Barbara H. Stuart

Forensic Analytical Techniques



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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 now 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, tables of SI units and important physical constants and, 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

The public profile of forensic science has dramatically increased in recent decades and there has been a corresponding rise in the number of students undertaking forensic science degree courses at a tertiary level with the view to a professional career in this field. During this period the application of modern analytical techniques to the examination of forensic problems has expanded, particularly due to the development of small and portable cost-effective instrumentation. The availability of new techniques has led to a greater choice of tools that can be employed to analyse forensic specimens. An understanding of a broad range of analytical tools is required by today's forensic chemists and is an important aspect of their training.

The aim of this book is to provide an overview of the most commonly used analytical techniques that are of interest to forensic chemists. A clear description of how each technique works and how to prepare specimens for analysis is provided. Some techniques are widely used as standard methods, while others are yet to be established but show great potential. An explanation of how to analyse the data obtained is also provided and, for each technique, the most common forensic applications are described. There are specific issues to consider when examining forensic samples. Apart from the applicability of a technique, the issues of dealing with small quantities of material, whether a technique is non-destructive and the cost and/or portability for fieldwork must be considered.

The reader will note that there is a deliberate focus on forensic chemistry and physical evidence. Topics such as DNA analysis are intentionally not dealt with here, and forensic biology topics are well covered elsewhere. The focus here is on how to analyse samples once collected – the process of evidence collection is, of course, an important aspect of a forensic scientist's training and is an expansive topic in its own right. This book is designed for students who are undertaking a forensic chemistry based programme and require a sound knowledge of analytical techniques. Some basic tertiary mathematical and chemistry knowledge is

assumed. The book will also provide a useful reference for forensic practitioners who may be interested in investigating new forms of evidence or techniques.

I hope that this book helps fill a gap in the world of forensic textbooks. Naturally many forensic science textbooks focus on the collection of evidence, but this book will provide a resource for the teaching of forensic analytical techniques. I would like to acknowledge the valuable conversations with and the data provided by a multitude of hardworking forensic scientists in police forces, law enforcement agencies and universities – not just in Australia, but worldwide. A special thanks to my colleagues and students past and present in the Centre of Forensic Science and the School of Chemistry and Forensic Science at the University of Technology, Sydney.

About the Author

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Barbara Stuart holds the position of Associate Professor at the School of Chemistry and Forensic Science and the Centre for Forensic Science at the University of Technology, Sydney (UTS) in Australia. She received BSc (Hons) and MSc degrees in chemistry from the University of Sydney in Australia and gained her PhD at Imperial College in London in 1993. Barbara held the position of lecturer at the University of Greenwich, London before returning to Australia to take up a position at UTS in 1995. Barbara has contributed to the teaching of a broad range of topics in the chemistry, forensic and materials programmes at UTS. She also has active research interests in the fields of forensic taphonomy and archaeology, as well as in materials conservation and environmental science, and has published many papers on these topics. Barbara is also the author of five other books published by John Wiley & Sons: Modern Infrared Spectroscopy and Biological Applications of Infrared Spectroscopy, both in the ACOL series of open learning texts, and Polymer Analysis and Infrared Spectroscopy: Fundamentals and Applications in the current AnTS series of texts, as well as Analytical Techniques in Materials Conservation.

Acronyms, Abbreviations and Symbols

AAS atomic absorption spectrometry
AES atomic emission spectrometry
AFM atomic force microscopy
ALS alternate light source
ANN artificial neural network

APCI atmospheric pressure chemical ionization

ATR attenuated total reflectance BAC blood alcohol concentration BSA N,O-bistrimethylsilylic acid

BSE backscattered electron

BSTFA N,O-bistrimethylsilyltrifluoroacetamide

CE capillary electrophoresis
CI chemical ionization
CNS central nervous system
COHb carboxyhaemoglobin

CZE capillary zone electrophoresis

DAC diamond anvil cell
 DAD diode array detector
 DART direct analysis in real time

DC direct current

DESI desorption electrospray ionization

DFO 1,8-diazafluoren-9-one

DRIFT diffuse reflectance infrared by Fourier transform

DSC differential scanning calorimetry
DTA differential thermal analysis
DTG derivative thermogravimetric

ECD electron capture detector

EDS energy dispersive X-ray spectroscopy
EDX energy-dispersive X-ray analysis
EDXRF energy-dispersive X-ray fluorescence
EELS electron energy loss spectroscopy

EI electron ionization

ESEM environmental scanning electron microscopy

ESI electrospray ionization
FID flame ionization detector
GC gas chromotography

GHB gamma-hydroxybutyric acid

GFAAS graphite furnace atomic absorption spectrometry

GRIM Glass Refractive Index Measurement

GSR gunshot residue Hb haemoglobin

HCA hierarchical clustering analysis HDPE high-density polyethylene

HPLC high-performance liquid chromatography

IBA ion beam analysis IC ion chromatography

ICDD International Centre for Diffraction Data
ICP-MS inductively coupled plasma-mass spectrometry

ILR ignitable liquid residue IMS ion mobility spectrometry IRMS isotope ratio mass spectrometry

LC liquid chromatography
LDA linear discriminant analysis
LDPE low-density polyethylene

LIBS laser-induced breakdown spectroscopy

MDA methylenedioxyamphetamine

MDMA methylenedioxymethylamphetamine MDEA 3,4-methylenedioxyethylamphetamine

MECC micellar electrokinetic capillary chromatography (also MEKC)

MI medullary index
MS mass spectrometry
MSP microspectrophotometry

MSTFA N-methyl-M-trimethylsilyltrifluoroacetamide

m/z mass-to-charge (ratio)

NMR nuclear magnetic resonance

NOE Nuclear Overhauser Effect

NRA nuclear reaction analysis

PC paper chromatography

PCA principal component analysis

PD physical developer PDMS polydimethylsiloxane

PE polyethylene

PET poly(ethylene terephthalate)
PETN pentaerythritol tetranitrate
PIXE particle-induced X-ray emission
PLM polarizing light microscope
PMMA poly(methyl methacrylate)

PP polypropylene
ppb parts per billion
ppm parts per million
PS polystyrene

PSA prostate-specific antigen (test)

PVC poly(vinyl chloride)

ρ density

 R^2 coefficient of determination

RBS Rutherford back scattering spectrometry

RF radiofrequency RI reflective index

RRS resonance Raman spectroscopy

SAN styrene-acrylonitrile
SAP seminal acid phosphatase
SBR styrene-butadiene rubber
SE secondary electron

SEM scanning electron microscopy

SERS surface-enhanced Raman spectroscopy
SIMS secondary ion mass spectrometry

SIM selected ion monitoring
SPE solid-phase extraction
SPME solid-phase microextraction
TEA thermal energy analyser

TEM transmission electron microscopy

TFAA trifluoroacetic anhydride TGA thermogravimetric analysis THC Δ^9 -tetrahydrocannabinol

THM thermally assisted hydrolysis methylation

TLC thin layer chromatography

TMAH tetramethylammonium hydroxide

TMB tetramethylbenzidine

TOF time-of-flight

TOF-SIMS time-of-flight secondary ion mass spectrometry