of Bill Pickering. The editors acknowledge their debt to him not only for his contribution in Chapter 2, which is still valid today, but also for his share in the discussions that consolidated the original concept of the book. The final chapter, *Trends and Developments* has been revised and written by one of the original authors, R.R. Barefoot. We wish the former co-author, J.C. van Loon, a full recovery from his recent illness. Chapter 9 of the first edition on *Speciation of Trace Metals in Sediments and Combustion Waste* by M. Kersten and U. Förstner has been entirely rewritten by M. Kersten as *Speciation of Trace Metals in Sediments* as Chapter 11 of this book. We take this opportunity to express our thanks for the inspirational contribution by Professor Förstner in the first edition. The updating of Chapter 14, *Speciation of Metals and Metalloids in Biological Systems*, originally written by B. Goodman, has been carried out by P.H.E. Gardiner of Sheffield Hallam University. K.S. Leonard (CEFAS, Lowestoft, UK) joins B.R. Harvey as co-author of Chapter 13 *Speciation of Radionuclides*.

It is hoped that these changes in content and authorship will have resulted in an up-to-date and comprehensive treatment of the topic of speciation.

1.3 Definition of speciation

In the first edition it was stated that 'there is no generally accepted definition of "speciation"' and this is still true. The definition used in this second edition is still that used in the first edition and is based on the broad definition given by Ure (Ure, 1990; Ure *et al.*, 1993a) and outlined below. IUPAC has now published a document on chemical speciation terminology, IUPAC, 2000, *Guidelines for terms related to chemical speciation and fractionation of trace elements. Definitions, structural aspects and methodological approaches*, which recommends the term 'chemical species' as the form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. This narrow definition is perfectly appropriate to speciation in solution samples but would exclude most studies on solid materials such as soils, sediments and geochemical and biological materials from the field of speciation and relegate the selective extraction and fractionation procedures relevant to such solid materials to the category of fractionation methodology. Most current usage would include such solid sample techniques in a broader definition of speciation which would encompass the above IUPAC type of narrow definition of species, perhaps best described as 'classical speciation', as well as speciation in which species are defined functionally or operational as illustrated below. The '1st International Conference on Trace Element Speciation in Biomedical, Nutritional and Environmental Sciences' (Michalke and Schramel, 1999b) also concluded that a narrow definition of speciation, on the lines of the IUPAC proposal, was still not attainable for solid samples and found merit in the use of functionally and operationally defined species.

In this context the term speciation may be defined as either

(1) the process of identifying and quantifying the different, defined species forms or phases present in a material or
(2) the description of the amounts and kinds of these species, forms or phases present.

In both cases the species, forms or phases are defined (a) functionally, (b) operationally, or (c) as specific chemical compounds or oxidation states. This usage is employed in this book but IUPAC has proposed a useful clarification in that definition (1) above is abandoned in favour of speciation analysis and the term speciation is reserved for the concept of a description of the distribution of species.

The terminology used here includes, therefore, three types of speciation based on species defined functionally, operationally or as specific chemical compounds or oxidation states.

Functionally defined species are exemplified by the plant-available species mentioned in Section 1.1 in which the 'function' is plant availability.

In operationally defined speciation the physical or chemical fractionation procedure applied to the sample defines the fraction isolated for measurement. For example, selective sequential extraction procedures are used to isolate metals associated with the 'water/acid soluble', 'exchangeable', 'reducible', 'oxidisable' and 'residual' fractions in a sediment. The reducible, oxidisable and residual fractions, for example, are often equated with the metals associated, bound or adsorbed in the iron/manganese oxyhydroxide, organic matter/sulfide and silicate phases, respectively. While this is often a convenient concept it must be emphasised that these associations are nominal and can be misleading. It is, therefore, sounder to regard the isolated fractions as defined by the operational procedure. Physical procedures such as the division of a solid sample into particle-size fractions or the isolation of a soil solution by filtration, centrifugation or dialysis are also examples of operational speciation. Indeed even the distinction between soluble and insoluble species in aquatic systems can be considered as operational speciation as it is based on the somewhat arbitrary definition of 'soluble' as the ability to pass a $0.45\,\mu$m filter.

The third form of speciation in which the precise chemical form of an element is measured or defined is the most difficult to achieve since analytical methodology of great selectivity, and usually, sensitivity is required. Some success has been achieved in this narrowly defined type of speciation of elements in waters by chromatographic and electrochemical methods and by the judicious choice of absorbent or reagent the oxidation states of elements such as chromium (Isshiki *et al.*, 1989) or antimony (Mohammad *et al.*, 1990) can be separated. For solid samples, including soils sediments and biological materials, this type of speciation is seldom possible and resort must be made to functionally or operationally defined speciation. Direct, usually non-destructive, methods may be able to identify the species but are generally unable to quantify it without resort to associated separation techniques (Ure *et al.*, 1993b).

Acknowledgement

Finally the authors of this introduction, in their editorial role, would like to acknowledge the patience, dedication and co-operation of the company of distinguished authors who have made this book possible.

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PART I
TECHNIQUES FOR SPECIATION

2 General strategies for speciation

W.F. PICKERING

2.1 Speciation – the analytical challenge

2.1.1 Introduction

Interest in chemical speciation procedures is predicted to expand rapidly as a wider spectrum of the scientific community recognises that assessments of health hazards, toxicity and bioavailability must be based on levels of specific chemical forms, rather than on total element levels. Literature listings on this topic, however, are not extensive and most reviews, conference proceedings and books have appeared from the 1980s onwards (a typical few are listed in 'Further reading' at the end of the chapter).

The aim in this contribution is to introduce the reader to some of the alternative experimental strategies that have been used to study two particular categories of inorganic chemical speciation, namely:

(1) the determination of a particular species in a given sample, involving both identification and quantification; and
(2) species distribution or abundance studies which provide a description of the numerical distribution (or abundance) of different species containing the same central element, in a given sample. (For a definition of 'speciation' see Chapter 1.)

The determination of species concentrations tends to be more challenging than determination of total element contents because

(1) there are difficulties associated with isolating the compound(s) of interest from complex matrices;
(2) most of the speciation techniques available disturb (to some extent) the equilibria existing between the various chemical species present in the system under study;
(3) for species present at ultra-trace levels, few analytical procedures possess the degree of sensitivity required; and
(4) suitable standard reference materials are often unavailable. The nature of the challenges varies with matrix type, i.e. different approaches are required for speciation analysis in waters, or biological materials, or soils/sediments.

2.1.2 Disturbance of equilibrium state

The potential for disturbing existing equilibrium conditions during speciation analysis is high, particularly during the sampling stage. This can be demonstrated by considering a polluted waterway containing heavy metals. Interactions between the metal ions and other components of the system result in the formation of many different metal species (e.g. simple hydrated ions, ion pairs, hydroxy polymers, complex ions (involving inorganic or organic ligands), sorbed on colloidal material or fine particulate matter, as well as associated with small marine organisms) and the final distribution pattern of an element in the water phase reflects its affinity for inorganic or organic ligands, modified by adsorption on particulate matter and interaction with biota.

The various chemical forms co-exist in an equilibrium, or quasi-equilibrium state, and all stages of prescribed analytical procedures can be intrusive. Not always recognised, however, are the changes in species which can occur during sampling, preparation steps and the sample storage period. For example, collection of a water sample isolates it from other components of the quasi-equilibrium system, and filtration to remove fine suspended matter causes further disturbance. Ions in the aqueous phase then tend to sorb on the walls of the collection vessel, a process which can be minimised by adding acid. Unfortunately, acidificiation of the aqueous phase also causes dissociation of complex species (and displacement of the fraction sorbed on colloidal matter).

If sediment was collected from a particular waterway, the distribution of the element of interest between different components of the sediment was found to vary with the degree of exposure to air and the temperature of any drying stages (Rapin *et al*., 1986; Kersten and Foerstner, 1986). The minor elements present in sediments (and soils) are not uniformly distributed. Part can be present as mineral fragments derived from the original parent rock, while other parts can be associated with distinct component phases such as carbonate compounds, hydrous oxides of Fe, Al, Mn and organic matter. Some fractions are loosely sorbed on particle surfaces or are held on ion exchange sites.

The distribution of an element in biological samples collected from an ecosystem can be equally complex. In plants, for example, the distribution of minor elements or particular species is not uniform throughout the whole organism, i.e. leaf material values differ from those derived from ribs, stems, roots and fruit. For speciation, sub-sectioning of the semi-rigid matrix may thus have to precede isolation of the component of interest.

2.1.3 Speciation based on calculation methods

In view of the errors that can be associated with sampling and sample preparation, and the limitations of many of the experimental procedures used in speciation, many investigators prefer to calculate the most likely species distribution pattern. This approach involves solution of multiple simultaneous equations, some describing the competing chemical equilibria and others defining mass balance relationships. Data inputs required include the total levels of cations, anions and ligand species present, and equilibrium constant values for all possible interactions between the various species. At times it is necessary to make assumptions about the number and type of 'species' present and 'best values' for the various equilibrium constants have to be selected from the range reported in the literature. These preliminary decisions can result in apparent major discrepancies in the values reported for individual species present in a common matrix (e.g. seawater). Further variations occur if one attempts to allow for the fractions associated with organic matter, colloids or particulate matter, because relevant equilibrium constant data are usually not readily available. Calculation procedures are considered in some detail in Chapter 5.