



Raman spectroscopy – Basic principle, instrumentation and selected applications for the characterization of drugs of abuse



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Abstract This review gives an overview of the developments in the analysis of drugs of abuse and other illicit substances by Raman spectroscopy for forensic purpose. The review covers the brief overview of basic principle and instrumentation of Raman spectroscopy along with selected and recent applications for characterization of drugs of abuse using this technique. These applications show the potential value of Raman spectroscopy in the qualitative and quantitative analysis of trace amounts of drugs of abuse and other illicit substances on different matrices such as cloth, currency notes, fiber etc., without extensive sample preparation in a non-destructive manner.

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Contents

1. Introduction	209
2. Basic principles and instrumentation	210
3. Selected applications for the analysis of drugs of abuse.	211
4. Conclusion	214
Funding	214
Conflict of interest	214
References	214

1. Introduction

Spectroscopy is the study of interaction of electromagnetic radiation with matter. Spectroscopic methods can be based on phenomena of emission, absorption, fluorescence or scattering.^{1,3} Different spectroscopic methods are frequently used

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for the characterization of a wide range of samples of forensic interest. These methods are used for qualitative and quantitative analysis of sample/s. The qualitative analysis is performed to establish the identity of sample while quantitative analysis is performed to estimate the concentration of analyte in sample.¹ Some of the spectroscopic methods (e.g. UV-Vis Spectrophotometry) are used as a screening method since it gives the tentative identification of sample and are not specific in nature while other spectroscopic methods (e.g. Infrared Spectroscopy and Mass Spectrometry) are used as a confirmatory method since they give the reliable identity of sample and are specific in nature.^{3,4,10}

Raman spectroscopy was named in the honor of its inventor, C.V. Raman, who, along with K.S. Krishnan, published the first paper on this technique.² Raman spectroscopy (RS) is a versatile method for analysis of a wide range of forensic samples. It resolves most of limitations of other spectroscopic techniques. It can be used for both qualitative as well as quantitative purpose. Qualitative analysis can be performed by measuring the frequency of scattered radiations while quantitative analysis can be performed by measuring the intensity of scattered radiations.^{3,4}

A review unfolding the utility of Raman spectroscopy in the forensic analysis of different types of inks in questioned documents is available.⁵ A review presenting a recent progress in characterizing trace amounts of body fluids using Raman spectroscopy is available.⁶ A recent review describing the application of infrared and Raman spectroscopy to the identification of explosives is also available.⁷ Infrared spectroscopy is a complementary technique to Raman spectroscopy and is discussed in many cases for completeness. This article discusses the basic principle and instrumentation of Raman spectroscopy. The chief purpose of this review is to briefly present an overview of some important recent and selected applications of Raman spectroscopy in the analysis of drugs of abuse and related illicit compounds.

2. Basic principles and instrumentation

Raman spectroscopy is a scattering technique. It is based on Raman Effect, i.e., frequency of a small fraction of scattered radiation is different from frequency of monochromatic incident radiation. It is based on the inelastic scattering of incident radiation through its interaction with vibrating molecules. It probes the molecular vibrations.^{1,8}

In Raman spectroscopy, sample is illuminated with a monochromatic laser beam which interacts with the molecules of sample and originates a scattered light. The scattered light having a frequency different from that of incident light (inelastic scattering) is used to construct a Raman spectrum. Raman spectra arise due to inelastic collision between incident monochromatic radiation and molecules of sample. When a monochromatic radiation strikes at sample, it scatters in all directions after its interaction with sample molecules. Much of this scattered radiation has a frequency which is equal to frequency of incident radiation and constitutes Rayleigh scattering. Only a small fraction of scattered radiation has a frequency different from frequency of incident radiation and constitutes Raman scattering. When the frequency of incident radiation is higher than frequency of scattered radiation,

Stokes lines appear in Raman spectrum. But when the frequency of incident radiation is lower than frequency of scattered radiation, anti-Stokes lines appear in Raman spectrum. Scattered radiation is usually measured at right angle to incident radiation.^{3,4,9}

Stokes shifted Raman bands involve the transitions from lower to higher energy vibrational levels and therefore, Stokes bands are more intense than anti-Stokes bands and hence are measured in conventional Raman spectroscopy^{3,4,9} while anti-Stokes bands are measured with fluorescing samples because fluorescence causes interference with Stokes bands.³ The magnitude of Raman shifts does not depend on wavelength of incident radiation.³ Raman scattering depends on wavelength of incident radiation.¹ A change in polarizability during molecular vibration is an essential requirement to obtain Raman spectrum of sample. Since Raman scattering due to water is low, water is an ideal solvent for dissolving samples. Glass can be used for optical components (mirror, lens, sample cell) in Raman spectrophotometer.^{3,4,9}

A Raman spectrum is presented as an intensity-versus-wavelength shift.¹ Raman spectra can be recorded over a range of 4000–10 $\text{cm}^{-1(10)}$. However, Raman active normal modes of vibration of organic molecules occur in the range of 4000–400 Δcm^{-1} . Depending on spectrophotometer's design and optical components, typical Raman spectra cover the wavenumber region between 400–5 Δcm^{-1} and 4000–3800 $\Delta\text{cm}^{-1(8)}$. A Raman spectrum is significantly simpler than their Infrared (IR) counterparts because in normal Raman overtones, combination and difference bands are rare.¹

Raman spectrophotometers can be dispersive or non-dispersive. Dispersive Raman spectrophotometer use prism or grating while non-dispersive Raman spectrophotometer uses an interferometer such as Michelson interferometer in Fourier Transform Raman spectrophotometer.¹

Mercury arc lamp was used as light source in Raman spectrophotometers in early days. 435.8 nm line of coiled low-pressure mercury arc lamp was used as light source until 1960's.^{1,3} Laser sources became available in late 1960's and completely replaced the mercury lamp.¹ These laser sources provide stable and intense beam of radiation. Wide range of lasers such as Argon ion laser (488 and 514.5 nm), Krypton ion laser (530.9 and 647.1 nm), Helium-Neon (He-Ne) (632.8 nm), Near Infrared (IR) diode lasers (785 and 830 nm), Neodymium-Yttrium Aluminum Garnet (Nd:YAG) and Neodymium-Yttrium Ortho-Vanadate (Nd:YVO₄) (1064 nm) and frequency doubled Nd:YAG and Nd:YVO₄ diode lasers (532 nm) can be used as light source in Raman spectrophotometers.⁸ Short wavelength sources such as argon ion and krypton ion lasers can produce significant fluorescence and cause photodecomposition of the sample. However, long wavelength sources such as diode or Nd:YAG lasers can be operated at much higher power without causing photodecomposition of sample and eliminates or reduces fluorescence in most cases.³

Band pass filters are used to isolate a single laser beam. A combination of notch filter and high quality grating monochromator is most frequently used in dispersive instruments. Double or even triple grating monochromators, super notch filters, rejection filters, holographic notch or edge filters and holographic filters are used to separate relatively weak Raman lines from intense Rayleigh scattered radiations.^{1,3,11,12}

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