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Classification of Narcotics in Solid Mixtures Using Principal Component Analysis and Raman Spectroscopy

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ABSTRACT: Eighty-five solid samples consisting of illegal narcotics diluted with several different materials were analyzed by near-infrared (785 nm excitation) Raman spectroscopy. Principal component analysis (PCA) was employed to classify the samples according to narcotic type. The best sample discrimination was obtained by using the first derivative of the Raman spectra. Furthermore, restricting the spectral variables for PCA to 2 or 3% of the original spectral data according to the most intense peaks in the Raman spectrum of the pure narcotic resulted in a rapid discrimination method for classifying samples according to narcotic type. This method allows for the easy discrimination between cocaine, heroin, and MDMA mixtures even when the Raman spectra are complex or very similar. This approach of restricting the spectral variables also decreases the computational time by a factor of 30 (compared to the complete spectrum), making the methodology attractive for rapid automatic classification and identification of suspect materials.

KEYWORDS: forensic science, substance abuse detection, classification, Raman, spectroscopy, chemometrics, narcotics, principal component analysis, discrimination

Raman spectroscopy has become a useful adjunct to IR absorption spectroscopy, which is used widely for forensic purposes. Developments in detector, microscope, and laser design have now opened Raman spectroscopy to a much wider audience and made the technique more applicable to routine analysis (1). Raman and IR-absorption spectroscopies are vibrational techniques deriving from the chemical structure of molecules, and therefore the spectra are unique, providing a chemical fingerprint suitable for identification and discrimination of materials (2).

The advantages of Raman spectroscopy over IR absorption spectroscopy in the analysis of forensically significant materials have already been outlined (3–5). These advantages have been utilized in the rapid analysis of amphetamine-type narcotics in tablet form (6,7) or aqueous solution (8). The high spatial resolution (~1 μm) inherent in microscope-based Raman systems allows for the analysis of micron-sized particles, such as explosives (9,10), and propellant residues (11). Trace analysis (< ppm) of narcotics and explosives has also been demonstrated by using techniques such as surface enhanced raman spectroscopy (SERS) and surface enhanced resonance raman scattering (SERRS) (12–14). Furthermore, the development of fiber optic Raman probes has allowed the implementation of portable devices for in situ examination of narcotic and explosive materials (15–18).

Raman spectroscopy is increasingly being used for the quantitative and qualitative analysis of a wide variety of materials (19–21). Problems experienced in the past such as: poor reproducibility of spectral intensities, poor signal/noise ratios, and the presence of variable fluorescence (22) have largely been overcome by dramatic improvements in instrumentation and the application of chemometric (multivariate analysis) methods. Chemometric methods correlate (statistically) observed spectral changes with properties such as octane number, concentration, density, and others (23). Chemometric methods for the classification and characterization of explosive materials using Raman spectroscopy have also been demonstrated (13,24–27). We have demonstrated in previous studies the use of Raman spectroscopy and chemometrics (partial least squares analysis) to accurately predict concentrations of narcotics in a binary (3) or a ternary solid mixture (28). Principal component analysis (PCA) was also shown to be a useful method for the qualitative discrimination of mixtures of narcotics according to concentration (28).

In reality, however, the composition of seized drug samples varies enormously and it is unlikely that suspect materials will contain only one or two pure diluents. The vast range of possible diluents and impurities that may be present pose several problems for the use of Raman spectroscopy for illicit drug analysis. The primary difficulty lies in the presence of fluorescent materials that can obscure the Raman signal, thus making measurements difficult or impossible. The practical solution to this problem is to use excitation wavelengths either in the UV or near-IR regions of the spectrum, with which fluorescence is minimized or prevented altogether (3,8,29,30). In this case 785 nm excitation was used, which reduces fluorescence interference to a large extent, but does not eliminate it totally. The second major complication is the overlap of Raman diluent and narcotic peaks and the relative intensities of these overlapping Raman peaks. If the Raman signal from the diluent is weak with respect to the narcotic signal, then detection is relatively straightforward down to concentrations in the 5 to 10% by weight range (3,28). Conversely, intense Raman signals from the diluent will mask signals from the target narcotics, making quantitative measurements especially difficult. The existence of several diluents in a drug mixture further exacerbates the problem of identification as well as making quantitative measurements more difficult.

The purpose of this study was to examine a wide range of diluents and narcotics by Raman spectroscopy and to determine

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whether or not simple chemometric methods such as PCA could be used to classify samples according to narcotic type.

Methods

MDMA hydrochloride ((±)3,4-methylenedioxymethamphetamine hydrochloride) and cocaine hydrochloride were supplied by Sigma-Aldrich Company Ltd., United Kingdom, and the heroin hydrochloride was obtained from MacFarlan Smith Ltd., Edinburgh, Scotland. The diluent materials anhydrous D-glucose (BDH), mannitol (BDH), maltose (Aldrich), and lactose (Aldrich), talc powder, $NaHCO_3$, and $MgSO_4 \cdot 7H_2O$ were reagent grade. The flour was normal-milled wheat flour, and the baby formula was a standard commercial preparation. All materials were used as received.

The sample set (Table 1, 2, and 3) covered a representative range of concentrations and mixtures with the sample mixtures (10 to 30 mg total weight) being made up by mixing known weights of drug and diluent, followed by grinding in an agate mortar and pestle to ensure sample homogeneity by thorough mixing of components. The mixtures were transferred to clean stainless steel hexagonal sample holders with an internal diameter of ~2 mm and tamped into place. The samples were made up over a period of 6.5 to 19 months prior to this Raman study with storage at room temperature and normal humidity (no precautions taken for storage). The average storage time of the samples prior to this study was 11.8 months.

TABLE 1—*Cocaine containing samples: % cocaine by weight with diluent in parentheses. Abbreviations: C&G = caffeine and glucose; SMA = baby milk formula.*

Sample	% Cocaine	Sample	% Cocaine
MA004	59.6 (glucose)	MA097	10.8 (C&G)
MA010	49.5 (glucose)	MA103	59.7 (caffeine)
MA016	36.5 (glucose)	MA106	8.8 (SMA)
MA019	39.6 (flour)	MA109	71.1 (C&G)
MA028	17.7 (glucose)	MA115	73.4 (caffeine)
MA031	27.4 (glucose)	MA118	65.2 (glucose)
MA034	50.6 (C&G)	MA124	70.4 (C&G)
MA037	5.15 (glucose)	MA130	7.7 ($NaHCO_3$)
MA040	56.3 (C&G)	MA133	20.0 (C&G)
MA043	9.84 (glucose)	MA136	94.7 (glucose)
MA046	48.3 (C&G)	MA139	10.4 (flour)
MA052	19.5 (C&G)	MA142	39.2 (glucose)
MA058	100 (pure)	MA145	10.3 (caffeine)
MA061	40.3 (C&G)	MA151	23.7 (flour)
MA064	28.7 (glucose)	MA181	61.5 (C&G)
MA067	90.8 (caffeine)	MA184	14.8 (glucose)
MA070	23.4 (maltose)	MA193	29.5 (C&G)
MA073	9.84 (C&G)	MA202	80.0 (glucose)
MA076	10.2 (lactose)	MA205	80.6 (C&G)
MA079	29.96 (C&G)	MA211	48.9 (SMA)
MA085	79.6 (caffeine)	MA220	28.3 ($NaHCO_3$)
MA088	90.0 (glucose)	MA235	20.0 (SMA)
MA091	61.9 (C&G)	MA238	39.3 (SMA)
MA094	45.0 (glucose)		

TABLE 2—*Diluent and MDMA containing samples: % MDMA by weight with diluent in parentheses. Abbreviations: C&G = 50:50 caffeine and glucose; SMA = baby milk formula.*

Sample	% MDMA	Sample	% MDMA
MA001	02.4 ($MgSO_4$)	MA187	25.0 (maltose)
MA022	15.5 (SMA)	MA190	8.1 (lactose)
MA025	09.3 (maltose)	MA232	20.0 ($NaHCO_3$)
MA049	24.8 (lactose)	MA241	10.4 (flour)
MA127	5.5 (maltose)	MA244	0 (SMA pure)
MA148	23.8 ($MgSO_4$)	MA247	0 (C&G)
MA154	100 pure	MA250	0 (maltose pure)
MA166	18.4 (mannitol)	MA253	0 (lactose pure)
MA175	24.0 (flour)		

TABLE 3—*Heroin-containing samples: % heroin by weight with diluent in parentheses. Abbreviations: SMA = baby milk formula.*

Sample	% Heroin	Sample	% Heroin
MA007	14.7 (caffeine)	MA178	18.9 (SMA)
MA013	16.5 ($MgSO_4$)	MA196	8.9 (caffeine)
MA055	8.1 ($MgSO_4$)	MA199	100 pure
MA082	10.0 (glucose)	MA208	21.4 (glucose)
MA100	9.1 (mannitol)	MA214	8.6 (SMA)
MA112	20.0 (maltose)	MA217	8.5 (lactose)
MA121	7.4 ($NaHCO_3$)	MA223	11.2 (maltose)
MA160	19.7 (flour)	MA226	22.7 ($NaHCO_3$)
MA163	18.1 (mannitol)	MA229	9.9 (flour)
MA172	21.0 (lactose)		

The modular instrument used for near-IR Raman spectroscopy has been described previously (3,28). All spectra were recorded at a set interval of 450 to 1100 cm^{-1} (510 data points) and a resolution of ~4 cm^{-1}. The exposure time was set at 30 s for all samples. The choice of spectral range was governed by the experimental setup [restricted by spectrometer dispersion and CCD (charge coupled device) array size]. Three Raman spectra at different surface locations were recorded for each sample to minimize the effect of sample morphology. Features in the spectra caused by cosmic rays incident on the detector were manually removed using the EasyPlot software package (ver. 3.00–7, Spiral Software+MIT). The three spectra were co-added, averaged, and smoothed over a five-point range. These spectra were then divided by a normalized white light spectrum to correct for detector response. Chemometric analysis was performed using the Unscrambler (V7.5, CAMO ASA, Trondheim, Norway) multivariate analysis software package. Calculations were performed using a Pentium III 450 MHz, 256 Mbytes RAM IBM-compatible personal computer (Windows NT 4.0 operating system). All analyses were performed with full cross validation. Five component PCA calculations on a data matrix of 85 samples by 515 variables took less than 5 min.

Results and Discussion

As our laboratory is not associated with a law enforcement agency or a forensic testing laboratory, we do not have access to "street" samples and therefore we must generate test standards of known composition by mixing pure narcotics with diluents in the laboratory. These test standards may not accurately reflect the type of samples commonly seized by law enforcement officials and analyzed in forensic laboratories. There will be differences in diluent type, adulterant content, environmentally caused changes, and morphology. However, in some cases, studies on "real world" samples and laboratory samples show no extensive differences in Raman spectra (6,7). Therefore laboratory standards can be used to demonstrate the utility and effectiveness of new instrumental methods of analysis prior to the application of the method in real world situations. An added bonus is that any laboratory can replicate the work from the information provided in the experimental section, allowing easy and accurate evaluation of different techniques for narcotic identification.

The data set employed in this study was chosen to represent as diverse a mixture of materials as possible that could be conveniently analyzed in a single session with our modular Raman instrumentation (3,28). This particular in-house assembled Raman instrument, which has now been superseded by more advanced

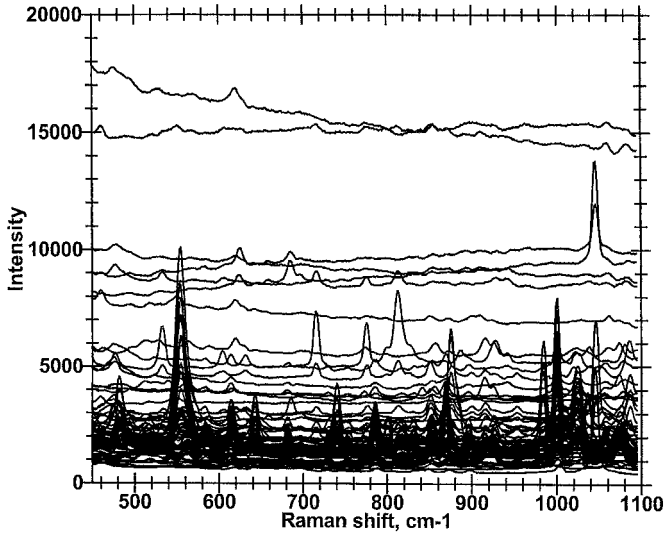

FIG. 1—*Raman spectra of the sample set illustrating the large spectral variations and complexity of vibrational bands.*

instruments, is limited to a low throughput because of tedious alignment and calibration procedures, which had to be repeated regularly due to spectrometer drift and environmental fluctuations. Three narcotics and nine different diluents were used to produce 49 cocaine, 13 MDMA, and 19 heroin-containing samples. An additional four narcotic-free samples were included in the test set (Tables 1, 2, and 3). Narcotic concentrations varied between 0 and 100%, with the majority of samples having a drug concentration of less than 40% by weight. The samples varied in appearance from clean white crystalline powders to amorphous dirty brown pastes.

Raman spectra of the samples show extreme variations in baseline and intensity of vibrational modes as illustrated in Fig. 1. Large variations in Raman signals, such as those shown in Fig. 1, would be expected from real world samples where the narcotics can be diluted with a range of materials. The samples with the most intense baselines tend to be the samples that were made up with complex amorphous materials such as flour and baby milk formula. Several of the diluents have sharp Raman peaks that are easily observed: caffeine at 555 cm^{-1}, $MgSO_4 \cdot 7H_2O$ at 982 cm^{-1}, and $NaHCO_3$ at 1043 cm^{-1}.

PCA on the original Raman spectral data (preprocessed using a multiplicative scatter correction) was not successful in discriminating the various narcotics, as can be seen by the PCA score plot in Fig. 2*A*. The loadings plot (Fig. 2*B*) for PC1 (98% explained

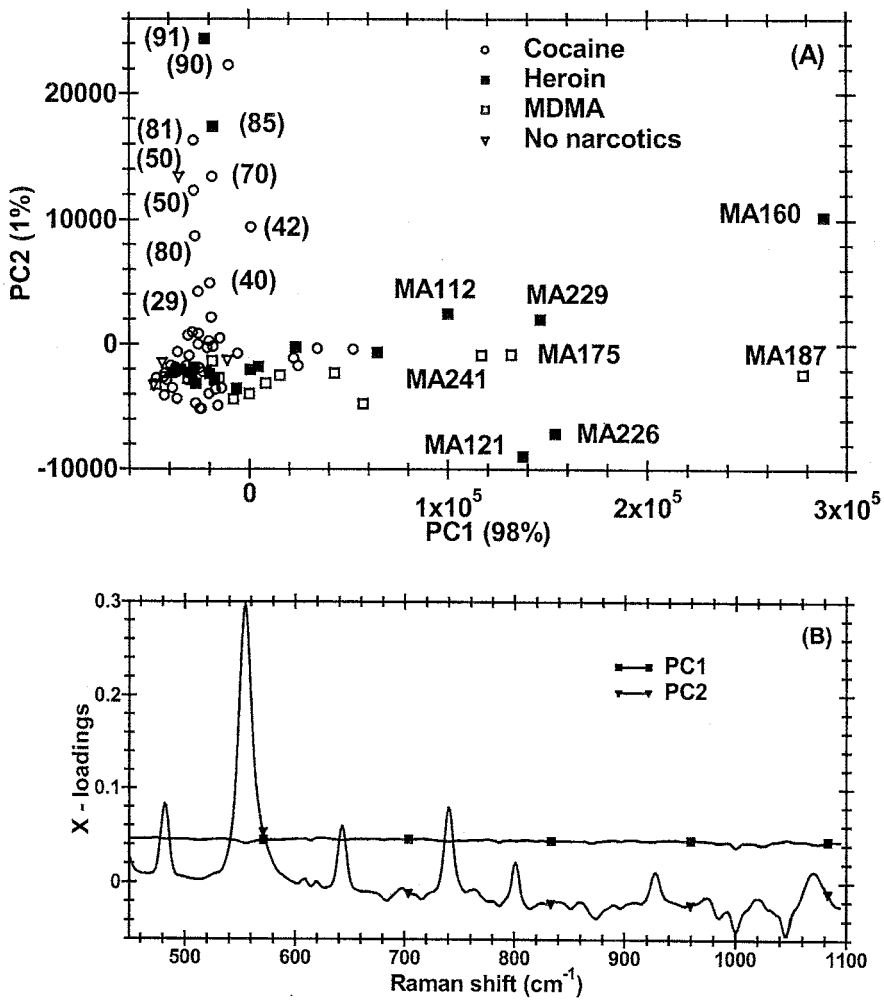

FIG. 2—(A) *Two-dimensional scores plot for PCA model of the Raman spectra from all 85 samples, showing poor discrimination except on the basis of caffeine content or baseline offset. Caffeine concentration in % weight is given in brackets for a selection of the samples.* (B) *X-loadings plots for PC1 and PC2.*

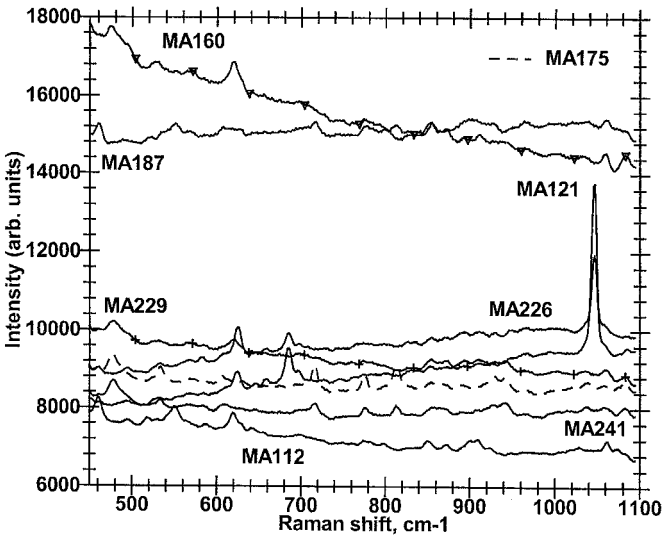

FIG. 3—*Raman spectra of labelled samples from Fig. 2 illustrating the high background signal from these samples.*

spectral variance) indicates that this component discriminates samples according to the intensity of the overall signal; the samples with the highest average backgrounds are distributed along the positive PC1 axis. This is evident from Fig. 3, which shows the Raman spectra of the samples discriminated along PC1 according to the baseline intensity. Samples containing diluents such as maltose, flour, and $NaHCO_3$ generated spectra with the largest backgrounds. The loadings plot (Fig. 2*B*) for the second component, PC2 (1% explained spectral variance), indicates clearly that this factor discriminates on the basis of caffeine concentration, as is shown by the values for caffeine content in Fig. 2*A*. This is to be expected since caffeine has the largest Raman cross section of the materials studied and its spectrum tends to dominate the weaker contributions from the narcotics or other diluents.

The data were then subjected to a variety of different preprocessing methods (2nd order integration, etc.) to try and improve the discrimination of narcotic-containing samples. After a trial and error process, it was established that the best results were obtained when the 1st derivative of the Raman spectra (normalized to 1.0) was used. The 1st derivative preprocessing reduced baseline-offset effects, while normalization (intensity of largest peak set to 1.0) helped to minimize the effect of Raman scatter intensity variations between samples. This case is illustrated in Fig. 4*A* where the cocaine-containing samples are partly discriminated from the re-

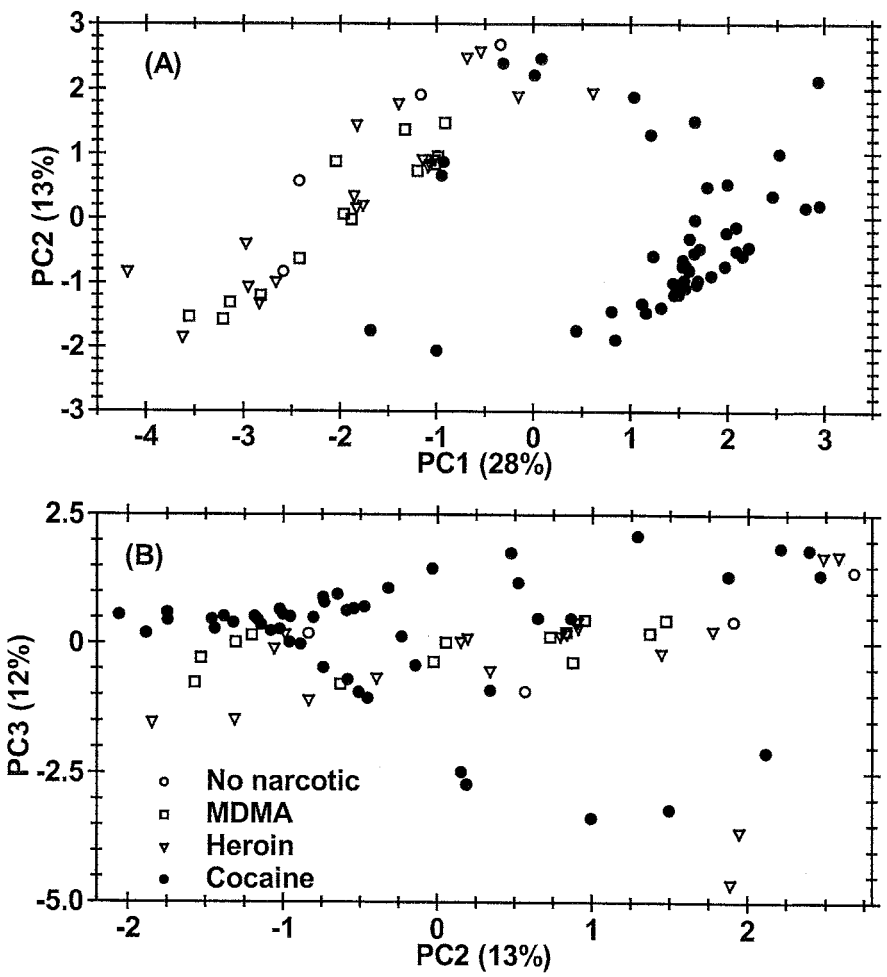

FIG. 4—*Two-dimensional score plots from PCA model of 1st derivative of Raman spectra from 85 samples with all spectral variables showing:* (A) *partial separation of the cocaine (•) containing samples from the remainder along PC1 axis, and* (B) *no narcotic discrimination along PC2 or PC3 axes.*

maining samples according to PC1 (Fig. 5*A*). Comparison of the PC1 X-loadings plot (Fig. 5*A*) with the 1st derivative normalized Raman spectrum of cocaine (Fig. 5*B*) reveals a considerable amount of overlap between the peaks. This confirms that PC1 discriminates the samples according to cocaine content. However, the remaining principal components failed to discriminate the other narcotic classes. This is shown in Fig. 4*B,* where it is clear that PC2 and PC3 fail to resolve the different narcotics. The X-loadings plots for these two components (Fig. 5*A*) when compared with the 1st derivative normalized Raman spectra of heroin and MDMA (Fig. 5*B*) show little overlap of peaks, indicating that these PCs describe other variations in the Raman spectra. PC4 (9% explained variance) and PC5 (9% explained variance) of this model provided no narcotic discrimination either. This type of PCA, while allowing for some degree of discrimination for a single narcotic, is not satisfactory for the unambiguous classification of a range of samples. This PCA required five components for a total explained *x*-variance of 71% and necessitated a considerable amount of computational time.

It was clear at this stage that the large variations in Raman intensities between components of the samples were skewing the results in favor of the more intense Raman scattering materials, thus leading to a situation where the weaker scatterers such as heroin and MDMA could not be discriminated. All PCA attempts used spectral data that had been equally weighted (each wavelength point weighted to 1.0), which was to the detriment of the weaker samples. It was decided to weight the spectral variables according to each individual target narcotic and produce an individual model for each target rather than using a global PCA to discriminate all three narcotics.

The data were weighted according to the six most intense peaks in the 1st derivative spectrum of cocaine (Table 4) with the remaining spectral points being weighted to zero (or not selected as variables). This approach worked well and can be seen in Fig. 6, where the discrimination of cocaine-containing samples has improved dramatically, and only two cocaine samples are not clearly discriminated from the bulk of the noncocaine-containing samples. Discrimination is affected along the PC1 axis according to the presence of cocaine, with the PC2 axis representing the degree of overlap between diluent and cocaine peaks. In this case, samples with a strong Raman peak at 875 cm^{-1} (mannitol) show the greatest separation along the PC2 axis. The low explained *x*-variance of 2% indicates very little impact on the discrimination of the cocaine-bearing samples. It is important, however, to include this second PC in the model as it gives us valuable information on the degree of spectral overlap between the target narcotic and the diluents and other narcotics. The two outliers (MA130 and MA220) are easily explained by looking at their Raman spectra illustrated in Fig. 7*A*. In both cases it is not possible to match all the peaks in the cocaine hydrochloride spectrum with the minor peaks in the sample spectra. This can be explained on the basis of a reaction between $NaHCO_3$ and the cocaine hydrochloride, which yielded the free base. This material has a different Raman spectrum to that of the salt and therefore discrimination does not occur. The Raman spectra depicted in Fig. 7A are very similar to the Raman spectrum of free base cocaine (crack cocaine) published in recent studies (17,31). In particular, the triplet of peaks between 840 and 900 cm^{-1} match up exactly. Both outlier samples had been stored for 19 months prior to this analysis, thus allowing plenty of time for the reaction to proceed. These outliers describe very clearly another potential pitfall of using laboratory-based samples for chemometric analysis, in that the effect of sample aging or conversion by environmental factors may not be sufficiently acknowledged. Figure 7*B* shows three Raman spectra from samples, which were cleanly discriminated from the noncocaine-containing samples. It is clearly evident from these spectra that this simplified PCA method can resolve samples with very different spectra from that of the target narcotic.

The same method of discrimination was applied to the MDMA-containing samples. Figure 8 shows that discrimination has been achieved. As shown with cocaine, discrimination is along PC1 for MDMA content, while the PC2 component describes the degree of target and nontarget Raman peak overlap. Again, however, there are a few outliers, and when the Raman spectra are studied (Fig. 9*A*), it is obvious that no peaks due to the MDMA are visible. In this case MA001 and MA232 Raman spectra show no trace of the MDMA or of its free base, and it is possible that all the MDMA evaporated over the 18-month interval between make-up and anal-

TABLE 4—*Listing of spectral peak pairs and the weighting values in parentheses applied for PCA models. All other spectral variables were set to a weighting of zero.*

Cocaine	Heroin	MDMA
611.3 cm^{-1} (0.41)	526.8 cm^{-1} (0.36)	473.8 cm^{-1} (0.20)
617.9 cm^{-1} (−0.42)	533.5 cm^{-1} (−0.38)	480.6 cm^{-1} (−0.21)
678.7 cm^{-1} (0.19)	616 cm^{-1} (1.0)	529.5 cm^{-1} (0.66)
685.3 cm^{-1} (−0.19)	623.3 cm^{-1} (−0.81)	536 cm^{-1} (−0.67)
781.7 cm^{-1} (0.32)	868.8 cm^{-1} (0.32)	600.6 cm^{-1} (0.25)
789.5 cm^{-1} (−0.28)	876.5 cm^{-1} (−0.32)	608.6 cm^{-1} (−0.23)
866.3 cm^{-1} (0.45)	908.1 cm^{-1} (0.26)	713 cm^{-1} (1.0)
872.6 cm^{-1} (−0.42)	914.4 cm^{-1} (−0.26)	719.4 cm^{-1} (−1.0)
997 cm^{-1} (1.0)	1057.4 cm^{-1} (0.29)	773 cm^{-1} (0.75)
1003 cm^{-1} (−0.88)	1066 cm^{-1} (−0.34)	779 cm^{-1} (−0.77)
1018.6 cm^{-1} (0.38)		808.8 cm^{-1} (0.82)
1030.4 cm^{-1} (−0.49)		816.5 cm^{-1} (−0.69)

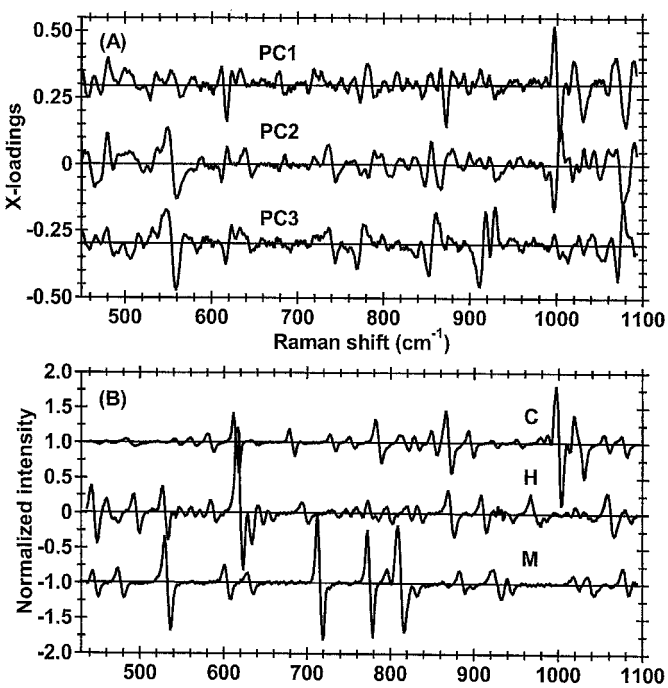

FIG. 5—(A) *Loading plots for the first three principal components of the PCA model shown in Fig. 4.* (B) *1st derivative, Raman spectra of cocaine hydrochloride* (C)*, heroin hydrochloride (H), and MDMA (M) with the spectra normalized to 1.0 and offset for clarity.*

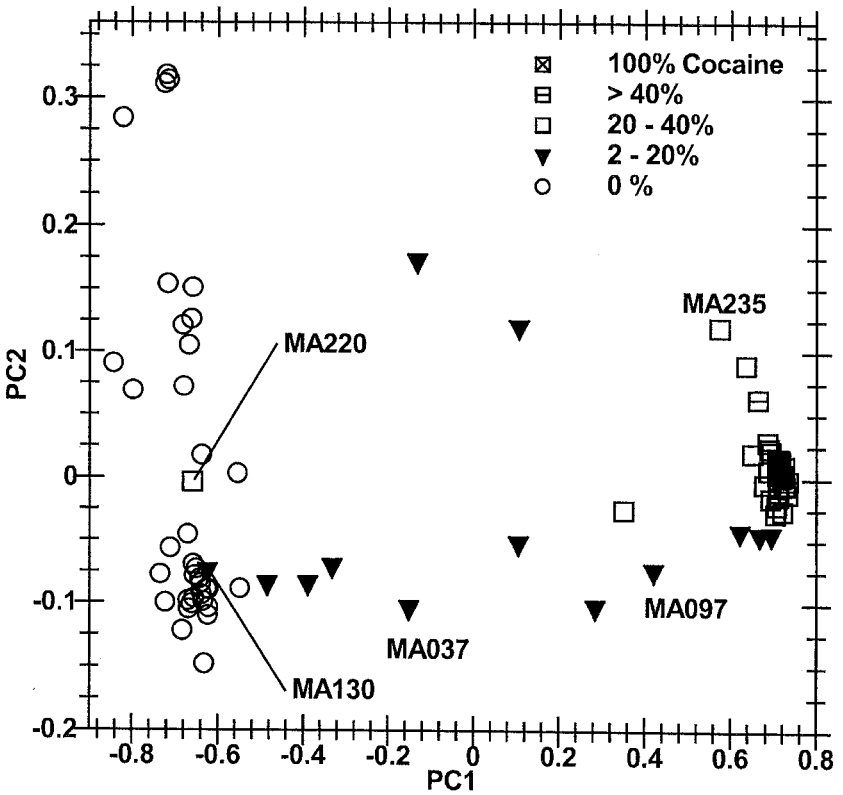

FIG. 6—*Scores plot from a PCA model of 1st derivative Raman spectra with selective weighting of cocaine peaks, showing separation of the cocaine containing samples. MA130 and MA220 outliers are also marked. The explained* x*-variance is 94% for PC1 and 2% for PC2.*

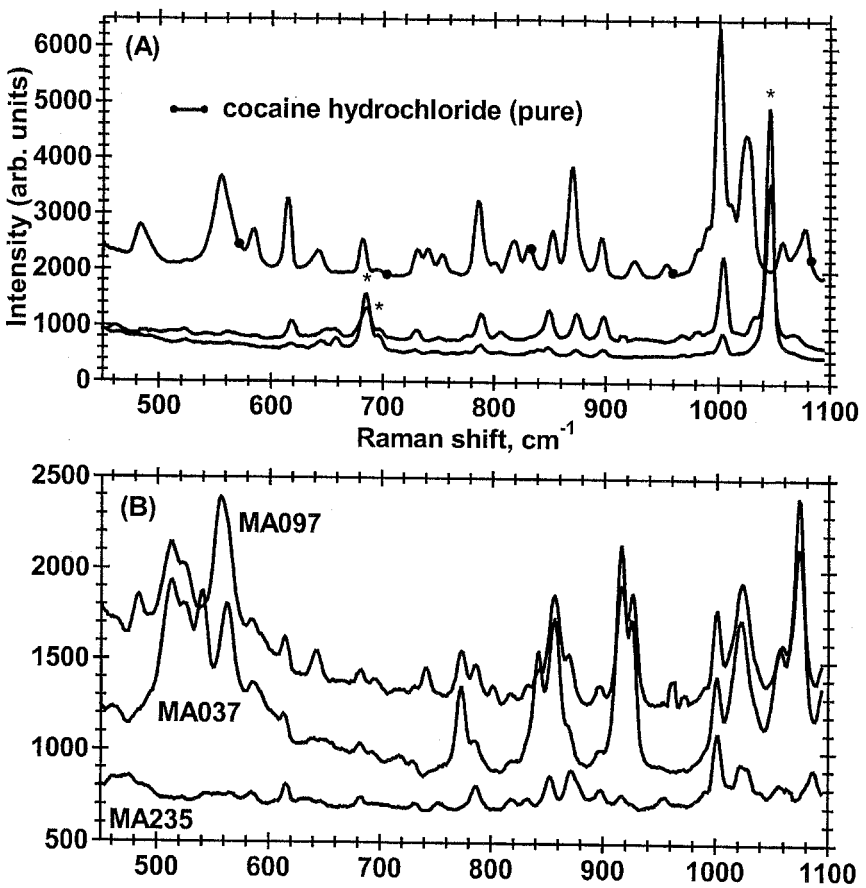

FIG. 7—(A) *Raman spectra of outliers, MA130 (lowest) and MA220 (middle) with spectrum of cocaine hydrochloride (top) for comparison.* $NaHCO_3$ diluent peaks are marked by an asterisk. (B) *Raman spectra of some of the discriminated samples.*

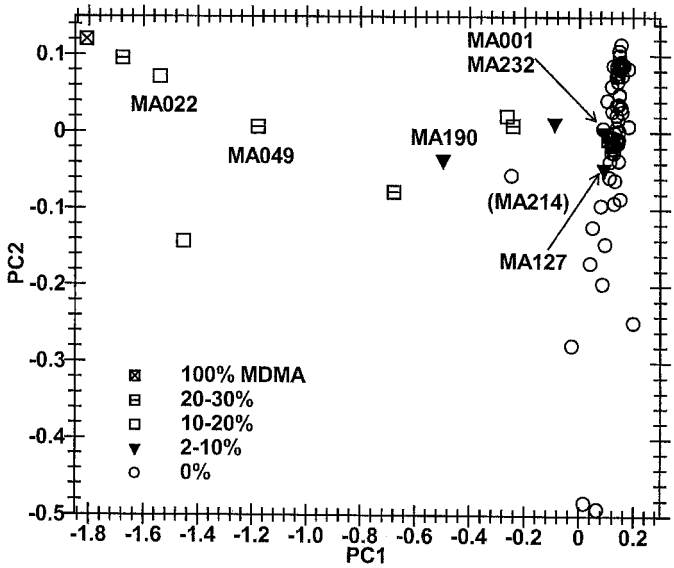

FIG. 8—*Scores plot from a PCA model of 1st derivative Raman spectra with selective weighting of MDMA peaks, showing separation of the MDMA containing samples. The explained* x*-variance is 84% for PC1 and 6% for PC2. Arrows and sample names indicate nondiscriminated samples.*

ysis. The case is less clear for MA127, where the diluent is maltose. Although the sample had a dirty brown pasty appearance, no attempt was made to ascertain conclusively what occurred with this sample. The Raman spectra of some discriminated samples are shown in Fig. 9*B,* illustrating the large variation in the original Raman data. Another outlier MA214—8.6% heroin in SMA—is also separated from the majority of the non-MDMA containing samples and is close to other low-MDMA concentration mixtures. The chances of spectral overlap between the weighted bands and weak features in the Raman bands is greater at low concentrations, making discrimination less likely for weaker scatterers such as MDMA and heroin.

Heroin-containing samples are discriminated in the final PCA model shown in Fig. 10 and the six outliers are displayed in Fig. 11*A*. In this case, the heroin is less easy to discriminate because of its relative weak Raman scattering properties and because there were only five weighted peak pairs used in the PCA model. All the samples had been mixed at the same time and had been stored for 15 months prior to this analysis. The Raman spectra of the outliers MA196 and MA007 are completely dominated by caffeine peaks, thus obscuring the heroin peaks. The Raman spectrum MA100 shows strong peaks due to the mannitol diluent and only a very weak peak at 622 cm^{-1} due to the most intense Raman peak of heroin. This was also the case when the sample was analyzed by Raman spectroscopy 15 months previously. MA055 and MA013 samples were diluted with $MgSO_4 \cdot 7H_2O$, and unfortunately there

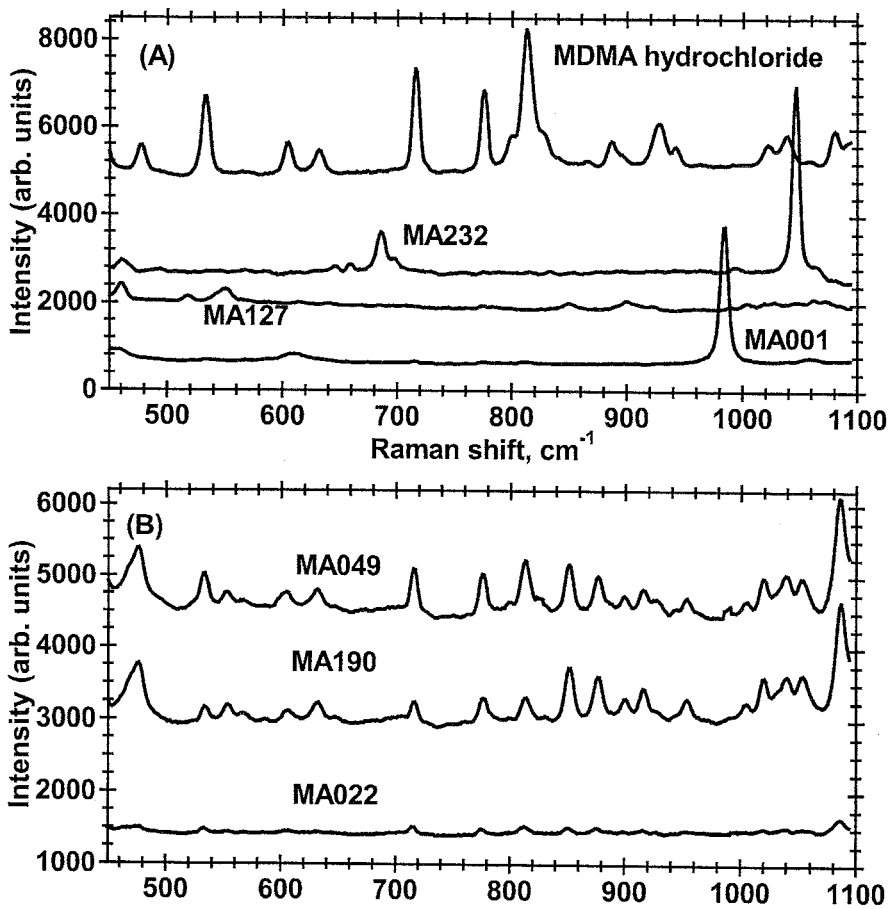

FIG. 9—(A) *Raman spectra of the outliers from the PCA model in Fig. 8 with the spectrum of MDMA hydrochloride for comparison. No MDMA peaks are evident in the Raman spectra of the outliers;* (B) *Raman spectra of three discriminated samples, showing the variation in spectra.*

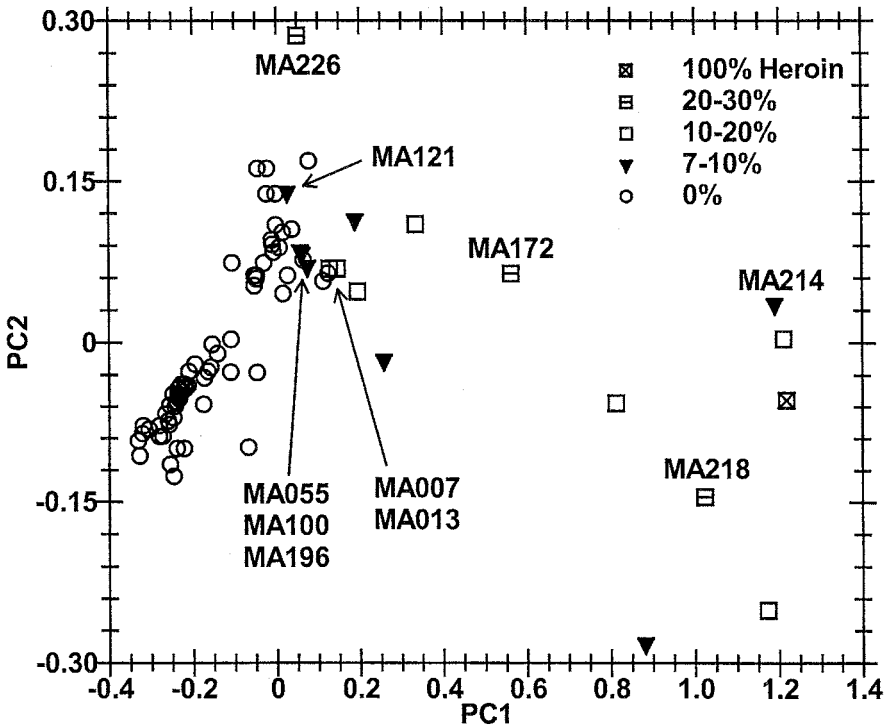

FIG. 10—*Scores plot from a PCA model of 1st derivative Raman spectra with selective weighting of heroin peaks, showing separation of the heroin-containing samples. The explained* x*-variance is 88% for PC1 and 6% for PC2. Poorly discriminated samples are marked by sample name.*

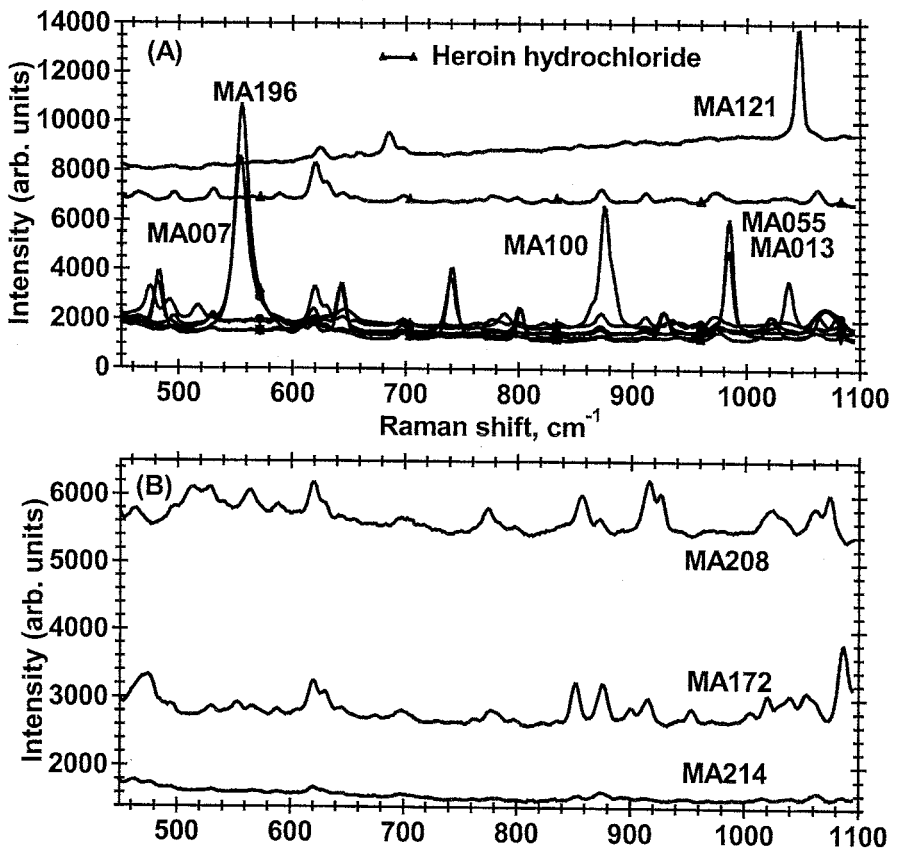

FIG. 11—(A) *Raman spectra of heroin containing outliers with spectrum of heroin hydrochloride for comparison;* (B) *Raman spectra of three discriminated samples, showing the variation in spectra.*

is significant overlap between diluent peaks and the narcotic peaks. In particular the 610 cm^{-1} Raman peak of $MgSO_4 \cdot 7H_2O$ is very close to the most intense peak in the Raman spectrum of heroin at 622 cm^{-1}. There is also a weak peak at 1059 cm^{-1} in the diluent spectrum, which overlaps the 1062 cm^{-1} peak of heroin. The only solution in cases where the Raman spectrum of the material is weak is to select the weighted Raman peaks to be those with little or no chance of overlap with the diluent. Specifically the discrimination would be improved if we had access to the complete fingerprint region 400 to 1000 cm^{-1} where the very specific carbonyl peaks are less likely to be obscured by diluent peaks.

Conclusions

This study has demonstrated that complex mixtures comprising a variety of narcotics dispersed in a selection of diluents can be successfully discriminated using a simple two factor PCA with a very restricted selective weighting of the most significant narcotic spectral features. In the case of the moderately strong Raman scatterers such as cocaine and MDMA, discrimination was fairly good with three of the five outliers being due to neutralization reactions that altered the chemical composition of the samples. In the case of heroin, which is a much weaker Raman scatterer, discrimination was not as good because of the much greater masking of the narcotic peaks by the diluent. The use of a very restricted subset of the spectral variables (10 to 12 points) for the PCA-based discrimination also provides a benefit in the computational resources required to generate classification models. These restricted wavelength PCA models were completed 30 times faster than traditional PCA using the full spectral range.

However, this is only a preliminary study with a very limited sample set. Development of a useful technique will require the analysis of larger sample sets with a much more diverse range of narcotics, diluents, and adulterants. Ideally, we require access to narcotic samples that have been seized by law enforcement agencies in order to accurately reflect the type of samples that are encountered on a day-to-day basis as shown by other researchers (7). This access would allow the creation of continually evolving databases that when subjected to PCA analysis by these methods could result in a facile route to a computerized analysis method for the classification of suspicious materials seized by law enforcement agencies. The proposed method would not be conclusive identification for a court of law, but may suffice for field operations with the new generation of portable Raman instruments being developed for law enforcement use. The method would allow police on site to search extensive laboratory-developed databases and models to instantly identify or classify an unknown material. In some cases the identification will be as good as that obtained by FT-IR spectroscopy, whereas in other cases the degree of identification will only suffice for an initial classification. A further advantage of a classification method as described in this paper is the fact that it doesn't have to be limited to narcotics but can easily be expanded to include explosives, pharmaceutical products, and hazardous chemicals. One possible application of this method would be in the screening of tablets for MDMA or other illegal narcotics. By conducting a Raman survey of illegal seizures of tablets for several months in conjunction with chemical analysis to determine narcotic and diluent content, a database would be available for PCA. Several models could then be constructed for each target narcotic (MDA/MDEA/MDMA), which could then be used to analyze future seizures using a portable Raman system. As Bell et al. (7) have shown, a Raman system should be capable of analyzing 50 samples or more per hour and in the case of a portable system this analysis would be conducted on site. This could allow law enforcement agencies to quickly make informed decisions about particular investigations without delay for costly or lengthy laboratory analysis. Furthermore, the spectra of seized samples can be recorded for later analysis at a central facility (or by a higher level investigative team) where variations in sample composition can be evaluated. These variations may provide information on the number and type of sources for illegal narcotics by tracking the compositional profile of the narcotic samples. For example, it could allow law-enforcement agencies in different jurisdictions to quickly compare compositional profiles of illegal narcotics.

This study has also demonstrated that prolonged storage of the hydrochloride salts of narcotics with basic inorganic salts such as $NaHCO_3$ can result in chemical reactions that can lead to the creation of different derivatives of the narcotic or complete decomposition. In this study some samples containing cocaine hydrochloride underwent a neutralization reaction yielding a decomposition product that was clearly identified from the Raman spectra as the relatively more volatile free amine or "crack cocaine." In the cases of heroin and MDMA hydrochlorides where the neutralization of these materials by $NaHCO_3$ may occur, we were not able to identify any product Raman spectrum with which we could prove that this had occurred. It is possible that other mechanisms may operate but these have not yet been identified. These decomposition reactions may also be accelerated by environmental factors such as heat and humidity, and this results in clear changes to the Raman spectra and hence hinders classification of samples using models developed in the laboratory that depend only on the acid salts (hydrochloride, sulphates, etc.). A model for the identification of outliers such as the byproducts of the neutralization reactions (free bases of cocaine, MDMA, etc.) could be generated by making up a series of samples with known concentrations of the free base in a series of diluents. Applying each model in turn until all the samples were identified would thus provide a general classification method. Further work into the Raman spectroscopy of the decomposition pathways and products of narcotics is necessary.

We are continuing to investigate ways of gaining access to real world samples in order to further refine and develop this method of sample identification and classification. In particular we will expand the spectral database of materials to include more adulterants and diluents. A new Raman instrument has just been procured and will allow full spectral coverage in the fingerprint region 200 to 1800 cm^{-1}, yielding better discrimination of narcotic-containing samples. Furthermore, a spectral database for Raman spectra of narcotic-containing samples is being established with a view to generating the large datasets required to validate this method as a possible fast screening method. Part of this database will involve monitoring samples for several years after makeup to investigate the effects of sample aging. The time series of spectra thus produced will serve as the basis of an identification method for the free bases of narcotics. We are also continuing to develop stronger models, which will give unequivocal classification at low ($<10\%$) narcotic concentrations.

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