Section I
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Introduction and Scope

John M. Chalmers¹, Howell G.M. Edwards² and Michael D. Hargreaves³

¹VS Consulting, Stokesley, UK
²Chemical and Forensic Science, University of Bradford, Bradford, UK
³Thermo Scientific Portable Optical Analyzers, Thermo Fisher Scientific, Wilmington, Mass., USA

1.1 Historical Prologue

Forensic science can be defined as the application of scientific principles to the public domain in courts of law, which were held by the Romans in the public forum.

Although evidence of the unlawful killing of a human being was presented in public fora from quite early times, such as the post mortem examination of the body of Julius Caesar after his assassination, which revealed 23 stab wounds but only one of which was judged to be fatal, and poisoning in particular, where the appearance of organ degradation gave rise to the conclusions that toxic materials had been ingested, these pronouncements were in the realm of the prototype medical examiners and pathologists and not chemical analysts [1].

The first chemical analysis of an historical artefact that can be viewed as “forensic” in its approach was reported in the literature by Sir Humphry Davy in 1815. The development of the Marsh test for arsenic poisoning in 1836 was a landmark event that launched the birth of analytical forensic science. This was followed quite rapidly by the public fascination for scientific analysis applied to crime as appeared in the Victorian gothic novel in detective stories such as Armadale [2], authored by Wilkie Collins in 1866, and culminating in the adventures of Sherlock Holmes, whose creator Sir Arthur Conan Doyle introduced in A Study in Scarlet [3] in December 1887, just one year before the notorious “Jack the Ripper” brought terror to the East End of London, England. Subsequently, some 56 of Conan Doyle’s short stories, published in the popular Strand Magazine between 1891 and 1927, commencing with A Scandal in Bohemia, established the Sherlock Holmes genre to an appreciative public; an unsuccessful attempt by Conan Doyle to terminate the Holmes character in a fatal meeting with his arch-enemy Professor Moriarty at the Reichenbach Falls in 1893 resulted in intense public outrage; such was the growing public perception of the scientific approach to
crime solution at that time, and the detective re-appeared to his public once more in *The Hound of the Baskervilles* in 1901.

The seemingly voracious appetite of readers for the scientific detection of crime in the mid-nineteenth century is illustrated in *Armadale* by the attempt by Miss Gwilt to murder her fiancé, the eponymous Armadale of the novel, using a chemical reaction between an unspecified liquid in a purple flask supplied by a mysterious admirer and the generation of an odourless, tasteless and undetectable gas whilst he was sleeping. The author had acknowledged appropriately the assistance and advice of an un-named professional chemist in the preface to his novel, thereby lending a veneer of respectability and credibility to the background science contained in the text! The activities of Sherlock Holmes and his analytical skills and observations pervade the Conan Doyle stories and hint at the prophetic accomplishments of Conan Doyle, said to be based upon his University mentor, Dr Joseph Bell, that were significantly in excess of the extant knowledge in the late 1880s.

It is, therefore, perhaps not surprising that the first recorded acceptance of forensic chemical analysis used in a court of law to secure a conviction occurred as late as 1912 in France when Emile Gourbin, who had a seemingly good, watertight alibi, was faced with evidence of his poisoning of his lover, Marie Latelle, using contaminated *poudre de riz*, a customised cosmetic preparation that was fashionable at that time. The scientific analyst at the centre of this landmark prosecution was Edmond Locard, who demonstrated that particles of material under the fingernails of the accused matched the composition of the cosmetic preparation purchased from a local pharmacist but with the addition of bismuth. It is interesting that some years later in 1927, this same Edmond Locard, then a professor at the University of Lyon, proposed his now famous and fundamental eponymous Exchange Principle that is at the basis of modern forensic science: that “every vigorous contact leaves a trace”.

There quickly followed the establishment of analytical laboratories internationally dedicated to forensic science, early examples of which in France was that of Edmond Locard in 1910 and in the United States by August Vollmer in 1924. The first Chair of Legal Medicine in a University, so establishing an academic forensic protocol, was established in Harvard in 1932.

A classic case of murder by poisoning that first escaped detection in the United Kingdom but which relied heavily upon chemical analysis to secure prosecution, was that of Major Herbert Armstrong, who systematically poisoned his wife using arsenic in 1921; only when he tried to repeat the exercise to remove a business rival did Major Armstrong receive his just desserts – a close relative of the business rival was the local pharmacist, who recollected that Armstrong had purchased large quantities of arsenic over the previous year. Exhumation of the Major’s wife revealed to the pathologist a large amount of arsenic in her remains – as exemplified by the adoption of the Marsh test; Armstrong was convicted of her murder and hanged in 1922 [4, 5].

The use of infrared spectroscopy to determine molecular structure has its roots firmly established in the nineteenth century, since the discovery of the infrared region of the electromagnetic spectrum in 1800 by Sir William Herschel. But the Raman effect was first observed experimentally only in 1928 by Sir Chandrasekhar Raman, following a theoretical prediction by Smekal in 1923, which resulted in the Nobel Prize for Physics for Raman in 1930. Lord Rayleigh, commenting on the observation of the Raman effect, judged this to be one of the four most important discoveries in physics of all time.

At first, the relative ease of recording photographically the wavenumber-shifted radiation of the weak Raman effect compared favourably with the point by point plotting of moving coil galvanometer signals used in infrared spectroscopy and gave an impetus to Raman spectroscopy in molecular structure analysis that surpassed the infrared investigations. However, it became quickly apparent that the onset of fluorescence emission swamped the weaker Raman data, often saturating the photographic emulsions used in the spectrographic recording. For many years this disadvantage was paramount in Raman spectroscopy and it was only the advent of tuneable laser excitation and novel methods of detection coupled with computerised
data acquisition that offered possibilities to circumvent it. Hence, although mid-infrared spectroscopy started to be applied to forensic analysis from the 1950s, Raman spectroscopy was only similarly used from the 1990s; in both cases, however, the coupling of a microscope to the analytical spectrometer was a necessary advancement. The advent of portable and handheld spectrometers has further advanced this application space, meaning analysts can analyse in situ artefacts of interest.

In the past, the greatest stumbling block to the application of both infrared spectroscopy and Raman spectroscopy to forensic structural analysis and molecular characterisation was the quantity of material that was required for analysis and the further requirement that in most cases the preparation of the specimen for the optical illumination processes necessitated the destruction, mechanically or chemically, of the sample itself. This was paralleled in chemical analysis, in that even as early as 1815 Davy [6] recognised that his experiments on the archaeological decorative wall painting artefacts from the recently excavated Pompeii archaeological site resulted in the complete destruction of the samples presented for analysis. Even 100 years later, Eccles and Rackham [7], in their comprehensive studies of porcelains in the British Museum and Victoria and Albert (V&A) Museum collections in the United Kingdom required the donation of multiple items from tea and dinner services which were sacrificed in the determination of factory body chemical compositions using wet chemical analysis. It was, therefore, a very important turning point in the mid-twentieth century when it was realised that advances in spectroscopic technology now made available for the first time the possibility of acquiring chemical molecular data from valuable specimens that was truly non-destructive of the sample [8–10].

In the 1970s great strides forward were made when optical microscopes were coupled with spectrometers to provide chemical identification data from spatially minimal regions of samples. The first infrared microspectrometer appeared in the mid-1960s and the first Raman microspectrometer was announced from the laboratory of Michel Delhaye and Paul Dhamelincourt in the University of Lille, France, in 1976; this was termed a molecular optical laser examiner (MOLE) which was quickly applied to the investigation of several interdisciplinary problems, including some fragments from oil paintings. The first papers in this area, which could perhaps be classified as ground-breakers for the later application of Raman microscopy in forensic science, then appeared from the laboratories of the Natural History Museum of Paris under the direction of Bernard Guineau, who analysed the inorganic pigments from mediaeval manuscripts in museum collections [11].

1.2 The Application of Infrared Spectroscopy and Raman Spectroscopy in Forensic Science

Both techniques share a microspectroscopic capability for the recording of data from particles in the nanogram to picogram range, which is paramount for the interrogation of specimens non-destructively; little if any sample preparation is required, which means that vibrational spectroscopy is often regarded as a first-pass analytical technique for the screening and identification of suspect materials which then may require some further analytical data from more destructive operations.

Naturally, infrared spectroscopy and Raman spectroscopy have particular advantages and disadvantages, which sometimes dictate that one or other technique is preferred for special applications: for example, the presence of water or hydrated chemical species in specimens can hamper the mid-infrared analysis and the ready inaccessibility with mid-infrared spectrometers of low wavenumber features below 400 cm\(^{-1}\) can severely limit the characterisation of drug polymorphs and heavy metal inorganics. The operational dependence of the Raman effect upon molecular polarisability rather than the dipole moment for the infrared means that polar groups such as –OH and C=O are better seen in the infrared spectrum, whereas homopolar unsaturation involving C≡C groups and N=N is better evidenced in the Raman spectrum. The degradation of keratotic materials such as skin, hair and nail associated with human remains in burial environments is best
followed through the –S–S– modes near 500 cm\(^{-1}\) in the Raman spectrum as this feature does not appear at all in the infrared spectrum.

A major factor in Raman spectroscopy applications to materials in a forensic context is the ability to overcome or circumvent fluorescence emission and this needed the advent of laser excitation at longer wavelengths from the visible into the near-infrared region of the electromagnetic spectrum, typically at 785, 830 or 1064 nm. Modern state of the art vibrational spectroscopic laboratories involved in forensic analysis therefore have several laser sources available for adoption in this respect, especially where samples are highly coloured, such as pigments and dyes.

Field–use capability of instrumentation is a desirable development for the adoption of miniaturised infrared and Raman spectrometers at crime scenes and for the examination of large or very fragile objects and artefacts. In this context, the penetration of packaging and the interrogation of specimens through transparent or semitransparent containers is also possible through shrewd selection of the radiation wavelength, and the possibilities of the terahertz (THz) region of the spectrum is affording much interest in this respect. An important factor here is the incorporation of database recognition packages within the chosen instrument to identify materials that are of relevance to forensic examination, such as drugs of abuse, explosives, chemical warfare agents and their chemical precursors, which may be correlated with drugs factories and synthetic bomb-making crime scenes. The use of such instrumentation by non-expert security forces and agents by the adoption of selection algorithms is also a real challenge for specialised spectroscopists.

Of special interest is the recording of seized specimens of suspect materials that can be examined whilst still contained in their evidential bags sealed at source and which need not be sampled or opened in the analytical laboratory; the data from such analyses carried out under these conditions can circumvent any doubts raised about the integrity of the preservation of the evidential material between the source and the analytical laboratory. This type of analysis has a distinct parallel in the scientific examination of artworks, which for operational reasons cannot be removed from their transparent covers or holders; in a “forensic art” study [12] of the Armada Jewel made for Queen Elizabeth I by Nicholas Hilliard, a prestigious court limner, in 1588, and now in the V&A Museum in London, the Raman spectroscopic characterisation of the pigments used was achieved by interrogation of the painting through its rock crystal cover plate, with some rather surprising results.

Finally, the so-called molecular fingerprint that is provided from the mid-infrared spectrum or Raman spectrum must be well-characterised and robust: for example, the question arises as to how many vibrational spectroscopic features are necessary to define a particular compound unequivocally – this is not easy to assess and sometimes it is relatively easy to differentiate between chemically similar materials and not so in other cases. In pigment characterisation, for example, the two forms of lead (II) oxide are readily differentiated in the low wavenumber region using Raman spectroscopy; in the geological field, anatase can readily be differentiated from rutile and brookite, yet all are titanium (IV) oxides; and the polymorphs of calcium carbonate, calcite and aragonite are easily discriminated by both mid-infrared and Raman spectroscopy. In each case, the detection of more than one vibrational spectroscopic feature is essential for correct identification of the specimen. In the area of drugs analysis, cocaine hydrochloride and freebase cocaine (crack cocaine) can be differentiated as can caffeine base and caffeine hydrate. The power of these techniques thus rests in an appreciation of the necessity for recording spectra of the best quality consistent with speed and rapid identification that is often a de rigueur requirement of the end user.

This book comprises overview chapters and case study chapters written by experts and practitioners who have a wealth of experience in the application of infrared, Raman and THz vibrational spectroscopic techniques to forensic analysis in which several of the points made above are investigated and exemplified; several outstanding challenges remain that need the collaboration of vibrational spectroscopists, forensic practitioners and front-line security forces in the advancement of technologies in the fight against crime, contraband trafficking and international terrorism.
References
