Forensic Sci Rev 30:137–169
July 2018

Applications of Raman Spectroscopy in Forensic Science. II: Analysis Considerations, Spectral Interpretation, and Examination of Evidence

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 138
I. ANALYSIS CONSIDERATIONS 139
A. Avoiding or Minimizing Fluorescence 139
B. Avoiding Photo/Thermal Degradation of Samples 140
C. A Note of Caution 141
D. Optimal Analysis Conditions 141
II. SPECTRAL INTERPRETATION 142
A. Spectral Artifacts 142
B. Dependence of Raman Spectra on Excitation Wavelength 142
C. Variations in Raman Spectra of Anisotropic Materials 145
D. Silicate Extender Pigments 147
III. EXAMINATION OF PHYSICAL EVIDENCE 147
A. Seized Drugs 147
B. Textile Fibers 149
C. Paint 151
D. Inks and Toners 153
E. Explosives 155
F. Bodily Fluids 158
G. Miscellaneous Evidence 159
ACKNOWLEDGMENTS 160
REFERENCES 160
ABOUT THE AUTHORS 169

* 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.

1042-7201/30-2/July 2018/137–169/$49.50 •

Applications of Raman Spectroscopy in Forensic Science. II: Analysis Considerations, Spectral Interpretation, and Examination of Evidence

REFERENCE: Suzuki EM, Buzzini P: Applications of Raman spectroscopy in forensic science. II: Analysis considerations, spectral interpretation, and examination of evidence; *Forensic Sci Rev* 30:137; 2018.

ABSTRACT: There have been several significant advances in Raman spectroscopy instrumentation during the past few decades, and this method is now a fully mature analytical technique on par with its counterpart, infrared spectroscopy. The latter method 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. However, this promising technique is finally making some inroads into the forensic science laboratory, and to facilitate this process, this article presents a comprehensive review of Raman spectroscopy; it emphasizes how and why this underutilized method can be a very valuable tool for the analysis of a wide variety of evidentiary materials. Part I of this article described the principles of Raman spectroscopy, including theory, instrumentation, and a comparison of spectral data obtained using infrared and Raman methods for various analytes. Part II discusses how different analytical conditions can affect Raman spectra, and what bearing this and other factors may have on spectral interpretation; it also presents a review of the literature describing applications of Raman spectroscopy for the examination of various types of evidence.

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

INTRODUCTION

Following the introduction of dependable, inexpensive Fourier transform infrared (FT-IR) spectrometers in the early 1980s, this instrument soon became an indispensable tool in the forensic science laboratory. This was particularly true for applications involving seized drugs, certain types of trace evidence, and unknown materials, and there are now few forensic science laboratories worldwide that are not equipped with an FT-IR spectrometer.

In contrast, an analogous revolution involving use of Raman spectroscopy in forensic science did not occur. Raman scattering is an inherently weak process that is completely dwarfed by Rayleigh scattering, and in some cases, fluorescence as well. Consequently, a number of technological developments and innovations were required before Raman spectrometers achieved a level of utility for routine analysis comparable to that of FT-IR spectrometers. Because these developments occurred over the span of several decades, as well as other factors, Raman spectroscopy did not enjoy the same overnight success as did FT-IR spectroscopy.

The first forensic science laboratory to use Raman microscopy was McCrone Associates, Inc., as reported by Andersen and Muggll in 1981 [16]. At least two decades passed, however, before there was a notable increase in the number of literature references describing applications of Raman spectroscopy for the analysis of evidence. There are now hundreds of such articles and this often-ignored and underutilized cousin to infrared spectroscopy is finally making inroads into the forensic science laboratory.

Part I of this article described the principles of Raman spectroscopy, including analytical features, theory of the Raman effect, and instrumentation [230]. Because forensic scientists are generally more familiar with infrared spectroscopy than Raman spectroscopy, a comparison of the data produced by these two related methods for various samples was also discussed. One very significant difference between the two is that Raman spectra can be much more dependent on analytical conditions than infrared spectroscopy. Some of the reasons for this were described in Part I, and other factors are discussed in Part II.

An important aspect of any spectroscopic analysis — but especially one where variable data may result — is interpretation. Accounting for spectral differences is a major issue for comparative examinations, as is often conducted for some types of trace evidence. Interpretation of Raman data is thus discussed at length in Part II, along with a comprehensive review of the literature describing applications of this method for the analysis of evidence.

Because many of the figures presented in Part I serve to illustrate both principles and applications, reference is made to some of them in the current article. These particular figures are denoted with a "I" after the figure number to distinguish them from those of the current article.

ABOUT THE AUTHORS

E. M. Suzuki; P. Buzzini

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.