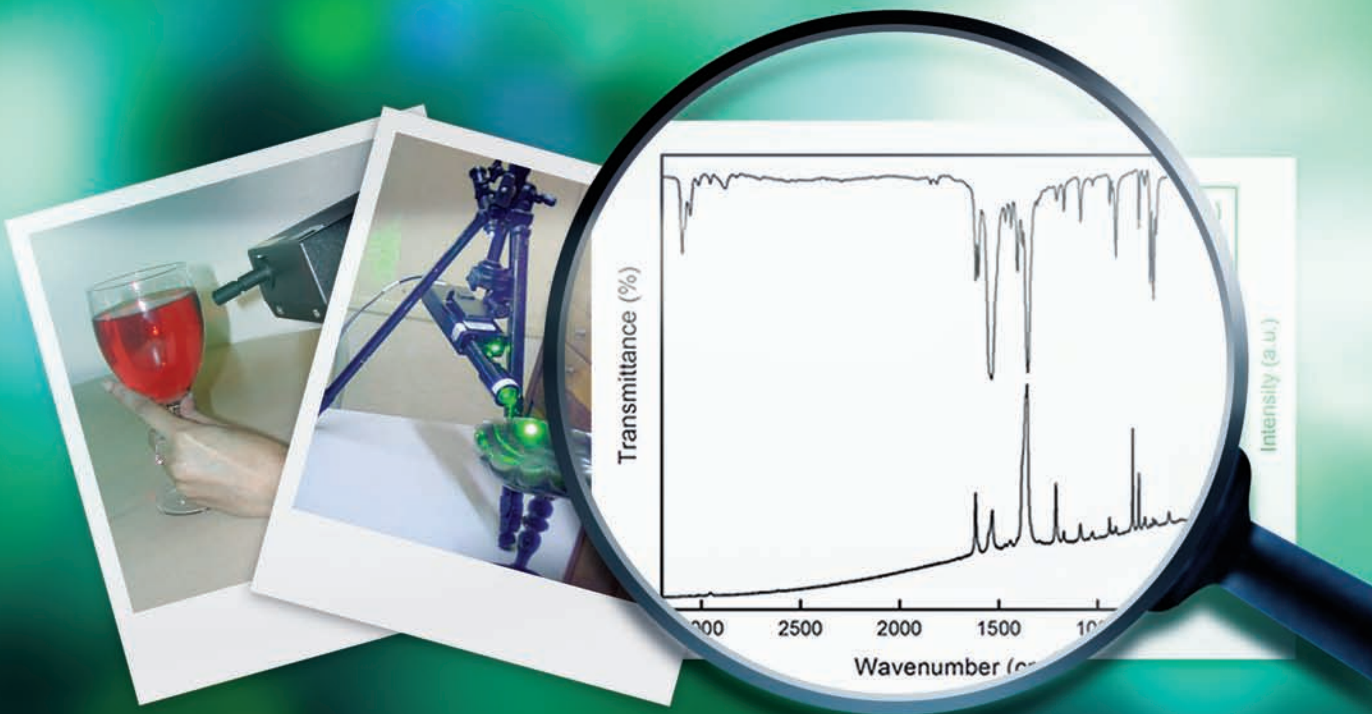
Editors John M. Chalmers | Howell G. M. Edwards | Michael D. Hargreaves

Infrared and Raman Spectroscopy in Forensic Science



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Infrared and Raman Spectroscopy in Forensic Science

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Edited by

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John Chalmers would like to, yet again, apologise to his wife Shelley for her enduring the role of being a book editor's partner, despite having promised previously not to take such a task on again; maybe this will be the last!

Howell Edwards dedicates this book to his wife Gillian and daughter Katharine who have supported him throughout and to his research supervisor, Dr Leonard Woodward at the University of Oxford, who first stimulated what proved to be his lifelong interest in Raman spectroscopy.

Mike Hargreaves would like to thank his partner Jen, family and his fellow editors for their patience and understanding and for sometimes failing to juggle everything.

John M. Chalmers
Howell G.M. Edwards
Michael D. Hargreaves
July 2011

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About the Editors

John M. Chalmers CChem FRSC
John Chalmers "early retired" at the end of 1999 from the United Kingdom chemical company ICI plc; John spent 34 years working with vibrational spectroscopy techniques while employed within research departments of ICI; he retired as a Business Research Associate in the Molecular Spectroscopy Team, Science Support Group, ICI Technology, Wilton Research Centre, UK. In 1994 John was the recipient of the Williams–Wright Award presented by The Coblentz Society for outstanding contributions in the *Field of Industrial Infrared Spectroscopy*. In 2000, John became a self-employed consultant (VS Consulting) specialising in vibrational spectroscopy; he also took up part-time positions as a Senior Research Fellow and then a Special Lecturer for a period of about 10 years within the School of Chemistry at the University of Nottingham. John has also been a visiting lecturer to the School of Chemical Sciences, University of East Anglia, from 1992–2000. Among his spectroscopic society activities, John is a Past President (2008) of the Society for Applied Spectroscopy (SAS), having served SAS previously as both a Governing Board Member and an International Delegate; John was Chair of the UK Infrared and Raman Discussion Group (IRDG) for nine years (1995–2003).

John has published over 50 peer-reviewed technical papers in scientific journals; he has also had published over 20 book chapters or reference articles. He has co-authored one book (*Industrial Analysis with Vibrational Spectroscopy*, with Geoffrey Dent, 1997, Royal Society of Chemistry, Cambridge); John has also edited or co-edited several books, including the highly acclaimed reference work the five-volume *Handbook of Vibrational Spectroscopy* (co-edited with Professor Peter Griffiths, 2002, published by John Wiley & Sons, Ltd, Chichester). Edited or co-edited book titles published include: *Spectroscopy in Process Analysis* (2000, Sheffield Academic Press, Sheffield), *Raman Spectroscopy in Archaeology and Art History* (with H.G.M. Edwards, 2005, Royal Society of Chemistry, Cambridge), *Molecular Characterization and Analysis of Polymers* (with Robert J. Meier, 2008, published by Elsevier, Amsterdam); and the books with titles published by John Wiley & Sons, Ltd., Chichester are: *Vibrational Spectroscopy of Polymers: Principles and Practice* (with Neil J. Everall and Peter R. Griffiths, 2007), *Applications of Vibrational Spectroscopy in Pharmaceutical Research and Development* (with Don E. Pivonka and Peter R. Griffiths, 2007), *Vibrational Spectroscopy for Medical Diagnosis* (with Max Diem and Peter R. Griffiths, 2008), *Applications of Vibrational Spectroscopy in Food Science* (two-volume set, with Eunice C.Y. Li-Chan and Peter R. Griffiths, 2010). John is also currently the Article Editor for *Spectroscopy Europe*.

Professor H.G.M. Edwards M.A., B.Sc., D.Phil., C.Chem. FRSC, Emeritus Professor of Molecular Spectroscopy
Howell Edwards studied Chemistry at Jesus College, University of Oxford, and carried out research for his DPhil at Oxford on chemical applications of Raman spectroscopy under the supervision of Dr. Leonard Woodward. Following a Research Fellowship at Jesus College in the University of Cambridge he took a

lectureship in Structural and Inorganic Chemistry at the University of Bradford where he became Reader and then Professor of Molecular Spectroscopy and Head of the Chemical and Forensic Sciences Division. In 2003, he received the Sir Harold Thompson Award from Elsevier Science for his international contributions to vibrational spectroscopy. He is the recipient of the Emanuel Boricky Medal for 2008/2009 from Charles University, Prague, for distinguished international contributions to geochemistry and mineralogical analysis. In his research career he has published over 1000 papers on Raman spectroscopy and its applications and is the co-editor of three books: *A Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line* (with I.R. Lewis, 2001, Marcel Dekker, New York), *Selected Topics in Raman Spectroscopic Applications: Geology, Biomaterials and Ar*t (with F. Rull Perez, P. Vandenabeele and D.C. Smith, 2007, Publidisa Valladolid), and *Raman Spectroscopy in Archaeology and Art His*tory (with J.M. Chalmers, 2005, RSC Publishing, Cambridge). He is the recipient of the 2011 Charles Mann Award of the international Federation of Analytical Spectroscopic Societies (FACSS) for distinguished work in applications of Raman spectroscopy. Professor Edwards is a member of the Editorial Boards of *J. Raman Spectroscopy*, *J. Molecular Structure*, *Spectrochimica Acta*, *Vibrational Spectroscopy*, *Drug Targeting and Analysis* and *Asian J. Spectroscopy*. He is Associate Editor of the *International Journal of Astrobiology*.

Professor Edwards has wide-ranging interests in the applications of Raman spectroscopy to the characterisation of materials in forensic, art historical, polymer, pharmaceutical and archaeological contexts, the characterisation of contraband biomaterials (ivories and drugs of abuse), and spectroscopic molecular signatures relating to the biological survival of cyanobacteria in putative Martian terrestrial analogues. He is international lead coordinator of the Science Team on the RLS Raman instrument with the NASA/European Space Agency on the ExoMars project for the construction and terrestrial evaluation of a miniature Raman spectrometer adopted for a planetary robotic lander for surface and subsurface exploration and search for life on Mars. The Raman spectroscopic characterisation of contraband biomaterials, including the evaluation of portable Raman spectrometers for the field acquisition of data on ivories and drugs of abuse of forensic relevance, has been carried out with support from the Engineering and Physical Sciences Research Council and sponsored by security and law enforcement agencies.

Michael D. Hargreaves MChem, PhD, CSci, CChem, MRSC

Michael Hargreaves studied chemistry at the University of Newcastle upon Tyne, United Kingdom, and carried out a PhD under the supervision of Professor Mike George and Associate Professor Barrie Kellam at the University of Nottingham, UK, on reaction monitoring using FT-IR and Raman spectroscopy.

He undertook two postdoctoral positions with Professor Howell Edwards, at Bradford University, UK, the first on portable Raman spectroscopy for identification/screening of biomaterials, drugs of abuse and explosives, the second on evaluation and development of the RLS Raman detector and geological library with European Space Agency/NASA on the ExoMars project.

After this Mike joined industry, working for Cobalt Light Systems, with Professor Pavel Matousek, commercialising SORS and transmission Raman spectroscopy. He left to join Ahura Scientific in the Application Development Group; Ahura Scientific was subsequently acquired by Thermo Fisher Scientific, where Mike remains within the Portable Analytical Instruments Group.

Michael Hargreaves has authored or co-authored over 30 publications, covering the application of vibrational spectroscopy to the fields of drugs of abuse, explosives, pharmaceutics, geology, biomaterials and works of art.

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July 2010

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Preface

For many years the practices of infrared and Raman spectroscopy were confined largely to dedicated academic, industrial or national research laboratories. Major technical advances over the past 10–20 years have afforded a significant broadening of the applicability of these vibrational spectroscopy techniques as a whole.

Instruments used to be large, complicated to operate, with even the simplest experiment often challenging to set up and run. Advances in technology have resulted in smaller, easier to use instrumentation that is much more user-friendly. Demands and needs from users for increased portability of scientific instrumentation have produced spectrometers and interferometers of small dimensions and of sufficient quality such that handheld Raman and Fourier transform infrared (FT-IR) instruments have been realized over the past few years, opening up much wider application of Raman and FT-IR spectroscopy to forensic science applications, particularly for adoption into field usage.

This book is intended to introduce a novice or established spectroscopic practitioner of analytical chemistry to the technical elements of Raman and infrared spectroscopy as applied to forensic science, outlining several proven and potential applications within this field. It is not intended to describe advanced topics such as non-linear Raman or time-resolved vibrational spectroscopy, but rather to address the applications of Raman and IR spectroscopy to the different fields of forensic work, from explosives to narcotics and from bio-agents to works of art.

The early chapters introduce the reader to the principles of forensic science and how Raman and IR spectroscopy can be applied. Chapter 2 introduces the basics of vibrational spectroscopy and the instrumentation that may be found routinely, ranging from bench-top through portable to handheld systems. To complement this, Chapter 3 discusses sampling techniques and considerations of analysis to aid in the non-destructive analysis of samples.

The following sections of the book are split into overviews and case-study chapters comprising topics covering the following areas: crime scene, counter terrorism/homeland security, drugs of abuse, archaeology/mineralogy and consumer products, including pharmaceutics. Each chapter is written by internationally respected scientists. This broad selection of topics is complemented by relevant application examples, highlighting how IR, Raman and terahertz (THz) spectroscopy can be applied to these fields. To complement this, each chapter is referenced so that users can read up on and investigate areas that interest them.

Commercial Raman, near-IR, mid-IR and THz spectrometers differ widely in their applicability, configuration and performance. No one system can be applied to all possible applications; specific manufacturers are mentioned within the text to identify a particular approach, configuration or application. Where manufacturers are mentioned, this does not infer an endorsement, but it may be useful to the reader to understand the special design or application objectives and requirements.

It is the editors' and contributors' hope that those just developing an interest in the application of infrared and Raman spectroscopy to forensic analysis and that those who practice it already will find this book useful not only as a source of new information, but also as a reference work. Furthermore, we hope that it will inspire readers to delve deeper into the applications of vibrational spectroscopy that have not yet been explored in this rapidly expanding field.

Notes on convention (or lack of them): it is usual practice to plot IR spectra from high wavenumber (on the left) to low wavenumber (on the right); this convention is held throughout the book. Raman shifts are often shown plotted either way, that is, low shift (on the left) to high shift (on the right) or vice versa. It has not been possible to ensure all the spectral plots have been standardised in this way, particularly those that have been reproduced from other publications, so readers are directed to check the individual plots. In addition, the Raman shift axis only shows the Stokes-shifted bands, unless stated otherwise. Mostly Raman shifts are noted in the unit cm^{-1}, rather than the more correct form of Δcm^{-1}.

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