

Contents

| | |
|---|----------|
| <i>About the Editors</i> | xxi |
| <i>List of Contributors</i> | xxiii |
| <i>Preface</i> | xxvii |
| SECTION I: INTRODUCTION | 1 |
| 1 Introduction and Scope | 3 |
| <i>John M. Chalmers, Howell G.M. Edwards and Michael D. Hargreaves</i> | |
| 1.1 Historical Prologue | 3 |
| 1.2 The Application of Infrared Spectroscopy and Raman Spectroscopy in Forensic Science | 5 |
| References | 7 |
| 2 Vibrational Spectroscopy Techniques: Basics and Instrumentation | 9 |
| <i>John M. Chalmers, Howell G.M. Edwards and Michael D. Hargreaves</i> | |
| 2.1 Introduction | 9 |
| 2.2 Vibrational Spectroscopy Techniques | 9 |
| 2.2.1 The basics and some comparisons | 9 |
| 2.2.1.1 Wavelength/Wavenumber Ranges and Selection Rules | 10 |
| 2.2.1.2 Sampling Considerations | 12 |
| 2.2.1.3 Sensitivity, Surfaces and Signal Enhancement Techniques | 13 |
| 2.2.1.4 IR and Raman Bands | 13 |
| 2.2.2 Quantitative and classification analyses | 16 |
| 2.2.2.1 Multivariate Data Analyses | 17 |
| 2.2.2.2 Data Pre-Processing | 20 |
| 2.2.3 Reference databases and search libraries/algorithms | 20 |
| 2.3 Vibrational Spectroscopy: Instrumentation | 22 |
| 2.3.1 Spectrometers | 22 |
| 2.3.1.1 Sources | 22 |
| 2.3.1.2 Detectors | 24 |
| 2.3.1.3 Spectrometers and Interferometers | 24 |
| 2.3.2 Vibrational spectroscopy–microscopy systems | 28 |
| 2.3.2.1 Mapping and Imaging | 30 |

| | |
|---|-----------|
| 2.3.3 Fibre optics and fibre-optic probes | 34 |
| 2.3.4 Remote, portable, handheld, field-use, and stand-off vibrational spectroscopy instrumentation | 35 |
| 2.4 Closing Remarks | 40 |
| References | 40 |
| 3 Vibrational Spectroscopy Sampling Techniques | 45 |
| <i>John M. Chalmers, Howell G.M. Edwards and Michael D. Hargreaves</i> | |
| 3.1 Introduction | 45 |
| 3.2 Vibrational Spectroscopy: Sampling Techniques | 47 |
| 3.2.1 Raman spectroscopy | 47 |
| 3.2.1.1 Raman Spectroscopy: Sampling Techniques and Considerations | 47 |
| 3.2.1.2 Resonance Raman Spectroscopy | 50 |
| 3.2.1.3 Surface Enhanced Raman Spectroscopy and Surface Enhanced Resonance Raman Spectroscopy | 51 |
| 3.2.1.4 Spatially Offset Raman Spectroscopy | 51 |
| 3.2.1.5 Transmission Raman Spectroscopy | 55 |
| 3.2.1.6 Raman Microscopy/Microspectroscopy and Imaging | 55 |
| 3.2.1.7 Remote and Fibre-Optic Probe Raman Spectroscopy | 56 |
| 3.2.2 Mid-infrared spectroscopy | 58 |
| 3.2.2.1 Mid-Infrared Transmission Spectroscopy: Sampling Techniques | 58 |
| 3.2.2.2 Mid-Infrared Reflection Spectroscopy Sampling Techniques | 62 |
| 3.2.2.3 Mid-Infrared Photoacoustic Spectroscopy | 70 |
| 3.2.2.4 Mid-Infrared Microscopy/Microspectroscopy and Imaging | 71 |
| 3.2.3 Near-infrared spectroscopy: sampling techniques | 76 |
| 3.2.3.1 Near-Infrared Transmission Spectroscopy | 77 |
| 3.2.3.2 Near-Infrared Diffuse Reflection Spectroscopy | 77 |
| 3.2.3.3 Near-Infrared Transflection Spectroscopy | 78 |
| 3.2.3.4 Near-Infrared Spectroscopy: Interactance and Fibre-Optic Probe Measurements | 78 |
| 3.2.3.5 Near-Infrared Microscopy and Imaging | 79 |
| 3.2.4 Terahertz/far-infrared spectroscopy: sampling techniques | 79 |
| 3.3 Closing Remarks | 81 |
| Acknowledgements | 81 |
| References | 82 |
| SECTION II: CRIMINAL SCENE | 87 |
| 4 Criminal Forensic Analysis | 89 |
| <i>Edward G. Bartick</i> | |
| 4.1 Introduction | 89 |
| 4.2 Forensic Analysis | 90 |
| 4.3 General Use of IR and Raman Spectroscopy in Forensic Analysis | 91 |
| 4.3.1 Progression of infrared spectroscopy development in forensic analysis | 91 |
| 4.3.2 Progression of Raman spectroscopy development in forensic analysis | 91 |
| 4.3.3 Sampling methods | 91 |

| | | |
|------------|--|------------|
| 4.3.3.1 | Microscopes | 91 |
| 4.3.3.2 | Reflection Methods | 92 |
| 4.3.3.3 | Gas Chromatography/IR | 92 |
| 4.3.3.4 | Spectral Imaging | 92 |
| 4.4 | Applications of Evidential Material Analysis | 93 |
| 4.4.1 | Polymers | 93 |
| 4.4.1.1 | General | 93 |
| 4.4.1.2 | Copy Toners | 94 |
| 4.4.1.3 | Fibres | 95 |
| 4.4.1.4 | Paints | 98 |
| 4.4.1.5 | Tapes | 99 |
| 4.4.2 | Drugs | 101 |
| 4.4.3 | Explosives | 103 |
| 4.4.4 | Fingerprint analysis | 104 |
| 4.5 | Summary and Future Direction | 105 |
| | Acknowledgements | 106 |
| | References | 106 |
| 4.1 | Forensic Analysis of Hair by Infrared Spectroscopy | 111 |
| | <i>Kathryn S. Kalasinsky</i> | |
| 4.1.1 | Introduction | 111 |
| 4.1.2 | Basic Forensic Hair Analysis | 113 |
| 4.1.3 | Uniqueness of Hair to Chemical Analysis | 114 |
| 4.1.4 | Mechanism for Chemical Substance Incorporation into Hair | 115 |
| 4.1.5 | Applications | 118 |
| 4.1.6 | Disease Diagnosis | 119 |
| 4.1.7 | Summary | 119 |
| | References | 119 |
| 4.2 | Raman Spectroscopy for Forensic Analysis of Household and Automotive Paints | 121 |
| | <i>Steven E.J. Bell, Samantha P. Stewart and W.J. Armstrong</i> | |
| 4.2.1 | Introduction | 121 |
| 4.2.2 | Paint Composition | 121 |
| 4.2.3 | Analysis of Resin Bases | 122 |
| 4.2.4 | White Paint | 125 |
| 4.2.5 | Coloured Household Paints | 126 |
| 4.2.6 | Multi-Layer Paints | 130 |
| 4.2.7 | Automotive Paint | 132 |
| 4.2.8 | Conclusions | 135 |
| | References | 135 |
| 4.3 | Raman Spectroscopy for the Characterisation of Inks on Written Documents | 137 |
| | <i>A. Guedes and A.C. Prieto</i> | |
| 4.3.1 | Introduction | 137 |
| 4.3.2 | Experimental | 139 |

| | | |
|------------|--|------------|
| 4.3.3 | Chemical Differences in the Composition of Writing Inks through Time, and Modern Inks: Major Groups | 141 |
| 4.3.4 | Ink Discrimination | 144 |
| 4.3.5 | Forensic Test | 146 |
| 4.3.6 | Conclusions | 149 |
| | References | 149 |
| 4.4 | Forensic Analysis of Fibres by Vibrational Spectroscopy | 153 |
| | <i>Peter M. Fredericks</i> | |
| 4.4.1 | Introduction | 153 |
| 4.4.1.1 | Forensic importance of fibres | 153 |
| 4.4.1.2 | Types of fibres | 153 |
| 4.4.1.3 | Dyes | 154 |
| 4.4.1.4 | Why use vibrational spectroscopy? | 154 |
| 4.4.2 | Infrared Spectroscopy | 154 |
| 4.4.2.1 | Instrumentation and sample preparation | 155 |
| 4.4.2.2 | Transmission mid-IR microspectroscopy | 157 |
| 4.4.2.3 | ATR IR microspectroscopy | 158 |
| 4.4.2.4 | IR synchrotron radiation | 160 |
| 4.4.2.5 | Mid-IR imaging | 160 |
| 4.4.3 | Raman Spectroscopy | 162 |
| 4.4.3.1 | Application to fibres | 162 |
| 4.4.3.2 | Surface-enhanced Raman scattering | 164 |
| 4.4.3.3 | Raman spectroscopy of titania filler | 165 |
| 4.4.4 | Data Analysis | 165 |
| 4.4.5 | Conclusions | 167 |
| | Acknowledgement | 168 |
| | References | 168 |
| 4.5 | <i>In Situ</i> Crime Scene Analysis | 171 |
| | <i>Edward G. Bartick</i> | |
| 4.5.1 | Introduction | 171 |
| 4.5.2 | Instrumentation | 172 |
| 4.5.2.1 | Raman spectrometers | 173 |
| 4.5.2.2 | Infrared spectrometers | 175 |
| 4.5.3 | Applications | 177 |
| 4.5.3.1 | Conditions of analysis | 177 |
| 4.5.3.2 | General chemical analysis | 177 |
| 4.5.3.3 | Explosives | 177 |
| 4.5.3.4 | Drugs | 178 |
| 4.5.4 | Conclusion | 183 |
| | Acknowledgements | 183 |
| | References | 183 |

| | |
|---|------------|
| 4.6 Raman spectroscopy gains currency | 185 |
| <i>R. Withnall, A. Reip and J. Silver</i> | |
| 4.6.1 Introduction | 185 |
| 4.6.2 Banknotes | 186 |
| 4.6.3 Postage Stamps | 194 |
| 4.6.4 Potential Forensic Applications | 198 |
| 4.6.5 Conclusions | 203 |
| Acknowledgements | 203 |
| References | 203 |
| SECTION III: COUNTER TERRORISM AND HOMELAND SECURITY | 205 |
| 5 Counter Terrorism and Homeland Security | 207 |
| <i>Vincent Otieno-Alego and Naomi Speers</i> | |
| 5.1 Introduction | 207 |
| 5.2 Infrared and Raman Spectroscopy for Explosives Identification | 208 |
| 5.2.1 Level of chemical identification | 209 |
| 5.2.2 Capability to analyse a large range of explosives and related chemicals | 210 |
| 5.2.3 Other positive features of IR and Raman spectroscopy in explosive analysis | 211 |
| 5.2.4 Case Studies – Example 1 | 211 |
| 5.3 Portable IR and Raman Instruments | 213 |
| 5.3.1 Case Studies – Example 2 | 214 |
| 5.4 Post-Blast Examinations | 217 |
| 5.5 Detection of Explosives in Fingerprints | 217 |
| 5.6 Spatially Offset Raman Spectroscopy | 218 |
| 5.6.1 Applications of SORS in explosive analysis | 220 |
| 5.7 Terahertz Spectroscopy of Explosives | 221 |
| 5.7.1 Sampling modes and sample preparation | 222 |
| 5.7.2 THz spectroscopy of explosives and explosive related materials | 223 |
| 5.8 Summary | 226 |
| Glossary | 227 |
| References | 228 |
| 5.1 Tracing Bioagents – a Vibrational Spectroscopic Approach for a Fast and Reliable Identification of Bioagents | 233 |
| <i>P. Rösch, U. Münchberg, S. Stöckel and J. Popp</i> | |
| 5.1.1 Introduction | 233 |
| 5.1.2 Toxins | 236 |
| 5.1.3 Viruses | 238 |

| | | |
|------------|---|------------|
| 5.1.4 | Bacteria | 238 |
| 5.1.4.1 | Bulk samples | 238 |
| 5.1.4.2 | Single bacterium identification | 240 |
| 5.1.5 | Conclusion | 246 |
| | Acknowledgement | 246 |
| | References | 246 |
| 5.2 | Raman Spectroscopic Studies of Explosives and Precursors: Applications and Instrumentation | 251 |
| | <i>Mary L. Lewis, Ian R. Lewis and Peter R. Griffiths</i> | |
| 5.2.1 | Background | 251 |
| 5.2.2 | Introduction | 252 |
| 5.2.3 | UV Excited Raman Studies of Explosives | 253 |
| 5.2.4 | FT-Raman Studies of Explosives | 255 |
| 5.2.5 | Neither FT-Raman nor Traditional Dispersive Raman | 258 |
| 5.2.6 | Surface Enhanced Raman and Surface Enhanced Resonance Raman Studies of Explosives | 258 |
| 5.2.7 | Dispersive Raman Studies of Explosives | 259 |
| 5.2.8 | Compact Dispersive Raman Spectrometers for the Study of Explosives | 260 |
| 5.2.9 | Spatially Offset Raman Spectroscopy | 265 |
| 5.2.10 | Stand-Off Raman of Explosives | 266 |
| 5.2.11 | Raman Microscopy and Imaging | 266 |
| 5.2.12 | Vehicle-Mounted Raman Analysers | 267 |
| 5.2.13 | Classification Schema for Explosives | 268 |
| 5.2.14 | Summary | 268 |
| | References | 269 |
| 5.3 | Handheld Raman and FT-IR Spectrometers | 275 |
| | <i>Michael D. Hargreaves, Robert L. Green, Wayne Jalenak, Christopher D. Brown and Craig Gardner</i> | |
| 5.3.1 | Introduction | 275 |
| 5.3.2 | Handheld/Portable Raman and FT-IR Devices | 276 |
| 5.3.3 | Explosives | 276 |
| 5.3.4 | Tactical Considerations | 277 |
| 5.3.5 | Sample Considerations | 279 |
| 5.3.6 | Raman and FT-IR Spectroscopy Explosive Identification Capabilities | 280 |
| 5.3.7 | Performance Characterisation | 285 |
| 5.3.8 | Summary | 285 |
| | Disclaimer | 286 |
| | References | 286 |
| 5.4 | Non-Invasive Detection of Concealed Liquid and Powder Explosives using Spatially Offset Raman spectroscopy | 289 |
| | <i>Kevin Buckley and Pavel Matousek</i> | |
| 5.4.1 | Introduction | 289 |

| | |
|---|------------|
| 5.4.2 Discussion and Examples | 290 |
| 5.4.3 Summary | 293 |
| References | 294 |
| 5.5 Terahertz Frequency Spectroscopy and its Potential for Security Applications | 295 |
| <i>A.D. Burnett, A.G. Davies, P. Dean, J.E. Cunningham and E.H. Linfield</i> | |
| 5.5.1 Introduction | 295 |
| 5.5.2 Terahertz Frequency Radiation | 296 |
| 5.5.3 Terahertz Time-Domain Spectroscopy | 296 |
| 5.5.4 Examples of the Use of THz Spectroscopy to Detect Materials of Security Interest | 298 |
| 5.5.4.1 Explosives | 298 |
| 5.5.4.2 Drugs of abuse | 301 |
| 5.5.4.3 Terahertz frequency imaging | 305 |
| 5.5.4.4 Spectroscopy and imaging of concealed materials | 307 |
| 5.5.5 Conclusions and Future Outlook | 309 |
| Acknowledgements | 309 |
| References | 310 |
| SECTION IV: DRUGS AND DRUGS OF ABUSE | 315 |
| 6 Raman Spectroscopy of Drugs of Abuse | 317 |
| <i>Steven E.J. Bell, Samantha P. Stewart and S.J. Speers</i> | |
| 6.1 Introduction | 317 |
| 6.2 Bulk Drugs | 317 |
| 6.2.1 General introduction | 317 |
| 6.2.2 Experimental considerations | 319 |
| 6.2.3 Laboratory-based methods | 322 |
| 6.2.3.1 Screening and Identification | 322 |
| 6.2.3.2 Quantitative Analysis | 323 |
| 6.2.3.3 Composition Profiling | 325 |
| 6.2.4 Raman outside the laboratory | 326 |
| 6.3 Trace Detection | 328 |
| 6.3.1 Drug microparticles | 328 |
| 6.3.2 Surface-enhanced Raman spectroscopy | 329 |
| 6.4 Conclusions | 335 |
| References | 336 |
| 6.1 Drugs of Abuse – Application of Handheld FT-IR and Raman Spectrometers | 339 |
| <i>Michael D. Hargreaves</i> | |
| 6.1.1 Introduction | 339 |
| 6.1.2 Advantages of Vibrational Spectroscopy | 339 |
| 6.1.3 General Drugs of Abuse – Introduction | 340 |
| 6.1.4 Vibrational Spectroscopy | 340 |
| 6.1.5 Analysis of Street Samples | 343 |

| | |
|--|------------|
| 6.1.5.1 Considerations when analysing in situ | 343 |
| 6.1.5.2 Considerations when analysing in the laboratory | 343 |
| 6.1.6 New Narcotic Threats | 344 |
| 6.1.7 Identification of Drug Precursors | 344 |
| 6.1.8 Case Studies | 346 |
| 6.1.8.1 Case study I | 346 |
| 6.1.8.2 Case study II | 347 |
| 6.1.9 Conclusion | 347 |
| Disclaimer | 348 |
| References | 348 |
| 6.2 Non-Invasive Detection of Illicit Drugs Using Spatially Offset Raman Spectroscopy | 351 |
| <i>Kevin Buckley and Pavel Matousek</i> | |
| 6.2.1 Introduction | 351 |
| 6.2.2 Application Examples | 352 |
| 6.2.3 Summary | 356 |
| References | 356 |
| 6.3 Detection of Drugs of Abuse Using Surface Enhanced Raman Scattering | 357 |
| <i>Karen Faulds and W. Ewen Smith</i> | |
| 6.3.1 Introduction | 357 |
| 6.3.2 Substrates | 358 |
| 6.3.3 Direct Detection | 360 |
| 6.3.4 Indirect Detection | 363 |
| 6.3.5 Conclusions | 365 |
| References | 365 |
| SECTION V: ART | 367 |
| 7 Vibrational Spectroscopy as a Tool for Tracing Art Forgeries | 369 |
| <i>A. Deneckere, P. Vandenameele and L. Moens</i> | |
| 7.1 Introduction | 369 |
| 7.2 How to Trace Art Forgeries with Vibrational Spectroscopy? | 371 |
| 7.2.1 Detection of anachronisms | 371 |
| 7.2.1.1 Examples | 371 |
| 7.2.1.2 Differentiation Between the Natural or Synthetic Form of a Pigment | 373 |
| 7.2.2 Comparing with the artist's palette | 375 |
| 7.2.3 Impurities | 377 |
| 7.2.3.1 The Mercatellis Manuscripts | 377 |
| 7.2.3.2 Spectroscopic Pigment Investigation of the Mayer van den Bergh Breviary | 378 |
| 7.3 Conclusion | 380 |
| Acknowledgements | 380 |
| References | 380 |

| | |
|---|------------|
| 7.1 Identification of Dyes and Pigments by Vibrational Spectroscopy | 383 |
| <i>Juan Manuel Madariaga</i> | |
| 7.1.1 Introduction | 383 |
| 7.1.2 Review of the Scientific Literature | 384 |
| 7.1.3 Databases of Reference Materials | 386 |
| 7.1.3.1 Chemometric analysis of the spectral information | 389 |
| 7.1.4 FT-IR and Raman Spectroscopy Applications | 390 |
| 7.1.4.1 Identification of dyes, pigments and bulk materials | 390 |
| 7.1.4.2 Attribution, authentication and counterfeit detection | 392 |
| 7.1.4.3 Identification of degradation products and degradation mechanisms | 394 |
| References | 396 |
| 7.2 The Vinland Map: An Authentic Relic of Early Exploration or a Modern Forgery – Raman Spectroscopy in a Pivotal Role? | 401 |
| <i>Howell G.M. Edwards</i> | |
| 7.2.1 Introduction | 401 |
| 7.2.2 The Scientific Analysis of the Vinland Map and Tartar Relation | 403 |
| 7.2.3 Raman Microspectroscopic Study | 403 |
| References | 407 |
| 7.3 Study of Manuscripts by Vibrational Spectroscopy | 409 |
| <i>Lucia Burgio</i> | |
| 7.3.1 Introduction | 409 |
| 7.3.2 Why Raman Microscopy? | 410 |
| 7.3.3 Dating and Authentication | 411 |
| 7.3.4 Provenance and Trade Routes | 413 |
| 7.3.5 Infrared Spectroscopy | 415 |
| Acknowledgements | 415 |
| References | 415 |
| SECTION VI: ARCHAEOLOGY AND MINERALOGY | 419 |
| 8 Infrared and Raman Spectroscopy: Forensic Applications in Mineralogy | 421 |
| <i>J. Jehlička</i> | |
| 8.1 Introduction | 421 |
| 8.2 Applications of Raman Spectroscopy for Provenancing | 423 |
| 8.3 Raman Spectroscopy of Minerals | 423 |
| 8.3.1 Class 1: Elements | 423 |
| 8.3.1.1 Carbon | 423 |
| 8.3.1.2 Carbon and Graphitisation | 425 |
| 8.3.2 Minerals from other groups of the mineralogical classification system | 426 |
| 8.3.2.1 Class 2: Sulfides | 426 |
| 8.3.2.2 Class 3: Halogenides | 426 |
| 8.3.2.3 Class 4: Oxides and Hydroxides | 426 |

| | | |
|------------|---|------------|
| 8.3.2.4 | Class 5: Carbonates and Nitrates | 427 |
| 8.3.2.5 | Class 6: Borates | 427 |
| 8.3.2.6 | Class 7: Sulfates | 427 |
| 8.3.2.7 | Class 8: Phosphates | 427 |
| 8.3.2.8 | Class 9: Silicates | 427 |
| 8.3.2.9 | Class 10: Organic Compounds | 427 |
| 8.4 | Opals | 428 |
| 8.5 | Natural Glass | 428 |
| 8.6 | Meteorites | 429 |
| 8.7 | Identification and Provenancing of Gemstones | 430 |
| 8.7.1 | Synthetic gemstones | 431 |
| 8.7.2 | Semi-precious minerals | 431 |
| 8.7.3 | Garnets | 431 |
| 8.8 | Common Minerals | 433 |
| 8.8.1 | Clays | 433 |
| 8.9 | Databases | 434 |
| 8.10 | Identification of Inclusions in Minerals | 434 |
| 8.11 | Raman Mapping Techniques | 436 |
| 8.12 | Analyses Outdoors and On Site | 437 |
| 8.13 | Applications of Raman Spectroscopy to the Provenancing of Rocks | 438 |
| 8.14 | Summary | 438 |
| | Acknowledgements | 439 |
| | References | 439 |
| 8.1 | Identification of Ivory by Conventional Backscatter Raman and SORS | 447 |
| | <i>Michael D. Hargreaves and Howell G.M. Edwards</i> | |
| 8.1.1 | Introduction | 447 |
| 8.1.2 | Application of Raman Spectroscopy | 449 |
| 8.1.2.1 | Preliminary screening method | 449 |
| 8.1.2.2 | Fake sample analysis | 451 |
| 8.1.2.3 | Concealed materials screening | 452 |
| 8.1.3 | Conclusions | 453 |
| | Disclaimer | 453 |
| | References | 454 |
| 8.2 | Applications to the Study of Gems and Jewellery | 455 |
| | <i>Lore Kiefert, Marina Epelboym, Hpone-Phyo Kan-Nyunt and Susan Paralusz</i> | |
| 8.2.1 | Introduction | 455 |
| 8.2.2 | Case Study Example I: Mid-Infrared and Raman Spectroscopy of Diamonds | 456 |
| 8.2.2.1 | Introduction | 456 |
| 8.2.2.2 | Background | 456 |
| 8.2.2.3 | Infrared spectroscopy of diamonds | 457 |
| 8.2.2.4 | Photoluminescence spectroscopy | 457 |
| 8.2.2.5 | Conclusions | 458 |
| 8.2.3 | Case Study Example II: Detection of Fissure Fillings in Emeralds | 458 |

| | | |
|------------|--|------------|
| 8.2.3.1 | Introduction | 458 |
| 8.2.3.2 | Detection of emerald fissure fillings using FT-IR spectroscopy | 461 |
| 8.2.3.3 | Detection of emerald fissure fillings using Raman spectroscopy | 463 |
| 8.2.3.4 | Conclusions | 464 |
| 8.2.4 | Case Study Example III: The Raman Identification of Turquoise | 464 |
| 8.2.4.1 | Introduction | 464 |
| 8.2.4.2 | Advanced analysis of turquoise | 464 |
| 8.2.5 | Summary | 466 |
| | Acknowledgements | 467 |
| | References | 467 |
| 8.3 | Raman Spectroscopy of Ceramics and Glasses | 469 |
| | <i>Paola Ricciardi and Philippe Colombar</i> | |
| 8.3.1 | Introduction | 469 |
| 8.3.1.1 | The Raman spectroscopic signature of ceramics, glasses and enamels | 470 |
| 8.3.2 | How to Discriminate Between Genuine Artifacts and Copies and Fakes | 470 |
| 8.3.3 | On-Site Measurements and Procedures | 472 |
| 8.3.3.1 | Tools for the identification of crystalline and amorphous phases in ceramics and glasses | 474 |
| 8.3.4 | Case Studies | 474 |
| 8.3.4.1 | Alhambra vases (Granada, Spain, fourteenth century) | 476 |
| 8.3.4.2 | Iznik fritware (Ottoman empire, fifteenth–seventeenth century) | 476 |
| 8.3.4.3 | Celadons (Viêt Nam, thirteenth–fifteenth century) | 476 |
| 8.3.4.4 | Medici porcelain (Florence, sixteenth century) | 476 |
| 8.3.4.5 | Glass cup with handles (Low Countries, sixteenth–seventeenth century) | 477 |
| 8.3.4.6 | Meissen porcelains (Saxony, eighteenth century) | 477 |
| 8.3.4.7 | Enamels on metal: Chinese cloisonnés and Limoges painted enamels (fifteenth–nineteenth century) | 478 |
| 8.3.5 | Conclusions | 478 |
| | References | 478 |
| 8.4 | Raman Spectroscopy at Longer Excitation Wavelengths Applied to the Forensic Analysis of Archaeological Specimens: A Novel Aspect of Forensic Geoscience | 481 |
| | <i>Howell G.M. Edwards</i> | |
| 8.4.1 | Introduction | 481 |
| 8.4.2 | Experimental | 486 |
| 8.4.3 | Results and Discussion | 486 |
| 8.4.3.1 | Resins | 486 |
| 8.4.3.2 | Ivories | 492 |
| 8.4.3.3 | Buried skeletal remains | 495 |
| 8.4.4 | Human Tissues and Skeletal Remains | 495 |
| 8.4.4.1 | Nail | 500 |
| 8.4.4.2 | Skin | 501 |
| 8.4.4.3 | Calcified tissues | 507 |

| | |
|---|------------|
| 8.4.4.4 Teeth | 507 |
| 8.4.4.5 Bone | 508 |
| 8.4.5 Conclusions | 509 |
| Acknowledgements | 509 |
| References | 510 |
| SECTION VII: COUNTERFEIT CONSUMER PRODUCTS | 513 |
| 9 Counterfeit Consumer Products | 515 |
| <i>Andrew J. O'Neil</i> | |
| 9.1 Background | 515 |
| 9.2 Anti-Counterfeiting Organisations | 515 |
| 9.3 Definition of a Counterfeit Product | 516 |
| 9.4 Counterfeit Product Spectroscopic Analysis | 516 |
| 9.4.1 Counterfeit alcoholic beverages and whisky | 517 |
| 9.4.2 Counterfeit stamps | 518 |
| 9.4.3 Counterfeit currency | 519 |
| 9.4.4 Counterfeit medicines | 520 |
| 9.4.4.1 Near-Infrared Spectroscopy and Imaging Microscopy | 522 |
| 9.4.4.2 Attenuated Total Reflection Mid-Infrared Spectroscopy and Imaging Microscopy | 526 |
| 9.4.4.3 Raman Spectroscopy, Spatially Offset Raman Spectroscopy and Mapping Microscopy | 527 |
| 9.4.4.4 Use of Portable Spectrometers for Medicines Authentication | 528 |
| 9.4.4.5 Combined Uses of Molecular Spectroscopic Techniques for Medicines Authentication | 529 |
| 9.5 Case Studies Using Mid-infrared, Raman and Near-infrared Spectroscopies and NIR Multispectral Imaging | 529 |
| 9.6 Case Study I: Counterfeit Clothing | 532 |
| 9.6.1 Case study Ia: counterfeit Burberry Classic Check Scarf | 532 |
| 9.6.1.1 Near-Infrared Spectroscopic Analysis | 532 |
| 9.6.1.2 ATR/FT-IR Analysis | 532 |
| 9.6.2 Case study Ib: counterfeit New Era 59fifty baseball caps | 532 |
| 9.6.2.1 Near-Infrared Spectroscopic Analysis | 533 |
| 9.6.2.2 ATR/FT-IR Analysis | 535 |
| 9.7 Case Study II: Counterfeit Aftershave | 536 |
| 9.8 Case Study III: Counterfeit Medicines | 540 |
| 9.8.1 Near-infrared spectrometry | 542 |
| 9.8.2 Raman spectrometry | 545 |
| 9.8.3 NIR Multispectral Imaging | 547 |
| 9.9 Case Study IV: Counterfeit Product Packaging | 549 |
| 9.9.1 ATR/FT-IR Spectroscopy | 549 |
| 9.9.1.1 Tablet Blister-Strip Polymer | 549 |
| 9.9.1.2 Tablet Carton | 550 |
| 9.10 Case Study V: Counterfeit Royal Mail First Class Stamps | 551 |
| 9.10.1 Near-infrared spectroscopic analysis | 551 |

| | |
|---|------------|
| 9.10.2 Near-infrared multispectral imaging | 551 |
| 9.11 Case Study VI: Counterfeit Bank of England Banknotes | 552 |
| 9.11.1 ATR/FT-IR Spectroscopic Analysis | 552 |
| 9.11.2 NIR Multispectral Imaging | 555 |
| 9.12 Conclusion | 555 |
| References | 557 |
| 9.1 Raman Spectroscopy for the Analysis of Counterfeit Tablets | 561 |
| <i>Kaho Kwok and Lynne S. Taylor</i> | |
| 9.1.1 The Pharmaceutical Counterfeiting Problem | 561 |
| 9.1.2 Analytical Techniques to Detect Counterfeit Products | 562 |
| 9.1.3 Using Raman Spectroscopy to Characterise Genuine and Counterfeit Tablets—A Case Study | 563 |
| 9.1.4 Conclusions | 571 |
| Acknowledgements | 571 |
| References | 571 |
| 9.2 Examination of Counterfeit Pharmaceutical Labels | 573 |
| <i>Mark R. Witkowski and Mary W. Carrabba</i> | |
| 9.2.1 Introduction | 573 |
| 9.2.2 Counterfeit Packaging Analysis | 574 |
| 9.2.3 Case Study I: Counterfeit Lipitor® Labels | 574 |
| 9.2.4 Case Study II: Counterfeit Zyprexa® Labels | 578 |
| 9.2.5 Conclusion | 581 |
| Disclaimer | 582 |
| Acknowledgements | 582 |
| References | 582 |
| 9.3 Vibrational Spectroscopy for “Food Forensics” | 583 |
| <i>Victoria L. Brewster and Royston Goodacre</i> | |
| 9.3.1 Introduction | 583 |
| 9.3.2 Adulteration | 584 |
| 9.3.3 Provenance | 587 |
| 9.3.4 Food Spoilage | 587 |
| 9.3.5 Micro-Organism Identification | 588 |
| 9.3.6 Conclusion | 589 |
| Acknowledgements | 589 |
| References | 589 |
| 9.4 Infrared Spectroscopy for the Detection of Adulteration in Foods | 593 |
| <i>Banu Özen and Figen Tokatlı</i> | |
| 9.4.1 Introduction | 593 |
| 9.4.2 Adulteration of Food Products and Application of IR Spectroscopy in the Detection of Adulteration | 594 |

xx *Contents*

| | |
|---|------------|
| 9.4.3 Case Study: Adulteration of Extra Virgin Olive Oils with Refined Hazelnut Oil | 596 |
| 9.4.4 Summary | 599 |
| References | 599 |
| <i>Index</i> | 603 |