



Applications of Raman Spectroscopy in Forensic Science. I: Principles, Comparison to Infrared Spectroscopy, and Instrumentation

E. M. Suzuki*

Washington State Crime Laboratory
Washington State Patrol
Seattle, Washington
United States of America

P. Buzzini

Department of Forensic Science
Sam Houston State University
Huntsville, Texas
United States of America

TABLE OF CONTENTS

INTRODUCTION	112
I. FEATURES OF RAMAN SPECTROSCOPY	113
II. THEORY	113
A. Rayleigh Scattering	114
B. Raman Scattering	115
C. Resonance Raman Scattering	118
D. Surface-Enhanced Raman Scattering (SERS)	120
E. Laser-Induced Fluorescence	121
III. COMPARISONS OF INFRARED AND RAMAN SPECTRAL DATA	121
A. Display Formats	121
B. Infrared Microscopy vs. Raman Microscopy	122
C. Organic Compounds	123
D. Inorganic Compounds	124
E. Composite Matrices: Paint	127
IV. INSTRUMENTATION	128
A. Source Lasers	128
B. Filters	128
C. Sampling Optical Configurations	129
D. Monochromators	130
E. Detectors	132
F. Raman Microscopes	132
ACKNOWLEDGMENTS	134
REFERENCES	134
ABOUT THE AUTHORS	135

* Corresponding author: Dr. Edward M. Suzuki, Washington State Crime Laboratory, Washington State Patrol, Seattle, WA 98134; +1 206 262 6020 (voice); edward.suzuki@wsp.wa.gov.

Applications of Raman Spectroscopy in Forensic Science. I: Principles, Comparison to Infrared Spectroscopy, and Instrumentation

REFERENCE: Suzuki EM, Buzzini P: Applications of Raman spectroscopy in forensic science. I: Principles, comparison to infrared spectroscopy, and instrumentation; *Forensic Sci Rev* 30:111; 2018.

ABSTRACT: There have been several significant advances in Raman spectroscopy instrument technology during the past few decades, including the introduction of several new laser sources, the development of holographic gratings, efficient Rayleigh line rejection filters, and CCD array detectors, and the advent of FT-Raman spectrometers. In view of these developments, Raman spectroscopy is now a fully mature analytical technique on par with its counterpart, infrared spectroscopy. The latter technique experienced a quantum leap in use in the forensic science laboratory following the introduction of inexpensive FT-IR spectrometers in the 1980s, but forensic scientists have been slower to embrace Raman spectroscopy. This may stem in part from the perception that fluorescence prevents its use for many samples. However, a more significant factor may be insufficient understanding of the unique capabilities of Raman spectroscopy, including how it can provide information not accessible using other methods. This promising technique is finally making some inroads into the forensic science laboratory, and this will continue as forensic scientists gain a greater appreciation of its features and merits. To facilitate this process, this article presents a comprehensive review of Raman spectroscopy, with an emphasis on how and why this underutilized cousin to infrared spectroscopy can be a very valuable tool for the analysis of a wide variety of evidentiary materials. Owing to the wide scope of this review, it is presented in two parts. Most forensic scientists are not very familiar with inelastic scattering and Part I of this article describes the principles and instrumentation of Raman spectroscopy. Forensic scientists, however, are generally more knowledgeable about infrared spectroscopy, and a comparison of the spectral data produced by these two related vibrational methods for various categories of analytes is also presented and discussed.

KEY WORDS: Criminalistics, evidence analysis, forensic applications, forensic science, FT-Raman spectroscopy, Raman microscopy, Raman scattering, Raman spectroscopy, trace evidence.

INTRODUCTION

The Raman effect, which involves inelastic scattering of light, was predicted theoretically by Smekal in 1923 [25] and was observed experimentally by Raman and Krishnan in 1928 [22]. It is an extremely weak process; Rayleigh (elastic) scattering, which occurs at the same time, is typically five to seven orders of magnitude greater in intensity. Early custom-built Raman spectrometers, which relied on mercury arc lamps as excitation sources, prisms as dispersive elements, and photographic films as detectors, required many hours of data collection. The first commercial Raman spectrometer was introduced in 1953 and it employed a photomultiplier tube instead of photographic film [3]. This allowed for a more quantitative measurement of Raman-scattered light, but at the cost of the multiplexing feature of a photographic film, as data would now have to be collected by sequentially scanning through the desired spectral range. Diffraction gratings replaced prisms in the late 1950s, but a system of two or three gratings in tandem was required to remove stray light from the very intense Rayleigh-scattered peak.

One of the most significant developments in Raman instrument technology occurred in the 1960s when visible lasers replaced mercury arc lamps. Not only were highly

monochromatic sources having greater power levels now feasible using coherent radiation, but use of a wider range of wavelengths to seek more favorable excitation conditions became available. The increased sensitivity afforded by the laser also led to the development of the first Raman microscope in 1973 [13]. However, even with laser excitation and photomultiplier detectors, Raman spectra were still acquired by scanning through the entire spectral range. When diode array detectors began to be used in the 1980s, their multiplexing ability allowed simultaneous collection of scattered light over a wide spectral range, permitting shorter collection times.

Other significant instrument developments that occurred in the 1980s were the advent of efficient rejection filters to remove Rayleigh-scattered light, and the introduction of near-infrared lasers. Interferometry, as employed in a Fourier transform infrared (FT-IR) spectrometer [11,27], cannot be used to disperse (mathematically) Raman-scattered light if a Rayleigh line is present, as the contribution of the latter to an interferogram would completely overwhelm the very feeble contributions from Raman bands. Using these new filters, however, FT-Raman spectrometers became a viable means to use near-infrared lasers for excitation, and the first Fourier transform instrument was developed in 1985 [3].

- interpretation, and examination of evidence; *Forensic Sci Rev*; 30:155; 2018.
30. Suzuki EM, Carrabba M: In situ identification and analysis of automotive paint pigments using line segment excitation Raman spectroscopy: I. Inorganic topcoat pigments; *J Forensic Sci* 46:1053; 2001.
 31. Suzuki EM, Nibler JW: Vibrational spectra of *cis*-3,4-dichlorocyclobutene; *Spectrochim Acta Part A* 30:15; 1974.
 32. Thermo Fisher Scientific: Raman spectroscopy, unveiling the secrets of limestone (Application Note 52569); Thermo Fisher Scientific: Madison, WI; 2014; <https://tools.thermofisher.com/content/sfs/brochures/CAD-Molecular-Raman-LimestoneCarbonates.pdf>(accessed June 12, 2018).
 33. Turrell G, Delhaye, Dhamelincourt: Characteristics of Raman microscopes; In Turrell G, Corset J (Eds): *Raman Microscopy: Developments and Applications*; Academic Press: London, UK; pp 27–50; 1996.
 34. Tuschel D: Selecting an excitation wavelength for Raman spectroscopy; In *Molecular Spectroscopy Workbench: The 2006 Collection*; Spectroscopy: Iselin, NJ; pp 11–17; December 2016; <http://images2.advanstar.com/PixelMags/spectroscopy/digitaledition/12-2016-sp.html#10>(Accessed June 20, 2018).
 35. Weimer R, Clary J, Heintz R, Wall M: Analysis of bicomponent fibers using confocal Raman mapping; *JASTEE* 3:21; 2012.



Edward M. Suzuki received his B.S. degree in chemistry from the University of Washington (Seattle, WA) in 1970 and his Ph.D. in chemistry (physical) from Oregon State University (Corvallis, OR) in 1975. Dr. Suzuki's doctoral dissertation involved the characterization of highly reactive chemical species trapped in low-temperature argon matrices using various spectroscopic methods, including infrared, Raman, and electron paramagnetic resonance.

Dr. Suzuki is currently a supervising forensic scientist at the Washington State Crime Laboratory (Seattle, WA). He has worked for over 38 years in the field of forensic science and has testified in over 750 criminal cases. His main research interests include applications of infrared, Raman, and X-ray fluorescence spectroscopies for the analysis of various types of evidence, and particularly, for the identification of pigments in automotive finishes. He has published over 30 research papers, primarily in the area of vibrational spectroscopy.

Dr. Suzuki has helped teach classes on forensic applications of infrared spectroscopy for the FBI Academy (Quantico, VA), IR Courses Inc. (Bowdoin College: Brunswick, ME), Eastern Washington University (Cheney, WA), the California Criminalistics Institute (Sacramento, CA), Microtrace LLC (Elgin, IL), and public forensic science laboratories in New Hampshire, Illinois, California, and Singapore. He is a fellow of the American Academy of Forensic Sciences; a member of the American Chemical Society, the Society for Applied Spectroscopy, the Coblentz Society, the American Society of Trace Evidence Examiners, and the Northwest Association of Forensic Scientists; and is certified as a fellow by the American Board of Criminalistics.

Patrick Buzzini graduated from the Institut de Police Scientifique of the School of Criminal Sciences with the University of Lausanne (Lausanne, Switzerland). In 2007, he obtained a doctoral degree in forensic science from the same institution on the application of Raman spectroscopy to criminalistics and particularly to the discrimination of dyed fibers. Dr. Buzzini is an associate professor in forensic science with the Department of Forensic Science at Sam Houston State University (Huntsville, TX).

Dr. Buzzini has more than 15 years of experience as an instructor, researcher, and caseworker in criminalistics, with emphasis in trace evidence. His research interests include the forensic applications of microscopic and spectroscopic methods (i.e., Raman spectroscopy, infrared spectroscopy, and microspectrophotometry) to various types of trace evidence and questioned documents as well as addressing problems of physical evidence interpretation. He has published over a dozen papers in the field of forensic science.

Dr. Buzzini has provided training nationally and internationally to practitioners in the field and to the legal community in the areas of trace evidence analysis and interpretation. He is a fellow of the American Academy of Forensic Sciences, a member of the Organization of Scientific Area Committees (OSAC) on Chemistry and Instrumental Analysis, a member of the American Society of Trace Evidence Examiners, and an associate member of the International Association for Identification.