

ENCYCLOPEDIA OF
ANALYTICAL SCIENCE

SECOND
EDITION

VOLUME

4
G-I

REFERENCE

QD
71.5
E53
2005
v. 4

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REF

ENCYCLOPEDIA
— OF —
ANALYTICAL
SCIENCE
SECOND EDITION

ENCYCLOPEDIA
— OF —
ANALYTICAL
SCIENCE
SECOND EDITION

Editors

PAUL WORSFOLD
ALAN TOWNSHEND
COLIN POOLE



Amsterdam Boston Heidelberg London New York Oxford
Paris San Diego San Francisco Singapore Sydney Tokyo

Elsevier Ltd., The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK
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MASS SPECTROMETRY /Forensic Applications

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PHARMACEUTICAL ANALYSIS /Drug Purity Determination**

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AIR ANALYSIS /Workplace Air

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Library of Congress Control Number: 2004104444

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

ISBN 0-12-764100-9

General Library System
University of Wisconsin - Madison
728 State Street
Madison, WI 53706-1494
U.S.A.

This book is printed on acid-free paper
Printed and bound in Spain

Contents

Volume 1

A

ACCREDITATION <i>See</i> QUALITY ASSURANCE: Accreditation	
ACID-BASE INDICATORS <i>See</i> INDICATORS: Acid-Base	
ACID-BASE TITRATION <i>See</i> TITRIMETRY: Overview; Potentiometric; Photometric	
ACTIVATION ANALYSIS	
Neutron Activation <i>SJ Parry</i>	1
Charged-Particle Activation <i>K Strijckmans</i>	10
Photon Activation <i>D Schulze, C Segebade</i>	20
ADHESIVES AND SEALANTS <i>RG Leonard, K Quigley</i>	28
AFFINITY CHROMATOGRAPHY <i>See</i> LIQUID CHROMATOGRAPHY: Affinity Chromatography	
AFM <i>See</i> MICROSCOPY TECHNIQUES: Atomic Force and Scanning Tunneling Microscopy	
AIR ANALYSIS	
Sampling <i>J McQuaid</i>	37
Outdoor Air <i>RM Harrison</i>	43
Workplace Air <i>J Yu, RMA Hahne</i>	48
ALCOHOL <i>See</i> ETHANOL. FORENSIC SCIENCES: Alcohol in Body Fluids	
ALKALOIDS <i>R Verpoorte</i>	56
ALKYLLEAD SPECIES <i>See</i> LEAD	
AMINO ACIDS <i>SM Lunte</i>	61
AMPEROMETRIC OXYGEN SENSORS <i>See</i> SENSORS: Amperometric Oxygen Sensors	
AMPEROMETRY <i>SB Adeloju</i>	70
AMPHETAMINES <i>JT Cody</i>	80
AMPLIFICATION REACTIONS <i>JM Wages Jr.</i>	88
ANALYTICAL REAGENTS	
Specification <i>EJ Newman</i>	96
Purification <i>EJ Newman</i>	103
ANODIC STRIPPING VOLTAMMETRY <i>See</i> VOLTAMMETRY: Anodic Stripping	
ANTIOXIDANTS <i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Antioxidants and Preservatives	
ANTIQUES <i>See</i> ARCHAEOLOGY AND ANTIQUE ANALYSIS: Dating of Artefacts; Metallic and Ceramic Objects; Art and Conservation; Organic and Biological Materials	
ARCHAEOLOGY AND ANTIQUE ANALYSIS	
Dating of Artefacts <i>J Ambers</i>	109
Metallic and Ceramic Objects <i>LT Gibson</i>	117
Art and Conservation <i>LT Gibson</i>	123
Organic and Biological Materials <i>M Richards</i>	127

ARSENIC	<i>A Raab, J Feldmann</i>	132
ASBESTOS	<i>H Janik, M Wrona</i>	141
ASV	<i>See</i> VOLTAMMETRY: Anodic Stripping	
ATMOSPHERIC ANALYSIS	<i>See</i> AIR ANALYSIS: Sampling; Outdoor Air; Workplace Air	
ATOMIC ABSORPTION SPECTROMETRY		
Principles and Instrumentation	<i>EH Ivanova</i>	149
Interferences and Background Correction	<i>DJ Butcher</i>	157
Flame	<i>SJ Hill</i>	163
Electrothermal	<i>P Fodor, I Ipolyi</i>	170
Vapor Generation	<i>R Sturgeon</i>	180
ATOMIC EMISSION SPECTROMETRY		
Principles and Instrumentation	<i>RM Tuymman</i>	190
Interferences and Background Correction	<i>RM Tuymman</i>	198
Flame Photometry	<i>EE Pickett</i>	203
Inductively Coupled Plasma	<i>JM Mernet</i>	210
Microwave-Induced Plasma	<i>GM Greenway</i>	215
ATOMIC FLUORESCENCE SPECTROMETRY	<i>DJ Butcher</i>	221
ATOMIC FORCE MICROSCOPY	<i>See</i> MICROSCOPY TECHNIQUES: Atomic Force and Scanning Tunneling Microscopy	
ATOMIC MASS SPECTROMETRY		
Inductively Coupled Plasma	<i>EH Evans</i>	229
Laser Microprobe	<i>L Van Vaeck</i>	237
ATOMIC SPECTROMETRY		
Overview	<i>JA Holcombe</i>	249
AUGER ELECTRON SPECTROSCOPY	<i>See</i> SURFACE ANALYSIS: Auger Electron Spectroscopy	
B		
BACKGROUND CORRECTION	<i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Interferences and Background Correction. ATOMIC EMISSION SPECTROMETRY: Interferences and Background Correction	
BIOASSAYS		
Overview	<i>J Chayen, L Bitemsky</i>	259
Microbial Tests	<i>N Christof</i>	265
Bioautography	<i>L Botz, B Kocsis, S Nagy</i>	271
BIOCHEMICAL OXYGEN DEMAND	<i>See</i> WATER ANALYSIS: Biochemical Oxygen Demand	
BIOLUMINESCENCE	<i>LJ Kricka</i>	277
BIOSENSORS	<i>See</i> SENSORS: Overview	
BLEACHES AND STERILANTS	<i>MA Busch, KW Busch</i>	284
BLOOD AND PLASMA	<i>EA Stein, J Pum</i>	294
BOD	<i>See</i> WATER ANALYSIS: Biochemical Oxygen Demand	

BUFFER SOLUTIONS	<i>A Hulanicki, S Glab</i>	300
BUILDING MATERIALS	<i>LW Cheriton, JP Gupta</i>	304
C		
CADMIUM	<i>A Rodríguez-Cea, MR Fernández de la Campa, A Sanz-Medel</i>	315
CALORIMETRIC SENSORS	<i>See SENSORS: Calorimetric/Enthalpimetric</i>	
CAPILLARY ELECTROCHROMATOGRAPHY	<i>M Macka, PR Haddad</i>	323
CAPILLARY ELECTROPHORESIS		
Overview	<i>M Bowser</i>	334
Pharmaceutical Applications	<i>GKE Scriba</i>	343
Low-Molecular-Weight Ions	<i>V Pacáková, K Štulík</i>	354
Environmental Applications	<i>Y Picó</i>	362
Food Chemistry Applications	<i>RA Frazier</i>	374
Clinical Applications	<i>ZK Shihabi</i>	381
CARBOHYDRATES		
Overview	<i>AM Stephen, EH Merrifield</i>	392
Sugars – Spectrophotometric Methods	<i>SC Churms</i>	408
Sugars – Chromatographic Methods	<i>SC Churms</i>	414
Sugar Alcohols	<i>ME Legaz, C Vicente</i>	427
Starch	<i>G Mitchell</i>	440
Dietary Fiber Measured as Nonstarch Polysaccharides in Plant Foods	<i>HN Englyst, GJ Hudson, ME Quigley</i>	448
CARBON	<i>M Nimmo</i>	453
CATALYTIC TECHNIQUES	<i>See KINETIC METHODS: Catalytic Techniques</i>	
CATHODIC STRIPPING VOLTAMMETRY	<i>See VOLTAMMETRY: Cathodic Stripping</i>	
CEMENT	<i>PW Hurley, RG Pritchard</i>	458
CENTRIFUGATION		
Analytical Ultracentrifugation	<i>A Furst, DN Taulbee</i>	463
Preparative	<i>DN Taulbee, A Furst</i>	469
CERAMICS	<i>GJ Oliver, RN White</i>	481
CEREBROSPINAL FLUID	<i>EJ Thompson</i>	489
CERTIFIED REFERENCE MATERIALS	<i>See QUALITY ASSURANCE: Reference Materials; Production of Reference Materials</i>	
CHARGE COUPLED DEVICES	<i>See OPTICAL SPECTROSCOPY: Detection Devices</i>	
CHEMICAL OXYGEN DEMAND	<i>See WATER ANALYSIS: Chemical Oxygen Demand</i>	
CHEMICAL WARFARE AGENTS	<i>PA D'Agostino</i>	495
CHEMICALLY MODIFIED ELECTRODES	<i>See SENSORS: Chemically Modified Electrodes</i>	
CHEMILUMINESCENCE		
Overview	<i>NW Barnett, PS Francis</i>	506
Liquid-Phase	<i>NW Barnett, PS Francis</i>	511
Gas-Phase	<i>NW Barnett, PS Francis, JS Lancaster</i>	521
Electrogenerated	<i>J Kankare, S Kulmala</i>	528

Volume 2

CHEMOMETRICS AND STATISTICS	
Statistical Techniques	<i>JN Miller</i> 1
Experimental Design	<i>G Hanrahan, J Zhu, S Gibani, DG Patil</i> 8
Optimization Strategies	<i>RG Brereton</i> 13
Multivariate Classification Techniques	<i>MJ Adams</i> 21
Multivariate Calibration Techniques	<i>G Hanrahan, F Udeh, DG Patil</i> 27
Expert Systems	<i>MJ Adams</i> 33
Multicriteria Decision Making	<i>S Kokot, GA Ayoko</i> 40
Signal Processing	<i>RG Brereton</i> 46
Spectral Deconvolution and Filtering	<i>RG Brereton</i> 51
CHIROPTICAL ANALYSIS	<i>H-G Kuball</i> 60
CHLOROFLUOROCARBONS AND OTHER HALOCARBONS	<i>DE Oram</i> 80
CHROMATOGRAPHY	
Overview	<i>VR Meyer</i> 89
Principles	<i>VR Meyer</i> 98
Multidimensional Techniques	<i>PJ Marriott, D Ryan</i> 105
CHROMIUM	<i>M Sperling</i> 113
CLINICAL ANALYSIS	
Overview	<i>ID Watson</i> 126
Sample Handling	<i>F Bressolle, O Nicolas, MT Kelly</i> 133
Electrolytes in Physiological Samples	<i>WR K��lpmann</i> 141
Glucose	<i>HM Heise, PU Abel</i> 152
Sarcosine, Creatine, and Creatinine	<i>T Smith-Palmer</i> 166
Inborn Errors of Metabolism	<i>DH Chace</i> 174
COAL AND COKE	<i>JA Pajares, MA D��ez</i> 182
COD	<i>See WATER ANALYSIS: Chemical Oxygen Demand</i>
COFFEE	<i>See FOOD AND NUTRITIONAL ANALYSIS: Coffee, Cocoa, and Tea</i>
COKE	<i>See COAL AND COKE</i>
COLLOIDS	<i>See FIELD-FLOW FRACTIONATION. WATER ANALYSIS: Particle Characterization</i>
COLOR MEASUREMENT	<i>JB Hutchings</i> 198
COMPLEXOMETRIC TITRATIONS	<i>See TITRIMETRY: Overview; Potentiometric; Photometric</i>
COMPUTER MODELING	<i>J Mocak</i> 208
CONDUCTIMETRY AND OSCILLOMETRY	<i>TS Light</i> 217
CONTINUOUS-FLOW ANALYSIS <i>See FLOW ANALYSIS: Overview. FLOW INJECTION ANALYSIS: Principles; Instrumentation; Detection Techniques; Environmental and Agricultural Applications; Clinical and Pharmaceutical Applications; Industrial Applications. SEGMENTED FLOW ANALYSIS. SEQUENTIAL INJECTION ANALYSIS</i>	
COSMETICS AND TOILETRIES	<i>A Salvador, MC Pascual-Mart��</i> 226
COULOMETRY	<i>PC Hauser</i> 234

COUNTERCURRENT CHROMATOGRAPHY

Overview	<i>Y Ito</i>	241
Solvent Extraction with a Helical Column	<i>Y Ito</i>	252
CRMs	<i>See QUALITY ASSURANCE: Reference Materials; Production of Reference Materials</i>	
CSV	<i>See VOLTAMMETRY: Cathodic Stripping</i>	
CYCLIC VOLTAMMETRY	<i>See VOLTAMMETRY: Linear Sweep and Cyclic</i>	

D

DAIRY PRODUCTS	<i>See FOOD AND NUTRITIONAL ANALYSIS: Dairy Products</i>	
DERIVATIZATION OF ANALYTES	<i>S Görög</i>	263
DETERGENTS	<i>See SURFACTANTS AND DETERGENTS</i>	
DIALYSIS	<i>See MEMBRANE TECHNIQUES: Dialysis and Reverse Osmosis</i>	
DIFFERENTIAL SCANNING CALORIMETRY	<i>See THERMAL ANALYSIS: Overview; Temperature-Modulated Techniques; Coupled Techniques; Sample-Controlled Techniques; Nonbasic Techniques</i>	
DIODE ARRAY	<i>See SPECTROPHOTOMETRY: Diode Array</i>	
DIOXINS	<i>K Kannan, KM Aldous</i>	274
DISSOLUTION TESTING	<i>See PHARMACEUTICAL ANALYSIS: Dissolution Testing</i>	
DISTILLATION	<i>JD Green</i>	281
DNA SEQUENCING	<i>KR Mitchelson</i>	286
DRUG METABOLISM		
Overview	<i>SA Roberts</i>	293
Metabolite Isolation and Identification	<i>IP Nnane, X Tao</i>	305
Isotope Studies	<i>IP Nnane, X Tao</i>	311
DRUG SCREENING IN SPORT	<i>See FORENSIC SCIENCES: Drug Screening in Sport</i>	
DRY ASHING	<i>See SAMPLE DISSOLUTION FOR ELEMENTAL ANALYSIS: Dry Ashing</i>	

E

ELECTROGRAVIMETRY	<i>AR Hillman</i>	317
ELECTRON ENERGY LOSS SPECTROMETRY	<i>J Verbeeck, S Hens, P Potapov, D Schryvers</i>	324
ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY	<i>See ELECTRON SPIN RESONANCE SPECTROSCOPY: Principles and Instrumentation; Specialized Techniques; Biological Applications</i>	
ELECTRON SPIN RESONANCE SPECTROSCOPY		
Principles and Instrumentation	<i>CJ Rhodes</i>	332
Specialized Techniques	<i>CJ Rhodes, H Morris</i>	337
Biological Applications	<i>AF Vanin, EEH van Faassen</i>	344
ELECTROPHORESIS		
Overview	<i>R Stringer</i>	356
Principles	<i>B Gas</i>	363
Isotachophoresis	<i>L Křivánková, P Boček</i>	370

xxii CONTENTS

Isoelectric Focusing	<i>PG Righetti</i>	382
Electrophoresis in Ionic Liquids	<i>CF Poole</i>	392
Polyacrylamide Gels	<i>PG Righetti</i>	396
Two-Dimensional Gels	<i>PG Righetti</i>	407
Affinity Techniques	<i>TC Bøg-Hansen</i>	419
Blotting Techniques	<i>BT Kurten, R Hal Scofield</i>	425
Carbohydrates	<i>H Scherz, CW Huck, GK Born</i>	433
Clinical Applications	<i>JA Beeley</i>	445
Nucleic Acids	<i>CM Roth</i>	456
Proteins	<i>V Kašička</i>	460
ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY <i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Electrothermal		
ELEMENTAL SPECIATION		
Overview	<i>A Sanz-Medel, ML Fernández-Sanchez</i>	472
Waters, Sediments, and Soils	<i>GE Batley, SC Apte</i>	481
Practicalities and Instrumentation	<i>DJ Butcher</i>	488
ENDOCRINE DISRUPTING CHEMICALS	<i>F Regan, B Fogarty</i>	495
ENTHALPIMETRIC SENSORS <i>See</i> SENSORS: Calorimetric/Enthalpimetric		
ENVIRONMENTAL ANALYSIS	<i>R Sandford, P Worsfold</i>	502
ENZYMES		
Overview	<i>A Narváez, E Domínguez</i>	508
Immobilized Enzymes	<i>RM Tuymann</i>	523
Enzyme-Based Electrodes	<i>FW Scheller, D Pfeiffer, F Schubert, U Wollenberger</i>	529
Enzymes in Physiological Samples	<i>N Kiba</i>	536
Industrial Products and Processes	<i>P Williams</i>	544
Enzyme-Based Assays	<i>K Matsumoto, H Ukedo</i>	549
ESSENTIAL OILS	<i>RPW Scott</i>	554
ESTROGENS <i>See</i> ENDOCRINE DISRUPTING CHEMICALS		
ETAAS <i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Electrothermal		
ETHANOL	<i>WJ Criddle</i>	562
EXPERT SYSTEMS <i>See</i> CHEMOMETRICS AND STATISTICS: Expert Systems		
EXPLOSIVES <i>See</i> FORENSIC SCIENCES: Explosives		
EXTRACTION		
Solvent Extraction Principles	<i>AM Sastre, J Szymanowski</i>	569
Solvent Extraction: Multistage Countercurrent Distribution	<i>CF Poole</i>	577
Microwave-Assisted Solvent Extraction	<i>JL Luque-García</i>	584
Pressurized Fluid Extraction	<i>JL Luque-García</i>	591
Supercritical Fluid Extraction	<i>E Björklund, C Sparr-Eskilsson</i>	597
Solid-Phase Extraction	<i>JS Fritz</i>	604
Solid-Phase Microextraction	<i>C Ross, J Pawliszyn</i>	608

Volume 3

F

FAAS *See* ATOMIC ABSORPTION SPECTROMETRY: Flame
FATS *See* FOOD AND NUTRITIONAL ANALYSIS: Oils and Fats

FATTY ACIDS <i>See</i> LIPIDS: Fatty Acids	
FERTILIZERS <i>JH Falls, SA Siegel</i>	1
FFF <i>See</i> FIELD-FLOW FRACTIONATION	
FIA <i>See</i> FLOW INJECTION ANALYSIS: Principles; Instrumentation; Detection Techniques; Environmental and Agricultural Applications; Clinical and Pharmaceutical Applications; Industrial Applications	
FIBERS <i>See</i> FORENSIC SCIENCES: Fibers. TEXTILES: Natural; Synthetic	
FIELD-FLOW FRACTIONATION <i>R Beckett</i>	9
FILTRATION <i>See</i> MEMBRANE TECHNIQUES: Ultrafiltration	
FINGERPRINTS <i>See</i> FORENSIC SCIENCES: Fingerprint Techniques	
FIRE ASSAY <i>GL Everett</i>	17
FLAME ATOMIC ABSORPTION SPECTROMETRY <i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Flame	
FLAME PHOTOMETRY <i>See</i> ATOMIC EMISSION SPECTROMETRY: Flame Photometry	
FLOTATION <i>See</i> FOAM FRACTIONATION AND FLOTATION	
FLOW ANALYSIS	
Overview <i>EAG Zagatto, PJ Worsfold</i>	24
FLOW INJECTION ANALYSIS	
Principles <i>MD Luque de Castro</i>	31
Instrumentation <i>MD Luque de Castro</i>	39
Detection Techniques <i>M Miró, W Frenzel</i>	48
Environmental and Agricultural Applications <i>M Miró, W Frenzel</i>	57
Clinical and Pharmaceutical Applications <i>JM Calatayud, MC Icardo</i>	76
Industrial Applications <i>AF Danet, M Badea</i>	89
FLUORESCENCE	
Overview <i>ME Díaz-García, R Badía-Laiño</i>	97
Instrumentation <i>JN Miller</i>	106
Multidimensional Fluorescence Spectrometry <i>TT Ndou, IM Warner, JB Zung</i>	112
High-Resolution Techniques <i>C Gooijer, F Ariese, NH Velthorst</i>	119
Time-Resolved Fluorescence <i>M E Díaz-García, R Badía-Laiño</i>	128
Derivatization <i>ME Díaz-García, R Badía-Laiño</i>	138
Fluorescence Labeling <i>ME Díaz-García, R Badía-Laiño</i>	149
Quantitative Analysis <i>JN Miller</i>	163
Clinical and Drug Applications <i>A Gómez-Hens</i>	170
Environmental Applications <i>SR Bravo</i>	178
Food Applications <i>A Gómez-Hens</i>	186
FOAM FRACTIONATION AND FLOTATION <i>M Hiraide</i>	195
FOOD AND NUTRITIONAL ANALYSIS	
Overview <i>V Jain, K Gupta</i>	202
Sample Preparation <i>K Matsumoto, H Ukeda</i>	211
Additives <i>M Gallego, M González</i>	217
Antioxidants and Preservatives <i>MH Gordon</i>	225
Contaminants <i>M O'Keeffe</i>	230
Water and Minerals <i>M González, V González</i>	241
Pesticide Residues <i>K Mastovska</i>	251

Mycotoxins	M Driffeld	261
Soft Drinks	J Sadecka, J Polonsky	272
Coffee, Cocoa, and Tea	SY Tse	279
Alcoholic Beverages	JF Cacho, R Lopez	285
Wine	MT Kelly, A Blaise	292
Meat and Meat Products	M O'Keeffe	302
Dairy Products	RJ Marshall	312
Vegetables and Legumes	RJ Pither	320
Oils and Fats	EW Hammond	328
Fruits and Fruit Products	RJ Pither	334
Packaging Materials	AW Lord	341

FORENSIC SCIENCES

Overview	P Margot	352
Alcohol in Body Fluids	F Moriya	358
Arson Residues	M Baron	365
Blood Analysis	C Brandt-Casadevall, N Dimo-Simonin	373
Carbon Monoxide and Cyanide from Fire and Accident	CN Gray	379
DNA profiling	R Cognoz	384
Drug Screening in Sport	L Rivier	391
Explosives	R Sleeman, JF Carter	400
Fibers	N Watson	406
Fingerprint Techniques	C Lennard	414
Glass	JA Lambert	423
Gunshot Residues	SW Lewis, KM Agg, SJ Gutowski, P Ross	430
Hair	N Watson	436
Illicit Drugs	NN Daéid	446
Paints, Varnishes, and Lacquers	P Buzzini, W Stoecklein	453
Questioned Documents	C Neumann, WD Mazzella	465
Systematic Drug Identification	NN Daéid	471
Thin-Layer Chromatography	RE Ardrey	481
Volatile Substances	RJ Flanagan	486

FOURIER TRANSFORM TECHNIQUES

PF Bernath

498

FRUITS See FOOD AND NUTRITIONAL ANALYSIS: Fruits and Fruit Products

FT TECHNIQUES See FOURIER TRANSFORM TECHNIQUES

FUELS

Gaseous	H Müller	505
Oil-Based	M Raudon	512

FULVIC SUBSTANCES See HUMIC AND FULVIC COMPOUNDS

FUNCTIONAL GROUP ANALYSIS

K Nakashima, K Inai

519

Volume 4

G

GAMMA-RAY SPECTROSCOPY See RADIOCHEMICAL METHODS: Gamma-Ray Spectrometry

GAS CHROMATOGRAPHY

Overview	K Robards	1
Principles	PJ Marriot	7
Column Technology	CF Poole	18

Gas-Solid Chromatography	<i>VG Berezkin</i>	35
Multidimensional Techniques	<i>PJ Marriott</i>	39
High-Temperature Techniques	<i>W Blum, R Aichholz</i>	47
High-Speed Techniques	<i>PJ Marriott, RA Shellie</i>	58
Instrumentation	<i>CF Poole</i>	65
Online Coupled LC-GC	<i>K Grob</i>	74
Pyrolysis	<i>TP Wampler</i>	81
Detectors	<i>CF Poole</i>	95
Mass Spectrometry	<i>DJ Harvey</i>	106
Fourier Transform Infrared Spectroscopy	<i>PR Griffiths</i>	116
Physicochemical Measurements	<i>T Paryczak, J Rynkowski, MI Szyrkowska</i>	122
Environmental Applications	<i>MT Galceran, FJ Santos</i>	129
Forensic Applications	<i>H Neumann</i>	139
Petrochemical Applications	<i>ER Adlard</i>	146
Chiral Separations	<i>V Schurig</i>	152
GAS SENSING PROBES <i>See</i> ION-SELECTIVE ELECTRODES: Gas Sensing Probes		
GASEOUS FUELS <i>See</i> FUELS: Gaseous		
GASTRIC JUICES	<i>TJ Gana, J Koo</i>	161
GEL PERMEATION CHROMATOGRAPHY <i>See</i> LIQUID CHROMATOGRAPHY: Size-Exclusion		
GEOCHEMISTRY		
Inorganic	<i>C Trueman</i>	171
Sediment	<i>GE Millward</i>	181
Soil, Major Inorganic Components	<i>H van der Jagt</i>	188
Soil, Minor Inorganic Components	<i>AC Edwards</i>	195
Soil, Organic Components	<i>M Bernoux, CEP Cerri</i>	203
GLASSES	<i>MP Syomov, OV Rakhimova</i>	208
GRAPHITE FURNACE <i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Electrothermal		
GRAVIMETRY	<i>RT Sane</i>	215
GUNSHOT RESIDUES <i>See</i> FORENSIC SCIENCES: Gunshot Residues		
H		
HAEMOGLOBINS (HEMOGLOBINS)	<i>RA Sherwood</i>	223
HAIR <i>See</i> FORENSIC SCIENCES: Hair		
HEADSPACE ANALYSIS		
Static	<i>JD Green</i>	229
Purge and Trap	<i>D Kou, S Mitra</i>	236
HERBICIDES	<i>MN Vasilescu, AV Medvedovici</i>	243
HEROIN	<i>ML Merves, BA Goldberger</i>	260
HISTORY OF ANALYTICAL SCIENCE	<i>D Thorburn Burns, F Szabadváry</i>	267
HORMONES		
Steroids	<i>S Görög</i>	277
HUMIC AND FULVIC COMPOUNDS	<i>M Filella, J Buffle, N Parthasarathy</i>	288
HYDRIDE GENERATION <i>See</i> ATOMIC ABSORPTION SPECTROMETRY: Vapor Generation		

ICP <i>See</i> ATOMIC EMISSION SPECTROMETRY: Inductively Coupled Plasma	
ICP-MS <i>See</i> ATOMIC MASS SPECTROMETRY: Inductively Coupled Plasma	
IMMOBILIZED ENZYMES <i>See</i> ENZYMES: Immobilized Enzymes	
IMMUNOASSAYS	
Overview <i>RM Twyman</i>	299
Production of Antibodies <i>S Stapleton, R O'Kennedy, E Tully</i>	306
IMMUNOASSAYS, APPLICATIONS	
Clinical <i>RM Twyman</i>	317
Food <i>S Iametti</i>	324
Forensic <i>S Miyaishi, F Moriya</i>	329
IMMUNOASSAYS, TECHNIQUES	
Radioimmunoassays <i>A Lacy, R O'Kennedy</i>	335
Enzyme Immunoassays <i>Y Seo</i>	344
Luminescence Immunoassays <i>G Gübitz, MG Schmid</i>	352
INDICATORS	
Acid-Base <i>J Barbosa</i>	360
Redox <i>JR Chipperfield</i>	371
Complexometric, Adsorption, and Luminescence Indicators <i>K Krishnankutty</i>	378
INDUCTIVELY COUPLED PLASMA <i>See</i> ATOMIC EMISSION SPECTROMETRY: Inductively Coupled Plasma	
INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY <i>See</i> ATOMIC MASS SPECTROMETRY: Inductively Coupled Plasma	
INFRARED SPECTROSCOPY	
Overview <i>PR Griffiths</i>	385
Sample Presentation <i>J Chalmers</i>	402
Near-Infrared <i>CNG Scotter</i>	415
Photothermal <i>SE Bialkowski</i>	426
Industrial Applications <i>SF Parker</i>	430
ION CHROMATOGRAPHY <i>See</i> ION EXCHANGE: Ion Chromatography Instrumentation; Ion Chromatography Applications; Chelation Ion Chromatography; Isotope Separation	
ION EXCHANGE	
Overview <i>PR Haddad</i>	440
Principles <i>J Ståhlberg</i>	446
Ion Chromatography Instrumentation <i>Ya I Yashin, Ya A Yashin, HF Walton</i>	453
Ion Chromatography Applications <i>B Paull</i>	460
Chelation Ion Chromatography <i>P Jones, PN Nesterenko</i>	467
Isolation of Biopolymers <i>PR Levison</i>	481
Isotope Separation <i>Y Marcus</i>	484
ION-SELECTIVE ELECTRODES	
Overview <i>K Štulík</i>	493
Glass <i>S Glab, A Hulanicki</i>	498
Solid-State <i>V Horváth, G Horvai</i>	502
Liquid Membrane <i>E Bakker</i>	509
Gas Sensing Probes <i>F Opekar, K Štulík</i>	515
Enzyme Electrodes <i>M Mascini, I Palchetti</i>	520
Clinical Applications <i>UE Spichiger-Keller</i>	526
Food Applications <i>A Hulanicki, M Maj-Żurawska</i>	534
Water Applications <i>RO Ansell</i>	540

ISE <i>See</i> ION-SELECTIVE ELECTRODES: Overview; Glass; Solid-State; Liquid Membrane; Gas Sensing Probes; Enzyme Electrodes; Clinical Applications; Food Applications; Water Applications	
ISOTOPE DILUTION ANALYSIS <i>EH Evans, R Clough</i>	545
ISOTOPE RATIO MEASUREMENTS <i>JF Carter, R Sleeman</i>	554

Volume 5

K

KINETIC METHODS	
Principles and Instrumentation <i>D Pérez-Bendito</i>	1
Noncatalytic Techniques <i>M Silva</i>	9
Catalytic Techniques <i>D Pérez-Bendito</i>	24

L

LAB-ON-A-CHIP TECHNOLOGIES <i>U Bilitewski</i>	37
LASER-BASED TECHNIQUES <i>A Quentmeier</i>	45
LASERS <i>See</i> ATOMIC MASS SPECTROMETRY: Laser Microprobe. LASER-BASED TECHNIQUES. SURFACE ANALYSIS: Laser Ionization	
LEAD <i>J Ruiz Encinar, M Moldovan</i>	56
LIMS <i>See</i> QUALITY ASSURANCE: Laboratory Information Management Systems	
LIPIDS	
Overview <i>A Kuksis</i>	63
Fatty Acids <i>I Brondz</i>	76
Polar Lipids <i>MH Gordon</i>	88
Determination in Biological Fluids <i>A Kuksis</i>	94
LIQUID CHROMATOGRAPHY	
Overview <i>MD Palamareva</i>	106
Principles <i>MD Palamareva</i>	112
Column Technology <i>UD Neue</i>	118
Packed Capillary <i>NW Smith, C Legido-Quigley, ND Marlin, V Melin</i>	126
Mobile Phase Selection <i>M Swartz</i>	135
Normal Phase <i>P Jandera</i>	142
Reversed Phase <i>RA Shalliker, S Kayillo</i>	152
Ion Pair <i>B-A Persson</i>	157
Micellar <i>MC García-Alvarez-Coque, JR Torres-Lapasió</i>	164
Size-Exclusion <i>J Janča</i>	173
Chiral <i>VR Meyer</i>	179
Affinity Chromatography <i>DS Hage</i>	190
Multidimensional <i>F Hernández, JV Sancho</i>	197
Instrumentation <i>RPW Scott</i>	205
Liquid Chromatography–Mass Spectrometry <i>WMA Niessen</i>	213
Fourier-Transform Infrared Spectroscopy <i>SJ Kok, G Somsen</i>	221
Liquid Chromatography–Nuclear Magnetic Resonance Spectrometry <i>J-L Wolfender, K Ndjoko, K Hostettmann</i>	230
Amino Acids <i>I Molnár-Perl</i>	239
Chiral Analysis of Amino Acids <i>J Haginaka</i>	252
Biotechnology Applications <i>R Freitag</i>	258
Clinical Applications <i>RA Sherwood</i>	267

Food Applications	<i>E Ibañez, FJ Señoráns</i>	276
Pharmaceutical Applications	<i>DM Diehl</i>	287
Isotope Separations	<i>L Lešetický</i>	297
LOW ENERGY ELECTRON DIFFRACTION <i>See</i> SURFACE ANALYSIS: Low Energy		
Electron Diffraction		
LUMINESCENCE		
Overview	<i>NW Barnett, PS Francis</i>	305
Solid Phase	<i>LF Capitán-Vallvey</i>	315
M		
MAGNETIC PROPERTIES	<i>E Sinn</i>	323
MALDI <i>See</i> MASS SPECTROMETRY: Matrix-Assisted Laser Desorption/Ionization		
MARINE <i>See</i> WATER ANALYSIS: Seawater – Organic Compounds; Seawater – Dissolved Organic Carbon; Seawater – Inorganic Compounds		
MASS SPECTROMETRY		
Overview	<i>R Sleeman, JF Carter</i>	337
Principles	<i>KJ Welham</i>	344
Ionization Methods Overview	<i>DJ Harvey</i>	350
Electron Impact and Chemical Ionization	<i>E Eljarrat, D Barceló</i>	359
Atmospheric Pressure Ionization Techniques	<i>AP Bruins</i>	366
Electrospray	<i>WMA Niessen</i>	373
Liquid Secondary Ion Mass Spectrometry	<i>NJ Haskins</i>	380
Matrix-Assisted Laser Desorption/Ionization	<i>DJ Harvey</i>	386
Mass Separation	<i>KJ Welham</i>	397
Ion Traps	<i>RE March</i>	404
Time-of-Flight	<i>M Guilhaus</i>	412
Selected Ion Monitoring	<i>R Sleeman, JF Carter</i>	423
Multidimensional	<i>RM Twyman</i>	430
Stable Isotope Ratio	<i>KJ Welham</i>	438
Pyrolysis	<i>RM Twyman</i>	445
Archaeological Applications	<i>TC O'Connell, AWG Pike</i>	450
Clinical Applications	<i>NJ Haskins</i>	456
Environmental Applications	<i>D Barceló, E Eljarrat, M Petrović</i>	468
Food Applications	<i>FA Mellon</i>	476
Forensic Applications	<i>RJ Lewis, RH Liu</i>	484
Gas Analysis	<i>R Wright</i>	493
Peptides and Proteins	<i>GP McMahon</i>	501
Polymerase Chain Reaction Products	<i>A Fox, KF Fox, E Castanha, WT Muhammad</i>	509
MEAT AND MEAT PRODUCTS <i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Meat and Meat Products		
MECA <i>See</i> MOLECULAR EMISSION CAVITY ANALYSIS		
MEMBRANE TECHNIQUES		
Dialysis and Reverse Osmosis	<i>U Spohn</i>	515
Ultrafiltration	<i>B Spivakov, V Shkinev</i>	524
Liquid Membranes	<i>SD Kolev</i>	531
Pervaporation	<i>A Jurado-López, MD Luque de Castro</i>	538
MERCURY	<i>M Horvat</i>	545

METABOLISM *See* **CLINICAL ANALYSIS: Inborn Errors of Metabolism. DRUG METABOLISM:**
Overview; Metabolite Isolation and Identification; Isotope Studies

Volume 6

MICELLAR ELECTROKINETIC CHROMATOGRAPHY	<i>S Terabe, J-B Kim</i>	1
MICRO TOTAL ANALYTICAL SYSTEMS	<i>T McCreedy</i>	10
MICROBIOLOGICAL TECHNIQUES	<i>GL Pettipher, JM Jay, HH Wang</i>	16
MICROELECTRODES	<i>T Zeuthen</i>	25
MICROSCOPY		
Overview	<i>PJ Evennett, C Hammond</i>	32
MICROSCOPY APPLICATIONS		
Biomedical	<i>A Warley</i>	41
Food	<i>RM Twyman</i>	50
Forensic	<i>CS Palenik, SJ Palenik</i>	57
Environmental	<i>D Perret, GG Leppard, D Mavrocordatos</i>	65
Liquid Crystals	<i>JW Goodby</i>	74
Semiconductors	<i>DJ Smith, MR McCartney</i>	84
Proteins and Nucleic Acids	<i>JR Harris</i>	91
MICROSCOPY TECHNIQUES		
Light Microscopy	<i>C Hammond, PJ Evennett</i>	100
Sample Preparation for Light Microscopy	<i>C Hammond, PJ Evennett</i>	106
Electron Microscopy	<i>J Pérez-Arantegui, T Mulvey</i>	114
Specimen Preparation for Electron Microscopy	<i>R Langford</i>	124
Scanning Electron Microscopy	<i>MI Szyrkowska</i>	134
Atomic Force and Scanning Tunneling Microscopy	<i>LA Bottomley, ED Gadsby, MA Poggi</i>	143
X-Ray Microscopy	<i>I Snigireva, A Snigirev</i>	151
MICROWAVE-ASSISTED DIGESTION	<i>See</i> SAMPLE DISSOLUTION FOR ELEMENTAL ANALYSIS: Microwave Digestion	
MICROWAVE-ASSISTED SOLVENT EXTRACTION	<i>See</i> EXTRACTION: Microwave-Assisted Solvent Extraction	
MICROWAVE SPECTROSCOPY	<i>JG Baker</i>	158
MICROWAVE-INDUCED PLASMA	<i>See</i> ATOMIC EMISSION SPECTROMETRY: Microwave-Induced Plasma	
MILK	<i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Dairy Products	
MIP	<i>See</i> ATOMIC EMISSION SPECTROMETRY: Microwave-Induced Plasma	
MIPs	<i>See</i> MOLECULARLY IMPRINTED POLYMERS	
MOLECULAR EMISSION CAVITY ANALYSIS	<i>AC Calokerinos</i>	166
MOLECULARLY IMPRINTED POLYMERS	<i>ME Díaz-García, A Fernández-González</i>	173
MULTIVARIATE CALIBRATION	<i>See</i> CHEMOMETRICS AND STATISTICS: Multivariate Calibration Techniques	
MULTIVARIATE CLASSIFICATION	<i>See</i> CHEMOMETRICS AND STATISTICS: Multivariate Classification Techniques	
MYCOTOXINS	<i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Mycotoxins. TOXINS: Mycotoxins	

N

NEAR-INFRARED SPECTROSCOPY	<i>See</i> INFRARED SPECTROSCOPY: Near-Infrared
NEPHELOMETRY	<i>See</i> SPECTROPHOTOMETRY: Turbidimetry and Nephelometry
NERVE AGENTS	<i>See</i> CHEMICAL WARFARE AGENTS
NEUROTOXINS	<i>See</i> TOXINS: Neurotoxins
NEUTRON ACTIVATION	<i>See</i> ACTIVATION ANALYSIS: Neutron Activation
NITRIC OXIDE	<i>EEH van Faassen, AF Vanin</i> 183
NITROGEN	<i>G Hanrahan, G Chan</i> 191
NITROSAMINES	<i>AR Fernández-Alba, A Agüera</i> 197
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	
Overview	<i>A Bainbridge</i> 203
Principles	<i>JB Grutzner</i> 211
Instrumentation	<i>JC Lindon</i> 238
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY-APPLICABLE ELEMENTS	
Hydrogen Isotopes	<i>JR Jones, S-Y Lu</i> 245
Carbon-13	<i>S Simova</i> 250
Fluorine-19	<i>JC Lindon</i> 263
Nitrogen-15	<i>A Lyčka</i> 272
Phosphorus-31	<i>RM Twyman</i> 278
Organometallic Compounds	<i>C Pettinari</i> 286
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY APPLICATIONS	
Food	<i>C Deleanu</i> 303
Forensic	<i>B Dawson</i> 315
Pharmaceutical	<i>JR Everett</i> 321
Proton NMR in Biological Objects Subjected to Magic Angle Spinning	<i>RA Wind, JZ Hu</i> 333
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TECHNIQUES	
Nuclear Overhauser Effect	<i>MP Williamson</i> 342
Multidimensional Proton	<i>JC Lindon</i> 350
Solid-State	<i>JW Zwanziger, H-W Spiess</i> 358
Surface Coil	<i>AN Priest, EB Cady</i> 366
In Vivo Spectroscopy Using Localization Techniques	<i>A Bainbridge, EB Cady</i> 374
NUCLEIC ACIDS	
Chromatographic and Electrophoretic Methods	<i>F Foret, K Klepárník</i> 382
Spectroscopic Methods	<i>M Vorlíčková, J Kypr, V Sklenář</i> 391
Electrochemical Methods	<i>E Paleček</i> 399
Immunoassays	<i>JM Wages, Jr.</i> 408
mRNA Identification and Quantification	<i>M Pfaffl</i> 417
NUCLEOTIDES	<i>See</i> PURINES, PYRIMIDINES, AND NUCLEOTIDES

O

OIL-BASED FUELS *See* FUELS: Oil-Based

OPTICAL SPECTROSCOPY

Radiation Sources	<i>C Burgess</i> 427
Wavelength Selection Devices	<i>C Burgess</i> 431
Detection Devices	<i>C Burgess</i> 438

Stray Light	<i>C Burgess</i>	443
Spectroscopic Materials	<i>C Burgess</i>	448
Refractometry and Reflectometry	<i>J Pawliszyn, RE Hummel</i>	452
OSCILLOMETRY <i>See</i> CONDUCTIMETRY AND OSCILLOMETRY		
OSMOSIS, REVERSE <i>See</i> MEMBRANE TECHNIQUES: Dialysis and Reverse Osmosis		
OUTDOOR AIR <i>See</i> AIR ANALYSIS: Outdoor Air		
OXYGEN FLASK COMBUSTION <i>See</i> SAMPLE DISSOLUTION FOR ELEMENTAL ANALYSIS: Oxygen Flask Combustion		
OZONE	<i>K Takeuchi</i>	462

Volume 7

P

PACKAGING MATERIALS <i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Packaging Materials		
PAHs <i>See</i> POLYCYCLIC AROMATIC HYDROCARBONS: Determination; Environmental Applications		
PAINTS		
Water-Based	<i>Christopher Carr</i>	1
Organic Solvent-Based	<i>S Garrigues Mateo</i>	9
PARTICLE SIZE ANALYSIS	<i>M Wedd</i>	18
PAS <i>See</i> PHOTOACOUSTIC SPECTROSCOPY		
PCBs <i>See</i> POLYCHLORINATED BIPHENYLS		
PCR <i>See</i> POLYMERASE CHAIN REACTION		
PEPTIDES	<i>M-I Aguilar, AW Purcell</i>	29
PERFUMES	<i>A Salvador-Carreno, A Chisvert</i>	36
PERSONAL MONITORING		
Active	<i>K Kuwata, Y Nishikawa</i>	42
Passive	<i>M Harper</i>	49
PERVAPORATION <i>See</i> MEMBRANE TECHNIQUES: Pervaporation		
PESTICIDES	<i>MN Vasilescu, AV Medvedovici</i>	55
pH	<i>S Głqb, A Hulanicki</i>	72
PHARMACEUTICAL ANALYSIS		
Overview	<i>A-M Tivert, J Vessman</i>	78
Drug Purity Determination	<i>PM Lacroix</i>	89
Stability Testing	<i>T Coomber</i>	95
Dissolution Testing	<i>S Bateman</i>	101
Sample Preparation	<i>R Whelpton</i>	107
Plant Extracts	<i>AR Bilia</i>	116
PHARMACOKINETICS		
Absorption, Distribution, and Elimination	<i>IP Nnane</i>	126
Pharmacodynamics	<i>IP Nnane</i>	133
PHEROMONES	<i>GR Jones, JE Parker</i>	140

PHOSPHORESCENCE	
Principles and Instrumentation <i>A Sanz-Medel, JM Costa-Fernandez</i>	149
Room-Temperature <i>ME Díaz-García, R Badía-Laiño</i>	157
PHOSPHORUS <i>ID McKelvie, A Lyddy-Meaney</i>	167
PHOTOACOUSTIC SPECTROSCOPY <i>RD Snook, L Mitchem</i>	174
PIEZOELECTRIC SENSORS <i>See SENSORS: Piezoelectric Resonators</i>	
PIXE <i>See SURFACE ANALYSIS: Particle-Induced X-Ray Emission</i>	
PLASTICS <i>V Pacáková, J Virt</i>	180
PLATINUM METALS <i>See PRECIOUS METALS</i>	
POLAROGRAPHY	
Overview <i>V Cerdà</i>	187
Techniques <i>V Cerdà</i>	193
Inorganic Applications <i>M Nimmo</i>	198
Organic Applications <i>CE Efstathiou</i>	206
POLYCHLORINATED BIPHENYLS <i>J de Boer</i>	214
POLYCYCLIC AROMATIC HYDROCARBONS	
Determination <i>AN Gachanja</i>	225
Environmental Applications <i>AN Gachanja</i>	234
POLYMERASE CHAIN REACTION <i>JM Wages Jr.</i>	243
POLYMERS	
Natural Rubber <i>A Krishen, MA Schafer</i>	250
Synthetic <i>S Podzimek</i>	257
Polyurethanes <i>TM Schmitt</i>	266
POTENTIOMETRIC STRIPPING ANALYSIS <i>M Honeychurch</i>	272
PRECIOUS METALS <i>Y Hayashibe</i>	277
PRESSURIZED FLUID EXTRACTION <i>See EXTRACTION: Pressurized Fluid Extraction</i>	
PRIONS <i>B Brenig</i>	287
PROCESS ANALYSIS	
Overview <i>C McGill</i>	298
Chromatography <i>PM Wiegand, CP Sears</i>	303
Electroanalytical Techniques <i>A Ivaska, J Bobacka</i>	309
Sensors <i>SB Adeloju</i>	316
Acoustic Emission <i>R Belchamber</i>	324
Maintenance, Reliability, and Training <i>J Sung, AC Alves</i>	332
Bioprocess Analysis <i>T Schweder, P Neubauer</i>	337
PROTEINS	
Overview <i>L Skipper</i>	344
Traditional Methods of Sequence Determination <i>DH Schlesinger</i>	352
Physiological Samples <i>A Bianchi-Bosisio</i>	357
Foods <i>F Bonomi</i>	375
PROTEOMICS <i>RM Twyman</i>	383
PSA <i>See POTENTIOMETRIC STRIPPING ANALYSIS</i>	
PURGE AND TRAP <i>See HEADSPACE ANALYSIS: Purge and Trap</i>	

PURINES, PYRIMIDINES, AND NUCLEOTIDES	<i>J-J Aaron, S Trajkovska</i>	394
PYRIMIDINES	<i>See</i> PURINES, PYRIMIDINES, AND NUCLEOTIDES	
PYROLYSIS	<i>See</i> GAS CHROMATOGRAPHY: Pyrolysis. MASS SPECTROMETRY: Pyrolysis	
Q		
QUALITATIVE ANALYSIS	<i>M Valcárcel, S Cárdenas</i>	405
QUALITY ASSURANCE		
Quality Control	<i>DB Hibbert</i>	412
Primary Standards	<i>R Wielgosz</i>	419
Spectroscopic Standards	<i>JP Hammond</i>	426
Internal Standards	<i>R Whelpton</i>	432
Instrument Calibration	<i>JGK Ševčík</i>	441
Interlaboratory Studies	<i>DB Hibbert</i>	449
Reference Materials	<i>P Quevauviller</i>	458
Production of Reference Materials	<i>P Quevauviller</i>	462
Method Validation	<i>DB Hibbert</i>	469
Traceability	<i>M Sargent</i>	477
Accreditation	<i>EJ Newman</i>	485
Laboratory Information Management Systems	<i>RD McDowall</i>	490
Clinical Applications	<i>A Taylor</i>	504
Water Applications	<i>JE Gaskin</i>	511

Volume 8

R		
RADIOCHEMICAL METHODS		
Overview	<i>K Buchtela</i>	1
Natural and Artificial Radioactivity	<i>J Tölgyessy, M Harangozó</i>	8
Radionuclide Monitoring	<i>J Tölgyessy, M Harangozó</i>	16
Technetium	<i>B Salbu, E Holm</i>	24
Radon	<i>L Tommasino</i>	32
Uranium	<i>M Keith-Roach, EP Achterberg</i>	44
Radiotracers	<i>P Viitanen</i>	50
Radio-Reagent Methods	<i>J Tölgyessy, M Harangozó</i>	58
Radioreceptor Assays	<i>JW Ferkany</i>	65
Gamma-Ray Spectrometry	<i>K Buchtela</i>	72
Food and Environmental Applications	<i>J Tölgyessy, M Harangozó</i>	79
Pharmaceutical Applications	<i>RE Stringer</i>	86
RADON	<i>See</i> RADIOCHEMICAL METHODS: Radon	
RAMAN SPECTROSCOPY		
Instrumentation	<i>MJ Pelletier, CC Pelletier</i>	94
Near-Infrared	<i>C Ross, KT Caron</i>	105
Surface-Enhanced	<i>RE Littleford, D Graham, WE Smith, I Khan</i>	110
REAGENTS	<i>See</i> ANALYTICAL REAGENTS: Purification	
REDOX INDICATORS	<i>See</i> INDICATORS: Redox	
REDOX TITRATION	<i>See</i> TITRIMETRY: Overview; Potentiometry; Photometric	

REFERENCE MATERIALS	<i>See</i> QUALITY ASSURANCE: Reference Materials; Production of Reference Materials	
REFLECTOMETRY	<i>See</i> OPTICAL SPECTROSCOPY: Refractometry and Reflectometry	
REFRACTOMETRY	<i>See</i> OPTICAL SPECTROSCOPY: Refractometry and Reflectometry	
REMOTE GAS SENSING		
Overview	<i>MJT Milton</i>	119
Integrated-Path Remote Sensing	<i>MJT Milton</i>	122
Range-Resolved Remote Sensing	<i>MJT Milton</i>	126
ROBOTICS	<i>See</i> SAMPLE HANDLING: Robotics	
RUTHERFORD BACKSCATTERING SPECTROMETRY	<i>See</i> SURFACE ANALYSIS: Ion Scattering	
S		
SAMPLE DISSOLUTION FOR ELEMENTAL ANALYSIS		
Dry Ashing	<i>M Hoenig</i>	131
Oxygen Flask Combustion	<i>YS Fung</i>	137
Wet Digestion	<i>RM Twyman</i>	146
Microwave Digestion	<i>CB Ojeda, FS Rojas</i>	153
SAMPLE HANDLING		
Comminution of Samples	<i>B Markert</i>	163
Sample Preservation	<i>RD McDowall</i>	169
Automated Sample Preparation	<i>RD McDowall</i>	177
Robotics	<i>MD Luque de Castro, F Priego-Capote</i>	183
SAMPLING		
Theory	<i>R-Q Yu</i>	192
Practice	<i>JGK Sevcik</i>	198
SAPONINS	<i>K Hostettmann, A Marston</i>	205
SCANNING TUNNELING MICROSCOPY	<i>See</i> MICROSCOPY TECHNIQUES: Atomic Force and Scanning Tunneling Microscopy	
SEALANTS	<i>See</i> ADHESIVES AND SEALANTS	
SEAWATER	<i>See</i> WATER ANALYSIS: Seawater – Organic Compounds; Seawater – Dissolved Organic Carbon; Seawater – Inorganic Compounds	
SECONDARY ION MASS SPECTROMETRY	<i>See</i> MASS SPECTROMETRY: Liquid Secondary Ion Mass Spectrometry. SURFACE ANALYSIS: Secondary Ion Mass Spectrometry of Polymers	
SEDIMENT	<i>See</i> GEOCHEMISTRY: Inorganic; Sediment	
SEGMENTED FLOW ANALYSIS	<i>S Coverly</i>	210
SELENIUM	<i>PC Uden</i>	216
SEM	<i>See</i> MICROSCOPY TECHNIQUES: Scanning Electron Microscopy	
SENSORS		
Overview	<i>K Lau</i>	224
Amperometric Oxygen Sensors	<i>PC Hauser, SS Tan</i>	231
Calorimetric/Enthalpimetric	<i>B Danielsson</i>	237
Chemically Modified Electrodes	<i>S Dong, Z Peng</i>	245
Microorganism-Based	<i>DM Rawson, BGD Haggett</i>	254
Photometric	<i>R Narayanaswamy</i>	262
Piezoelectric Resonators	<i>C Steinem, A Janshoff</i>	269
Tissue-Based	<i>SB Adeloju</i>	276

SENSORY EVALUATION	<i>F Sinesio</i>	283
SEQUENTIAL INJECTION ANALYSIS	<i>C Lenehan</i>	290
SEWAGE	<i>See</i> WATER ANALYSIS: Sewage	
SIA	<i>See</i> SEQUENTIAL INJECTION ANALYSIS	
SIGNAL PROCESSING	<i>See</i> CHEMOMETRICS AND STATISTICS: Signal Processing	
SIZE-EXCLUSION CHROMATOGRAPHY	<i>See</i> LIQUID CHROMATOGRAPHY: Size-Exclusion	
SOFT DRINKS	<i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Soft Drinks	
SOIL	<i>See</i> GEOCHEMISTRY: Inorganic; Soil, Major Inorganic Components; Soil, Minor Inorganic Components; Soil, Organic Components	
SOLID-STATE ELECTRODES	<i>See</i> ION-SELECTIVE ELECTRODES: Solid-State	
SOLID-PHASE EXTRACTION	<i>See</i> EXTRACTION: Solid-Phase Extraction	
SOLID-PHASE MICROEXTRACTION	<i>See</i> EXTRACTION: Solid-Phase Microextraction	
SOLVENTS	<i>B Buszewski</i>	298
SPECIATION	<i>See</i> ELEMENTAL SPECIATION: Overview; Waters, Sediments, and Soils; Practicalities and Instrumentation	
SPECTRAL DECONVOLUTION	<i>See</i> CHEMOMETRICS AND STATISTICS: Spectral Deconvolution and Filtering	
SPECTROELECTROCHEMISTRY	<i>JA Crayston</i>	304
SPECTROPHOTOMETRY		
Overview	<i>PJ Worsfold</i>	318
Diode Array	<i>AV Medvedovici, V David</i>	321
Derivative Techniques	<i>F Vogt</i>	335
Turbidimetry and Nephelometry	<i>DM Lawler</i>	343
Inorganic Compounds	<i>MA Zezzi-Arruda, RJ Poppi</i>	351
Organic Compounds	<i>T Prasada Rao, VM Biju</i>	358
Biochemical Applications	<i>F Sánchez Rojas, JM Cano Pavón</i>	366
Pharmaceutical Applications	<i>J Martinez Calatayud</i>	373
SPOT TESTS	<i>E Jungreis</i>	383
STABLE ISOTOPE RATIO MASS SPECTROMETRY	<i>See</i> MASS SPECTROMETRY: Stable Isotope Ratio	
STANDARDS	<i>See</i> QUALITY ASSURANCE: Primary Standards; Spectroscopic Standards; Internal Standards	
STATISTICS	<i>See</i> CHEMOMETRICS AND STATISTICS: Statistical Techniques	
STERILANTS	<i>See</i> BLEACHES AND STERILANTS	
STEROIDS	<i>See</i> HORMONES: Steroids	
STM	<i>See</i> MICROSCOPY TECHNIQUES: Atomic Force and Scanning Tunneling Microscopy	
STRUCTURAL ELUCIDATION	<i>M Novič, J Zupan</i>	401
SUBLIMATION	<i>JD Green</i>	410
SULFUR	<i>J Räisänen</i>	415

SUPERCritical FLUID CHROMATOGRAPHY	
Overview <i>TA Berger</i>	423
Applications <i>TA Berger</i>	431
SUPERCritical FLUID EXTRACTION <i>See EXTRACTION: Supercritical Fluid Extraction</i>	
SURFACE ANALYSIS	
Overview <i>RM Twyman</i>	440
X-Ray Photoelectron Spectroscopy <i>S Tougaard</i>	446
Particle-Induced X-Ray Emission <i>E Koltay</i>	456
Auger Electron Spectroscopy <i>WES Unger</i>	466
Appearance Potential Spectroscopy <i>AR Chourasia</i>	474
Desorption Techniques <i>M Sasaki</i>	481
Ion Scattering <i>I Stensgaard</i>	487
Nuclear Reaction Analysis and Elastic Recoil Detection <i>RW Smith</i>	495
Secondary Ion Mass Spectrometry of Polymers <i>D Briggs</i>	503
Secondary Neutral Mass Spectrometry <i>H Oechsner</i>	514
Laser Ionization <i>L Van Vaeck</i>	526
Low Energy Electron Diffraction <i>K Sakamoto</i>	535
Infrared Spectroscopy <i>H Hoffmann, T Leitner</i>	543
SURFACE-ENHANCED RAMAN SPECTROSCOPY <i>See RAMAN SPECTROSCOPY: Surface-Enhanced</i>	
SURFACTANTS AND DETERGENTS <i>P López-Mahía, S Muniategui, D Prada-Rodríguez, MC Prieto-Blanco</i>	554
SWEETENERS <i>MC Yebra-Biurrun</i>	562

Volume 9

T

TEA <i>See FOOD AND NUTRITIONAL ANALYSIS: Coffee, Cocoa, and Tea</i>	
TECHNETIUM <i>See RADIOCHEMICAL METHODS: Technetium</i>	
TEXTILES	
Natural <i>M Halbeisen</i>	1
Synthetic <i>M Schmid</i>	8
THERMAL ANALYSIS	
Overview <i>JO Hill</i>	17
Temperature-Modulated Techniques <i>JO Hill</i>	22
Coupled Techniques <i>JO Hill</i>	29
Sample-Controlled Techniques <i>JO Hill</i>	35
Nonbasic Techniques <i>JO Hill</i>	44
THERMAL LENSING SPECTROMETRY <i>T Imasaka</i>	50
THERMOGRAVIMETRIC ANALYSIS <i>See THERMAL ANALYSIS: Overview</i>	
THIN-LAYER CHROMATOGRAPHY	
Overview <i>E Reich, A Blatter</i>	57
Principles <i>CF Poole</i>	66
Plate Technology <i>F Rabel</i>	77
Method Development <i>E Reich, A Blatter</i>	83
Instrumentation <i>E Reich, A Blatter</i>	91
TIME-OF-FLIGHT MASS SPECTROMETRY <i>See MASS SPECTROMETRY: Time-of-Flight</i>	
TIN <i>LG Mackay</i>	99

TITRIMETRY	
Overview	<i>A Townshend</i> 105
Potentiometric	<i>A Hulanicki, S Glab</i> 114
Photometric	<i>C McGill</i> 121
TOILETRIES <i>See</i> COSMETICS AND TOILETRIES	
TOTAL ANALYTICAL SYSTEMS, MICROFABRICATION <i>See</i> MICRO TOTAL ANALYTICAL SYSTEMS	
TOXINS	
Mycotoxins	<i>S Dragacci</i> 124
Neurotoxins	<i>M-T Fernández-Sánchez, A Ferrero, A Pérez-Gómez, A Novelli</i> 134
TURBIDIMETRY <i>See</i> SPECTROPHOTOMETRY: Turbidimetry and Nephelometry	
 U	
ULTRAFILTRATION <i>See</i> MEMBRANE TECHNIQUES: Ultrafiltration	
URANIUM <i>See</i> RADIOCHEMICAL METHODS: Uranium	
 V	
VEGETABLES <i>See</i> FOOD AND NUTRITIONAL ANALYSIS: Vegetables and Legumes	
VITAMINS	
Overview	<i>V Spitzer, U Höller</i> 147
Fat-Soluble	<i>CJ Bates</i> 159
Water-Soluble	<i>CJ Bates</i> 172
VOLTAMMETRY	
Overview	<i>RJ Forster, DA Walsh</i> 181
Linear Sweep and Cyclic	<i>G Bontempelli, R Toniolo</i> 188
Anodic Stripping	<i>S Daniele</i> 197
Cathodic Stripping	<i>EP Achterberg, JL Barriada, CB Braungardt</i> 203
Inorganic Compounds	<i>SB Adeloju</i> 211
Organic Compounds	<i>RJ Forster, DA Walsh</i> 217
VOLUMETRIC GAS MEASUREMENTS <i>L Feltl</i> 226	
 W	
WATER ANALYSIS	
Overview	<i>H van der Jagt, HF Reijnders</i> 233
Potable Water	<i>CWK Chow</i> 253
Freshwater	<i>G Hanrahan, H Casey, P Worsfold</i> 262
Seawater – Organic Compounds	<i>MR Preston</i> 269
Seawater – Dissolved Organic Carbon	<i>G Spyres, M Nimmo</i> 277
Seawater – Inorganic Compounds	<i>TD Jickells, AR Baker</i> 283
Industrial Effluents	<i>R Guerra</i> 289
Sewage	<i>C Bendicho, I Lavilla</i> 300
Organic Compounds	<i>MR Preston</i> 307
Biochemical Oxygen Demand	<i>R Kumar, A Kumar</i> 315
Chemical Oxygen Demand	<i>Z Hu, D Grasso</i> 325
Oil Pollution	<i>E Smith</i> 330

Microbiological	<i>FM Schets, AM de Roda Husman, AH Havelaar</i>	336
Algal and Microbial Toxins	<i>C Robillot, LE Llewellyn</i>	343
Particle Characterization	<i>GG Leppard</i>	349
WATER DETERMINATION	<i>SA Margolis, PH Huang</i>	357
WET DIGESTION	<i>See SAMPLE DISSOLUTION FOR ELEMENTAL ANALYSIS: Wet Digestion</i>	
WINE	<i>See FOOD AND NUTRITIONAL ANALYSIS: Wine</i>	
WORKPLACE AIR	<i>See AIR ANALYSIS: Workplace Air</i>	
X		
X-RAY ABSORPTION AND DIFFRACTION		
Overview	<i>F Adams</i>	365
X-Ray Absorption	<i>A Markowicz, D Wegrzynek</i>	378
X-Ray Diffraction – Powder	<i>S Garcia-Granda, JM Montejo-Bernardo</i>	389
X-Ray Diffraction – Single Crystal	<i>S Garcia-Granda, JM Montejo-Bernardo</i>	397
X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY	<i>See X-RAY ABSORPTION AND DIFFRACTION: Overview; X-Ray Absorption</i>	
X-RAY FLUORESCENCE AND EMISSION		
X-Ray Fluorescence Theory	<i>PJ Potts</i>	409
Wavelength Dispersive X-Ray Fluorescence	<i>PJ Potts</i>	419
Energy Dispersive X-Ray Fluorescence	<i>PJ Potts</i>	429
Total Reflection X-Ray Fluorescence	<i>M Schmeling</i>	440
Particle-Induced X-Ray Emission	<i>W Maenhaut, F Adams</i>	448
Synchrotron X-Ray Fluorescence	<i>F Adams</i>	458
X-RAY PHOTOELECTRON SPECTROSCOPY	<i>See SURFACE ANALYSIS: X-Ray Photoelectron Spectroscopy</i>	
Z		
ZONE REFINING	<i>HB Singh</i>	463

Volume 10

Contributors List	1
Appendices	
1. Nomenclature of Analytical Science	25
2. Wavelength Scale	26
3. Definitions and Symbols for Units	27
4. Fundamental Physical Constants	33
5. Properties of Particles, Elements, and Nuclides	34
6. Conversion of Units	49
7. Statistical Tables	54
8. Biological Buffers	58
9. pH Scale for Aqueous Solutions	59
10. Standard Potentials in Aqueous Solutions	62
11. Solvents for Ultraviolet Spectrophotometry	66
12. Important Peaks in the Mass Spectra of Common Solvents	67
Index	69

within a region of hemoglobin that can be altered in the hemoglobinopathies.

Reference method A reference method has been established that involves cleavage of hemoglobin into peptides by the endoproteinase Glu-C, followed by separation and quantitation of the hexapeptides by LC-electrospray ionization mass spectrometry or LC-capillary electrophoresis.

See also: **Blood and Plasma. Clinical Analysis:** Overview. **Immunoassays, Applications:** Clinical.

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HAIR

See FORENSIC SCIENCES: Hair

HEADSPACE ANALYSIS

Contents

Static

Purge and Trap

Static

J D Green, Beverley, UK

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Introduction

Headspace analysis is a technique for sampling and examining the volatiles associated with a solid or liquid sample. The actual headspace itself is the

volume of vapor or gas above the sample. For most headspace analysis purposes the sample and its associated headspace are held within an enclosed container (Figure 1). Often, it is the volatiles that are of primary importance when, for example, the chemical composition of the mixture giving rise to the aroma of the sample is to be determined. In other circumstances, examination of the volatiles rather than the whole sample greatly simplifies the analysis and still gives information relating to the whole sample. In effect, the analytical complications that are often apparent as a result of a complex matrix are considerably decreased.

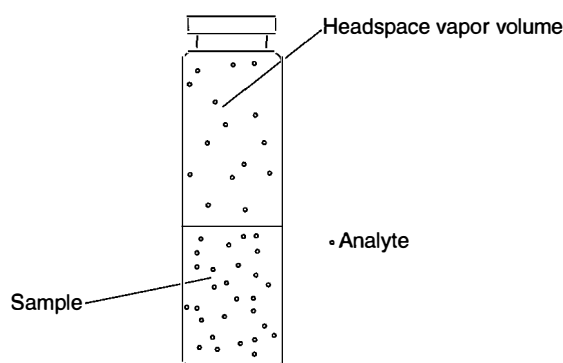


Figure 1 The fundamental concept of headspace analysis.

Principles

Headspace volatiles can be examined by a number of analytical methods and, although the technique is most often associated with gas chromatography (GC), it is perfectly feasible for headspace samples to be analyzed by other analytical methods. Such methods as mass spectrometry (MS), molecular spectrometric techniques, and voltammetry have been used, although infrequently and, if the component of interest exists in a volatile form, there is no reason why atomic spectrometry should not be used.

Sampling of headspace vapors at its simplest can be effected by using a gas-tight syringe. In this case a sample of the headspace contained in a closed volume above the sample is drawn into the syringe and subsequently introduced into the analytical instrumentation. Alternatively, an automated system can be used in which the sample can be conditioned in various ways according to the capabilities of the instrumentation prior to introduction into the analytical system using autosampler syringe technology or a sample transfer line. The results obtained depend upon the analytical technique chosen to supplement the headspace sampling procedure.

Static and dynamic headspace sampling techniques may be distinguished; this is shown diagrammatically in Figure 2 together with the closely related technique of 'purge and trap'. Static methods involve the removal of a small fraction of the headspace in equilibrium with the liquid. Dynamic methods involve the continuous removal of the headspace sample from above the sample as an enrichment step followed by a concentration of the vapors either cryogenically or using a porous adsorbent. The concentrated sample from the dynamic sampling may then be revaporized (from a cryogenic trap) or desorbed (from a solid adsorbent) and analyzed by an appropriate technique. Less commonly, a headspace sampling technique known as 'continuous flow thin

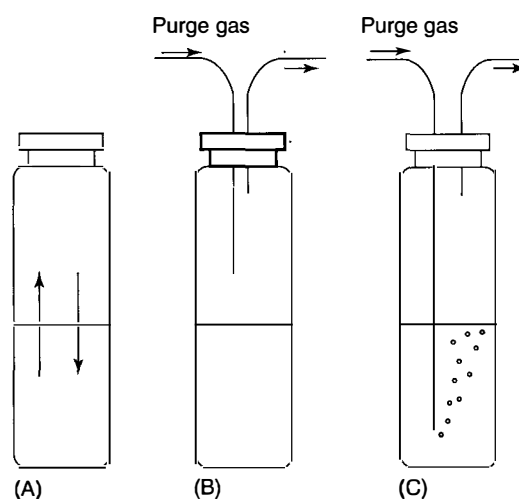


Figure 2 Concepts of 'static' headspace (A), 'dynamic' headspace (B), and purge and trap (C) sampling systems.

layer headspace' can be used to concentrate headspace volatiles in a thin layer of a flowing liquid. The concentrate can then be analyzed by the appropriate technique, including those such as voltammetry that are not usually associated with headspace methods.

Qualitative headspace analysis is used in many applications to determine differences between selected samples and to assess the importance of specific compounds in defining the aroma character of certain substances. This approach is often termed 'fingerprinting' as in many instances the composition remains chemically unknown. For additional qualitative data, headspace may be used in conjunction with knowledge of GC retention data or with GC-MS techniques for a more definitive chemical identification.

Quantitative relationships exist between the concentrations of volatiles in equilibrium with liquid samples and these form the basis of quantitative theory for headspace techniques. The partition coefficient, K , is the parameter of fundamental importance and it is defined as the ratio of concentration of analyte a in the sample phase s , C_a^s and that in the vapor phase v , C_a^v , at equilibrium (eqn [1]):

$$K = \frac{C_a^s}{C_a^v} \quad [1]$$

The sensitivity of headspace analysis is influenced principally by two sample-related parameters: the partition coefficient of the analyte between the phases and the phase ratio of sample to vapor. Consideration of the mass balance of an analyte in a sample under headspace conditions of equilibrium allows a simple expression to be developed relating sensitivity

to these two parameters (eqn [2]):

$$M_a^o = M_a^s + M_a^v \quad [2]$$

where M_a^o is the mass of analyte in the original sample, M_a^s is the mass of analyte in the sample phase under headspace conditions, and M_a^v is the mass of analyte in the vapor phase under the headspace conditions. This develops to

$$C_a^o V^s = C_a^s V^s + C_a^v V^v \quad [3]$$

where C_a^o is the concentration of analyte in the original sample, V^s is the volume of the sample phase, and V^v is the volume of the vapor phase under headspace conditions.

Incorporating $K = C_a^s/C_a^v$ from eqn [1] gives

$$C_a^o V^s = K C_a^v V^s + C_a^v V^v \quad [4]$$

and therefore

$$\begin{aligned} C_a^o &= K C_a^v + C_a^v \left(\frac{V^v}{V^s} \right) \\ &= C_a^v \left[K + \frac{V^v}{V^s} \right] \end{aligned} \quad [5]$$

Now, V^v/V^s is the phase ratio β , and therefore

$$C_a^o = C_a^v [K + \beta] \quad [6]$$

It is C_a^v that is proportional to the analytical response, therefore

$$C_a^v = \frac{C_a^o}{K + \beta} \quad [7]$$

Equation [7] shows that for a given concentration of analyte in the original sample, C_a^o , the analytical response, which is proportional to C_a^v , will depend upon K and β . With a large value of K (e.g., 1000 for ethanol in water), the phase ratio has no influence. Conversely, for a small value of K (e.g., $K \approx 0$ for halogenated species in water), the phase ratio has a significant bearing upon the sensitivity. Chemical methods for modifying the partition characteristics of the system are appropriate in some cases, perhaps the most well known being the addition of salts to the liquid phase to induce a higher concentration of organics in the vapor phase. In addition, the sensitivity of the detector used and the capacity of the analytical system for the sample will influence the sensitivity achievable as it does in any analytical method.

Quantitative analysis using headspace techniques is dependent upon the partition of the analyte between the sample and vapor phases. The concentration of the analyte in the sample phase is usually

the value sought, although it is the vapor phase that is sampled and analyzed. Four different approaches to headspace analysis quantification are discussed below. These are total vaporization, matrix-matched standards of analyte, multiple headspace extraction, and standards addition.

Total Vaporization

Total vaporization of the analyte into the vapor phase can be realized for a limited number of samples and this provides the simplest case for quantification. As an example, a polymeric matrix containing residual water could be heated to 150°C to effectively drive all the water into the vapor. Headspace analysis of the vapor phase in conjunction with external calibration will give the concentration of water in the vapor phase. From this and knowledge of the vapor phase volume, the total amount of water present in the sample can be calculated. This is expressed in the trivial relationship:

$$M_a^s = M_a^v \quad [8]$$

which becomes

$$M_a^s = C_a^v V^v \quad [9]$$

when the concentration term is introduced, where the terms have the same meanings as given earlier. With a known mass or volume of sample the concentration of analyte in the sample may be calculated.

Matrix-Matched Analyte Standards

In most practical cases the analyte will be distributed between the sample and vapor phases. Calibration involves preparing standards in a matrix identical to that of the sample with known concentrations of the analyte. The headspaces of these standards are then analyzed under identical conditions to the sample and thereby a calibration graph can be constructed. This procedure is practical for liquids and gives eqn [10]:

$$C_a^s = C_a^{\text{std}} \frac{A_a}{A_{\text{std}}} \quad [10]$$

In eqn [10], C_a^{std} is the concentration of analyte in the prepared standard, A_a is the analytical response to the analyte in the sample, and A_{std} is the analytical response to the analyte in the prepared standard. For solid samples, preparation of valid calibration standards is more difficult because the analyte in the real sample may be bound in a different form from that in the standard. These so-called matrix effects are difficult to overcome; however, the method described next provides a viable approach.

Multiple Headspace Extraction

Multiple headspace extraction is a simple concept. As the headspace is extracted several times from one sample, the analyte concentration is progressively decreased. If the procedure were carried out a sufficient number of times then no analyte would be detected in later extracts. Summing all the values obtained would allow the analyte concentration in the original sample to be calculated. While this procedure would be tedious and time consuming, simpler practical approaches using this concept are available. Multiple headspace extraction is a variant of methods known as stepwise gas extraction and discontinuous gas extraction. Such procedures can be applied to a variety of samples and can be used to quantify analytes in samples for which it is difficult or impossible to set up calibration standards as a result of the matrix complications or difficulties in preparing standards. These methods are therefore particularly valuable for quantification of volatiles in solid samples or for quantifying highly volatile analytes for which the preparation of accurate standards is experimentally difficult.

A series of headspace analyses is carried out on the same sample, which is conditioned to equilibrium between each analysis step. From the progressive, measured decrease in concentrations determined, the analyte concentration in the original sample can be calculated. The theory is outlined below.

With a continuous gas extraction, the decrease in concentration of analyte with time will be proportional to the remaining concentration of analyte (eqn [11]):

$$\frac{-dC_a}{dt} = kC \quad [11]$$

This integrates to give an expression for the concentration of analyte present at time t :

$$C = C_a^0 e^{-kt} \quad [12]$$

in which C_a^0 is the initial concentration and k is an exponent that includes the partition coefficient K . Where concentrations are proportional to the analytical responses of the techniques used, the expression may be transposed to

$$A_n = A_1 e^{(1-n)k'} \quad [13]$$

where concentrations become analytical responses (A_n is the analytical response of the n th extraction, etc.) and t is replaced by the number of extraction steps (n) in a multiple sequence having equal time intervals. The new exponent k' includes contributions from both K and some instrumental parameters.

From eqn [13], using the mathematics of geometric progression, an expression may be developed to give the

sum of the analytical responses for a series of analyses:

$$\sum A_n = \frac{A_1}{1 - e^{-k'}} \quad [14]$$

in which $k' = \ln(A_1/A_2)$. For practical purposes this can be simplified to a procedure involving two extractions, and the sum of analytical responses becomes

$$\sum A_n = \frac{A_1^2}{A_1 - A_2} \quad [15]$$

Further details of the mathematical derivation of these relationships can be found in the texts cited in the 'Further Reading'.

Standard Addition

Standard addition is also a method commonly used to quantify headspace analysis and can be used in cases where a standard solution of the analyte can be added to the sample in such a way that it exists in an identical form in relation to the matrix as the analyte itself. Analysis of the original sample and the sample with added standard analyte can then provide a value for the concentration of analyte in the original sample.

The analytical response A_a to the analyte from the sample and the concentration of analyte in the sample, C_a^s , are related by

$$A_a = K' C_a^s \quad [16]$$

where K' is a function of the distribution coefficient and the detector response. In a similar way, when a standard is added to the sample to be analyzed the analytical response, A_a^* , may be expressed as

$$A_a^* = K' \left[C_a^s \left(\frac{V_a}{V_a + v} \right) + C_{std} \right] \quad [17]$$

in which C_a^s is the concentration of the analyte in the sample that is to be determined, C_{std} is the concentration of the standard added, V_a is the volume of the solution (liquid phase) in which the analyte is dispersed, and v is the volume of standard solution added (of known concentration).

This expression may be developed to give

$$\begin{aligned} A_a^* &= \frac{A_a}{C_a^s} \left[C_a^s \left(\frac{V_a}{V_a + v} \right) + C_{std} \right] \\ &= A_a \left[\left(\frac{V_a}{V_a + v} \right) + \frac{C_{std}}{C_a^s} \right] \end{aligned} \quad [18]$$

$$\frac{A_a C_{std}}{C_a^s} = A_a^* - A_a \left(\frac{V_a}{V_a + v} \right) \quad [19]$$

$$C_a^s = \frac{C_{std} A_a}{(A_a^* - A_a [V_a / (V_a + v)])}$$

$$= \frac{C_{std} A_a (V_a + v)}{(A_a^* (V_a + v) - A_a V_a)} \quad [20]$$

This simplifies to

$$C_a^s = \frac{A_a C_{std}}{A_a^* - A_a} \quad [21]$$

when the volume added as a result of the standard addition is small.

The choice of quantification in headspace analysis therefore depends on the sample and the analyte. Procedures include total vaporization, the use of matrix-matched standards, multiple extractions, and standard additions. A method using an internal standard may be used provided knowledge of the equilibrium constants for the standard and the analyte can be determined.

Apparatus

The equipment used for headspace analysis in its simplest form may comprise a vial of suitable volume with a septum turn closure through which the sample may be drawn using a gas-tight syringe. With the use of a means of temperature control, this method of sampling headspace volatiles can be effective for simple applications where a qualitative or semiquantitative analytical screening procedure is required.

For more demanding applications, a range of apparatus has been designed for the sampling and

collection of headspace vapors. Commercially available systems exist from several of the major instrument manufacturers (Table 1). Modern equipment is designed for flexibility and can be used for static headspace methods, dynamic sampling, sometimes includes the option of multiple headspace extraction together and a capability to do solid-phase microextraction (SPME) injections. Some equipment is aimed at the electronic nose market for aroma profiling and the identification of odor components. Most manufacturers provide the means for automatic conditioning of samples and provide features to allow vial shaking, constant equilibration times for the sample vials, and method development options whereby the parameters can be progressively changed over a number of samples. Methods for introducing samples into the analytical instrumentation differ from automated syringe technology through sample valve and loop techniques to direct coupling using pressure-balanced sampling.

A wider range of equipment that has particular features for special applications is described in the literature. For example, special apparatus has been designed and reported, for sampling the headspace of canned foods and whole cheeses, and from single cigarettes.

Applications

Headspace techniques have been used for examining a wide variety of samples including environmental samples of soil, water, and air, biological fluids,

Table 1 Commercially available headspace sampling and injection equipment

<i>Manufacturer (web address)</i>	<i>Models available</i>	<i>Selected features</i>
Agilent (www.agilent.com)	7694 Headspace sampler	Flexible sample conditioning for 44 samples with inert interface options to Agilent and other gas chromatographs
Alpha MOS (www.presearch.co.uk)	HS 100 – Odorscanner	Sampler aimed at providing headspace samples to ‘electronic nose’ equipment
Gerstel (www.gerstel.com)	Headspace Chemsensor 4440	Provides an odor sample to a MS (quadrupole) or GC/MS analyzer for identification or comparative profiling
Perkin Elmer (http://uk.instruments.perkinelmer.com)	Turbomatrix Headspace Samplers HS-110/-16/-40	Pressure balanced sampling with flexible sample numbers and conditioning
Shimadzu (www.shimadzu.co.uk)	Liquid, Headspace & SPME GC Injection system	Combined injection capability including headspace
Teledyne Tekmar (www.teledynetekmar.com)	7000HT Headspace Autosampler (also 7050 with 50 sample vial positions)	Sample equilibration temperatures of up to 300°C, inert sample path and method optimization mode
Thermo Finnigan (www.thermo.com)	HS 2000 Headspace Sampler	Robotic system to control sample equilibration, allow method optimization
Varian (www.varianinc.com)	Combi PAL autosampler injection system	Combines headspace with liquid and SPME injections. Flexible sample conditioning and headspace injection modes

foodstuffs and related materials, forensic samples, pharmaceuticals, natural products, and polymers. Such samples are examined to ensure environmental protection, to diagnose medical conditions, to establish compliance with regulations in the food, pharmaceutical, and packaging industries, and for the direct determination of aroma volatiles with their associations to taste and smell. All these applications of the headspace analysis benefit either from the simplification of the analysis by removing some of the matrix effects or as a result of the technique being directly related to the examination of aroma volatiles. As mentioned above, headspace analysis is closely associated with techniques of purge and trap, which also direct attention to the volatiles 'extracted' from a sample by the purge gas.

Environmental samples including soils, water, and air have been examined using various headspace techniques. Soils, estuarine sediments, and industrial wastes have been examined for volatile organics including chlorinated hydrocarbons, benzene, and other aromatics. Groundwater samples have been examined for a wide range of volatile substances including chlorinated hydrocarbons, carbon disulfide, components of gasoline spillages, and methyl-mercury. The latter analysis was carried out using GC with atomic emission detection. Drinking water has been analyzed for volatile constituents including halocarbons, aromatics, and chloral hydrate using headspace sampling techniques. Dissolved gases and light hydrocarbons have been determined in seawater. In some cases headspace methods give improved limits of detection compared to direct injection procedures, and the problems of column overloading and detector memory effects that can occur with aqueous samples are eliminated. Headspace sampling is also used for determining solvents in waste gases and for a variety of substances in workplace and domestic environments including vulcanization volatiles in the rubber industry, and alkylated benzenes and formaldehyde from particle board products.

Trace components in alcoholic drinks can be determined following headspace concentration procedures, although great care is required to establish that the major components present in the sample are not influencing the partition of the analyte of interest between the liquid and headspace phases.

Volatile components of packaging materials in foods can be detected and quantified using headspace techniques. As an example, vinyl chloride as a component of poly(vinyl chloride) (PVC) has been determined in olive oil after storage in PVC containers.

Analysis of gases associated with fresh food packaging is carried out using a headspace technique, with

instruments being available to determine oxygen and carbon dioxide concentrations using a zirconia oxygen probe and an infrared detector for carbon dioxide.

The requirements for the determination of the impurities present in gases and especially in air are frequently so demanding that direct determination (usually by GC and therefore direct injection) is not feasible. The technique of reverse headspace analysis has been applied to such samples. The gas, the minor impurities of which are to be determined, is equilibrated with a liquid, usually in a special flow cell. The liquid may then be directly injected into a gas chromatograph or, in the case of a nonvolatile liquid being used to trap the impurities, thermal elution of the volatiles can be effective prior to analysis. Such methods have been used to determine sulfur-containing compounds in natural gas and air.

Monomeric residues in polymeric formulations or products can be determined using headspace techniques. Thus, monomeric impurities in aqueous suspensions of polymers for subsequent processing can be determined as a means of reducing possible off-odors in the processed materials. In commercial polymers, monomeric species can be identified and quantified using headspace sampling techniques with the appropriate analytical method. Such monomers may be undesirable with respect to subsequent usage, especially as packaging for food that may then become tainted by the volatile species present.

Clinical samples of urine, blood, expired air, and tissue have been examined using headspace sampling approaches. Thus, chlorinated organic compounds, methanol, acetone, methyl ethyl ketone, and phenols have been determined in urine. Volatile substances in urine have also been used as a guide to acute poisoning, and the determination of stimulants in urine has been proposed as screening test for 'field' use. The determination of the concentration of blood alcohol is the most well-known application of headspace techniques to biological samples. Blood has also been examined for cyanide, methyl sulfide, and formaldehyde levels, the last as a measure of methanol intoxication. The headspace approach for blood samples overcomes the difficulties associated with the alternative direct injection of two-phase samples.

Milk, being a two-phase substance, also creates some analytical difficulties for direct injection methods and therefore headspace techniques have been used to overcome these and to determine the odor components that have a bearing upon milk quality in processing and storage.

Volatiles associated with solids such as polymers and tablet formulations of pharmaceuticals can be

Table 2 Standard methods using headspace techniques

<i>Application</i>	<i>Standard(s)^a</i>
<i>Determination of residual volatiles</i>	
Residual acrylonitrile content of styrene–acrylonitrile copolymers and nitrile rubber	ASTM D4322
Residual vinyl chloride monomer (ng g^{-1} range) in vinyl chloride homopolymers and copolymers	ASTM D4443
Residual vinyl chloride monomer in poly(vinyl chloride) resins	ASTM D3749
Acetaldehyde content of freshly blown poly(ethylene terephthalate) bottles	ASTM D4509
<i>Fire debris samples</i>	
Separation/concentration of flammable and combustible residues from fire debris samples by dynamic headspace analysis	ASTM E1413
Separation/concentration of flammable and combustible residues from fire debris samples by passive headspace analysis	ASTM E1412
<i>Recommended methods and apparatus</i>	
Practice of sampling of headspace vapors from fire debris samples	ASTM E1388
Small-scale environmental chamber determinations of organic emissions from indoor materials/products	ASTM D5116
Volatile matter content in polymers by headspace chromatography	ASTM D4526
<i>Water samples</i>	
Examination of water, wastewater and sludge for individual constituents	DIN 38413
<i>Foodstuffs</i>	
Tests for vegetables, fruits, and their products including headspace techniques	SASO 440

^a Sources: ASTM, American Society for Testing and Materials; DIN, Deutsche Institute für Normung; SASO, Saudi Arabian Standards Organization.

determined using headspace techniques. Those samples that dissolve completely can be dealt with as solutions, when the headspace approach allows the volatiles to be analyzed separately from the nonvolatile solids. For insoluble solids the volatiles can be identified but quantification, which has been discussed above, is less straightforward.

Numerous applications of headspace analysis to the determination of the volatile aroma compounds of natural products, their essential oils and extracts have been reported. Thus, fruits, tobacco, hops, mushrooms, and various plants have been examined to determine the volatiles present. Such investigations provide information relating to the important chemistry of aroma, taste, and flavor. This has advanced the understanding of the development of odor in fresh, processed, and preserved food products as well as in flowers, from which fragrances are extracted and developed. Consequently, criteria of quality have been established and an understanding has developed of the changes in volatile composition occurring as a result of aging, storage, and processing procedures. As diverse examples, headspace techniques have been used to examine truffle aroma, volatiles in canned salmon, and from kiwi fruit flowers, and garlic volatiles. Synthesis of nature-identical flavors has been significantly advanced by the results of headspace analysis in this area of aroma and flavor research.

Household and personal hygiene products comprise another group of samples that can be screened and examined for volatile components. Thus, 1,4-dioxane in shampoos, ethylene oxide in cosmetics, and fragrances in soaps and cleaning fluids are examples of typical applications of the technique.

In a small number of selected examples it is possible to use headspace sampling techniques as part of an analytical procedure to determine involatile components in a sample. The headspace sampling usually follows a chemical treatment to produce a volatile compound from the analyte of interest. It is thus possible to determine fluoride in fluorinated milk following initial treatment to produce volatile trifluorosilane.

Headspace techniques are used in a number of standard methods for the examination of a wide variety of samples. Details are given in Table 2.

Headspace analysis has largely been neglected in the area of process analysis, although, with the inherent matrix complications that can slow down and complicate such analyses, significant benefits may be realized from such an approach.

Headspace techniques can be used to determine a number of thermodynamically important properties relating to vapor–liquid equilibria. The technique has been used to develop distillation procedures specifically where the selection of solvents in extractive distillation is required. Vapor pressures of pure

substances and activity coefficients may also be determined using headspace techniques.

See also: **Blood and Plasma. Cosmetics and Toiletries. Essential Oils. Food and Nutritional Analysis:** Pesticide Residues; Alcoholic Beverages; Dairy Products. **Polymers:** Natural Rubber; Synthetic; Polyurethanes. **Process Analysis:** Chromatography. **Quality Assurance:** Primary Standards; Spectroscopic Standards;

Internal Standards. Sensory Evaluation. Sulfur. Water Analysis: Organic Compounds.

Further Reading

Kolb B and Ettre L (1997) *Static Headspace-Gas Chromatography: Theory and Practice*. New York: Wiley. Manufacturers' Websites (see Table 1) and additionally www.atas.co.uk.

Purge and Trap

D Kou, Hoffmann-La Roche Inc., Nutley, NJ, USA
S Mitra, New Jersey Institute of Technology, Newark, NJ, USA

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Introduction

Purge and trap refers to the technique in which volatile organic compounds (VOCs) are purged out of the sample matrix by an inert gas and carried on to a sorbent trap, where they are concentrated and later introduced into an instrument (gas chromatography (GC) or GC/mass spectrometry (MS)) for analysis. After its introduction in the 1970s, purge and trap quickly gained widespread acceptance, and was adopted by regulatory agencies as a standard method. Today, it is still the workhorse for the analysis of low-concentration VOCs in solids and liquids. The instrumentation and procedures are slightly different for liquid and solid samples. This article discusses its basic theory, instrumentation, operational procedures, quantification methods, and selected applications.

Theoretical Considerations

Purge and trap is also known as dynamic headspace extraction, which is closely related to static headspace extraction. In both techniques, organic compounds migrate from the sample matrix into its headspace. This is illustrated in Figure 1. In static headspace, equilibrium is reached between the sample and its headspace. In purge and trap, an inert gas is used to continuously remove the analytes out of the sample, thus creating a higher concentration gradient. This enhances the mass transfer of the analytes. Consequently, purge and trap is more sensitive than static headspace analysis. It is suitable for trace analysis with detection limits at parts per billion to

parts per trillion levels. On the other hand, static headspace is often used as a complementarily screening method for high-concentration samples.

There are three main processes in purge and trap: extraction (purging), simultaneous adsorption (trapping), and subsequent desorption (heating). The overall purge-and-trap performance depends on the efficiency of each individual process.

Purging efficiency (the percentage of analytes removed from the sample) depends upon the properties of the analytes, purge temperature, flow rate, duration of the purging, and sample matrix. Purging is most efficient for VOCs that are insoluble or

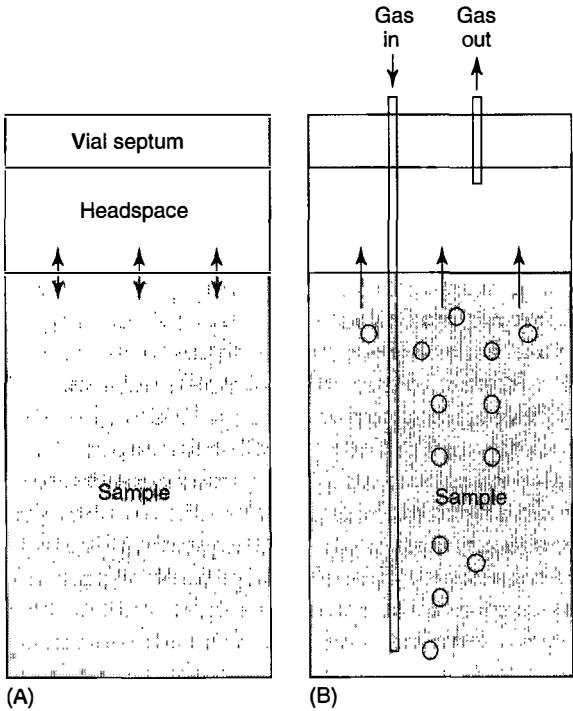


Figure 1 Comparison of purge and trap with static headspace extraction. (A) Static head space and (B) purge and trap.