HORIBA Scientific

Application Note

Forensics

Raman

RA19

The Non-Destructive and in-situ identification of controlled drugs and narcotics

Over the past few years, Raman spectroscopy has been recognised as an efficient and powerful analytical tool in the field of Forensic Science. There are several reasons for this rapid evolution: it is a non contact and non destructive technique which does not need any sample preparation. In many cases, this hence allows the preservation of small traces of evidence for further analyses of the same specimen for confirmation of results. In addition only minimal quantities of material are required to perform a complete analysis resulting from the high spatial resolution of the confocal system.
The Raman effect is highly sensitive to slight differences in chemical composition and crystallographic structure. These features are very useful for the investigation of illegal drugs as it enables the detection of very small differences and therefore to provide valuable information regarding the origin of the synthesis method of the drug.
The aim of this note is to review the main advantages of this technique for drug investigation and to illustrate them with a specific study of cocaine and its derivatives.

Identification of different drug substances

1. Experimental

Experiments were carried out on a LabRAM equipped with a 633nm laser and a 785nm diode laser. Raman spectra of all types were recorded on the LabRam by using a diode laser at 785nm; this laser wavelength inhibits interfering fluorescence which could be emitted by impurities. However, a cursory look at samples using the standard 633nm HeNe laser indicated results that were as good, if not better, than those recorded with the diode laser.
At 785nm, glass emits a fluorescence spectrum. Thus the spectra recorded in glass vials may show a large background around 1400cm^{-1} due to the glass being close to the focal volume. However, by using the standard feature of the LabRAM software, it is possible to effectively subtract the glass background and produce a spectrum of the sample without the glass contribution.

2. Cocaine Raman bands

Free base cocaine (Crack) is prepared from cocaine HCl with ammonia or sodium bicarbonate and water. The mixture isv heated to remove the hydrochloride. The spectra of cocaine hydrochloride and free base cocaine are shown in Figure 1.

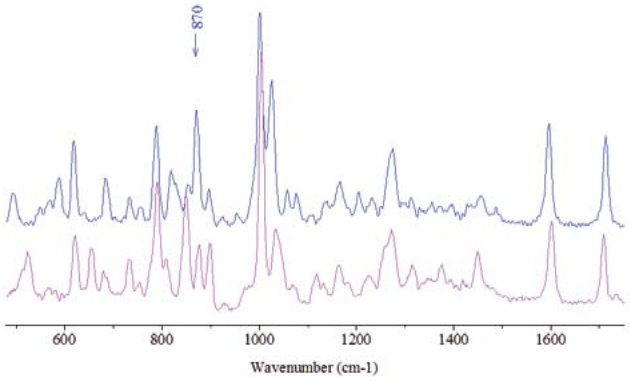

Figure 1: Spectra of free base cocaine (bottom) and of cocaine HCl. 785nm.

Spectra were collected directly through the glass vials containing the free particles, using a long working distance objective to analyse particles far behind the glass window. Thus, there is no risk of contamination or degradation of the sample.
For convenience, the most prominent features in the spectra are tabulated below (Table 1).

Free Base	HCl
788 cm^{-1}	786 cm^{-1}
847 cm^{-1} (s)	851 cm^{-1} (m)
872 cm^{-1} (m)	870 cm^{-1} (s)
896 cm^{-1}(m)	894 cm^{-1} (m)
1003 cm^{-1}	999 cm^{-1}
1601 cm^{-1}	1596 cm^{-1}
1713 cm^{-1}	1709 cm^{-1}

Table 1: Position of the main Raman bands of Cocaine HCl and free base cocaine in the [700-1800] cm^{-1} range.

Since the precision of the measurements is about 1cm^{-1}, these differences between frequencies of very similar samples are significant. However the easiest method to distinguish the two species of cocaine is to compare the signatures in the spectral region [845-900]cm^{-1} (grey cells in Table 1). In the HCl form, the central band (870cm^{-1}) is the most intense of the triplet whereas, in the free base form, the lowest frequency band (847cm^{-1}) is the most intense.

3. Cocaine related compounds

Figure 2 shows the spectra of compounds related to cocaine which all present distinct Raman features and are easily distinguishable.

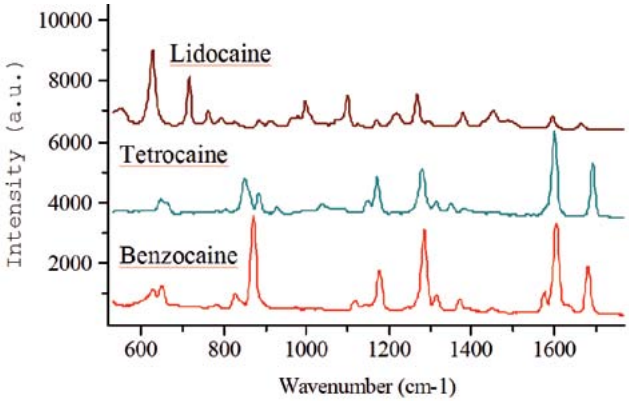

Figure 2 : Spectra of three cocaine related compound.

Detection of drug substances within a mixture

The purpose of the following measurements is to provide a means to characterize the chemical or physical form of the cocaine powders.

1. Mixture with Cutting Agents

Often, the analyst has to investigate mixtures of drug particles and cutting agents. Three compounds have been examined as possible cutting agents: manitol, myoinositol and sorbitol (three sugars). Their spectra have been reported Figure 3. We can clearly notice that the three spectra differ from each other and from the reported spectra of drugs.

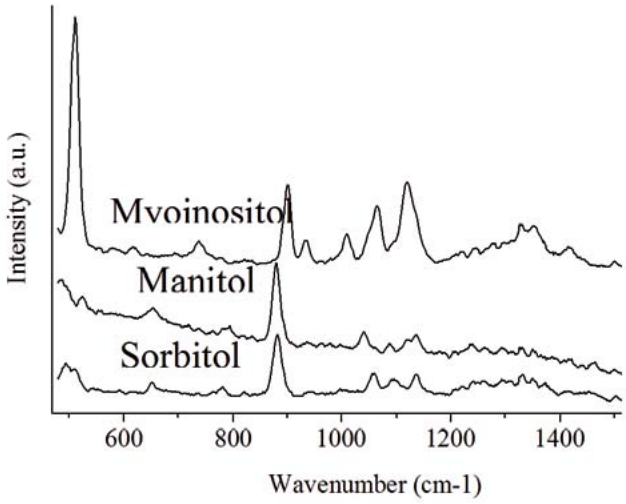

Figure 3: Spectra of three possible cutting agents.

Vials of calibrated mixtures of cocaine and various possible cutting compounds were examined to determine if the presence of cocaine could be documented and its form identified.
The example presented here (Fig. 4) is a (50:50)%w. mixture of cocaine HCl with Manitol. The Raman signal of Manitol in these spectra is very low and the intensity pattern between 845 and 900 cm^{-1} enabled identification of cocaine HCl rather than the free base.

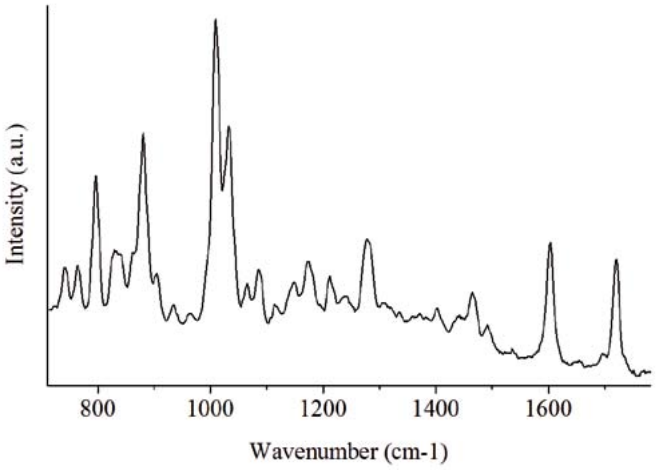

Figure 4: Spectrum obtained after substraction of a (50:50)%w. mixture of cocaine-HCl:manitol.

2. Traces analysis: mixture of three drugs

The following shows spectra maps of a surface contaminated with minute amounts of regularly controlled drug substances (i.e. Cocaine, Caffeine and Amphetamine). Spectral features of the three different drugs were identified from the reference spectra (Fig.5). An area of 25µmx35µm on the contaminated surface was analysed by confocal point mapping. By integrating the area of the characteristic band of each compound (Fig.6), a two-dimensional Raman image was then produced revealing the localisation of the three substances.

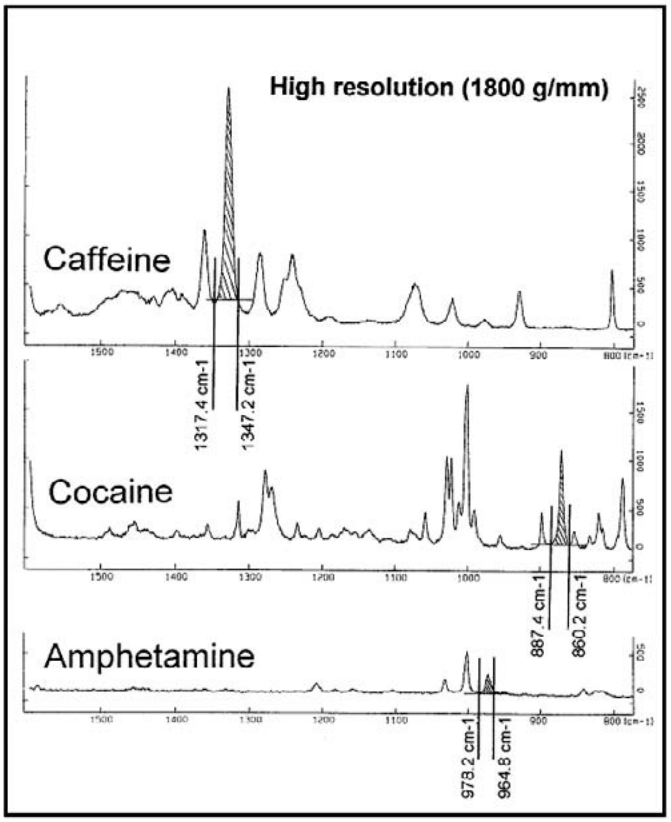

Figure 5: Reference Raman spectra of three drug compounds and the integration range under their characteristic band.

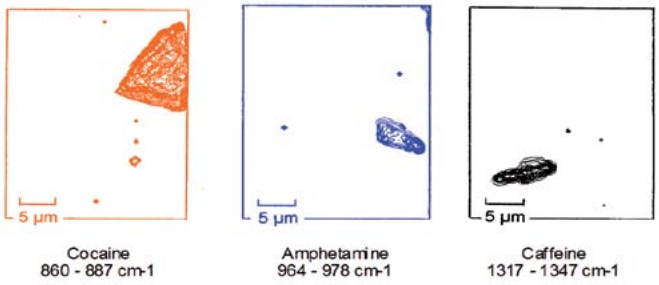

Figure 6: Confocal mapped images generated from Raman spectra by the integration under the characteristic band of each compound.

Conclusion

Suspected drug products can be analysed by Raman spectroscopy to confirm the nature of the material. Small differences can be identified from the Raman analysis (ex: cocaine HCl / free base cocaine). By confocal Raman spectroscopy, traces can be identified on surfaces or in vials transparent to the visible excitation wavelength (glass, polymer..). Mixtures of different drug compounds or mixtures of a drug substance with additives (cutting agents) can give characteristic Raman features allowing the determination of the nature of each component and the generation of Raman maps showing their distribution.

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