Handbook of Elemental Speciation II – Species in the Environment, Food, Medicine and Occupational Health

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Preface

Speciation has evolved over the past two (or is it three?) decades into an important sub-discipline of analytical chemistry having considerable impact on environmental monitoring and the life sciences. In its embryonic phase, elemental speciation was an academic curiosity, "a rebel without a cause", straddling the boundary between the two large and well-developed areas of inorganic and organic analytical chemistry. Gradually, it became apparent that elemental speciation bridged the gap between both fields as it borrowed and combined the major methodologies and techniques, notably chromatography in its various modes and sensitive spectroscopic detection methods that coalesced into hyphenated techniques. It is now clear that the incremental development of speciation analysis was not born as a trivial academic pursuit but as the solution to major problems in environmental chemical measurement. I mention just a few examples: challenges due to massive worldwide emission of organolead compounds in the atmosphere through the extensive use of tetra-alkyl lead compounds in automobile fuel; several mercury pollution incidents connected with the indiscriminate use and disposal of methylmercury compounds, without recognising its extreme toxicity; severe disruptions of the marine environment with effects on aquaculture, connected with the use of organotin compounds, for example, as anti-fouling agents in the marine environment and agricultural applications.

Currently, elemental speciation is well respected and has established itself as a real bridge, the paranymph between organic and inorganic analytical chemistry, utilising the best of both fields for its development, specific methodology and fundamental paradigms.

Despite many potential application areas, speciation analysis, at least until recently, seemed rather slow in finding practical exploitation. This is not surprising. There is a definite induction period needed for any new development before it finds its place in technology and society. We cannot force the pace. Despite scientific achievements, ultimately the applications need to be triggered by societal needs, pushed from practice rather than pulled from science.

A handbook such as this one is a welcome compendium of information that would otherwise be scattered throughout the scientific literature. It can serve as a reference book for those interested in the subject in academe, government and industry and those involved with important questions related to the differences in behaviour between atoms and molecules.

The first volume of the Handbook of Elemental Speciation with the subtitle "Techniques and Methodology" appeared in mid-2003. It deals with the experimental basis and contains chapters on the collection and storage of samples and their problems, on the various methods used in sample preparation and sample preseparation for analysis, the full range of different separation and detection techniques that together provide the necessary sensitivity and selectivity for trace and ultra-trace analysis with a number of hyphenated techniques from solution, the important topic of calibration and quality assurance/quality control. The work also provides a detailed description of the actual status of direct speciation methods in solid samples on the basis of, on one side, different beam methods of analysis based on electrons and X-rays and, on the other side, with solid or solution applications using new possibilities offered by synchrotron X-ray methods through the exploitation of the fine structure of the X-ray absorption edge. The first volume is concluded with an overview of rapid screening methods and risk assessment/regulatory issues concerned with speciation. It provides the necessary background material and a thorough description of the practice of elemental speciation.

If the first volume deals with the analytical chemistry of *elemental speciation*, according to the IUPAC definition, and, as such, is a basic scientific discipline, this accompanying second volume deals largely with *speciation* and *chemical species* as defined by the IUPAC. The material belongs to applied science and, as far as its routine application of scientific concepts is concerned, can even be considered as technology.

What follows in this volume of the Handbook of Elemental Speciation, as a welcome and practical complement to Volume I, is a thorough survey of chemical speciation of the different elements, treated systematically, more or less from alpha to omega, within sequence: the compounds of aluminium, antimony, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, platinum (and the other noble metals), selenium, silicon, sulphur, thallium, tin vanadium and finally, zinc. This systematic survey of the different relevant elements for speciation is followed by a review of groups of elemental species, the actinide elements, halogens as present in the atmosphere, the volatile metals and, finally, a chapter on proteins and one on the metals' behaviour in humic/fulvic acids and their implications for elemental bio-availability in the soil/water environment. For all these topics, the analytical chemistry aspects are completed with data on the physical and chemical properties, environmental, toxicological, health and legislative aspects of the species of interest, in short everything important for the issues in hand. The text concludes with chapters on various modelling aspects connected with speciation issues.

It is obvious that for a complex topic such as this one, the preferable way to deal with the rather disparate contents is through assembling the experience of a number of different expert authors, as no single person would master in sufficient detail all the topics to be developed. As in the previously published volume, the editors selected experts carefully, to provide overall a high-quality work.

Is this volume going to be the end of the series and the collaboration among the four editors? I sincerely hope not! The present and previous volume, as comprehensive as they are, still leave numerous gaps in the field. The two volumes are heavily centred on the environmental and health sciences, evidently the most important areas of application up to now. However, it is clear that as the subdiscipline develops, a myriad of new analytical challenges will arise in other areas. We can only hope that the present two volumes will become the start of further complements in a continuing series of handbooks. Speciation analysis in materials science and especially in the microscopic and nano-size spatial domains, the pursuit of speciation analysis and its exploitation in speciation in solid samples, the growing applications and the challenges of elemental speciation of metal-containing proteins in the bio-sciences (metalloproteomics) and the global issues connected with elemental speciation in bio-geochemistry will be further areas of expansion for this important methodology.

Freddy Adams

Antwerp, Belgium, October 2004

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Rita Cornelis
Helen Crews
Joe Caruso
Klaus Heumann

Technical Abbreviations and Acronyms

Abbreviations

AAS	atomic absorption spectrometry
ACD	allergic contact dermatitis
ACGIH	American Conference of Governmental Industrial Hygienists
ACSL	Advanced Continuous Simulation Language
ACSV	adsorptive cathodic stripping voltammetry
ACW	artificial cement water
ADI	acceptable daily intake
ADME	absorption distribution metabolism and excretion
ADP	adenosine diphosphate
AE	acrodermatitis enteropathica
AED	atomic emission detection
AEM	analytical electron microscopy
AFS	atomic fluorescence spectrometry
ALA	aminolevulinic acid
ALA-D	delta aminolevulinic acid dehydratase activity
ALA-U	delta aminolevulinic acid (urine)
ALS	amyothrophic lateral sclerosis
AMP	adenosine monophosphate
AMS	accelerator mass spectrometry
AOAC	Association of Official Agricultural Chemists
AOS	activated oxygen species
APCI	atmospheric pressure chemical ionisation
APDC	ammonium pyrrolidine dithiocarbamate
API-MS	atmospheric pressure ionization-mass spectrometry
APP	amyloid precursor protein
APXS	alpha proton X-ray spectrometry
AROI	acceptable range of oral intake
ASV	anode stripping voltammetry
ATCUN	amino terminal Cu(II) and Ni(II)-binding
ATN	acute tubular necrosis
ATP	adenosine triphosphate
ATR	attenuated total reflectance
ATR-FTIR	attenuated total reflection Fourier transform infrared
ATSDR	Agency for Toxic Substances and Disease Registry
AUC	area under the curve
AWQC	ambient water quality criteria
BBM	brush border membrane
BCM-ESR	blood circulation monitoring-electron spin resonance
BCR	Community Bureau of Reference (Commission of the European Communities)
BDE	bromodiphenyl ether
BLM	biotic ligand model
BMD	bench mark dose
BRHS	British Regional Heart Study
BSE	back scattered electrons
BW	body weight
CA	cellulose acetate
CAC	Codex Alimentarius Commission
CAPD	continuous ambulatory peritoneal dialysis
CCA	chromium(VI) trioxide – copper oxide – arsenic trioxide
CCD	charge coupled device
CCFAC	Codex Committee for Food Additives and Contaminants
CCP	capacitively coupled plasma
CCS	copper chaperone for superoxide dismutase

CE	capillary electrophoresis
CFC	chlorinated and fluorinated carbon
CGC	capillary gas chromatography
CHD	coronary heart disease
CI	chemical ionisation
CIEF	capillary isoelectric focusing
CIMS	chemical ionization mass spectrometry
CJD	Creutzfeldt-Jacob disease
CMT	cylcopentadienyl manganese tricarbonyl
CNS	central nervous system
CONSAAM	Conversational Simulation Analysis and Modeling
COX	cytochrome oxidase
CP	caeruloplasmin
CPVC	chlorinated PVC
CRM	certified reference material
CSF	cerebrospinal fluid
CSV	cathodic stripping voltammetry
CV	cold vapor
Cys	cysteine
CZE	capillary zone electrophoresis
DAD	diode array detector
D-DDC	diethylammonium diethyl dithiocarbamate
DAO	diamine oxidase
DBT	dibutyltin
DCI	desorption chemical ionisation
DCP	direct-current plasma
DDT	dichlorodiphenyltrichloroethane
DEAE	diethylaminoethyl
DEGS-PS	diethylene glycol succinate
DFG	German Research Community
DFO	desferroxiamine
DGE	The German Society for Nutrition
DI	deiodinases
DIHEN	direct injection high efficiency nebulizer
DIN	direct injection nebulizer
DIT	diiodothyrosine
DL-AAS	diode laser atomic absorption spectrometry
DMA	dimethylarsinic acid
DMDSe	dimethyl diselenide
DMPS	2,3-dimercapto-1-propane sulfonate
DMS	dimethyl sulfide
DMSA	dimercaptosuccinic acid
DMSD	dimethyl silanediol
DMSe	dimethyl selenide
DMSeP	dimethylselenonium propionate
DMSO	dimethyl sulfoxide
DMSP	dimethylsulfoniopropionate
DMT	divalent metal transporter
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DOM	dissolved organic matter
DPASV	differential pulse anodic stripping voltammetry
DPC	diphenyl carbazide
DPCSV	differential pulse cathodic stripping voltammetry
DRC	dynamic reaction cell
DTPA	diethylenetriamine-pentaacetic acid
DTPA-TEA	diethylenetriamine-pentaacetic acid-triethanolamine
DTT	dithiothreitol
DV	Daily Value
ECD	electron capture detector
EDS	energy dispersive spectrometry
EDTA	ethylenedinitrilotetraacetic acid or ethylenediaminetetraacetic acid
EDXA	energy-dispersive X-ray analysis
EELS	electron energy loss spectroscopy
EFSA	European Food Safety Authority
EHMA	ethylhexylmercaptoacetate
EIA	enzyme immunoassay
EI-MS	electron impact mass spectrometry
ELISA	enzyme linked immunosorbent assay
ELNES	energy loss near-edge structure
ELSD	evaporative light-scattering detection
EMPA	electron micro probe analysis
ENDOR	electron nuclear double resonance

EP	erythrocyte porphyrin
EPA	Environmental Protection Agency
EPR	electron paramagnetic resonance
EPXRS	electron-probe X-ray spectrometry
EQA	external quality assurance
ES	electrospray
ESADDI	estimated safe and adequate daily dietary intakes
ESCA	electron spectroscopy for chemical analysis
ESEEM	electron spin echo envelope modulation
ESI MS-MS	electrospray ionisation tandem mass spectrometry
ESI	electrospray ionisation
ESI-MS	electrospray ionization mass spectrometry
ESR	electron spin resonance
ET-AAS	electrothermal atomic absorption spectrometry
EtSH	ethyl mercaptan
EXAFS	extended X-ray absorption fine structure spectroscopy
EZP	exchangeable zinc pool
FA	fulvic acid
FAAS	flame atomic absorption spectrometry
FCAW	flux-cored arc welding
FDA	Food and Drug Administration
FEP	fluoroethylene polymer
FIA	flow-injection analysis
FIA	fluorescence immunoassay
FPD	flame photometric detector
FPLC	fast protein liquid chromatography
FR	flame retardants
FT-IR	Fourier-transform infrared radiation
FVC	forced vital capacity
GABA	gamma-aminobutyric acid
GC	gas chromatography
GC-AAS	gas chromatography-atomic absorption spectrometry
GC-AED	gas chromatography-atomic emission detection
GC-ECD	gas chromatography – electron capture detection
GC-MS	gas chromatography mass spectrometry
GEM	Gibbs energy minimisation
GF	graphite furnace
GFAAS	graphite furnace atomic absorption spectrometry
gHb	glycated hemoglobin
GI	gastrointestinal
GIME	gel-integrated microelectrode array
GLC	gas–liquid chromatography
GMAW	gas metal arc welding
GMP	guanosine monophosphate
GPC	gel permeation chromatography
GPEC	gradient polymer elution chromatography
GPX	glutathione peroxidase
GSGD	gas sampling glow discharge
GSH	glutathione (reduced form)
GT	gammaglutamyl-transpeptidase
GTAW	gas tungsten arc welding
GTF	glucose tolerance factor
HA	humic acids
HbA	hemoglobin A
HbF	fetal hemoglobin
HDEHP	bis(2-ethyl-hexyl)-hydrogen-phosphate
HDL	high density lipoprotein
HEDP	1-hydroxyethane-1,1-diphosphonic acid
HEPA	high efficiency particulate air
HFBA	heptafluorobutanoic acid
HFO	hydrous ferric oxide
HG	hydride generation
HG-AAS	hydride generation-atomic absorption spectrometry
HG-AFS	hydride generation – atomic fluorescence spectrometry
HG-GC	hydride generation gas chromatography

HG-ICP AES	hydride generation – inductively coupled plasma – atomic emission spectrometry
HHPN	hydraulic high pressure nebulizer
HKF	Helgeson-Kirkham-Flowers
HLA	human lymphocyte antigens
HMM	high molecular mass
HPLC	high performance liquid chromatography
HPLC-ICP	high performance liquid chromatography-inductively coupled plasma
HRIDMS	high resolution isotope dilution mass spectrometry
HRSEM	high resolution scanning electron microscopy
HS	humic substances
IAP	ion activity product
IARC	International Agency for Research on Cancer
IBMK	isobutyl methyl ketone
IC	ion chromatography
ICNCM	International Committee on Nickel Carcinogesis in Man
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICT	idiopathic copper toxicosis
IDLH	immediately dangerous to life or health
IDMS	isotope dilution mass spectrometry
IEF	isoelectric focusing
IEUBK	integrated exposure uptake biokinetic
IFCC	International Federation of Clinical Chemistry
IgE	immunoglobulin E
IMO	International Maritime Organisations
INAA	instrumental neutron activation analysis
IOMA	isooctyl mercaptoacetate
IPM	interior points method
IQC	internal quality control
IRMA	immunoradiometric assay
IUPAC	International Union of Pure and Applied Chemistry
JECFA	Joint Expert Committee on Food Additives
K_{sp}	solubility constant
K-XRF	K-shell X-ray fluorescence
LA	laser ablation
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LC	liquid chromatography
LC-MS	liquid chromatography-mass spectrometry
LDH	lactate dehydrogenase
LDL	low density lipoprotein
LDR	linear dynamic range
LFER	linear free-energy relationships
LI TOF	laser-induced time of flight
LIA	luminescence immunoassay
LIBD	laser-induced breakdown detection
LIBS	laser-induced breakdown spectroscopy
LIPAS	laser-induced photo acoustic spectroscopy
LMA	law of mass action
LMM	low molecular mass
LOAEL	lowest-observed-adverse-effect level
LOD	limit of detection
LPAS	laser-induced photoacoustic spectroscopy
LP/RP-ICP-MS	low pressure/reduced pressure-ICP-MS
LT	low temperature
LT-GC	low temperature – gas chromatography
L-XRF	L-shell X-ray fluorescence
MAC	maximum allowable concentration

MALDI	matrix assisted laser desorption ionization
MALDI-MS	matrix assisted laser desorption ionization mass spectrometry
MBT	monobutyltin
MCH	mean corpuscular hemoglobin
MCHC	mean corpuscular hemoglobin concentration
MCLG	maximum contamination level goal
MEKC	micellar electrokinetic chromatography
MEPC	Marine Environment Protection Committee
MeSH	methyl mercaptan
Met	methionine
MIBK	methyl isobutyl ketone
MIC	minimal inhibitory concentrations
MIG	metal inert gas
MIP	microwave-induced plasma
MIP-AED	microwave-induced plasma-atomic emission detector
MIP-AES	microwave-induced plasma atomic emission spectrometry
MIT	monoiodothyrosine
ML	one ligand complexes
ML$_2$	two-ligand complexes
μLC	liquid chromatography of micro-scale
MLs	maximum limits
MMA	manual metal arc
MMA	monomethylarsonic acid
MMM	medium molecular mass
MMT	methylcyclopentadienyl manganese tricarbonyl
MNK	Menkes protein (P-type ATPase)
MnSOD	manganese superoxide dismutase
MRL	maximum residue limit
MS	mass spectrometry
MSA	methanesulfonic acid
MSIA	methanesulfinic acid
MT	metallothionein
NAA	neutron activation analysis
NAC	*N*-acetyl cysteine
NaDDTC	sodium diethyldithiocarbamate
NAG	*N*-acetyl-β-D-glucosaminidase
NASA	National Aeronautic and Space Administration
NCOMP	noncompartmental programs
NCV	nerve conduction velocity
NEM	non-electrostatic model
NEQAS	national external quality assurance system
NHANES	national health and nutrition examination surveys
NIES	National Institute of Environmental Studies
NIOSH	National Institute for Occupational Safety and Health
NIR	near infra-red
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NN	1-nitroso-2-naphthol
NOEL	no-observed-effect level
NOM	natural organic matter
NPDES	national pollution discharge regulations
NTA	nitrilotriacetic acid
NTBI	nontransferrin-bound Fe
OEL	occupational exposure limit
OMCTS	octamethylcyclotetrasiloxane
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OTC	organotin compounds
PAA	proton activation analysis
PAD	pulse amperometric detection
PAGE	polyacrylamide gel electrophoresis
PAR	4-(2-pyridylazo)resorcin
PBDE	polybrominated diphenyl ethers
PBPK	physiologically based pharmacokinetic
PC	polycarbonate
PCA	principal component analysis
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxanes

PEC	predicted environmental concentration
PEL	permissible exposure limit
PES	polyethersulfon
P-FPD	pulsed flame photometric detector
PGC	packed-column gas chromatography
PGE	platinum group element(s)
PIXE	proton induced X-ray emission
PKC	protein kinase C
PNC-PAGE	preparative native continuous polyacrylamide gel electrophoresis
PNEC	predicted no effect concentration
PNS	peripheral nervous systems
PP	polypropylene
PrP	prion protein
PSA	potentiometric stripping analysis
pTDI	predicted tolerable daily intake
PTFE	polytetrafluoroethylene
PTI-IDMS	Positive thermal ionisation isotope dilution mass spectrometry
PTWI	provisional tolerable weekly intake
PVC	polyvinylchloride
PVDF	poly(vinylidene fluoride)
QMS	quadrupole mass spectrometry
RA	relative area
RBC	red blood cell
RBP	retinol-binding protein
RC	regenerated cellulose
RDF	radial distribution function
RDI	recommended daily intakes
REACH	registration evaluation and authorization of chemicals
RfC	reference concentration
RI	refractive index
RIA	radioimmunological assays
RoHS	restriction of the use of certain hazardous substances
ROS	reactive oxygen species
SAAM	simulation analysis and modeling
SAE-SPE	strong anion exchange solid phase extraction
SAT	salinities and temperatures
SAW	submerged arc welding
SAX	strong anion exchange
SBI	silicone breast implant
SBSE	stir bar sorptive extraction
SCF	Scientific Committee for Food
SCOEL	Scientific Committee on Occupational Exposure Limits
SDDC	sodium dimethyl dithiocarbamate
SDS	sodium dodecyl sulfate
SDS-PAGE	sodium dodecyl sulfate polyacrylamide gel electrophoresis
SE	secondary electrons
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SeP	selenoprotein-P
SFC	supercritical fluid chromatography
SFE	supercritical fluid extraction
SFMS	sector field mass spectrometer
SIDMS	speciated isotope dilution mass spectrometry
SIDS	sudden infant death syndrome
SIMS	secondary ion mass spectrometry
SIT	specific ion interaction theory
SMAW	shielded metal arc welding
SOD	superoxide dismutase
SOP	standard operation procedure
SPARC	secreted protein acidic rich in cysteine
SPE	solid phase extraction
SPME	solid-phase microextraction
SSAS	solid solution-aqueous solution
SVD	singular value decomposition
TARL	tolerable average residue level
TBG	thyroid hormone binding globulin
TBP	tributylphosphate
TBT	tributyltin
TBTO	bis tri-n-butyloxide
TCyT	tricyclohexyltin

TDI	tolerable daily intake
TEL	tetraethyl lead
TEM	transmission electron microscopy
TEP	total exchangeable pool
TFA	trifluoroacetic acid
TGN	trans-golgi network
THF	tetrahydrofurane
TIBC	total iron binding capacity
TIG	tungsten inert gas
TIMS	thermal ionisation mass spectrometry
TLC	thin layer chromatography
TLV	threshold limit value
TLV-TWA	threshold limit value-time-weighted average
TML	tetramethyl lead
TMSOL	trimethyl silanol
TOC	total organic carbon
TOF-MS	time of flight-mass spectrometry
TOF-SIMS	time-of-flight secondary ion mass spectrometry
TPhT	triphenyltin
TPTZ	tripyridyl-triazine
TR	thioredoxin reductase
TRLFS	time-resolved laser-induced fluorescence spectroscopy
TRW	Technical Review Workgroup
TTA	α-thenoyltrifluoroacetone
TWA	time weighted average
TXRF	total reflection X-ray fluorescence
UHT	ultra high temperature
UIBC	unsaturated iron-binding capacity
UNEP	United Nations Environmental Programme
USEPA	US Environmental Protection Agency
UV-VIS	ultraviolet-visible
VC	vital capacity
VLDL	very low density lipoprotein
VLMM	very low molecular mass
VMC	volatile metal compounds
VMS	volatile methylsiloxanes
VOC	volatile organic compounds
VSC	volatile sulfur compound
WEEE	waste from electrical and electronic equipment
WFD	water framework directive
WHO	World Health Organization
WIPP	waste isolation pilot plant
WND	Wilson disease protein
WQC	water quality criteria
WWTP	wastewater treatment plant
XAFS	X-ray absorption fine structure spectroscopy
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction
XRF	X-ray fluorescence
XRFS	X-Ray fluorescence spectroscopy
ZnPP	zinc protoporphyrin

CHAPTER 1

Introduction

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Elemental Speciation has become a challenging part of analytical chemistry. The short-, medium-, and long-term perspectives are far-reaching, and it may be interesting to dwell upon the ways the scientific community will continue its progress. It is to be expected that a renewed legal framework will come into effect, in which essentiality and toxicity of the elemental species, instead of total trace element concentration, becomes the key issue.

During the past 20 to 30 years, elemental speciation has grown into a full-fledged analytical discipline. The technological and methodological achievements in recent years have considerably increased the possibilities of analytical chemistry. Today, it is possible to determine numerous element species accurately at concentration levels that were inconceivable some 10 years ago.

The first volume of this Handbook gave a comprehensive overview of the analytical possibilities and the general technical and methodological aspects of speciation analysis [1].

The present – second – volume will cover the species by element or group of compounds (actinides, halogens, volatile metals, proteins, and humic acids) describing the state of the art for the sections environment, food, clinical, and occupational health and hygiene. Special chapters on the possibilities of modeling will introduce the reader to the modern way of predicting chemical situations through theoretical calculations, made possible by the availability of modern high-performance computers.

Newcomers in the field will appreciate the total overview that this Handbook provides. Experienced analysts will value the comprehensive detailing of the most current developments in the different sectors of elemental speciation.

The current situation in Speciation Analysis is complex. On the one hand, there is a group of elemental species that has been thoroughly investigated and described (e.g. methylmercury, organotin compounds, and organoarsenicals). On the other hand, there are those compounds for which only preliminary scientific knowledge has

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been gained (e.g. elements bound to proteins, to humic acids, etc.).

For the first group, the technological progress in instrumental analysis has reached a level of performance that enables analysts to determine elemental species accurately at picogram levels and below. In principle, these procedures already allow comprehensive survey measurements. Unfortunately, the number of laboratories with the necessary skills and analytical instrumentation is still much too limited for routine control activities.

Although in research laboratories there exist reliable analytical instrumentation and validated standard operation procedures (SOPs), almost every analytical approach turns out to be only applicable to a few elemental species, in a narrow range of matrices. While it would not be too difficult for instrument manufacturers to transfer such know-how into routinely usable analytical instruments, such instrumentation would lack in general applicability and would therefore only appeal to a limited market segment. As long as laws, regulations, and directives do not force industrial and governmental controlling bodies to systematically analyze elemental species, the size of the market will remain too small to guarantee a reasonable return on investment for routine-instrument development.

The support for scientific research through universities and research institutions must increasingly be justified on the basis of the relevance decided by external funding bodies. Many traditional fields of application such as environmental sciences do not offer a promising outlook in this respect. As a consequence, analytical research groups face a substantial reduction of support because of the reallocation of funds to more "fashionable" sciences such as molecular biology or nanotechnology. To adjust to this situation, analytical scientists need to use their creativity in finding ways to participate by creating their niche in, for example, nanotechnology, cancer research, or proteomics. This requires an open mind in terms of new opportunities, evaluating strengths and weaknesses of existing techniques and methodologies and a departure from technique-oriented toward problem-oriented research. Analytical chemistry provides basic information about the status of humans and their environment and about the characteristics of materials, its cycling, and interactions. There is little doubt that the role of speciation analysis is crucial in answering questions about the bioavailability, biological activity, toxicity, or nutritional value and metabolism of trace elements. The important role of speciation analysis is evident from the more than 500 publications every year on the subject and from the gradual introduction of chemical species, rather than total amounts, in rules and regulations. These developments were possible only because different scientific disciplines have crossed their respective borderlines.

Analytical chemistry

More and more sensitive analytical techniques have reached a detection power limited only by mere contamination problems. At the same time, the risk of contamination has been drastically reduced by on-line coupling of separation and detection into a closed system. There remain, however, limitations imposed by the presence of contaminants in the reagents and the release of impurities by the packing material and many utensils through contact with the sample. Nevertheless, the quality of the information obtained through these techniques has been enhanced drastically by the increased sensitivity gained through hyphenation [2]. Modern mass spectrometric techniques allow to collect information on the atomic as well as the molecular species [3, 4]. Fast separation techniques such as Flow Injection [5], Fast Protein Liquid Chromatography (FPLC) [6], Capillary Electrophoresis [7], and Multicapillary Gas Chromatography [8] reduce the analysis time and therefore the possibilities for species transformation during analysis. Sample preparation has also been made instrumental, benefiting from automation and feedback control (e.g. microwave extraction with temperature and pressure control [9]). Solvent-less extraction [10] and other soft enzymatic extraction methods try to keep fragile species intact. Some X-ray spectroscopic and microbeam techniques are available for direct elemental speciation analysis in the solid state, thus bypassing sample preparation [11]. Additionally, increasing Quality Management has caused the comparability and traceability of analytical measurements to get possible even for trace and ultra-trace analyses. Manufacturers of certified reference materials (CRMs) have started to market CRMs for speciation analysis [12, 13]. Research groups have established the state of the art in speciation analysis and discussed shortcomings and artifacts during intercomparison studies and workshops. Species-specific isotope dilution analysis has been proven to be a very versatile tool for studying species transformation even during the analysis and enables accurate determination even under dynamic conditions [14, 15].

Toxicology

The toxicologists have developed increasingly reliable investigation and calculation models to determine the toxicity of chemical species. These data form the basis for comprehensive characterization and description of chemical species to be used in legislation.

Chemometrics

Analytical chemistry, toxicology, and other disciplines can be improved significantly by using chemometrical methods. The continuing development in data processing techniques allows the use of highly complex algorithms suited to improve the quality and quantity of information extractable from huge sets of data. Accordingly, this discipline offers valuable support tools.

Medicine, biology, and food science

The assessment of the effect of elemental species in medicine, biology, and food science depends heavily on the quality of the analytical and toxicological input. The most recent developments in this connection are coming from the field of proteomics and metallomics, dealing with the determination of trace metals in biomolecules. These new scientific fields will hopefully provide a more fundamental understanding of the essential role of trace metals in life processes and enhance our knowledge of their physiological effect on different organisms. Although this research field has only recently emerged, the very first results are already exciting.

It is obvious from this list of disciplines and their interactions that only interdisciplinary, targeted approaches will be able to generate the momentum for further development in elemental speciation analysis. This supposes well-coordinated research aimed at answering complex and important questions. It will be interesting to see whether initiatives such as the European Virtual Institute for Speciation Analysis (http://www.speciation.net) can provide an efficient platform for such activities [16].

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CHAPTER 2

Element by Element Review

2.1 Introduction

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Volume 2 of the Handbook of Elemental Speciation endeavors to compile the state of the art in elemental speciation for a large number of chemical elements. The reader will clearly see why it is important to measure chemical species rather than total element concentrations, especially in relation to environment and living organisms, in health or disease.

Roughly 90 elements are present on earth in an as yet unknown number of chemical species.

Our interest went to those species that occur in low concentrations in environmental matrices and in living systems. Left out are the abundant elements, carbon, hydrogen, oxygen, nitrogen and phosphor, and calcium, lithium, sodium, potassium, magnesium, chlorine and fluorine and those elements for which the elemental species have not yet been substantially investigated and little or no speciation knowledge is available. It is expected that our knowledge in chemical species will expand greatly during the coming decades, in line with the increasing analytical competence. The analytical methodology is the subject of Volume 1 of this Handbook [1]. This second volume covers in detail the various species of 21 elements, of the actinides, and of four groups of compounds (halogens, volatile metal compounds of biogenic origin, metal complexes of humic substances and metal complexes of proteins). Chapters on modeling of trace element species in the environment, food, health and disease illustrate the power of modern chemometric techniques in describing the behavior of elemental species in complicated systems.

The chapters intend to provide basic knowledge about the chemical species of each element or group of compounds. The general structure of each chapter aims at following a logical progression, starting with the elemental species as they occur naturally in the environment, in many cases upset by dumping practices and further worsened by input of synthetic species and their derivatives of purely anthropogenic origin. (The organotin compounds are undoubtedly one of the worst examples.) The next step deals with the chemical form under which they end up in the life cycle, including the food chain. The study is complete

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when it is known which elemental species are being inhaled or ingested by man, how they are incorporated, excreted and, last but not least, how they have either been beneficial to the health of the subjects or, on the contrary, posed a health risk.

The rudimentary depth of fundamental knowledge in this relatively young discipline made it impossible to impose a strict organization of the chapters. Each contribution has been written by specialists in the field, who have aimed at being as informative as possible. The individual style of each author plays, however, a decisive role in the way the existing knowledge is presented. It is inevitable that every author be conditioned by his or her personal focus and academic background in either analytical chemistry, medical sciences, occupational medicine or environmental sciences.

We hope that the knowledge contained in the two volumes of this Handbook will provide a stimulus for further research in this young and exciting scientific domain.

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2.2 Speciation of Aluminum

2.2.1 Speciation of Aluminum in the Environment

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1 INTRODUCTION

Aluminum (Al) is the most abundant metal in the lithosphere. It is bound predominantly in sparingly soluble oxides (bauxite) and complex alumosilicates, comprising 8% of the Earth's crust. Its chemistry depends strongly on pH. In contrast, because Al is very insoluble in the neutral pH range, its abundance in the oceans is much less, the Al concentration being below 1 μg dm^{-3}. Nevertheless, its solubility is significantly increased under acidic ($pH < 6.0$) or alkaline ($pH > 8.0$) conditions and/or in the presence of inorganic and organic complexing ligands. Acid rain may substantially mobilize and release Al into soil solution, and into underground and surface waters. This effect is observed especially in poorly buffered soils [1, 2]. Al solubility in soil also increases as a response to elevated nitrification that causes an increase in acidity and consequently mobilizes Al into soil solution [3]. The released mononuclear ionic Al species may undergo polymerization or may be complexed by available inorganic or organic ligands [4]. Al^{3+} is a very reactive species. It reacts 10^7 times faster than Cr^{3+}. In the environment and in biological systems, Al exists only in Al^{3+} oxidation state. Al is too reactive to be found free in nature. It is widely used in the industry, representing an additional burden to the environment. $Al_2(SO_4)_3$ is added to drinking water as a coagulant to clarify turbid drinking waters. Alums, double sulfate salts of Al^{3+} and Na^+, K^+ or $NH_4{}^+$ such as $KAl(SO_4)_2 \cdot 12H_2O$ are used in the paper industry for tanning (to replace Cr^{3+} salts) and dyeing. Alums are also added to foods, and $Al(OH)_3$ can be found in pharmaceutical products, such as antacids [5]. With the increased release of

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Al to the environment, its toxic effects on humans, animals and plants have been observed.

2 THE AQUEOUS CHEMISTRY OF ALUMINUM

Al is a small, highly charged ion. The effective ionic radius of Al^{3+} is 0.054 nm. Because of its charge, in aqueous solutions at low pH values, Al^{3+} is coordinated by six water molecules in an octahedral configuration. In solutions more acidic than pH 5.0, $Al(H_2O)_6{}^{3+}$ exists (abbreviated as Al^{3+}). In less acidic solution, $Al(H_2O)_6{}^{3+}$ undergoes hydrolysis to yield $Al(H_2O)_5(OH)^{2+}$ (abbreviated as $Al(OH)^{2+}$) and $Al(H_2O)_4(OH)_2{}^{+}$ (abbreviated as $Al(OH)_2{}^{+}$) species. In the neutral pH range, Al is mainly precipitated as $Al(OH)_3$. In basic solutions, the precipitate redissolves, resulting in formation of tetrahedral $Al(OH)_4{}^{-}$. The equilibria among mononuclear Al species in aqueous solutions may be expressed by the following reactions with corresponding equilibrium constants [5]:

$$Al(H_2O)_6{}^{3+} + H_2O \rightleftarrows Al(H_2O)_5(OH)^{2+} + H_3O^{+}$$

$$K_1a = 10^{-5.5} \tag{2.2.1.1}$$

$$Al(H_2O)_5(OH)^{2+} + H_2O \rightleftarrows Al(H_2O)_4(OH)_2{}^{+} + H_3O^{+}$$

$$K_2a = 10^{-5.6} \tag{2.2.1.2}$$

Significant amounts of soluble $Al(OH)_3$ are not formed in solution, but deprotonation from two more $Al(H_2O)_4(OH)_2{}^{+}$ bound waters yields the soluble tetrahydroxy aluminum species.

$$Al(H_2O)_4(OH)_2{}^{+} + 2H_2O \rightleftarrows Al(H_2O)_2(OH)_4{}^{-} + 2H_3O^{+}$$

$$K_4a = 10^{-12.1} \tag{2.2.1.3}$$

Martin [5] reported the distribution of soluble mononuclear Al species in aqueous solutions at various pH values, calculated on the basis of thermodynamic equilibrium constants at 25 °C and an ionic strength of 0.16. Al^{3+} is the prevailing species below pH 5.0. In the pH range between 5.0 and 6.2, there is a mixture of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$ and colloidal $Al(OH)_3$ species. At a pH higher than 6.2, the dominant species is $Al(OH)_4{}^{-}$.

When the pH of an acidic aqueous solution increases, the charge density of Al, due to hydrolysis, decreases and Al begins to polymerize [4]. Polynuclear Al species represent important metastable dissolved constituents that may remain in solution for many years. The smallest polynuclear Al complex in solution is the Al dimer, which is linked by a dihydroxide bridge $(Al_2(OH)_2(H_2O)_8)^{4+}$. This Al dimer is not a stable species. The ring structure of six aluminum hydroxide octahedra $(Al_6(OH)_{12})^{6+}$, the double-ring $(Al_{10}(OH)_{22}{}^{8+})$ and the triple-ring $(Al_{13}(OH)_{30}{}^{9+})$ structures are more stable Al polymers [4]. The most widely used method for direct observation of polynuclear Al species is nuclear magnetic resonance (NMR) spectroscopy. Various polynuclear Al complexes with the general formula $[Al_2(OH)_3]_n{}^{3+}$ and other polynuclear structures of Al have been proposed in the literature [6]. The extent of polymerization and the distribution of polymers depend on the degree of oversaturation, pH, temperature and age of the solution. Elevated concentrations of polynuclear species are found only in highly saturated solutions that are not in contact with adsorbing surfaces. Higher temperatures and aging of solutions favor the polymerization process. It was demonstrated that Al also tends to hydrolyze at clay surfaces, resulting in polymer formation in soil solution and aquatic systems. Coalescing of polymers increases the molecular mass, leading to precipitation of Al from solution as amorphous $Al(OH)_3$. If suspended particulate matter is present in natural water samples, it will readily adsorb polynuclear Al species [6].

3 THE DISTRIBUTION OF ALUMINUM IN ENVIRONMENTAL SOLUTIONS

In environmental solutions, F^{-}, $SO_4{}^{2-}$ and organic ligands compete with OH^{-} for formation of Al complexes. Al^{3+} forms stronger complexes with F^{-} than $SO_4{}^{2-}$. In acidic solutions, containing more fluoride than Al, almost all Al^{3+} exists in the form of fluoride complexes. Unless there are very high concentrations of sulfate present, fluoride is the most important inorganic ligand that complexes Al in acidic environmental solutions. However, under alkaline conditions, F^{-} or $SO_4{}^{2-}$ are displaced by the OH^{-} ion [7]. There is evidence of interactions between