

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)

Analytical Chemistry in Archaeology

An introductory manual that explains the basic concepts of chemistry behind scientific analytical techniques and that reviews their application to archaeology. It explains key terminology, outlines the procedures to be followed in order to produce good data, and describes the function of the basic instrumentation required to carry out those procedures. The manual contains chapters on the basic chemistry and physics necessary to understand the techniques used in analytical chemistry, with more detailed chapters on atomic absorption, inductively coupled plasma emission spectroscopy, neutron activation analysis, X-ray fluorescence, electron microscopy, infrared and Raman spectroscopy, and mass spectrometry. Each chapter describes the operation of the instruments, some hints on the practicalities, and a review of the application of the technique to archaeology, including some case studies. With guides to further reading on the topic, it is an essential tool for practitioners, researchers, and advanced students alike.

MARK POLLARD is Edward Hall Professor of Archaeological Science, Research Laboratory for Archaeology and the History of Art, University of Oxford.

CATHY BATT is Senior Lecturer in Archaeological Sciences, University of Bradford.

BEN STERN is Lecturer in Archaeological Sciences, University of Bradford.

SUZANNE M. M. YOUNG is NASA Researcher and Lecturer in Chemistry at Tufts University.

Cambridge University Press
978-0-521-65209-4 - Analytical Chemistry in Archaeology
A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young
Frontmatter
[More information](#)

CAMBRIDGE MANUALS IN ARCHAEOLOGY

General Editor

Graeme Barker, *University of Cambridge*

Advisory Editors

Elizabeth Slater, *University of Liverpool*

Peter Bogucki, *Princeton University*

Books in the series

Pottery in Archaeology, Clive Orton, Paul Tyers, and Alan Vince

Vertebrate Taphonomy, R. Lee Lyman

Photography in Archaeology and Conservation, 2nd edn, Peter G. Dorrell

Alluvial Geoarchaeology, A.G. Brown

Shells, Cheryl Claasen

Zooarchaeology, Elizabeth J. Reitz and Elizabeth S. Wing

Sampling in Archaeology, Clive Orton

Excavation, Steve Roskams

Teeth, 2nd edn, Simon Hillson

Lithics, 2nd edn, William Andrefsky Jr.

Geographical Information Systems in Archaeology, James Conolly and Mark Lake

Demography in Archaeology, Andrew Chamberlain

Analytical Chemistry in Archaeology, A.M. Pollard, C.M. Batt, B. Stern,
and S.M.M. Young

Cambridge Manuals in Archaeology is a series of reference handbooks designed for an international audience of upper-level undergraduate and graduate students, and professional archaeologists and archaeological scientists in universities, museums, research laboratories, and field units. Each book includes a survey of current archaeological practice alongside essential reference material on contemporary techniques and methodology.

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)

ANALYTICAL CHEMISTRY IN ARCHAEOLOGY

A.M. Pollard

*Research Laboratory for Archaeology and the History of Art,
University of Oxford, UK*

C.M. Batt and B. Stern

*Department of Archaeological Sciences,
University of Bradford, UK*

S.M.M. Young

*NASA Researcher, Department of Chemistry, Tufts University,
Medford, Massachusetts, USA*



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press
978-0-521-65209-4 - Analytical Chemistry in Archaeology
A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young
Frontmatter
[More information](#)

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521655729

© Mark Pollard, Catherine Batt, Benjamin Stern, and Suzanne M. M. Young 2006

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 2006

Printed in the United Kingdom at the University Press, Cambridge

A catalogue record for this publication is available from the British Library

ISBN-13 978-0-521-65209-4 hardback
ISBN-10 0-521-65209-X hardback
ISBN-13 978-0-521-65572-9 paperback
ISBN-10 0-521-65572-2 paperback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for
external or third-party internet websites referred to in this publication, and does not guarantee
that any content on such websites is, or will remain, accurate or appropriate.

CONTENTS

<i>List of figures</i>	<i>page ix</i>
<i>List of tables</i>	<i>xii</i>
<i>Preface</i>	<i>xiii</i>
PART I THE ROLE OF ANALYTICAL CHEMISTRY IN ARCHAEOLOGY	1
1. ARCHAEOLOGY AND ANALYTICAL CHEMISTRY	3
1.1 The history of analytical chemistry in archaeology	5
1.2 Basic archaeological questions	10
1.3 Questions of process	25
2. AN INTRODUCTION TO ANALYTICAL CHEMISTRY	31
2.1 What is chemistry?	31
2.2 Analytical chemistry	38
2.3 Special considerations in the analysis of archaeological material	42
PART II THE APPLICATION OF ANALYTICAL CHEMISTRY TO ARCHAEOLOGY	45
3. ELEMENTAL ANALYSIS BY ABSORPTION AND EMISSION SPECTROSCOPIES IN THE VISIBLE AND ULTRAVIOLET	47
3.1 Optical emission spectroscopy (OES)	47
3.2 Atomic absorption spectroscopy (AAS)	48
3.3 Inductively coupled plasma atomic emission spectroscopy (ICP–AES)	57
3.4 Comparison of analysis by absorption/emission spectrometries	60
3.5 Greek pots and European bronzes – archaeological applications of emission/absorption spectrometries	62
4. MOLECULAR ANALYSIS BY ABSORPTION AND RAMAN SPECTROSCOPY	70
4.1 Optical and UV spectrophotometry	70
4.2 Infrared absorption spectroscopy	77

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)vi *Contents*

4.3 Raman spectroscopy	83
4.4 Soils, bone, and the “Baltic shoulder” – archaeological applications of vibrational spectroscopy	85
5. X-RAY TECHNIQUES AND ELECTRON BEAM MICROANALYSIS	93
5.1 Introduction to X-rays	93
5.2 X-ray fluorescence (XRF) spectrometry	101
5.3 Electron microscopy as an analytical tool	109
5.4 X-ray diffraction	113
5.5 Other X-ray related techniques	116
5.6 A cornucopia of delights – archaeological applications of X-ray analysis	118
6. NEUTRON ACTIVATION ANALYSIS	123
6.1 Introduction to nuclear structure and the principles of neutron activation analysis	123
6.2 Neutron activation analysis in practice	128
6.3 Practical alchemy – archaeological applications of NAA	130
7. CHROMATOGRAPHY	137
7.1 Principles of chromatography	137
7.2 Classical liquid column chromatography	139
7.3 Thin layer chromatography (TLC)	139
7.4 Gas chromatography (GC)	142
7.5 High performance liquid chromatography (HPLC)	146
7.6 Sticky messengers from the past – archaeological applications of chromatography	147
8. MASS SPECTROMETRY	160
8.1 Separation of ions by electric and magnetic fields	160
8.2 Light stable isotopes (δD , $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$)	169
8.3 Heavy isotopes (Pb, Sr) – thermal ionization mass spectrometry (TIMS)	173
8.4 Combined techniques – GC–MS	174
8.5 Isotope archaeology – applications of MS in archaeology	176
9. INDUCTIVELY COUPLED PLASMA–MASS SPECTROMETRY (ICP–MS)	195
9.1 Types of ICP analysis	195
9.2 Comparison with other techniques	200
9.3 Instrument performance	202
9.4 Splitting hairs – archaeological applications of ICP–MS	208

<i>Contents</i>	vii
PART III SOME BASIC CHEMISTRY FOR ARCHAEOLOGISTS	215
10. ATOMS, ISOTOPES, ELECTRON ORBITALS, AND THE PERIODIC TABLE	217
10.1 The discovery of subatomic particles	217
10.2 The Bohr–Rutherford model of the atom	227
10.3 Stable and radioactive isotopes	230
10.4 The quantum atom	238
10.5 The periodic table	243
11. VALENCY, BONDING, AND MOLECULES	249
11.1 Atoms and molecules	249
11.2 Bonds between atoms	253
11.3 Intermolecular bonds	258
11.4 Lewis structures and the shapes of molecules	260
11.5 Introduction to organic compounds	263
11.6 Isomers	269
12. THE ELECTROMAGNETIC SPECTRUM	275
12.1 Electromagnetic waves	275
12.2 Particle–wave duality	279
12.3 Emission lines and the Rydberg equation	281
12.4 Absorption of EM radiation by matter – Beer’s law	286
12.5 The EM spectrum and spectrochemical analysis	288
12.6 Synchrotron radiation	290
13. PRACTICAL ISSUES IN ANALYTICAL CHEMISTRY	294
13.1 Some basic procedures in analytical chemistry	294
13.2 Sample preparation for trace element and residue analysis	302
13.3 Standards for calibration	306
13.4 Calibration procedures and estimation of errors	309
13.5 Quality assurance procedures	319
<i>Epilogue</i>	322
<i>Appendices</i>	326
I Scientific notation	326
II Significant figures	327
III Seven basic SI units	328
IV Physical constants	329
V Greek notation	330
VI Chemical symbols and isotopes of the elements	331
VII Electronic configuration of the elements (to radon, $Z = 86$)	335

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)viii *Contents*

VIII Some common inorganic and organic sample preparation methods used in archaeology	337
IX General safe practice in the laboratory	340
X COSHH assessments	342
<i>References</i>	350
<i>Index</i>	391

FIGURES

3.1	Schematic diagram of an AAS spectrometer	<i>page</i> 51
3.2	Beam chopper in AAS	52
3.3	Schematic diagram of an ICP torch	58
3.4	Schematic comparison of limits of detection in solution for various absorption/emission spectrometries	61
3.5	A “decision tree” for allocating European Bronze Age copper alloys to metal type	65
4.1	Copper sulfate pentaquo complex	71
4.2	Schematic diagram of a charge-coupled device (CCD) imaging sensor	76
4.3	Vibrational modes of a nonlinear triatomic molecule such as H ₂ O	78
4.4	Infrared correlation chart	79
4.5	Schematic diagram of a Fourier transform infrared (FTIR) spectrometer	81
4.6	Infrared absorption spectrum of phosphomolybdenum blue solution	86
4.7	Measurement of crystallinity index from IR spectrum of bone apatite	88
4.8	Infrared absorption spectrum of amber from the Baltic coast	90
4.9	FT–Raman spectrum of mammalian ivory	91
5.1	The X-ray emission and Auger processes	95
5.2	Electronic transitions giving rise to the K X-ray emission spectrum of tin	97
5.3	K and L absorption edges of tungsten	98
5.4	X-ray tube output spectrum	100
5.5	Comparison of EDXRF and WDXRF detection systems	103
5.6	Interaction of a beam of primary electrons with a thin solid sample	110
5.7	Derivation of Bragg’s law of X-ray diffraction	114
5.8	A Debye–Scherrer powder camera for X-ray diffraction	116
6.1	Schematic diagram of the nuclear processes involved in NAA	125
7.1	Diagram of classical liquid column chromatography	140
7.2	Diagram of a TLC plate	142
7.3	Derivatization of organic acid and alcohol compounds	143
7.4	Schematic diagram of a gas chromatography (GC) system	144
7.5	Schematic diagram of a high performance liquid chromatography (HPLC) system	147
7.6	Possible transformation processes of residues in or on pottery vessels	150
7.7	Structures of some fatty acids and sterols found in archaeological residues	151
7.8	2-methylbutadiene (C ₅ H ₈), “the isoprene unit”	153
7.9	Some diagnostic triterpenoid compounds from birch bark tar	155
7.10	Some triterpenoid compounds found in mastic (<i>Pistacia</i> resin)	156
7.11	C ₄₀ wax ester	157

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)x *Figures*

7.12	Potential biomarkers in bitumen	158
8.1	Schematic diagram of electron impact (EI) source for mass spectrometry	162
8.2	Schematic diagrams of single focusing and double focusing mass spectrometers	165
8.3	Schematic diagram of a quadrupole mass spectrometer	167
8.4	Typical total ion count (TIC) of a bitumen extract from an archaeological shard obtained by GC-MS	176
8.5	Mass chromatogram for $m/z = 71$	176
8.6	Mass spectrum of C_{34} <i>n</i> -alkane ($C_{34}H_{70}$)	178
8.7	Relationship between bone collagen carbon isotope ratio and latitude for modern carnivorous terrestrial mammals	180
8.8	Variations in mammalian bone collagen carbon and nitrogen isotope values over the last 40 000 radiocarbon years	181
8.9	Carbon isotope composition of human bone collagen from the lower Illinois Valley, North America	183
8.10	Carbon isotope ratios in bone collagen plotted against radiocarbon ages for British Mesolithic and Neolithic humans	187
8.11	Kernel density estimate of the lead isotope data for part of the Troodos orefield, Cyprus	193
9.1	The number of published scientific papers (1981–2003) with keywords relating to ICP and NAA	196
9.2	Schematic diagram of a quadrupole ICP-MS	198
9.3	Schematic diagram of a multicollector ICP-MS (MC-ICP-MS)	200
9.4	The first and second ionization energies for selected elements	203
9.5	ICP-MS survey data from masses 203 to 210	204
9.6	Examples of calibration lines produced during ICP-MS analysis	205
9.7	Sensitivity as a function of mass number in ICP-MS analysis	206
9.8	Trace element profile along a single hair using LA-ICP-MS	211
9.9	REE abundances from archaeological glass, showing the effect of chondrite normalization	212
10.1	Thomson's method for measuring e/m , the mass-to-charge ratio of an electron	223
10.2	The radioactive stability of the elements	232
10.3	Schematic diagram of the four common modes of radioactive decay	237
10.4	Shapes of the <i>s</i> , <i>p</i> , and <i>d</i> atomic orbitals	240
10.5	Energy levels of atomic orbitals	242
10.6	The modern "extended" periodic table	246
11.1	Simple model of valency and bonding	253
11.2	Electronegativity values (χ) for the elements	255
11.3	Arrangement of atoms in an ionic solid such as NaCl	255
11.4	Metallic bonding	256
11.5	Covalent bonding	257
11.6	Variation of bond energy with interatomic distance for the hydrogen molecule	258
11.7	van der Waals' bond caused by the creation of an instantaneous dipole	259

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)

<i>Figures</i>	xi
11.8 Dipole–dipole bonds in polar molecules such as HCl	260
11.9 Hydrogen bonding	261
11.10 Lewis structures of water (H ₂ O)	262
11.11 The resonance structure of a generalized organic acid RCOO [−]	263
11.12 The three-dimensional tetrahedral structure of carbon	264
11.13 Hybridization of <i>s</i> - and <i>p</i> - atomic orbitals	265
11.14 σ - and π -bond formation	266
11.15 Four different representations of the structure of <i>n</i> -hexane, C ₆ H ₁₄	267
11.16 The Kekulé structures of benzene (C ₆ H ₆)	267
11.17 Structure of 1,4-hexadiene	269
11.18 Two conformational isomers of ethane, C ₂ H ₆	272
11.19 Two structural isomers having the molecular formula C ₄ H ₁₀	272
11.20 Diastereoisomers of 2-butene	273
11.21 Stereoisomerism in 2-iodobutane (CH ₃ CH ₂ CHICH ₃)	273
11.22 Determination of absolute configuration of a stereoisomer	274
12.1 Constructive and destructive interference	277
12.2 Sine wave representation of electromagnetic radiation	278
12.3 Regions of the electromagnetic spectrum	279
12.4 Young's slits	280
12.5 The photoelectric effect	280
12.6 The emission spectrum of hydrogen in the UV, visible, and near infrared	282
12.7 Electronic transitions giving rise to the emission spectrum of sodium in the visible	284
12.8 Schematic plan of a synchrotron	291
13.1 Illustration of the terms <i>accuracy</i> and <i>precision</i> in analytical chemistry	314
13.2 Plot of hypothetical calibration data from Table 13.1	315

TABLES

7.1 Definition of the four main chromatographic techniques	<i>page</i> 138
7.2 Structural formulas of the terpenoids groups	154
8.1 Typical mass fragment ions encountered during GC–MS of organic archaeological compounds	177
8.2 Some of the isotopes used in “isotope archaeology”	179
9.1 Abundance of REE in a chondrite meteorite used for normalization	213
10.1 Definition of electron orbitals in terms of the four orbital quantum numbers (n, l, m_l, s)	241
11.1 Examples of calculating valency from the combining capacity of some simple compounds	251
11.2 Prefix for the number of carbons in the parent chain when naming organic compounds	268
11.3 Some common organic functional groups	270
12.1 The wavelengths of the major spectral lines in the emission spectrum of sodium	284
12.2 Relationship between the wavelength and source of electromagnetic radiation	289
13.1 Some hypothetical analytical calibration data	315
13.2 Critical values of t at the 95% confidence interval	317

PREFACE

The purpose of this book is to provide an introduction to the applications of analytical chemistry to archaeology. The intended audience is advanced students of archaeology, who may not have all of the required background in chemistry and physics, but who need either to carry out analytical procedures, or to use the results of such analyses in their studies. The book is presented in three parts. The first is intended to contextualize analytical chemistry for students of archaeology – it illustrates some of the archaeological questions which have been addressed, at least in part, by chemical analysis, and also chronicles some of the long history of interaction between chemistry and archaeology. Additionally, it introduces chemistry as a scientific discipline, and gives a brief historical introduction to the art and science of analytical chemistry.

The second part consists of seven chapters, which present a range of analytical techniques that have found archaeological application, grouped by their underlying scientific principles (absorption/emission of visible light, absorption of infrared, etc.). Each chapter describes the principles and instrumentation of the methods in some detail, using mathematics where this amplifies a point. The majority of each chapter, however, is devoted to reviewing the applications of the techniques to archaeology. We do not pretend that these application reviews are comprehensive, although we do hope that there are enough relevant references to allow the interested reader to find her or his way into the subject in some depth. We have also tried to be critical (without engaging in too much controversy), since the role of a good teacher is to instill a sense of enthusiastic but critical enquiry! Nor can we pretend that the topics covered in these chapters are exhaustive in terms of describing all of the analytical methods that have been, or could profitably be, applied to serious questions in archaeology. The critical reader will no doubt point out that her or his favorite application (e.g., NMR, thermal methods, etc.) is missing. All that we can say is that we have attempted to deal with those methods that have contributed the most over the years to archaeological chemistry. Perhaps more attention could usefully have been applied to a detailed analysis of how chemical data has been used in archaeology, especially when hindsight suggests that this has been unhelpful. It is a matter of some

Cambridge University Press

978-0-521-65209-4 - Analytical Chemistry in Archaeology

A. M. Pollard, C. M. Batt, B. Stern and S. M. M. Young

Frontmatter

[More information](#)xiv *Preface*

debate as to whether it is worse to carry out superb chemistry in support of trivial or meaningless archaeology, or to address substantial issues in archaeology with bad chemistry. That, however, could fill another book!

In order for the intended audience of students to become “informed customers” or, better still, trainee practitioners, we present in the final part some of the basic science necessary to appreciate the principles and practice underlying modern analytical chemistry. We hope that this basic science is presented in such a way that it might be useful for students of other applied chemistry disciplines, such as environmental chemistry or forensic chemistry, and even that students of chemistry might find some interest in the applications of archaeological chemistry.

Chapters 10 and 11 introduce basic concepts in chemistry, including atomic theory and molecular bonding, since these are necessary to understand the principles of spectrometry, and an introduction to organic chemistry. Chapter 12 discusses some basic physics, including wave motion and the interaction of electromagnetic waves with solid matter. Chapter 13 is an introduction to some of the practicalities of analytical chemistry, including how to make up standard solutions, how to calibrate analytical instruments, and how to calculate such important parameters as the minimum detectable level of an analyte, and how to estimate errors. We also outline quality assurance protocols, and good practice in laboratory safety. Much of this material has been used in teaching the underlying maths, physics, and chemistry on the BSc in Archaeological Science at the University of Bradford, in the hope that these students will go on to become more than “intelligent consumers” of analytical chemistry. It is gratifying to see that a number of ex-students have, indeed, contributed significantly to the literature of archaeological chemistry.

In this background material, we have taken a decidedly historical approach to the development of the subject, and have, where possible, made reference to the original publications. It is surprising and slightly distressing to see how much misinformation is propagated through the modern literature because of a lack of acquaintance with the primary sources. We have also made use of the underlying mathematics where it (hopefully) clarifies the narrative. Not only does this give the student the opportunity to develop a quantitative approach to her or his work, but it also gives the reader the opportunity to appreciate the underlying beauty of the structure of science.

This book has been an embarrassing number of years in gestation. We are grateful for the patience of Cambridge University Press during this process. We are also grateful to a large number of individuals, without whom such a work could not have been completed (including, of course, Newton’s Giants!). In particular, we are grateful to Dr Janet Montgomery, who helped to collate some of the text and sought out references, and to Judy Watson, who constructed the figures. All errors are, of course, our own.