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Composition profiling of seized ecstasy tablets by Raman spectroscopy

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Raman spectroscopy with far-red excitation has been investigated as a simple and rapid technique for composition profiling of seized ecstasy (MDMA, *N*-methyl-3,4-methylenedioxyamphetamine) tablets. The spectra obtained are rich in vibrational bands and allow the active drug and excipient used to bulk the tablets to be identified. Relative band heights can be used to determine drug/excipient ratios and the degree of hydration of the drug while the fact that 50 tablets per hour can be analysed allows large numbers of spectra to be recorded. The ability of Raman spectroscopy to distinguish between ecstasy tablets on the basis of their chemical composition is illustrated here by a sample set of 400 tablets taken from a large seizure of $>50\,000$ tablets that were found in eight large bags. The tablets are all similar in appearance and carry the same logo. Conventional analysis by GC-MS showed they contained MDMA. Initial Raman studies of samples from each of the eight bags showed that despite some tablet-to-tablet variation within each bag the contents could be classified on the basis of the excipients used. The tablets in five of the bags were sorbitol-based, two were cellulose-based and one bag contained tablets with a glucose excipient. More extensive analysis of 50 tablets from each of a representative series of sample bags gave distribution profiles that showed the contents of each bag were approximately normally distributed about a mean value, rather than being mixtures of several discrete types. Two of the sorbitol-containing sample sets were indistinguishable while a third was similar but not identical to these, in that it contained the same excipient and MDMA with the same degree of hydration but had a slightly different MDMA/sorbitol ratio. The cellulose-based samples were badly manufactured and showed considerable tablet-to-tablet variation in their drug/excipient ratio while the glucose-based tablets had a tight distribution in their drug/excipient ratios. The degree of hydration in the MDMA feedstocks used to manufacture the cellulose-, glucose- and sorbitol-based tablets were all different from each other. This study, because it centres on a single seizure of physically similar tablets with the same active drug, highlights the fact that simple physical descriptions coupled with active drug content do not in themselves fully characterize the nature of the seized materials. There is considerable variation in the composition of the tablets within this single seizure and the fact that this variation can be detected from Raman spectra demonstrates that the potential benefits of obtaining highly detailed spectra can indeed translate into information that is not readily available from other methods but would be useful for tracing of drug distribution networks.

Introduction

Raman spectroscopy has been proposed as a useful method for screening of seized tablets and powders for illicit substances.[1–6] The two features of the technique which make it attractive for this purpose are the ability to record spectra with no sample preparation and the reasonably short (<1 min) collection times required. We have previously shown that Raman methods can be used to distinguish between ecstasy (*i.e.* MDMA, *N*-methyl-3,4-methylenedioxyamphetamine) and various other phenethylamine ecstasy analogues commonly seized in the UK. The compounds can be identified even when they are mixed with bulking agents (excipients) in seized tablets, as well as when they are presented as pure samples.[7] In itself, this rapid identification of the active drugs is useful but the fact that the spectra can also be used to identify excipient(s), the relative concentration of drug to excipient and even the degree of hydration of the active compounds means that the Raman spectrum of a seized sample has the potential to provide a more complete profile of the composition of seized tablets than other, more established, analytical methods. For example, gas chromatography-mass spectrometry (GC-MS) analysis, which is currently the method of choice for criminal prosecutions,[8] can be used to identify and quantify the active compound present but does not give any other information on tablet composition.

Seized ecstasy tablets are typically marked with an identifying logo (a form of product branding): these logos can be symbols of any type, such as animals or birds, but they are often copies of the logos of internationally recognized brand names, such as Rolex or McDonalds. Unfortunately, the logos are not a reliable guide to the source or composition of tablets, not least because as 'brands' become popular the logos they carry are simply copied by other illicit manufacturers.

Since Raman spectra can be acquired rapidly it has been suggested that it should be possible to test hundreds of samples in a few hours, although to our knowledge this has not actually been done. In contrast, with conventional GC-MS analysis only small numbers of individual tablets are normally analysed because of the time taken for each measurement. The ability to test relatively large numbers of samples within reasonable times is obviously a useful characteristic of any method, since it increases the sample throughput and reduces cost, but in the case of ecstasy seizures it is particularly useful because it opens up the possibility of determining the degree of homogeneity within a single sample set composed of hundreds of apparently similar tablets. This information on the composition of many tablets might be used to determine if all the tablets in large

seizures are simply a single batch which has been sub-divided for distribution or whether they have actually been manufactured in a different way and only later tableted in the same form. Similarly, information on sample homogeneity is needed if the composition data are to be used to determine whether samples that have been seized at a different time (and possibly even carry different identifying marks) in fact have the same chemical constituents and therefore have the same origin, which their manufacturers have tried to conceal by changing logos *etc*. In these comparisons of different seizures, the degree of homogeneity within the two sample sets to be compared must be known. Clearly with very inhomogeneous mixed batches of tablets sampling errors could easily lead to erroneous conclusions about the similarity of seized samples from different sources.

The purpose of this paper is to explore the extent to which possible potential advantages of Raman profiling of composition can be realised in practice. In particular, a large sample set consisting of 400 tablets taken from a single seizure has been studied. This seizure was composed of a series of bags of physically-similar tablets all bearing the same 'Mitsubishi' logo, so it is almost ideal for testing the discriminating power of Raman methods.

Experimental

Raman spectra were recorded using 810 nm excitation (Spectra-Physics (San Jose, CA, USA, Ti/sapphire laser pumped by a Spectra-Physics 2020 Ar^+ laser, typically 70 mW at sample) using a 180° backscattering geometry. Typically, the laser was line focused (< 100 μm × 10 mm) with a cylindrical lens onto the sample, which was mounted on a rotating platform so that an averaged spectrum from the tablet was obtained. Scattered light was collected, passed through a Kaiser Optical Systems (Ann Arbor, MI, USA) holographic notch filter and then dispersed by a Jobin-Yvon (Longjumeau, France) HR640 single stage spectrograph (600 lines per mm grating) onto a Princeton Instruments (Trenton, NJ, USA) LN1152 liquid N_2 cooled charge-coupled device (CCD) detector. Spectra were typically accumulated for 40 s and were exported to the 'Labcalc' spectral manipulation package for processing and presentation.[9] Due to the nature of the samples all the spectra were superimposed on a smooth background of stray light which rose smoothly to the low cm^{-1} end of the spectrum. This background was removed from all the spectra shown by digitally subtracting a similar stray light signal which was generated by placing a piece of normal blackboard chalk in the sample position. The spectrometer was calibrated using a standard 50/50 mixture of toluene and acetonitrile.[10] The positions of strong sharp bands are considered accurate to ± 2 pixels (*ca.* 3 cm^{-1}).

Seized ecstasy tablets were obtained from the Forensic Service Agency for Northern Ireland and were used as received.

Results

At the outset, the only information available for the samples was that they were in eight bags, each containing 50 off-white tablets with the 'Mitsubishi' logo. Each of these sets of 50 tablets had been taken at random from one of the eight very large bags of tablets that comprised the original seizure of > 50 000 tablets. Conventional analysis of a random selection of the tablets had shown that they all contained MDMA. Due to the large number of tablets received, a preliminary data set consisting of the Raman spectra of 6 tablets from each bag was obtained, so that gross variations in MDMA and excipient content between the various sample bags could be determined. Fig. 1 shows this data as the averages of the spectra of each set of 6 tablets. All the spectra show clear sets of bands due to their MDMA content (marked on the figure as bands 716, 771 and 810 cm^{-1}) but they also have features due to the excipients present. Cursory examination of the spectra in Fig. 1 shows that the tablets in Item 1, bags 1, 2, 3 and 4, and Item 2, bag 3 are similar, as are Item 2, bags 1 and 2, leaving Item 2, bag 4 as a unique set. Since the samples clearly divide into three main types we have relabelled the samples as **1(a)**–**(e)**, **2(a)** and **(b)**, and **3**. All the samples **1(a)**–**(e)** contain the same excipient, which was identified as sorbitol (band at 880 cm^{-1}) by comparison with the spectrum of pure sorbitol, samples **2(a)** and **(b)** have cellulose as the excipient (band at 1124 cm^{-1}), while sample **3** is glucose-based (band at 896 cm^{-1}).

The spectra shown in Fig.1 were all collected from tablets which were mounted on a rotating platform in the spectrometer and with the laser line-focused (not point-focused) onto them. This sampling method was chosen so that the spectra were obtained over as large an area of the tablet face as possible, minimizing any problems due to inhomogeneity of the distribution of drug and excipient throughout the tablets. Illegally-

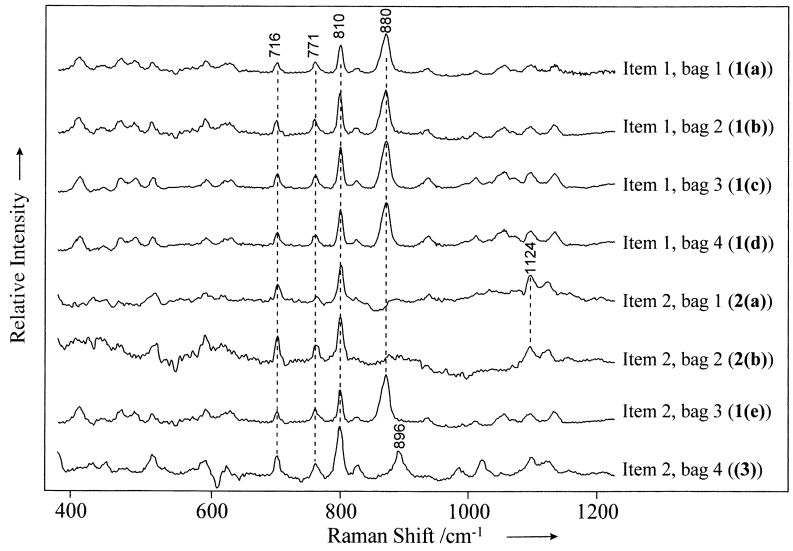

Fig. 1 The averaged Raman spectra of 6 tablets randomly selected from each of the eight large bags of tablets in the seizure. The strongest MDMA bands are at 716, 771 and 810 cm^{-1}, the strongest excipient band in each of the spectra is also labelled. The excipients are: samples **1(a)**–**(e)**, sorbitol; **2(a)** and **(b)**, cellulose, and **(3)**, glucose.

produced tablets are not manufactured under conditions of strict quality control, so that sample inhomogeneity due to poor mixing of drug and excipient is likely to be encountered.

To determine the extent of any inhomogeneity, a single tablet from sample bag **1(e)** was chosen at random for more detailed study. This tablet was mounted on a linear translation stage and the laser spot-focused rather than line-focused onto its surface. A series of spectra were then recorded as the sample was moved in 100 μm increments across the diameter of the tablet. A plot of the absolute peak heights of the MDMA band at 810 cm^{-1} and the excipient band at 880 cm^{-1} across the tablet is shown in Fig. 2. It is clear from the figure that there is not a homogeneous distribution of MDMA or excipient throughout the tablet.

Even without further analysis, it is clear that the Raman data in Fig. 1 can be used to show that all the tablets studied do indeed contain MDMA (as opposed to MDA or MDEA, for example) and further, that they broadly classify into the three groups labelled **1**, **2** and **3** which have different excipients. However, the spectra clearly contain more information than these two simple measures of composition and measurement of appropriate relative peak heights or areas can be used to extract quantitative data on, for example, the relative amounts of drug and excipient present.

In the initial data set, analysis of the variance of the relative peak heights of the strongest bands of the MDMA and excipients showed that the sets of 6 tablets taken from four of the bags with sorbitol-containing tablets (samples **1(a)** and **1(c)**–**(e)**) were indeed statistically similar, giving an F value of 0.58 compared with the critical value of 3.10 at the 5% confidence level. However, somewhat surprisingly, the tablets taken from the fifth sorbitol bag, (sample **1(b)**) were found to be slightly different. The sets of tablets taken from the bags with cellulose excipient (sample **2(a)** and **(b)**) were indistinguishable from each other (F = 0.062, F_{crit} = 4.96 at the 5% level), while sample **3** was unique.

In the preliminary data we found a considerable degree of variation in drug/excipient ratios, even in tablets taken from the same bag. To provide more statistically-valid data and to confirm that the variation within each sample set was not due to the bags containing mixtures of just two or three distinct types of tablets, each with a different fixed composition, we recorded spectra of all 50 tablets from each of a representative series of sample bags. The samples chosen were: two of the bags with similar apparent drug/sorbitol ratios (**1(a)** and **(e)**), the sorbitol-containing sample (**1(b)**) which the preliminary data had suggested was different from the others, one cellulose-containing sample (**2(a)**) and the glucose-containing sample **3**.

Fig. 3 shows the averages of the 50 spectra taken for each of the three sorbitol-containing samples. In all the 150 spectra used to make these averages there were variations in relative peak heights *etc.* but all the tablets were of the same general type *i.e.* there were no anomalous stray glucose- or cellulose-containing tablets in the sorbitol samples, similarly the bags of cellulose- or glucose-containing samples did not contain any sorbitol tablets.

In the spectra shown in Fig. 3 there is a clear difference in the relative intensities of the strongest MDMA (810 cm^{-1}) and sorbitol (880 cm^{-1}) bands between samples from bag **1(b)** and the samples from the other 2 bags examined. However, comparison of averaged spectra can be misleading and to make a well-founded conclusion about whether samples are indeed statistically similar or distinct it is necessary to look at the distribution of values as well as their averages.

The tablet-to-tablet variations in the ratio of MDMA/excipient band heights are illustrated in Fig. 4, which shows histograms of the number of tablets found with given MDMA/sorbitol ratios in samples **1(a)**, **(b)** and **(e)**. Also shown in the figure are Gaussian curves with the same mean and standard deviation as the data shown in the histograms. The mean and standard deviations of these are given in Table 1. From the data in Fig. 4 it is clear that the bags do not contain mixtures of distinct types of tablets with different MDMA/sorbitol ratios but rather that there is an approximately normal distribution about the mean values for each sample set. This is consistent with the observation that all the bags contain samples with a single excipient and, for example, there are no cellulose-containing tablets mixed in with sorbitol-containing samples.

ANOVA tables can be used to compare the MDMA/sorbitol ratios for the three sorbitol-containing samples that were studied in detail. Comparison of samples from bag **1(b)** with **1(a)** and **1(e)** gives F values of 46.31, and 93.03, respectively ($F_{crit\ (5\%)}$

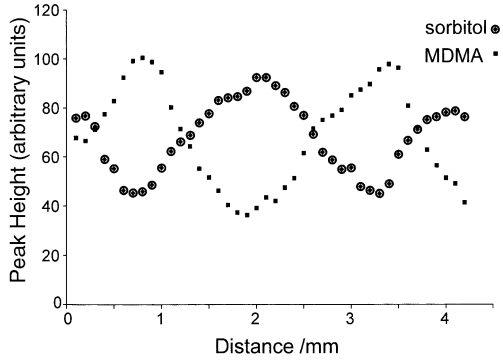

Fig. 2 Plot of the absolute peak heights of the MDMA band at 810 cm^{-1} and the excipient band at 880 cm^{-1} in a series of spectra recorded as a spot focused laser was moved in 100 μm increments across the diameter of a randomly-selected tablet from bag **1(e)**. The variation arises from inhomogeneous distribution of MDMA and excipient in the tablet.

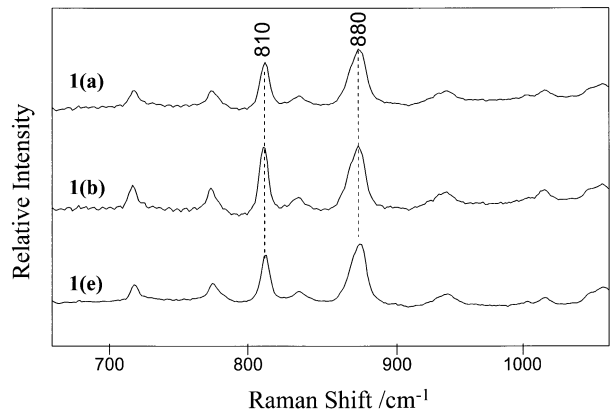

Fig. 3 The averaged Raman spectra of sets of 50 tablets taken from three sample bags, **1(a)**, **1(b)** and **1(e)**, all of which have sorbitol as the excipient. The relative intensities of the MDMA band at 810 cm^{-1} and the excipient band at 880 cm^{-1} are similar for samples **1(a)** and **1(e)** but different in **1(b)**.

Table 1 Mean and standard deviations of the ratios of bands characteristic of the degree of hydration of MDMA (upper section) and the drug/excipient ratio (lower section) in samples of 50 tablets taken from sample bags **1(a)**–**(e)** (sorbitol-based), **2(a)** (cellulose) and **(3)** (glucose)

Peak ratio measured/cm^{-1}	Sample number	Height ratio (mean ± s)
810:716	**1a**	3.057 ± 0.168
810:716	**1b**	3.041 ± 0.210
810:716	**1e**	3.005 ± 0.198
810:717	**2a**	1.507 ± 0.195
807:714	**3**	2.591 ± 0.139
810:879	**1a**	0.737 ± 0.165
810:880	**1b**	0.959 ± 0.162
810:880	**1e**	0.686 ± 0.119
810:1124	**2a**	4.564 ± 0.567
807:896	**3**	1.968 ± 0.077

= 3.94), whereas comparison of those from bags **1(a)** and **1(e)** yields an F value of 3.23 ($F_{crit(5\%)}$ = 3.94), which shows that these two bags have the same MDMA/excipient ratio but that **1(b)** has a statistically different ratio.

A similar analysis was carried out on two sets of tablets (6 tablets and 50 tablets) taken from the two bags of cellulose-containing tablets (samples **2(a)** and **2(b)**). This showed that the MDMA/cellulose ratio in the samples from both these bags were indistinguishable.

The final sample for which more extensive Raman data were recorded was sample **3** which displays a band at 896 cm^{-1} and contains a different excipient from the other seven lots.

The second parameter which was measured in the spectra is related to the degree of hydration of the MDMA present. We have previously found evidence for two differently hydrated forms of MDMA which form under different crystallisation conditions. The spectra of these two forms have very similar band positions but have pronounced differences in the relative intensities of the strongest MDMA band at 810 cm^{-1} to the weaker bands at 771 and 716 cm^{-1}.[7] To determine if there were differences between the degree of hydration in the MDMA components of the samples studied here we have measured the ratio of the heights of the MDMA peaks at 810 cm^{-1} and 716 cm^{-1}. The more intense MDMA peak at 771 cm^{-1} was not used because a sorbitol peak also lies close to this position and variations in sorbitol content could result in apparent variations in MDMA hydration. Table 1 shows a summary of the mean and standard deviation of the 810 : 716 cm^{-1} ratio for those samples where 50 spectra were available for analysis. As was the case for the MDMA/excipient ratios, there is a spread in the values observed, even for tablets taken from a single sample bag, but the standard deviations are considerably lower than those for the MDMA/sorbitol ratios, despite the fact that the intensity of the 716 cm^{-1} band is low so that an increase in scatter due to experimental uncertainty would be expected.

Figs. 5 and 6 show histograms of relative peak heights of the two MDMA bands of interest for 5 of the sets of samples. Interestingly, ANOVA shows that the sorbitol-containing samples, **1(a)**, **1(b)** and **1(e)**, all have similar MDMA peak ratios

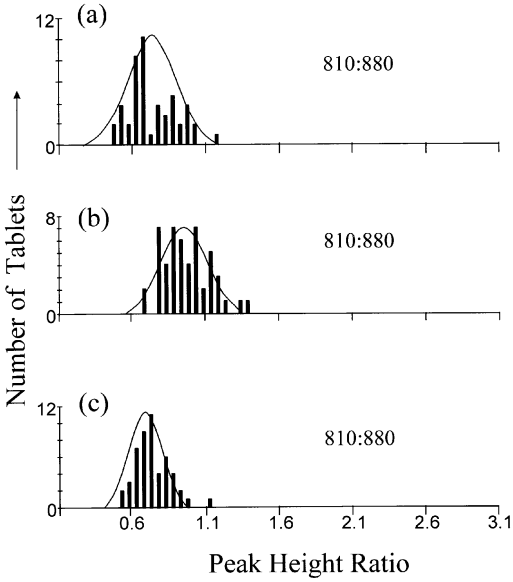

Fig. 4 An illustration of the tablet-to-tablet variations in the ratio of MDMA/excipient band heights in (a)–(c) the sorbitol-containing samples **1(a)**, **(b)** and **(e)**. The histograms show the number of tablets found with given MDMA/sorbitol ratios while the Gaussian curves are drawn with the same mean and standard deviation as the data shown in the histograms. There is a statistically-significant difference in the average value of the ratio in sample **1(b)** compared to **1(a)** and **(e)** but the distribution is approximately normal and there is no evidence that this difference in the average arises because the samples are composed of distinct types of tablets mixed in different proportions.

(F = 0.947 at the 5% level; F_{crit} = 3.058) while samples **2(b)**(cellulose) and **3** (glucose) are different both from each other and from the sorbitol-containing samples **1(a)**, **1(b)** and **1(e)** (F = 649.01 at the 5% level; F_{crit} = 2.41 between the 5 sets of data).

Discussion

This study highlights the advantages of Raman spectroscopy as a rapid and non-destructive technique for the characterization of

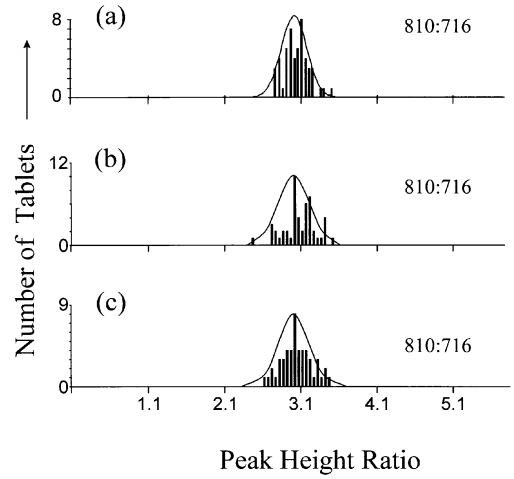

Fig. 5 An illustration of the tablet-to-tablet variations in the ratio of MDMA bands at 810 and 716 cm^{-1} in (a)–(c) the sorbitol-containing samples **1(a)**, **(b)** and **(e)** which are characteristic of the degree of hydration of the drug. The histograms show the number of tablets found with given MDMA/sorbitol ratios while the Gaussian curves are drawn with the same mean and standard deviation as the data shown in the histograms. There is no statistically-significant difference in the degree of hydration found in these samples.

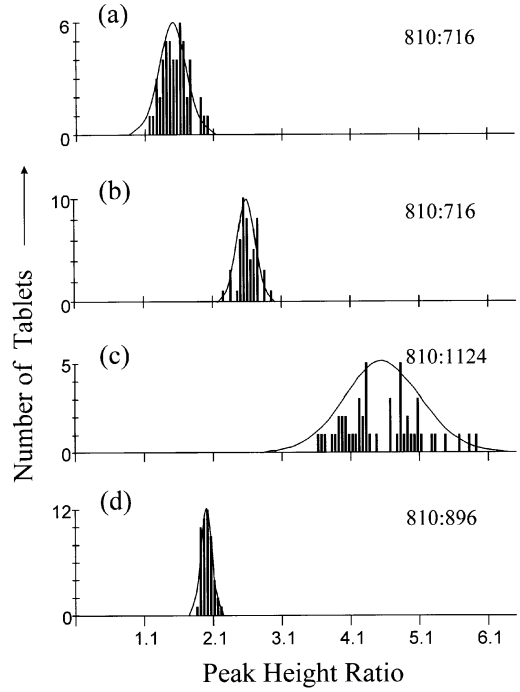

Fig. 6 An illustration of the tablet-to-tablet variations in bands characteristic of the MDMA and drug/excipient ratio in the cellulose and glucose-containing samples **2(a)** and **3**. Upper traces, (a) and (b): the ratio of bands at 810 and 716 cm^{-1} (MDMA hydration) in cellulose and glucose samples, respectively. Lower traces, (c) and (d): ratio of strongest MDMA and excipient bands for the same cellulose and glucose samples. The degree of hydration and variation in drug/excipient ratio are very different for these samples.

seized tablets containing ecstasy or related phenethylamines. There is little difficulty in obtaining data of sufficient quality for analysis with a simple dispersive instrument using red (810 nm) excitation and accumulation times as short as 40 s. The sample tablets do not have to be prepared in any way before analysis and we have found that the spectra of 50 tablets can be obtained in one hour. Simple visual inspection of the spectra can be used to identify the drug and excipient, which gives a gross characterisation, while measurement of relative peak heights gives quantitative data on drug/excipient ratios, degree of hydration of the active compound and sample homogeneity. However, there are clear lessons to be learned for use of Raman methods for analysis of actual seized samples, rather than model samples which have been prepared from commercially-available drugs and pure excipients in a research laboratory.

The most obvious problem in the real samples is that homogeneity is not guaranteed, even in single tablets. The data in Fig. 2 show that for the particular samples we studied there was a very marked variation ($> \times 5$) in the ratio of drug to excipient at different points on the tablet. We did not find a point in the line segment which was scanned where there was no detectable MDMA but there were patches on the surface > 1 mm in diameter with low drug content and there are undoubtedly regions of almost pure excipient in these samples. This inhomogeneity is most likely to cause problems if microscopic illumination/collection is used because it means that for every tablet a series of spectra will need to be taken at different points on the surface to ensure that the Raman data are representative of the composition of the sample. With macroscopic optical collection, line focus coupled with sample rotation provides a much simpler solution because it allows almost the entire surface of the seized sample to be characterized by a single spectrum.

The inhomogeneity observed within single tablets is reflected in tablet-to-tablet variation of drug/excipient ratios. For the sorbitol-containing tablets we studied there was a significant degree of random variation in drug/excipient ratios, so that even for tablets taken from a single sample bag the differences between the highest and lowest ratios were $> \times 2$ (see Fig. 4). In contrast, the drug/excipient ratio for the unique sample bag **3** had significantly less spread (Fig. 6(d)) and the difference between the highest and lowest values was only *ca.* 20%. This gives us confidence that the much larger spread in values for the sorbitol-containing samples reflects a real distribution in composition rather than statistical noise in the experimental data. It is clear that when using Raman methods it is important to sample over large areas of each tablet and characterise more than a few tablets since this allows true mean values to be established and also would allow detection of 'mixed' samples composed of several discrete types.

An additional advantage of the Raman method is that, as well as identifying the drug and excipient(s) present, the measurement of relative intensities of some of the MDMA bands in the spectra gives information on the degree of hydration of the drug which was used to prepare the tableted form.[7] This gives an additional parameter which can be used to characterise the drug content of the tablets. For example, in the samples studied here all three of the sorbitol-containing samples contained MDMA with the same degree of hydration (see Fig. 5), despite the fact that one of these bags had a different drug/sorbitol ratio from the other two. The other samples, which had cellulose and glucose excipients, were clearly not prepared by taking the same batch of MDMA as the feedstock and mixing it with different excipients, since they had hydration states different both from each other and from the sorbitol-containing sets (see Fig. 5 and 6 and Table 1). In effect, the only similarity between them and the majority of the seizure, which was composed of sorbitol-containing samples, was that they were MDMA tablets marked with the 'Mitsubishi' logo that had been seized at the same time.

This study serves to highlight the amount of information available from the Raman spectra of these samples and in particular shows that simply noting drug content and physical appearance alone misses clues that allow different tablets to be distinguished. Since the sample set chosen was from a large seizure of bags of physically similar tablets, all off-white colour, which were confirmed by GC-MS analysis as containing MDMA and which bore the same impressed mark, our expectation was that all these tablets would be identical *i.e.* that they had been produced in a large production run and had been divided for transport and distribution. In fact, the Raman analysis shows that this was far from the case. Although we found that the contents of each of the large bags in the seizure contained tablets of a particular composition normally distributed about an average value, *i.e.* there were no mixtures of distinct tablets in each of the bags, the composition varied between bags. Only two of the bags that were studied in detail contained identical sorbitol-based tablets, although there was a third bag of sorbitol-containing tablets that were very similar to these and differed only in the MDMA/sorbitol ratio. Presumably the tablets in this bag were made by the same method as the others but in a different production run. However, we also found that two of the bags contained only cellulose-based tablets, these had a very broad range of drug/excipient ratios and contained MDMA with hydration intermediate between that of the sorbitol tablets and the final bag of tablets, which were glucose-based. The tablets in this final bag had a very different degree of hydration from any of the others and appeared to have been carefully manufactured, since their MDMA/glucose ratios spanned a very narrow range (see Fig. 6(d)) compared to those of the tablets in the other sample bags.

Overall, we have found that composition profiling by Raman methods is a fast and effective method of discriminating between ecstasy tablets that have been manufactured in different ways and with different drug feedstocks. In the example shown here the task was made marginally more difficult than usual because all the samples contained MDMA as the active compound but, as we have shown previously, it is also easy to discriminate between tablets containing different, related phenethylamines.[7] It is clear that the potential benefits of obtaining highly detailed spectra can indeed translate into information that is not readily available from other methods but which will be useful for tracing of drug distribution networks.

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