Electronic Supplementary Material (ESI) for ChemComm.

Surface-enhanced Raman spectroscopy of novel psychoactive substances using polymer-stabilized Ag nanoparticle aggregates

W. W. Y. Lee,[a] V. A. D. Silverson,[a] L. E. Jones,[a] Y. C. Ho,[b] N. C. Fletcher,[c] M. McNaul,[d] K. L. Peters,[d] S. J. Speers [e] and S. E. J. Bell[a]*

Experimental

Reagents and materials

Silver nitrate (99.9999 %) trisodium citrate, hydroxylamine hydrochloride, sodium hydroxide and magnesium sulphate were purchased from Sigma Aldrich. Natrosol ® hydroxyethylcellulose (HEC) 250 pharm HX was purchased from Ashland Inc. All drug samples were supplied by Forensic Science Northern Ireland (FSNI). Methiopropamine samples were seized bulk materials. Other cathinones were commercial analytical standards.

Raman analysis of methiopropamine

Methiopropamine powder samples were homogenised before a Raman spectrum was recorded using a PerkinElmer RamanMicro 200 Raman microscope, 20 × objective lens, 30 % laser power and accumulation times of 300 s.

Poly-SERS films

Citrate reduced silver colloid (CRSC) was prepared using the Lee and Meisel method, [1] and hydroxylamine reduced silver colloid (HRSC) using the Leopold method [2]. Ag (CRSC) [3] and Ag (HRSC) Poly-SERS films were prepared by isolating pre-aggregated aqueous colloid into HEC polymer before drying down in a mould to form a 100 × 100 mm thin film which was then cut with scissors into individual sections for individual use. Characterisation of Ag films and studies into their reproducibility and lifetime has been carried out in previous work. [4] The SERS background for the Poly-SERS films are shown in the Supplementary Data, Fig S1. Both CRSC and HRSC Poly-SERS films gave identical backgrounds (due to Ag-Cl covered surfaces) and SERS spectra so were used interchangeably.

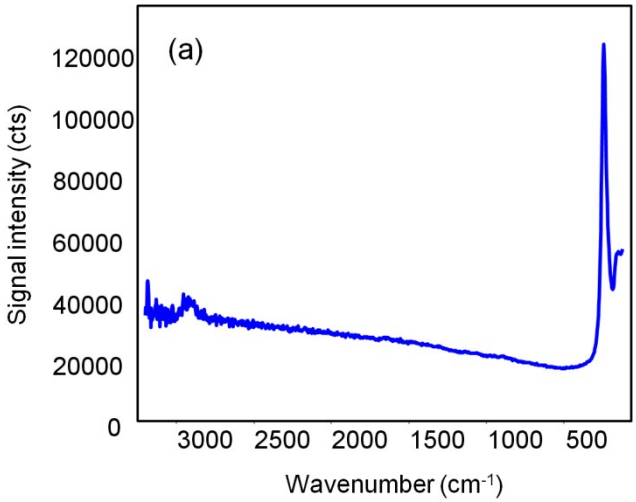


Figure S1: Background SERS spectrum of Poly-SERS films

SERS analysis of methiopropamine

Pure methiopropamine was characterised using ^{1}H on a 400 MHz instrument and ^{13}C NMR on a 100 MHz instrument. In both cases $CDCl_3$ was the solvent. Their spectra are shown in Figure S1 and S2, along with their peak positions in Table S1.

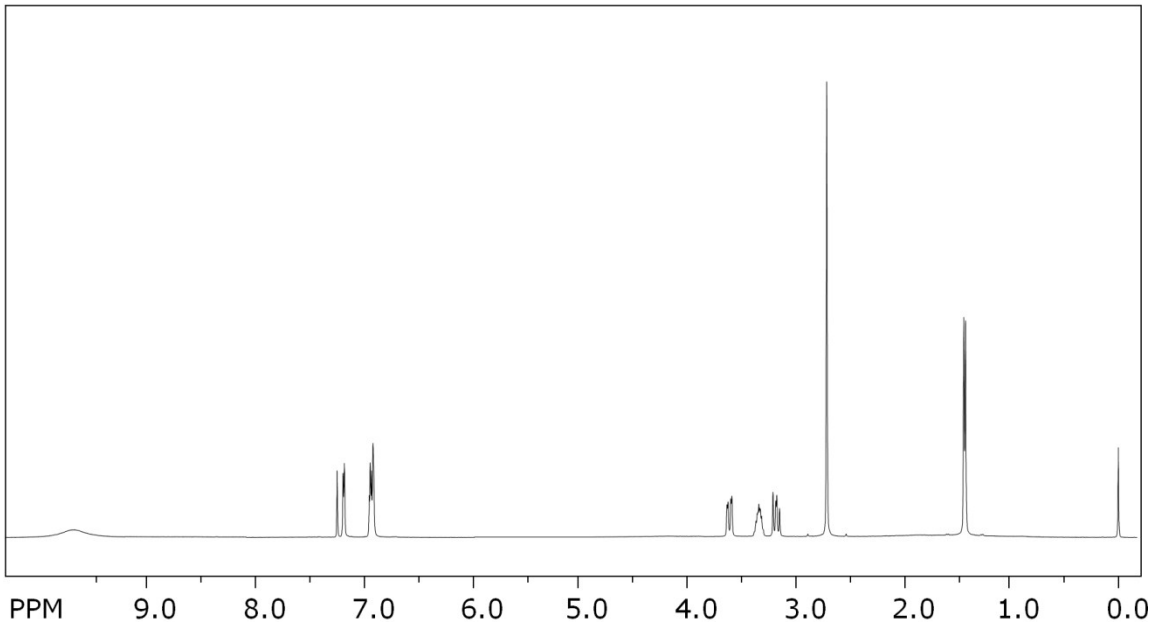


Figure S2a: ^{1}H NMR spectrum of pure methiopropamine.

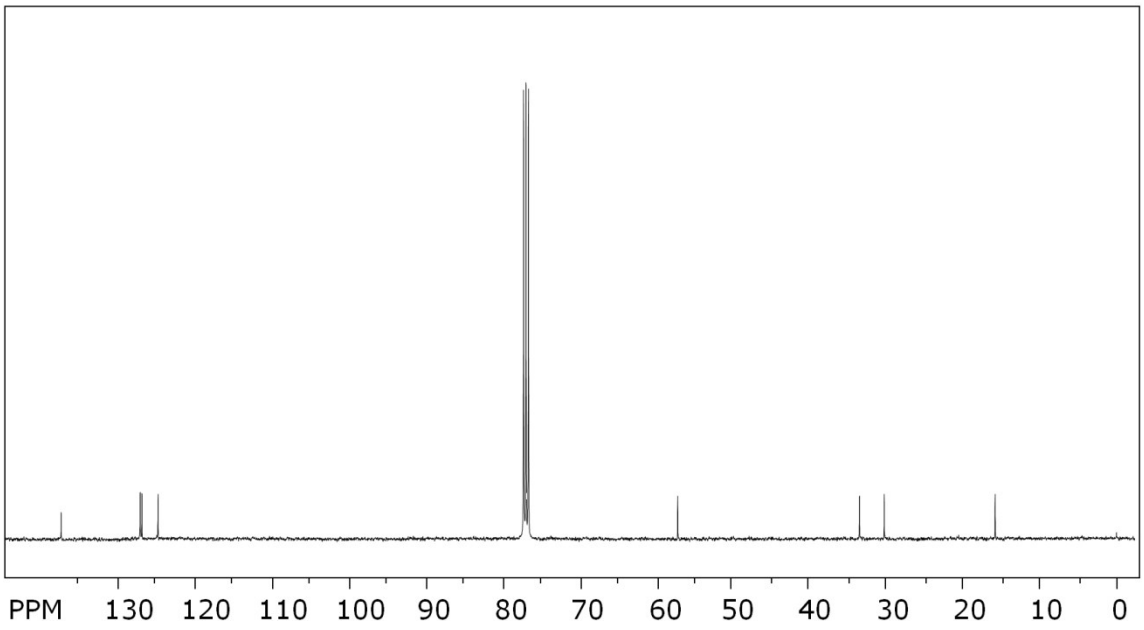
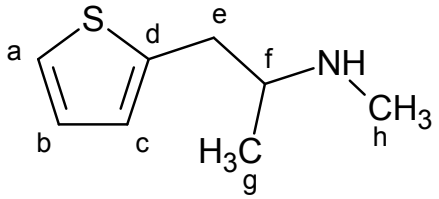


Figure S2b: ^{13}C NMR spectrum of pure methiopropamine.



Position	Carbon (ppm)	Proton (ppm, J)
d	137.6	-
b	127.3	6.95 (1H, dd)
c	127.1	6.92 (1H, d)
a	124.9	7.20 (1H, d)
f	57.2	3.34 (1H, m)
e	33.5	3.61 (1H, dd), 3.17 (1H, dd)
h	30.3	2.70 (3H, s)
g	15.8	1.42 (3H, d)

Table S1: ^{1}H and ^{13}C NMR data.

For SERS analysis, all methiopropamine samples (7.8 mg) were dissolved in 5 mL water containing 25 % ethanol and were tested with Ag (CRSC) Poly-SERS films. A droplet of aqueous analyte was placed onto a section of the Poly-SERS film which was sitting on an aluminium foil backing substrate. The droplet was then allowed to dry at room temperature. The probe laser from a PerkinElmer RamanMicro 200 Raman microscope was directed onto the film surface and a 30 s SERS spectrum was collected. The microscope uses a 785 nm cavity diode laser (80 mW) with a Czerny-Turner spectrometer with a spectral range of 95-3200 cm^{-1}. It is composed of an

Olympus microscope (BX51 reflected illumination frame) which is connected to a spectrometer through fibre optic cables. The spot diameter is 230 µm.

Figure S3a, Mass spectrum of sample A:

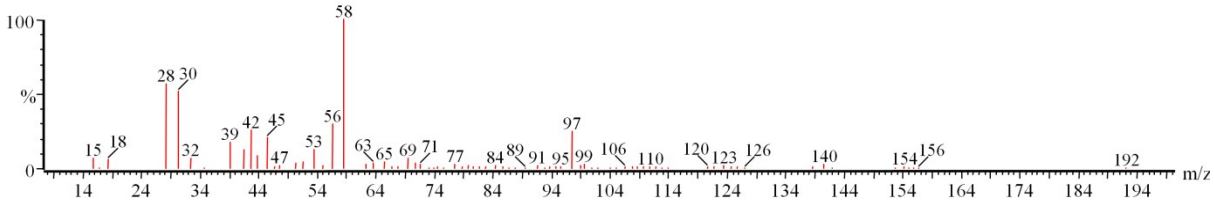
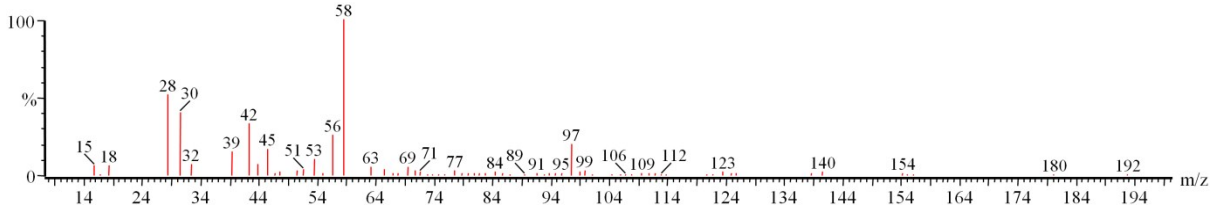


Figure S3b, Mass spectrum of sample B:



Both samples had major peaks with retention times of approximately 7.9 min and virtually identical mass spectra. Both samples had a prominent mass fragment at m/z 58 (base peak). A smaller fragment at m/z 97 was also seen with both samples and was thought to be from the thiopyrillium ion, $C_5H_5S^+$. Another small fragment seen in both samples at m/z 154 was from the molecular ion analogous to the M-1 ion for methamphetamine. [4] The molecular structures of the mass fragments are shown in Table S1a.

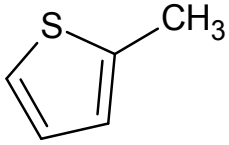
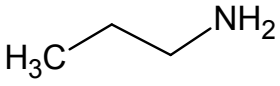
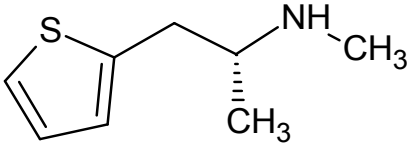
m/z	Ion fragments
97	
58	
154	

Table S2: Molecular structures of methiopropamine GC-MS mass fragments.

Figure S4a, IR spectrum of methiopropamine sample A:

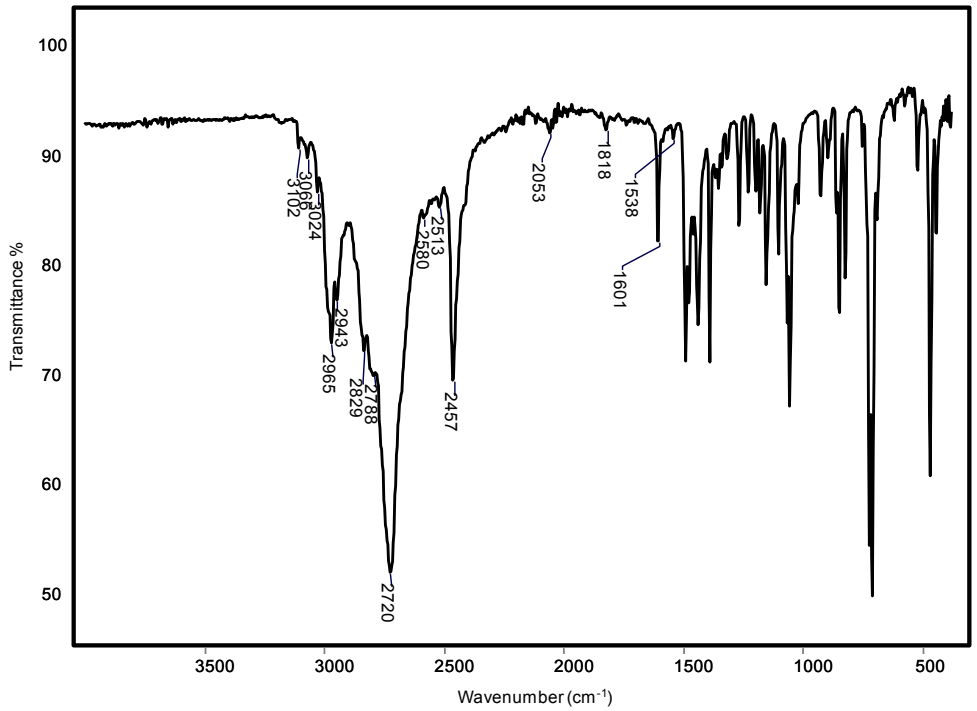
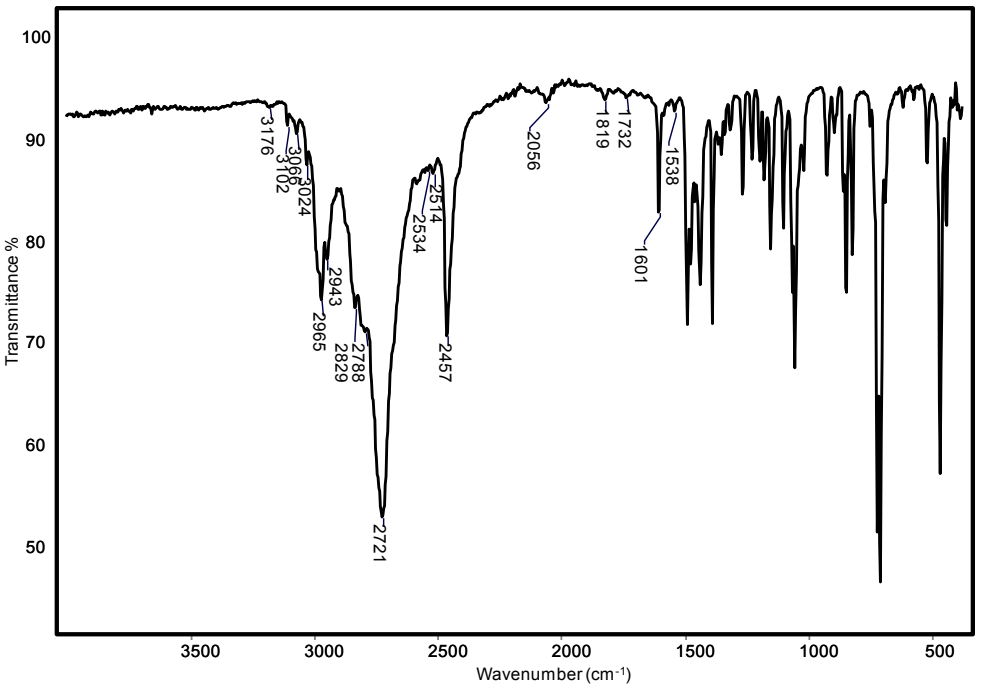


Figure S4b, IR spectrum of methiopropamine sample B:



SERS analysis of cathinones

Pure samples of cathinones were dissolved in methanol and were analysed with Ag (CRSC) or Ag (HRSC) Poly-SERS films using pre-swelled films or by using swab transfer. Using pre-swelled films allowed analytes in pure methanol solvent to be analysed. [3] In use, Poly-SERS films were first swelled by depositing 10 µL of DDI water onto its

surface before allowing it to sit for approximately 5 minutes. This was followed by a droplet of analyte dissolved in methanol which was then allowed to sit in air at RT until dry. The SERS spectrum was then collected using a hand-held DeltaNu ReporterR Raman spectrometer (785 nm excitation, spectral range 300-2000 cm^{-1} and excitation spot diameter is 50 µm). In all cases the accumulation time was 30 s.

Water soaked cotton swabs (containing approximately 50 µL) DDI water were also used to swipe over glass slides carrying trace cathinones and then swiped over a pre-swollen Ag (HRSC) Poly-SERS film which were then allowed to dry. Cathinones tested with the swabbing method were analysed with the PerkinElmer RamanMicro 200 Raman microscope using 30 s accumulation times.

References

1 P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391–3395.

2 N. Leopold, M. Haberkorn, T. Laurell, J. Nilsson, J. R. Baena, J. Frank and B. Lendl, *Anal. Chem.,* 2003, **75**, 2166–2171.

3 W. W. Y. Lee., V. A. D. Silverson, C. P. McCoy, R. F. Donnelly and S. E. J. Bell, *Anal. Chem*., 2014, **86**, 8106−8113.

4 J. F. Casale, and P. A. Hays, *Microgram Journal,* 2012, 2*,* 53–57.