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Characterization of street drugs using handheld Fourier transform Raman spectroscopy

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Abstract

Handheld Raman spectroscopy offers a rapid and mobile technique for determining drugs non-destructively. The technique offers further advantage for drug products' (DPs) analysis in its ability to measure samples through packaging thus preserving the evidence integrity and continuity. This research evaluated the use of handheld FT-Raman spectroscopy for characterization of street DPs (n = 254) of diverse formulations. Raman spectra of DPs inside their packaging were collected and matched against the instrumental in-built library then exported to Matlab 2020a for offline spectral interpretation. Reference analysis was confirmed using gas chromatography-mass spectrometry and infrared spectroscopy. The main drugs present were 1,3-trifluoromethylphenylpiperazine, cocaine, ketamine, 3,4-methylenedioxymethamphetamine, mephedrone, and 1-benzylpiperazine. The main impurities present in DPs were benzocaine, caffeine and lactose. The impurities affected the Raman signature (enhanced or inhibited) of DPs, enabling profiling DPs and visualizing patterns among different products. These latter patterns were featured in the similarities highlighted by the correlation coefficient values between different DPs, and by adjacent clusters of different DPs envisaged in the principal component analysis scores plot.

Introduction

Crime and violent behaviors have increased due to the widespread use of illicit drugs in contemporary societies. Amsterdam (1027.7), London (701.1), and Copenhagen (780 mg/1000p/day) had the highest weekend daily mean cocaine usage in 2020 (1). Drug addiction endangers public health, safety and welfare, and the nations' security. Researchers and authorities require quick and accurate drug detection methods that

can be adapted to the ever-increasing spectrum of the illicit drugs. Nowadays, the primary goal of drug analysis is to detect and identify drugs of abuse.

Analytical techniques such as thin layer chromatography, gas chromatography-mass spectrometry (GC-MS), gas chromatography-flame ionization detector, high-performance liquid chromatography and liquid chromatography-mass spectrometry have all been proposed, developed, and used to detect illicit drugs (2). These techniques provide reliable and accurate results in drug analysis, but they are costly, time consuming, destructive that limits their practical ability. Vibrational spectroscopic methods such as Fourier transform infrared (FTIR) and Raman address the aforementioned limitation and have also been applied for qualitative and quantitative investigations of illicit drugs (3,4).

Raman spectroscopy measures the vibrational modes of a sample. The spectrum is a wavelength distribution of bands that correspond to molecular vibrations in the sample under investigation. The Raman bands frequencies and intensities could be used to identify and quantify the measured samples (5). Raman spectroscopy generates molecular-specific spectra with minimum or no sample preparation, permitting for non-destructive in-situ analysis for different forms of drugs (liquids, tablets, and powders) (6). These features are very useful when substantial number of samples need to be analyzed and are essential for avoiding sample contamination, reducing analysis time, and protecting the evidence under investigation. Raman spectroscopy has been used in a variety of applications, including forensics (6), industrial process control (7), biomedical purposes (8), and medical diagnostics (9). When identifying drugs, Raman can distinguish between salts, stereoisomers, and homologs with a sample size of more than 5 mg (10). It reveals a high level of specificity for drugs concealed in alcohol (11). Minor variations in chemical structures can be identified which provide a characteristic spectrum for each chemical compound and makes the identification of drugs more reliable (12). Raman spectroscopy has recently been used to check drug contents within their packaging (13), evaluate the composition and homogeneity of drug tablets (14), classify street drugs (15), and determine drug authenticity (16). Raman spectra of drug blends are often highly complex because they include spectral features corresponding to all components in the sample. Consequently, chemometric methods must be used to obtain quantitative information from complex spectra (17). This study complements previous studies in

evaluating the use of handheld Raman spectroscopy for on-spot identification and characterization of street drugs in their packaging.

Experimental

Street samples of drug products (DPs) (n = 254) were measured as received and included powders, tablets, capsules, liquids, and rocks of different colors. Samples were measured through glass vials using a handheld FT-Raman spectrometer equipped with 490 mW laser powder, 1064 nm laser wavelength and cooled InGaAs detector. Spectra were collected over the wavenumber range of 250 – 2000 cm^{-1} with a spectral resolution of 10 cm^{-1} . The inbuilt spectral algorithm was used to search matches of the drug samples against the instrumental libraries. For each sample, the library algorithm gave matches for the drug(s) and/or additives that showed spectral features. For offline analysis, the spectra of the products were interpreted considering spectral quality, functional groups and similarities among products using correlation in wavenumber space (CWS) and principal component analysis (PCA) algorithms. Spectral quality was evaluated for the measured drug products, considering the low spectral resolution in FT-Raman (18). For CWS method, the momentum product was calculated between the spectra of different products reporting a common drug. A threshold of 0.95 or more was considered a match and vice versa (19). For PCA, drug products' spectra were explored for patterns among their scores. A false negative was seen when a drug product score was not grouped with product scores of the same drug, where false positives were seen when a drug product score was clustered with scores of different drugs. Reference analysis was conducted using GC-MS and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. GC-MS and ATR-FTIR confirmed the identity of the drugs or common impurities present in DPs respectively (Table 1).

Results and discussion

Out of the measured drug products, 153 contained drugs/mixtures most of which were not pure. The main drugs found were 1,3-trifluoromethylphenylpiperazine (TFMPP) (n=42), cocaine (n = 36), ketamine (n = 29), 3,4-methylenedioxymethamphetamine (n = 24), mephedrone (n = 9), 1-benzylpiperazine (BZP) (n= 7) butylone (n =2), 3,4-methylenedioxypyrovalerone (MDPV) (n = 2), 1-(3-chlorophenyl)piperazine (mcPP) (n

= 2), dibenzylpiperazine (DBZP) (n = 1), and 1-methyl-4-benzylpiperazine (mBZP) (n=1).

The main impurities detected were caffeine (n = 57) and benzocaine (n = 35) that were both Raman active. Lidocaine and procaine were detected less than benzocaine and were found in seven and two products respectively. Benzocaine and lidocaine were mainly found as impurities in cocaine drug products alongside other impurities such as phenacetin and caffeine. Thus, the pattern of adulterants varied between DPs. For instance, caffeine was also an adulterant in MDMA and piperazine derivatives. On the other hand, lactose was a bulking agent reported in diazepam tablets and it contributed to the low Raman activity of these products. Likewise, dextrose and sucrose were also found in DPs of tablet- and powder-formulations; and contributed to the low Raman activity of these products. Hence, drugs adulterated with the aforementioned sugars were not detected in tablets/powders using Raman spectroscopy where the Raman signal of these tablets was masked by lactose fluorescence.

Spectral quality of DP

Spectral quality was evaluated considering five parameters: the number of peaks (N), maximum peak position and intensity, wavenumber range, and signal to noise ratio (SNR) (19). In this respect, synthetic piperazine, cocaine, and mephedrone products showed strong Raman activity, ketamine products showed medium Raman activity, whereas MDMA products showed low Raman activity.

Synthetic piperazines' spectral quality varied depending on the purity of the DPs and the types of impurities present in them (Figure 1). TFMPP samples showed stronger Raman activity than other piperazines and that was related to their being either pure or cut with caffeine that in turns was Raman active. The ranges of N, maximum intensity and SNR values for piperazine derivatives were 15-25, 1500-15000 a.u., and 10-20 respectively. Cocaine products demonstrated strong Raman activity but that depended on the adulterants present in cocaine sample and that affected the Raman activity (Figure 2). For cocaine, Raman active samples, N, maximum intensity, and SNR were in the range of 11-27, 1,744 – 51,242 a.u. and 15 – 39 respectively. Likewise, mephedrone showed strong Raman activity with ranges of N, maximum intensity and SNR in the ranges of 25-29, 1500-8000 a.u., and 18-37 respectively (Figure 3). Ketamine products showed medium Raman activity with N, maximum intensity and SNR in the ranges of 16-30, 700-4000 a.u., and 5.75-39 respectively

(Figure 4). On the other hand, MDMA products exhibited low Raman activity with low SNR (<20) despite the high N in most spectra (up to 25) (Figure 5). The maximum intensity seen for MDMA products was in the range of 1500-5000 a.u..

3.3. Spectral interpretation

Spectral interpretation showed characteristic scattering band for the major drugs/impurities present in the measured DPs (Table 1). Most drugs showed key bands between 500-1700 cm^{-1} (21-25). In this respect, Raman spectra indicated key differences between different drug analogues as well as base/salt forms of the same drug. For drug analogues, piperazine derivatives (TFMPP and BZP) could be differentiated over the ranges 500-1000 and 1300-1700 cm^{-1} respectively (Figure 1). Likewise, cocaine could be discriminated from cocaine HCl mainly in the range between 850-890 cm^{-1} , where cocaine based showed three bands around 850, 870, and 890 cm^{-1} corresponding to the C-C stretch of the tropane ring in cocaine base (20). On the other hand, cocaine HCl only showed two C-C stretching bands corresponding to the tropane ring around 850 and 890 cm^{-1} (20,21). Where benzocaine was present in cocaine DPs, it could be traced by the strong absorption intensity and by the characteristic bands in the range of 850-1700 cm^{-1} (Figure 2).

3.4. Classification of DPs

When CWS was applied to the spectra of the top encountered DPs, variable r value ranges were observed and that depended on the amount of drug in DPs and on the purity of the specific DP (Figure 6). For instance, TFMPP-related products (DPN213-DPN254) did not show high r values against each other and that could not be considered a false negative because of the inconsistency in constituents in TFMPP products that indicated the presence of other additives such as caffeine, dextrose, ephedrine, lactose, phenmetrazine, and sucrose. In this respect, the Raman activity of the constituents impacted the Raman scattering in terms of number of bands and Raman activity of the DP. For instance, caffeine had strong Raman scattering and that influenced the signature of the TFMPP products containing them (DPN234-249). Nonetheless the latter products contained impurities such as lactose that was only detected by Raman (and not GCMS) and this in turns influenced their Raman activity. Lactose and other sugars introduced fluorescence in the Raman spectra of TFMPP products (Figure 1). It is important to mention that the physical properties of the DPs

did not influence the Raman signature. Hence, TFMPP products of similar chemical makeup and different physical characteristics (formulation, color) showed high r values against each other. For example, DPN217 (white tablet formulation) showed r value of 0.95 against DPN220 (white crystal formulation). Also, DPN228 (pink tablets), DPN235 (white tablets), and DPN246 (blue tablets) showed r values of 0.95 against each other. It is worth noting that no false positives were seen for TFMPP-DPs except against a DP containing BZP and this mismatch could be related to the structural similarity between TFMPP and BZP.

Cocaine DPs featured less false negatives and that could be attributed to the consistency in the types of impurities detected in the measured cocaine DPs. For instance, samples with cocaine/benzocaine mixture (DPN48-DPN62) showed r values > 0.95 against each other where both constituents in the matrix were Raman active and were strong scatterers. Where more than two constituents were present in the cocaine DP, the r value changed and the also depended on the Raman activity of the constituent(s). Yet overall, the constituents were unique to cocaine mixtures where no false positives were observed with cocaine mixtures against other drugs. Similar patterns in r values results were seen for ketamine samples that were mainly pure and showed r values > 0.95 against each other and < 0.95 against different drugs. Only four ketamine DPs showed low r values against other ketamine products (one Raman active and three Raman inactive samples). The remaining DPs (containing MDMA and mephedrone) showed false positives and false negatives related to the high number of impurities present in them and that had been reported in the literature especially in mephedrone DPs.

Hence, CWS results were only conclusive when the exact number of impurities were present in the reference and test tablets. Considering the aforementioned challenge in identification, PCA recognized patterns in the DPs scores that corresponded to spectral features contributing to high variances (Figure 6). The first three PCs contributed 88.8% of the variance among the DPs' spectra with cocaine DPs' scores recording the highest variance. This was followed by ketamine DPs' scores and TFMPP DPs' scores. Cocaine, ketamine, and TFMPP DPs' scores showed three distinct clusters with slight overlap in few scores and that could be related to the caffeine/lactose that were impurities present in DPs of the three drugs. Some MDMA DPs' that contained lactose overlapped with products of the same impurity. On the

other hand, mephedrone DPs were clearly distinguished from other DPs and that showed their unique composition/chemical make-up.

Conclusion

In summary, handheld FT-Raman spectroscopy complemented GC-MS and IR in characterizing street DPs. It indicated information regarding certain impurities that could not be detected by GC-MS (e.g. lactose and sucrose). Another advantage encountered over IR was the ability of Raman to characterize Raman active drugs non-destructively regardless of the physical differences between the matrices (tablets, powders, or liquids). However, some limitations were encountered in processing the spectra of the drug products relating to the sensitivity of Raman in detecting drug(s) in presence of impurities especially fluorescent ones such as lactose. Moreover, the presence of multiple impurities introduced a challenge in the identification/characterization of the drug product. Further understanding of Raman spectra particularly in samples of multiple impurities is needed. Therefore, future work will consider investigating drugs in mixtures using a more quantitative approach.

Acknowledgments

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List of tables

Table 1. GC-MS, IR and Raman libraries' matches of the drug products measured

DPN(s)	Form(s)	Color(s)	Libraries matches		
			GCMS	IR	Raman
DPN1	crystal	white	benzocaine/procaine	benzocaine	p-hydroxy cocaine, p-hydroxy benzoyl ecgonine
DPN2-3	powders	white and grey	butylone, MDPV	ketamine	NR
DPN4-10	tablets	beige, white, yellow	BZP, caffeine, mCPP	buclizine, benzocaine, pemoline	acacia, caffeine
DPN11-31	crystals, powders, powder lumps, tablets	beige, brown, grey, off-white, white	caffeine, methyl salicylate, MDPV	aminophylline, caffeine, clonidine, ethambutol, ganciclovir, metrizamide, nicotinic acid, phosphoric acid, sulfamide, theobromine	caffeine, cyclodextrin, ketamine, paracetamol

DPN32-82	powders, powder lumps, rocks, tablets	beige, brown, off-white, white, yellow	cocaine, benzocaine, caffeine, lidocaine, phenacetin, procaine	cocaine, 4-aminobenzoic acid, benzocaine, boric acid, dextrose, hydroquinone, ketamine, lactose, levodopa, lidocaine, MDMA, methicillin ethyl acetate, n-butyl-p-amino-benzoate, opium powder, phenacetin.	cocaine HCl, caffeine, ephedrine, ketamine, lactose, p-hydroxy cocaine, p-hydroxy benzyl ecgonine.
DPN83	powder	pink	DBZP, TFMPP	NR	NR
DPN84-89	powder, tablet	blue, white	diazepam	cocaine, dextrose, lactose	cyclodextrin, lactose
DPN90-122	crystal, powder	white	ketamine	benzocaine, harmine, ketamine, THC	ketamine, MDMA, sucrose
DPN123-152	crystal, powder, tablet	grey, off-white, orange, pink, red, white, violet, yellow	MDMA, caffeine, cocaine, lidocaine	betaxolol, dextrose, ethambutol, histamine, kanamycin sulfate, MDMA, MDPV	ketamine, lactose, MDMA, p-hydroxy cocaine, p-hydroxy benzoyl ecgonine,
DPN153	powder	white	MDPV	NR	dextrin
DPN154-162	crystal, powder	brown, white	mephedrone	benzocaine, levodopa, monoethyl-glycinexylidide, paramethoxymethamphetamine, protriptyline	NR
DPN163	tablets	white	methcathinone	NR	NR
DPN164	powder	white	methylone	NR	NR
DPN165-210, DPN254	blue, capsule, crystal, gel, liquid, powder, tablet	beige, blue, brown, clear, green, grey, off-white, orange, pink, white, yellow	inconclusive	carbetapentane, chloroquine, ephedrine, epsom salt, ethambutol, ethylene glycol, ketamine, lactose, levodopa, MDMA, MDPV, morphine, opium powder, paracetamol, pilocarpine, sucrose, sugar, sulfuric acid, triolein.	1,2-propanediol, amphetamine sulfate, benzyl alcohol, chlorobenzene, cyclodextrin, quinine sulfate, ketamine, lactose, MDMA, paracetamol, strontium sulfate, titanium dioxide.
DPN211-253	capsules, crystals, powder, tablet	beige, blue, pink, turquoise, white	TFMPP, BZP, caffeine, deodecyl acrylate, MBZP, phenmetrazine, piperazine	dextrose, ephedrine, formaldehyde, harmine, levallorphan, MDMA, morphine, phenelzine sulfate, sucrose, thiamine	benzene, benzyl alcohol, caffeine, lactose, sodium sulfate,

DPN: drug product number; BZP: benzyl piperazine, MBZP: 1-methyl-4-benzylpiperazine; DBZP: dibenzylpiperazine; GC-MS: gas chromatography mass spectrometry; IR: infrared spectroscopy; mCPP: metachlorophenylpiperazine; MDMA: 3,4-methylenedioxyamphetamine; MDPV: 3,4-methylenedioxypropylamphetamine; MDPV: 3,4-methylenedioxypropylamphetamine; NR: not reported by libraries; TFMPP: 3-trifluoromethylphenyl piperazine; THC: delta nine tetrahydrocannabinol.

Table 2. Functional groups attributed to the main substances present in the drug products

DPN	Drug	Band position (cm ⁻¹)	Corresponding group
DPN211-253	TFMPP (15)	538	C-CF ₃ asymmetric stretch
		621	C-CF ₃ asymmetric stretch
		729	C-CF ₃ symmetric stretch
		893	C-C stretch
		993	CH out-of-plane bending
		1050	CH ₂ rocking
		1322	CH ₂ twisting
		1375	C-C stretch
		1441	CH ₂ wagging
		1606	C-C asymmetric stretch
DPN4-10	BZP (15)	993	C=C-C bending
		1208	CH ₂ twist and C-N stretch
		1463	CH ₂ scissoring
		1599	C=C-C asymmetric stretch and CH ₂ bending
DPN32-82	Cocaine (20, 21)	1001	symmetric stretching/ breathing of the aromatic ring
		1599	C=C stretching of the aromatic ring
		850, 870 and 890	C-C stretch of the tropane ring
		1183	C-N stretching
		1319	C-H twisting
		1735	C=O asymmetric stretching
DPN1, DPN48- DPN80	Benzocaine (20)	860	C-O stretching
		1170	in-plane H-C-H bending,
		1280	C-C/C-N/C-O stretching of aromatic ring,
		1600	stretching and bending of aromatic ring/NH ₂ scissoring
		1680	C=O stretching
DPN11- DPN31, DPN64- DPN70, DPN81, DPN152, DPN234- DPN250	Caffeine (20)	1075	C-C stretching
		1239	H-C=N bending
		1278	C-N stretching
		1323	C-N stretching
		1352	C-N stretching
		1599	C=C stretching
		1655	C=O stretching

		1696	C=O stretching
DPN90-122	Ketamine (22)	594	C-Cl stretching,
		649	aromatic C-H bending,
		1042	o-disubstituted aromatic C-H bending,
		1082	C-N stretching,
		1441	CH ₃ and CH ₂ deformation,
		1585	aromatic C=C stretching,
		1724	C=O stretching
DPN123-152	MDMA (23, 24)	773	aryl C-H wagging
		808	O-C=C-O
		885	CNC stretch
		1009	CH ₃ twist
		1247	CH
		1441	CH ₃ bending/CH ₂ scissors
		1613 and 1627	C=C stretch
DPN154-162	Mephedrone (25)	804	phenyl ring breathing
		1249	=C-H in plane deformation
		1299	=C-H in plane deformation
		1606	C=C stretch

List of figure legends

Figure 1. Raman spectra of (a) TFMPP and (b) BZP DPs measured using an FT-Raman spectrometer equipped with 1064 nm laser wavelength.

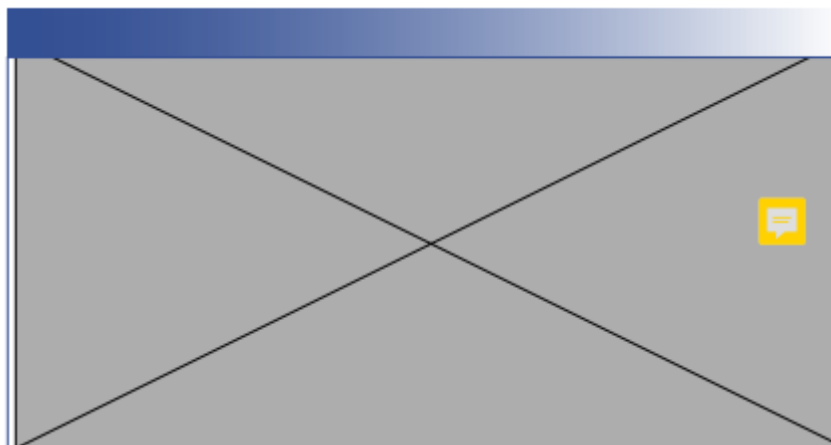


Figure 2. Raman spectra of DPs containing (a) cocaine, (b) cocaine and benzocaine, and (c) cocaine and caffeine measured using an FT-Raman spectrometer equipped with 1064 nm laser wavelength.

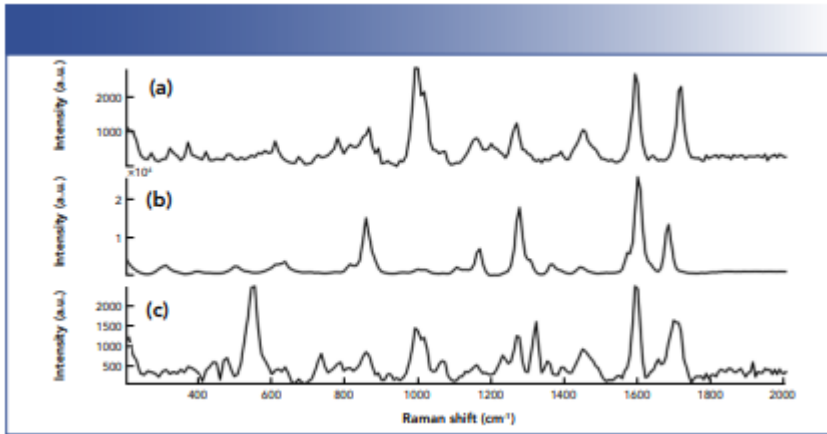


Figure 3. Raman spectra of mephedrone samples in crystal (black) and powder (red) forms measured using an FT-Raman spectrometer equipped with 1064 nm laser wavelength.

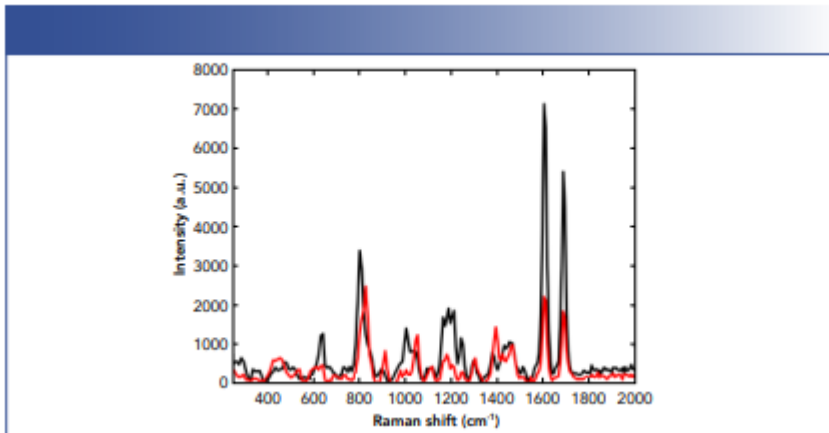


Figure 4. Raman spectra of ketamine DPs measured using an FT-Raman spectrometer equipped with 1064 nm laser wavelength.

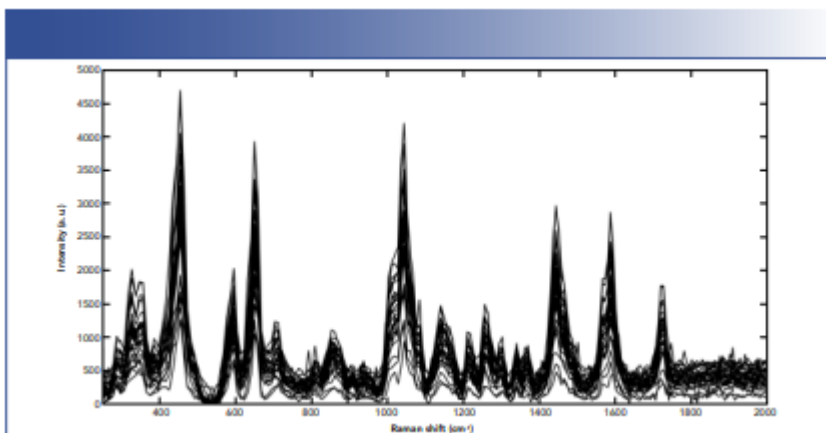


Figure 5. Raman spectra of MDMA DPs in the following colors/forms: (a) grey crystal, (b) white crystal, (c) orange powder, and (d) pink tablet measured using an FT-Raman spectrometer equipped with 1064 nm laser wavelength.

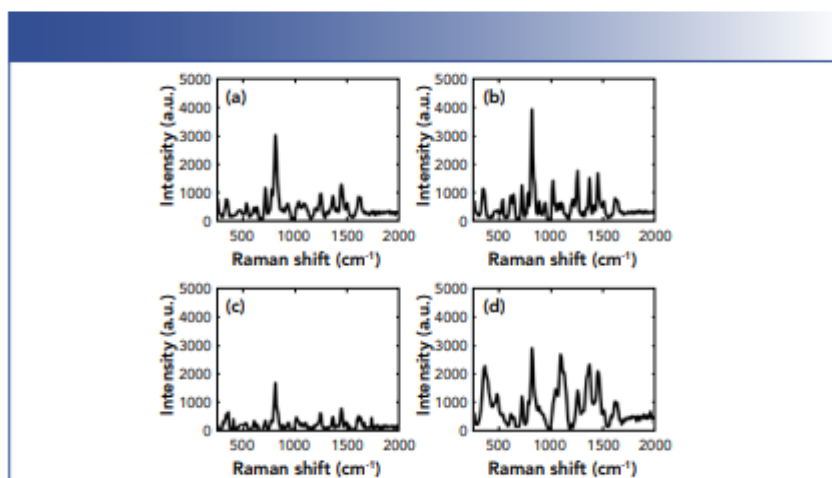


Figure 6 (a) Correlation map of the Raman spectra of TFMPP (1:42), cocaine (43:78), ketamine (79:107), MDMA (108:131), caffeine (132:150), mephedrone (151:159) and BZP (160:166) DPs where r values above 0.95 are marked in yellow and those below 0.95 are marked in red. (b) PCA scores plot of the Raman spectra of TFMPP (black circle), cocaine (blue square), ketamine (red star), MDMA (green triangle), mephedrone (cyan triangle) and BZP (black star) DPs.

