EXTRACTION TECHNIQUES IN ANALYTICAL SCIENCES

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To Lynne, Sam and Naomi (and the border terrier, Emmi) for allowing me the time to sit and write this book

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Series Preface

There has been a rapid expansion in the provision of further education in recent years, which has brought with it the need to provide more flexible methods of teaching in order to satisfy the requirements of an increasingly more diverse type of student. In this respect, the *open learning* approach has proved to be a valuable and effective teaching method, in particular for those students who for a variety of reasons cannot pursue full-time traditional courses. As a result, John Wiley & Sons, Ltd first published the *Analytical Chemistry by Open Learning* (ACOL) series of textbooks in the late 1980s. This series, which covers all of the major analytical techniques, rapidly established itself as a valuable teaching resource, providing a convenient and flexible means of studying for those people who, on account of their individual circumstances, were not able to take advantage of more conventional methods of education in this particular subject area.

Following upon the success of the ACOL series, which by its very name is predominately concerned with Analytical *Chemistry*, the *Analytical Techniques in the Sciences* (AnTS) series of open learning texts has been introduced with the aim of providing a broader coverage of the many areas of science in which analytical techniques and methods are now increasingly applied. With this in mind, the AnTS series of texts seeks to provide a range of books which will cover not only the actual techniques themselves, but *also* those scientific disciplines which have a necessary requirement for analytical characterization methods.

Analytical instrumentation continues to increase in sophistication, and as a consequence, the range of materials that can now be almost routinely analysed has increased accordingly. Books in this series which are concerned with the *techniques* themselves will reflect such advances in analytical instrumentation, while at the same time providing full and detailed discussions of the fundamental concepts and theories of the particular analytical method being considered. Such books will cover a variety of techniques, including general instrumental analysis, spectroscopy, chromatography, electrophoresis, tandem techniques, electroanalytical methods, X-ray analysis and other significant topics. In addition, books in

the series will include the *application* of analytical techniques in areas such as environmental science, the life sciences, clinical analysis, food science, forensic analysis, pharmaceutical science, conservation and archaeology, polymer science and general solid-state materials science.

Written by experts in their own particular fields, the books are presented in an easy-to-read, user-friendly style, with each chapter including both learning objectives and summaries of the subject matter being covered. The progress of the reader can be assessed by the use of frequent self-assessment questions (SAQs) and discussion questions (DQs), along with their corresponding reinforcing or remedial responses, which appear regularly throughout the texts. The books are thus eminently suitable both for self-study applications and for forming the basis of industrial company in-house training schemes. Each text also contains a large amount of supplementary material, including bibliographies, lists of acronyms and abbreviations, and tables of SI Units and important physical constants, plus where appropriate, glossaries and references to literature sources.

It is therefore hoped that this present series of textbooks will prove to be a useful and valuable source of teaching material, both for individual students and for teachers of science courses.

Dave Ando
Dartford, UK

Preface

This book introduces a range of extraction techniques as applied to the recovery of organic compounds from a variety of matrices. In line with other texts in the Analytical Techniques in the Sciences (AnTS) Series, discussion and self-assessment questions provide the reader with the opportunity to assess their own understanding of aspects of the text. This book has been designed to be 'user-friendly' with illustrations to aid understanding. This text is arranged into thirteen chapters as follows.

Chapter 1 introduces all the key aspects that need to be considered, pre- and post-extraction. In particular, it highlights the range of organic compounds that are extracted in analytical sciences. This chapter then addresses pre-sampling issues by way of a desk-top study of a contaminated land site using historic maps. Specific sampling strategies for solid, aqueous and air samples are considered. The natural progression in any analytical protocol would then be to carry out the extraction technique. However, as the rest of the book details how to perform different extractions no details are provided at this point. Post-extraction details focus on the main chromatographic approaches for analysing organic compounds, i.e. gas chromatography and high performance liquid chromatography. Both techniques are covered from a practical perspective. Issues around sample pre-concentration post-extraction are also discussed in terms of the most popular approaches used. Finally, quality assurance aspects and health and safety issues are considered.

Chapter 2 considers the classical approaches for extracting organic compounds from aqueous samples, namely liquid–liquid extraction (LLE). Details of the basic theory applicable to LLE are explained together with important practical aspects, including choice of solvents, the apparatus and procedure to undertake LLE and practical problems and remedies for undertaking LLE. Finally, the specific extraction technique of purge and trap and its application for recovering volatile organic compounds from aqueous samples is explained.

Chapter 3 considers the use of solid phase extraction (or SPE) for the recovery of organic compounds from aqueous samples. The different types of SPE media are considered as well as the different formats in which SPE can be performed, solvent selection and factors influencing SPE. The five main aspects of SPE operation are reviewed both generically and then via a series of applications using normal phase, reversed phase, ion exchange and molecularly imprinted polymers. Finally, the use of automated and in-line SPE is considered using a selected example.

Chapter 4 considers the use of solid phase microextraction (or SPME) for the recovery of organic compounds from aqueous samples (although mention is also made of its applicability for headspace sampling), followed by either GC or HPLC. The practical aspects of using the fibres are described in detail as well as their applicability for a range of sample types in different modes of operation.

Chapter 5 describes new developments in microextraction. Particular developments highlighted include stir-bar sorptive extraction (SBSE), liquid phase microextraction (specifically, single drop microextraction (SDME)), membrane microextraction (specifically, the semipermeable membrane device (SPMD), the polar organic chemical integrative sampler (POCIS), 'Chemcatcher', the ceramic dosimeter and membrane enclosed-sorptive coating (MESCO)), as well as microextraction in a packed syringe (MEPS).

Chapter 6 considers the classical approaches for extracting organic compounds from solid samples, namely Soxhlet extraction (LLE). Practical guidance on the use of Soxhlet extraction is provided along with choice of solvent, and the apparatus and procedure to undertake extraction. In addition, automated Soxhlet (or 'Soxtec') extraction is discussed alongside other approaches that utilize sonication or shake-flask extraction for the recovery of organic compounds from solid matrices.

Chapter 7 describes the use of pressurized fluid extraction (PFE) (also known as accelerated solvent extraction or pressurized liquid extraction) for the recovery of organic compounds from solid matrices. The theoretical aspects of the approach are described, as well as the range of commercial apparatus that is currently available. Approaches for method development for PFE are described, as well as a range of applications including approaches for parameter optimization, *in situ* clean-up (also known as selective PFE) and shape selective, fractionation PFE.

Chapter 8 describes the use of microwave-assisted extraction (MAE) for the recovery of organic compounds from solid matrices. Instrumentation for both atmospheric and pressurized MAE are highlighted, with the latter dominating in its applicability. A range of applications is considered, as well as some recommendations on the use of MAE in analytical sciences.

Chapter 9 considers developments in matrix solid phase dispersion (MSPD) for solid samples. The procedure for performing MSPD is highlighted, as well as its applicability to a range of sample types. A range of factors that can influence

MSPD is then discussed. Finally, a comparison between MSPD and solid phase extraction is made.

Chapter 10 describes the technique of supercritical fluid extraction (SFE). After an initial description of what is a supercritical fluid, the option of carbon dioxide as the fluid of choice is discussed. A detailed description of the instrumentation for SFE is outlined, together with the options for adding modifiers to the system. Finally, a range of applications for SFE in analytical sciences is described.

Chapter 11 considers the analysis of volatile organic compounds (VOCs) in gaseous samples. A discussion on the techniques for air sampling, including whole air collection in containers, enrichment into solid sorbents (active and passive sampling), desorption techniques and on-line sampling, is also included.

Chapter 12 includes a detailed discussion on the important extraction method criteria, namely, sample mass/volume, extraction time, solvent type and consumption, extraction method, sequential or simultaneous extraction, method development time, operator skill, equipment cost, level of automation and extraction method approval. This chapter then considers the above criteria in the context of comparing extraction techniques for (semi-) solid samples and liquid samples. A comparison is also made of the approaches for air samples. In addition, this chapter also considers the role and use of certified reference materials.

The final chapter (Chapter 13) considers the resources available when considering the use of extraction techniques in analytical sciences. The role of the Worldwide Web in accessing key sources of information (publishers, companies supplying instrumentation and consumables, institutions and databases) is highlighted.

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Acknowledgements

This present text includes material which has previously appeared in three of the author's earlier books, i.e. *Extraction Methods for Environmental Analysis* (1998), *Methods for Environmental Trace Analysis* (AnTS Series, 2003) and *Bioavailability, Bioaccessibility and Mobility of Environmental Contaminants* (AnTS Series, 2007), all published by John Wiley & Sons, Ltd. The author is grateful to the copyright holders for granting permission to reproduce figures and tables from his three earlier publications.

Dr Marisa Intawongse is acknowledged for her assistance with the compilation of Chapters 3 and 4. Dr Pinpong Kongchan is thanked for the drawing of Figures 6.3, 8.2, 8.3, 8.5 and 8.6, Dr Michael Deary for providing Figure 1.1 and Naomi Dean for the drawing of Figures 1.5 and 1.6.

The front cover shows a photograph of Sycamore Gap located on Hadrian's Wall in Northumberland, UK, where the tree, sky and ground symbolize the areas of soil, air and water aspects of this book. This location was used in the 1991 film 'Robin Hood Prince of Thieves' starring Kevin Costner and so to my family it is known as 'Robin's tree' – Robin Hood is also immortalized in my family with the phrase 'after them you hools!'. Picture provided by John R. Dean, Northumbria University, Newcastle, UK.

Acronyms, Abbreviations and Symbols

ACN	acetonitrile
ACS	American Chemical Society
AOAC	Association of Official Analytical Chemists
APCI	atmospheric pressure chemical ionization
ASE	accelerated solvent extraction
ASTM	American Society for Testing and Materials
BAM	The Federal Institute for Materials Research and Testing
BCR	Community Bureau of Reference
BNAs	bases, neutral species, acids
BTEX	benzene, toluene, ethylbenzene and xylenes
CAR	carboxen
CI	chemical ionization
COSHH	Control of Substances Hazardous to Health
CRM	certified reference material
DCM	dichloromethane
DIN	Deutsches Institut für Normung
DVB	divinylbenzene
ECD	electron capture detector
EI	electron impact
ES	electrospray
EU	European Union
EVACS	evaporative concentration system
FDA	Food and Drug Administration
FID	flame ionization detector
GC	gas chromatography

HPLC	high performance liquid chromatography
HS	headspace
HTML	hypertext markup language
ICP	inductively coupled plasma
ID–GC–MS	isotope dilution–gas chromatography–mass spectrometry
IR	infrared
IRMM	Institute for Reference Materials and Measurements
IT–MS	ion trap–mass spectrometry
LC	liquid chromatography
LDPE	low-density polyethylene
LGC	Laboratory of the Government Chemist
LLE	liquid–liquid extraction
LOD	limit of detection
LOQ	limit of quantitation
MAE	microwave accelerated extraction
MCL	maximum concentration level
MEPS	microextraction in a packed syringe
MESCO	membrane enclosed-sorptive coating
MIP	molecularly imprinted polymer
MS	mass spectrometry
MSD	mass selective detector
MSPD	matrix solid phase dispersion
NIST	National Institute of Science and Technology
NMIJ	National Metrology Institute of Japan
NP (HPLC)	normal phase (high performance liquid chromatography)
NRC	National Research Council (of Canada)
NRCCRM	National Research Centre for Certified Reference Materials
NWRI	National Water Research Institute
ODS	octadecylsilane
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
pdf	portable document format
PDMS	polydimethylsiloxane
PEEK	poly(ether ether ketone)
PFAs	perfluoroalkoxy fluorocarbons
PFE	pressurized fluid extraction
PHWE	pressurized hot water extraction
PLE	pressurized liquid extraction
POCIS	polar organic chemical integrative sampler
POPs	persistent organic pollutants
ppb	parts per billion (10^9)

ppm	parts per million (10^6)
ppt	parts per thousand (10^3)
PSE	pressurized solvent extraction
PTV	programmed temperature vaporizer
PVC	poly(vinyl chloride)
QA	quality assurance
RAM	restricted access media
RP (HPLC)	reversed phase (high performance liquid chromatography)
RSC	The Royal Society of Chemistry
RSD	relative standard deviation
SCX	strong cation exchange
SBSE	stir-bar sorptive extraction
SDME	single drop microextraction
SFC	supercritical fluid chromatography
SFE	supercritical fluid extraction
SIM	single (or selected) ion monitoring
SPE	solid phase extraction
SPLE	selective pressurized liquid extraction
SPMD	semipermeable membrane device
SPME	solid phase microextraction
SSSI	site of special scientific interest
SI (units)	Système International (d'Unitès) (International System of Units)
TFM	tetrafluoromethoxy (polymer)
TIC	total ion current
TOF–MS	time-of-flight–mass spectrometry
TSD	thermionic specific detector
URL	uniform resource locator
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VOCs	volatile organic compounds
WWW	Worldwide Web

c	speed of light; concentration
D	distribution ratio
E	energy; electric field strength
f	(linear) frequency
I	electric current
K_d	distribution coefficient
K_{ow}	octanol–water partition coefficient
log P	log of octanol–water partition coefficient
m	mass

P	pressure
R	molar gas constant
t	time; Student factor
V	electric potential
z	ionic charge
λ	wavelength
ν	frequency (of radiation)
σ	measure of standard deviation
σ^2	variance

About the Author

John R. Dean, B.Sc., M.Sc., Ph.D., D.I.C., D.Sc., FRSC, C.Chem., C.Sci., Cert. Ed., Registered Analytical Chemist

John R. Dean took his first degree in Chemistry at the University of Manchester Institute of Science and Technology (UMIST), followed by an M.Sc. in Analytical Chemistry and Instrumentation at Loughborough University of Technology, and finally a Ph.D. and D.I.C. in Physical Chemistry at the Imperial College of Science and Technology (University of London). He then spent two years as a postdoctoral research fellow at the Food Science Laboratory of the Ministry of Agriculture, Fisheries and Food in Norwich, in conjunction with the Polytechnic of the South West in Plymouth (now the University of Plymouth). His work there was focused on the development of directly coupled high performance liquid chromatography and inductively coupled plasma–mass spectrometry methods for trace element speciation in foodstuffs. This was followed by a temporary lectureship in Inorganic Chemistry at Huddersfield Polytechnic (now the University of Huddersfield). In 1988, he was appointed to a lectureship in Inorganic/Analytical Chemistry at Newcastle Polytechnic (now Northumbria University). This was followed by promotion to Senior Lecturer (1990), Reader (1994), Principal Lecturer (1998) and Associate Dean (Research) (2004). He was also awarded a personal chair in 2004. In 2008 he became the Director of The Graduate School at Northumbria University as well as Professor of Analytical and Environmental Sciences in the School of Applied Sciences.

In 1998, he was awarded a D.Sc. (University of London) in Analytical and Environmental Science and was the recipient of the 23rd Society for Analytical Chemistry (SAC) Silver Medal in 1995. He has published extensively in analytical and environmental science. He is an active member of The Royal Society of Chemistry (RSC) Analytical Division, having served as a member of the Atomic

Spectroscopy Group for 15 years (10 as Honorary Secretary) as well as a Past Chairman (1997–1999). He has served on the RSC Analytical Division Council for three terms and is a former Vice-President (2002–2004), as well as a past-Chairman of the North-East Region of the RSC (2001–2003).

Chapter 1

Pre- and Post-Extraction Considerations

Learning Objectives

- To appreciate the wide ranging types of organic compounds that are investigated in environmental and food matrices.
- Using an example, to be aware of pre-sampling issues associated with a contaminated land site.
- To be aware of the information required for a desk-top study (in a contaminated land situation).
- To understand the different sampling strategies associated with solid, aqueous and air samples.
- To be aware of the different types of contaminant distribution on a site.
- To understand the practical aspects of soil and sediment sampling.
- To understand the practical aspects of water sampling.
- To understand the practical aspects of air sampling.
- To be aware of the different analytical techniques available to analyse organic compounds.
- To understand and explain the principle of operation of a gas chromatography system.
- To understand and explain the principle of operation of a high performance liquid chromatography system.
- To be able to understand the principles of quantitative chromatographic analysis.

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- To be aware of the approaches and limitations for sample pre-concentration in the analysis of organic compounds.
- To appreciate the importance of quality assurance in quantitative analysis.
- To understand the health and safety aspects of performing laboratory work and the consequences for non-compliance.

1.1 Introduction

This book is concerned with the removal of organic compounds, principally persistent organic compounds (POPs), from a range of sample matrices including environmental matrices (soil, water and air samples), but also some other matrices including foodstuffs. The book is designed to be an informative guide to a range of extraction techniques that are used to remove organic compounds from various matrices. The use of discussion questions (DQs) and self-assessment questions (SAQs) throughout the text should allow you (the reader) to think about the main issues and to allow you to consider alternative approaches.

1.2 Organic Compounds of Interest

The range of organic compounds of interest in the environment and in other matrices varies enormously. They range from simple aromatic cyclic structures, for example, benzene, toluene, ethylbenzene and xylene(s) (collectively known as BTEX), to larger molecular weight compounds, such as polycyclic aromatic hydrocarbons (PAHs), and more complicated structures, e.g. pesticides and polychlorinated biphenyls (PCBs). A list of organic compounds that are measured in environmental (and other) matrices is shown in Table 1.1.

SAQ 1.1

What are the important physical and chemical properties of these organic compounds that are useful to know when extracting them from sample matrices?

1.3 Pre-Sampling Issues

Prior to sampling it is necessary to consider a whole range of issues that are directly/indirectly going to influence the quality of the final data that is produced after what is often a long and costly process. Therefore it is imperative to think