An Investigation into the Role of Portable Attenuated Total Reflectance Fourier Transform Infra Red Spectroscopy in the Presumptive Testing of Illicit Drugs

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Abstract

Attenuated Total Reflectance Fourier Transform Infra Red Spectroscopy (ATR-FTIR) was evaluated as a presumptive test for illicit drugs. Five hundred and forty five unknown substances collected between November 2009 and May 2010 from three large London nightclubs were analysed first by ATR-FTIR and later screened by Gas Chromatography-Mass Spectrometry (GC-MS). The identification of mephedrone, ketamine, methamfetamine, plaster-of-Paris tablets, MDMA in powder and crystalline forms were successful in over 99 % of the true positive samples by ATR-FTIR. The success rate was lower in the case of cocaine (43 %), piperazine derivatives (31-61 %) and MDMA in tablets (50%). Seventy two liquid samples were found to be GBL. Ninety-six per cent of identifications were achieved through the TICTAC library, created in our laboratory. This study indicates that portable ATR-FTIR will be a useful tool for the presumptive testing of the new synthetic powdered drugs available in high purity on the streets providing that the appropriate library is used.

Introduction

Police Forces often use presumptive tests to rapidly screen and tentatively identify seized materials.
The Scott colour test has long been used for field testing cocaine, as well as the Marquis colour test to indicate the presence of heroin, amfetamine/methamfetamine and ecstasy type compounds. Currently there is no available field test for the identification of new synthetic drugs (eg. ketamine, mephedrone, GBL).
Fourier transform infrared (FTIR) spectrometers have been developed with attenuated total reflection (ATR) sampling devices. The sample is placed directly onto the surface of an IR transparent crystal. The radiation enters the crystal, reflects through it, penetrates into the sample to a small degree, passes back to the IR beam and the changes in light intensity is measured [1] (Figure 1).

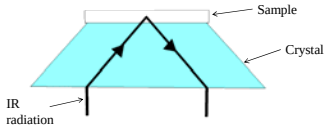

Figure 1. ATR analysis

There is no need for sample preparation, a small amount of liquid (one drop) or solid sample (0.5mg) is placed on the crystal and the measurement takes less than a minute.

Materials and methods

The contents of amnesty bins were received in eight sealed evidence bags and analysed by diamond ATR Infra Red Spectroscopy and GC-MS under a United Kingdom Home Office license. A Bruker Alpha P Spectrometer controlled by Opus software was used for the spectroscopic analysis [2] (Figure 2).
Spectra of unknown samples can be identified by searching built in libraries and evaluating the quality of possible matches. The use of spectral libraries enables untrained law enforcement officers to identify suspected drugs.

Spectral libraries

- Bruker Drug Library 742 spectra
- Enhanced Georgia State Crime Lab 2,165 spectra of controlled substances
- BIO-RAD Commonly Abused Drugs (Acid-Base) 580 spectra
- Merck database 2,940 spectra of compounds from the Merck Index

The above libraries were all collected in transmission mode using KBr disks.

- TICTAC library 90 spectra of frequently encountered drug substances

The TICTAC library was created using ATR.

Figure 2. Bruker Alpha P

Results and discussion

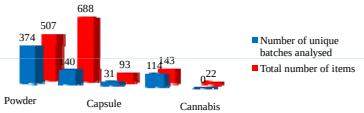

Figure 3.Total number of items in the eight evidence bags and the number of unique batches analysed

The eight sealed police evidence bags contained 1453 items (bags or wraps of powders, tablets, capsules, glass bottles, plastic containers, sealed straws and cannabis material.
Figure 3 shows the total number of items found in the eight evidence bags and the number of unique samples analysed.

Mephedrone

Forty per cent (151) of the powders and 29 % (9) of the capsules were identified as mephedrone (4-methylmethcathinone) by ATR-FTIR. Figure 4 shows the overlaid spectra of a sample and mephedrone standard.
Figure 5 shows the other compounds detected in these samples. One powder which did not show a match to the library was later identified as mephedrone by GC-MS. This sample was likely to have been diluted with a mixture of sugars. The identification of these samples was from the TICTAC library.

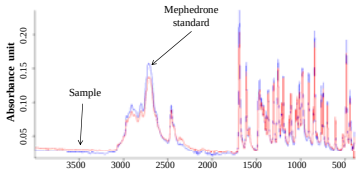

Figure 4. Overlaid spectra of a sample and mephedrone standard

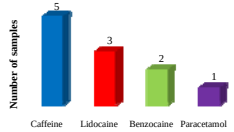

Figure 5. Other compounds detected in mephedrone samples

The library search of one powder resulted in a low quality match to 4-methylethcathinone and mephedrone. Subsequent GC-MS analysis identified this substance as 4'-methyl-alpha-pyrrolidinopropiophenone (MPPP) a compound previously only seen Germany's illicit drug market [3]. Figure 6 shows the overlaid spectra of MPPP and mephedrone.

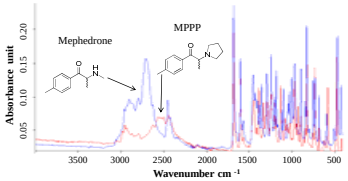

Figure 6. Chemical structures and overlaid spectra of mephedrone and MPPP

Ketamine

Twenty-eight per cent (105) of powders were identified as ketamine by ATR-FTIR. Figure 7 shows the other compounds detected in these samples.
All ketamine samples were identified from the TICTAC library.

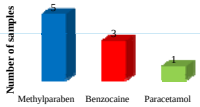

Figure 7. Other compounds detected in ketamine samples by GC-MS

Cocaine

Figure 8 shows compounds identified by ATR spectra of the 46 samples subsequently confirmed to contain cocaine by GC-MS. Figure 9 shows the overlaid spectra of a cocaine sample and cocaine standard (from Bruker Library as KBr disk).

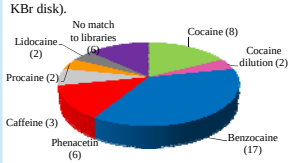

Figure 8. ATR-FTIR results of the 46 samples subsequently confirmed to contain cocaine by GC-MS

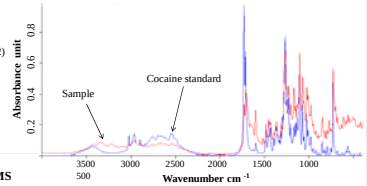

Figure 9. Overlaid spectra of a sample and cocaine standard

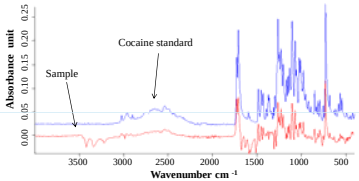

Figure 10. Overlaid spectra of a sample after subtraction and cocaine standard

Using OPUS software spectrum subtraction program the detection of cocaine increased from 17 % to 43 %.
Figure 10 shows the superimposed spectra of a cocaine sample after the subtraction of benzocaine and the standard cocaine.
Sixty nine per cent of the cocaine identifications were made from the TICTAC Library.

Piperazine derivatives

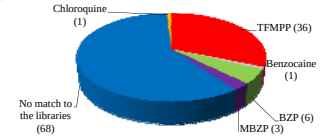

Figure 11. ATR-FTIR results of the 113 samples subsequently confirmed to contain piperazine derivatives by GC-MS.

The most common piprerazine derivatives in tablets, capsules and powders were 1-benzylpiperazine (BZP), 1-(3-trifluoromethylphenyl) piperazine (TFMPP), 1-(4-dibenzyl) piperazine (DBZP), 1-(4methylbenzyl) piperazine (MBZP), 1-(3-chlorophenyl) piperazine (CPP) and 1-(4-methoxyphenyl) piperazine (pMeOPP) [4].
Figure 11 shows the ATR-FTIR results for 113 samples subsequently confirmed to contain piperazine derivatives by GC-MS.

MDMA

Eleven crystalline samples were identified as methylenedioxymethamfetamine (MDMA) hydrate and one powder as anhydrous MDMA by ATR-FTIR.
MDMA-HCl was found in distinct crystalline states: fully hydrated and anhydrous polymorphic forms [5]. Figure 12 shows the overlaid spectra of the hydrate and anhydrous standards.
Three tablets were found to contain MDMA by ATR-FTIR in the EGSCL Library. GC-MS analysis also detected MDMA in one tablet that was identified as lactose by IR and also in two tablets where the spectra did not match any of the libraries.

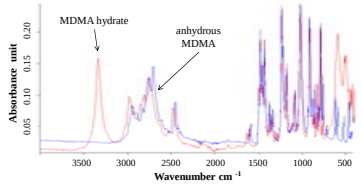

Figure 12. Overlaid spectra of fully hydrated and anhydrous MDMA standards

Amfetamine, and methamfetamine

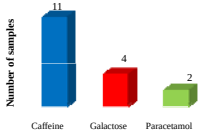

Figure 13. Other compounds detected in amfetamine samples by GC-MS

Four powder samples were found to contain methamfetamine by ATR-FTIR and the TICTAC Library. Amfetamine detection was unsuccessful by ATR-FTIR in all 12 samples. Figure 13 shows the other compounds detected in these samples by GC-MS. Six of these samples were identified as caffeine by IR and six of them gave no match to the libraries.

GBL and GHB

Seventy-two liquid samples were identified as gamma-butyrolactone (GBL) by ATR-FTIR.
Two liquid samples were found to be sodium gamma-hydroxybutyrate (GHB).
All samples were identified through the TICTAC library. No GC-MS method was available to conform these results.

Plaster-of-Paris

Eight tablets were identified as plaster-of-Paris (calcium sulphate hemihydrates) by ATR-FTIR. No drugs were detected by GC-MS. It is likely that these tablets were to be passed off as ecstasy.

Table 1. Summary of the results

Drug	Number of samples	Samples identified by ATR-FTIR
Mephedrone	161	99%
Ketamine	106	99%
Cocaine	46	17%- 43%
Piperazine derivatives (powders and capsules)	30	63%
Piperazine derivatives (tablets)	83	31%
MDMA powder and crystals	12	100%
MDMA tablets	6	50%
Methamfetamine	4	100%
Amfetamine	12	0
GBL	72	100%
GHB	2	100%
Plaster-of-Paris	8	100%
Butylone	3	100%
Methylone	3	100%
3-Fluoromethcathinone	1	100%
4-Methylethcathinone	1	100%
Methedrone	1	100%
MPPP	1	100%

Conclusion

Table 1 shows the result achieved during this study. Portable FTIR spectrometers with ATR accessories have the potential to be used for the identification of illicit drugs in the field. Although the initial cost of this instrument is high (about £20,000), there are no consumables and no routine service is required. Its biggest advantages are the lack of sample preparation, ease of use and that the results can be achieved in less than a minute. The use of spectral libraries allows a non-spectroscopist to perform identifications.
Limitation of this technique was noted when used for the identification of tablets, complex mixtures, and low purity drugs.
This study shows that ATR-FTIR can be used accurately and reliably for the identification of **essentially pure** samples and for the presumptive testing of the new synthetic powdered drugs available in high purity on the streets if the appropriate library is used.

References

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[2] www.brukeroptics.com/alpha.html, Accessed Aug 30, 2010
[3] D. Springer, F.T. Peters, G. Fritschi, H.H. Maurer, Studies on the metabolism and toxicological detection of new designer drug 4-methyl-a-pyrrolidinopropiophenone in urine using gas chromatography-mass spectrometry, *J Chromatogr*, 2002, **773**:25-33
[4] F.Staack, Piperazine designer drugs of abuse, *The Lancet*, 2007, **369**:1411-1413.
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