Electronic Supplementary Material

Direct detection of illicit drugs from biological fluids by desorption/ionization mass spectrometry with nanoporous silicon microparticles

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Material and methods

Determination of Plasma Oxycodone and Metabolite Concentration via SPE-LC-MS-MS:

Plasma oxycodone and metabolite concentrations were analyzed from liquid chromatography mass spectrometry (LC-MS) using a a Shimadzu Nexera LC-30AD UHPLC system and an AB Sciex 5600 TripleTOF™ mass spectrometer. Chromatographic separation was performed using a Phenomenex Gemini pentafluorophenyl C18 column (5 um, 100 A, 250 x 4.6 mm). AFCV-32AH switching valve (Shimadzu Corp., Japan) was employed to divert only the LC eluent between 5 and 9 min to mass spectrometer to protect it from potential contamination. The mass spectrometer was operated in positive ion mode. The m/z 316/298 ion was monitored for oxycodone, the m/z 302/284 for oxymorphone and noroxycodone and the m/z 305/287 for noroxycodone-d3, respectively.

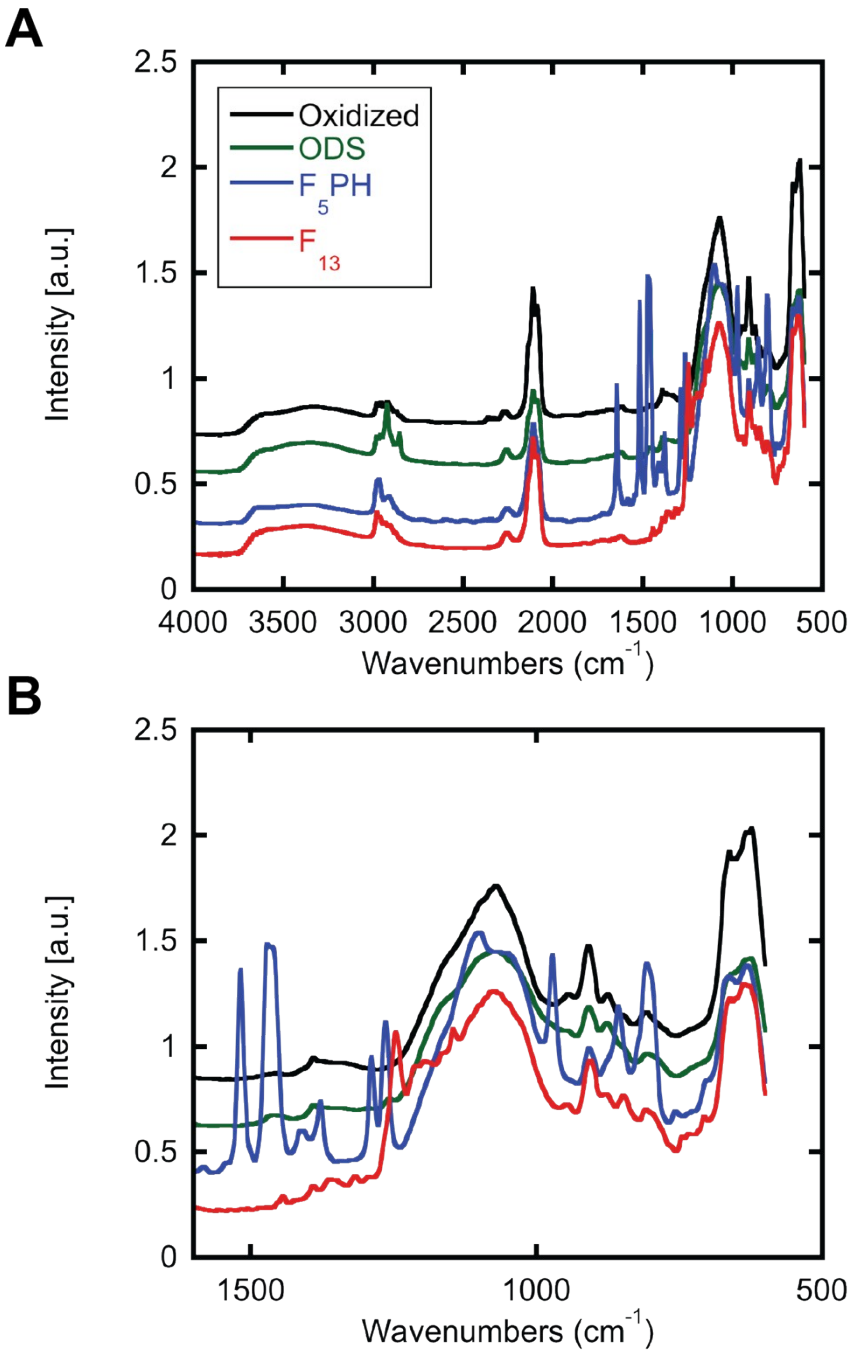

Fig. S1. A) DRIFT-IR spectra of oxidized, F_5Ph, F_{13} and ODS functionalized pSi-MPs. B) Inset of (A) showing the fingerprint region between 1700 and 500 cm^{-1}.

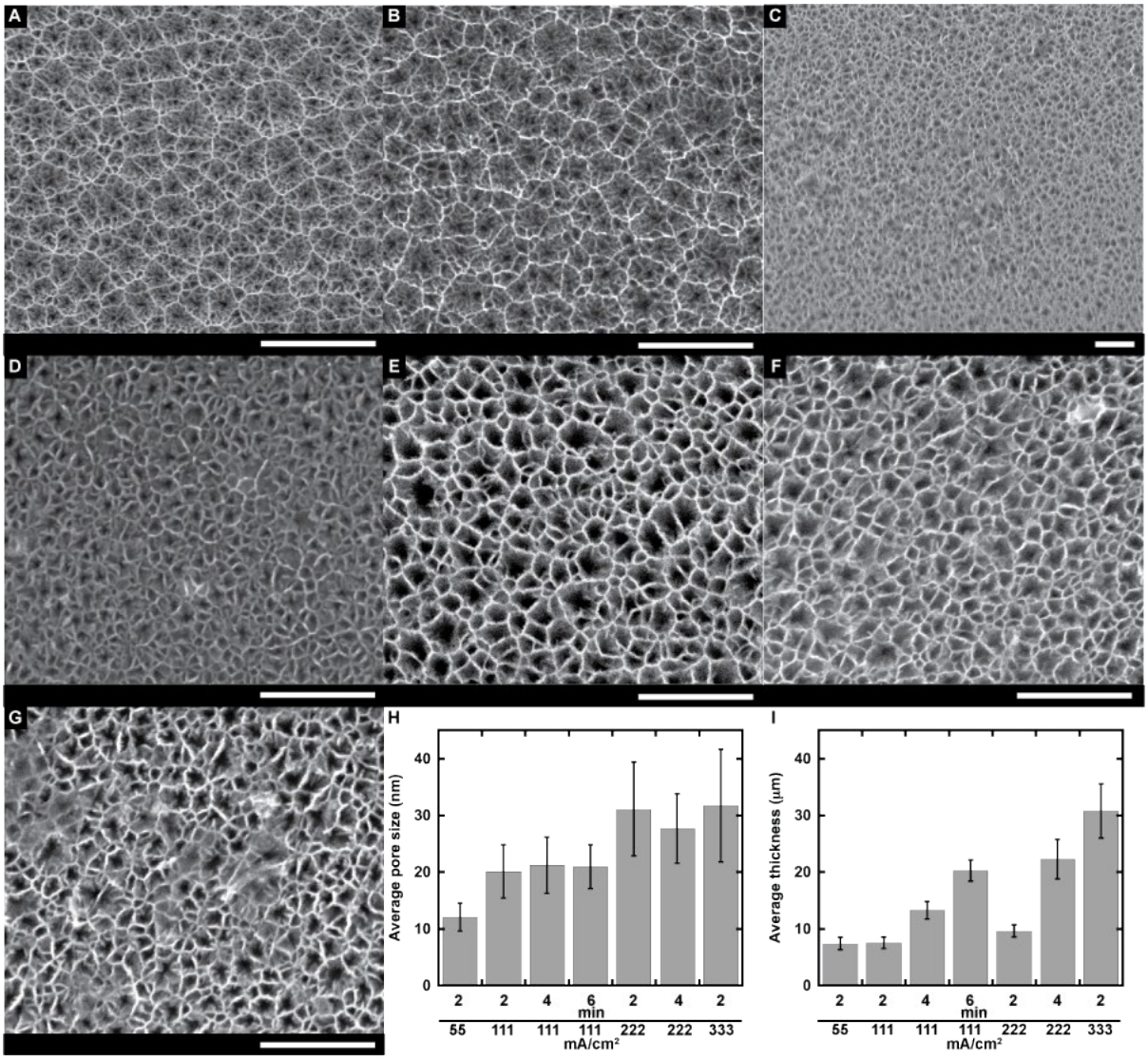

Fig. S2. SEM micrographs of pSi-MPs etched at A) 55 mA/cm^2, 4 min, B) 111 mA/cm^2, 2 min, C) 111 mA/cm^2, 4 min, D) 111 mA/cm^2, 6 min, E) 222 mA/cm^2, 2 min, F) 222 mA/cm^2, 4 min and G) 333 mA/cm^2, 4 min. Scale bar is 300 nm. Graphs representing average pore size (H) and thickness (I) for n=20 replicates.

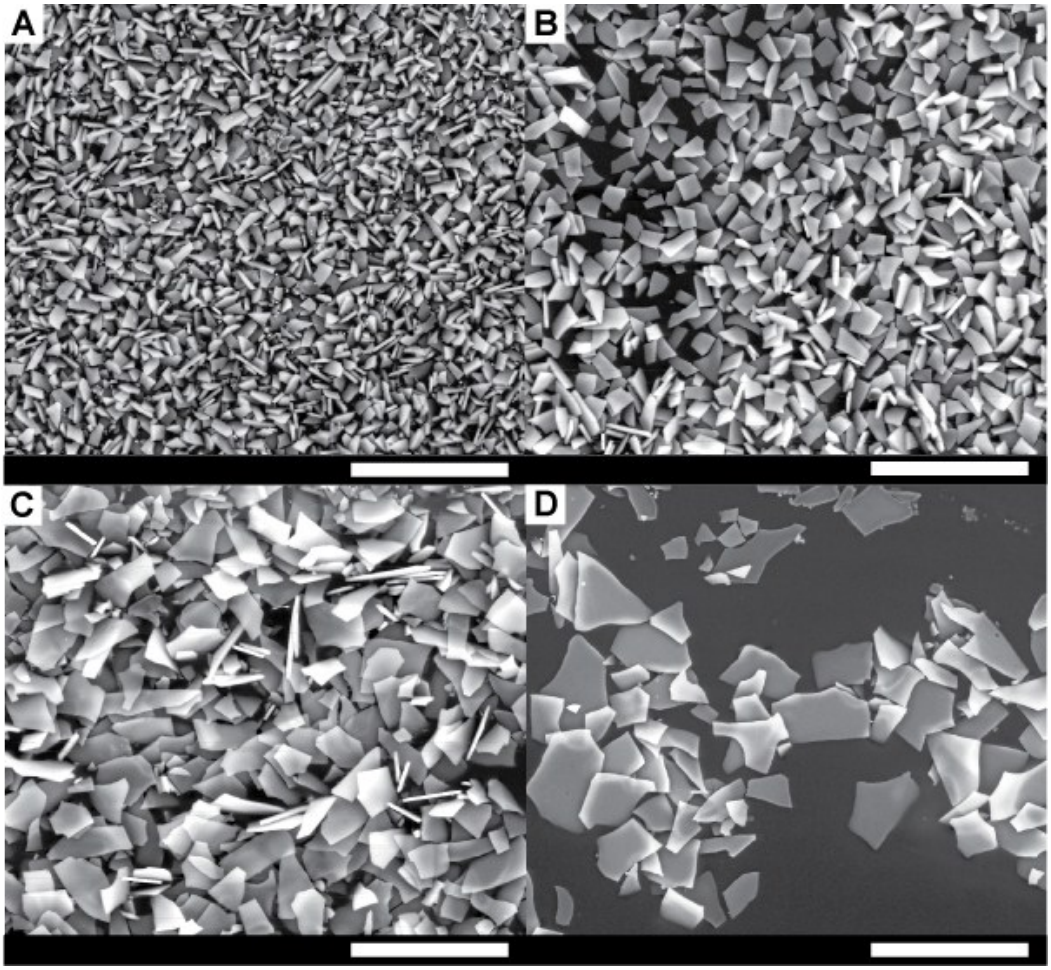

Fig. S3. SEM micrographs of sieved pSi-MPs using 25, 53 and 75 µm sieves, respectively. Sieving produced pSi-MPs with particle sizes of A) 19.2 ± 2.4 µm, B) 35.2 ± 7.2 µm, C) 56.1 ± 8.3 µm and D) 85.0 ± 17.2 µm.

Table S1. Turkey HSD Test for post ANOVA pair-wise comparisons in a one way ANOVA.

Cocaine (1000 ng/mL)	***85.0 ± 17.2 µm***	***35.2 ± 7.2 µm***	***19.2 ± 2.4 µm***
85.0 ± 17.2 µm	P<.01	P<.05	P<.01
56.1 µm± 8.3 µm		P<.01	P<.01
35.2 ± 7.2 µm			P<.01
MDMA (1000 ng/mL)	***85.0 ± 17.2 µm***	***35.2 ± 7.2 µm***	***19.2 ± 2.4 µm***
85.0 ± 17.2 µm	n/s	P<.05	P<.01
56.1 µm± 8.3 µm		P<.01	P<.01
35.2 ± 7.2 µm			P<.01
Methadone (1000 ng/mL)	***85.0 ± 17.2 µm***	***35.2 ± 7.2 µm***	***19.2 ± 2.4 µm***
85.0 ± 17.2 µm	n/s	n/s	P<.01
56.1 µm± 8.3 µm		n/s	P<.01
35.2 ± 7.2 µm			P<.01

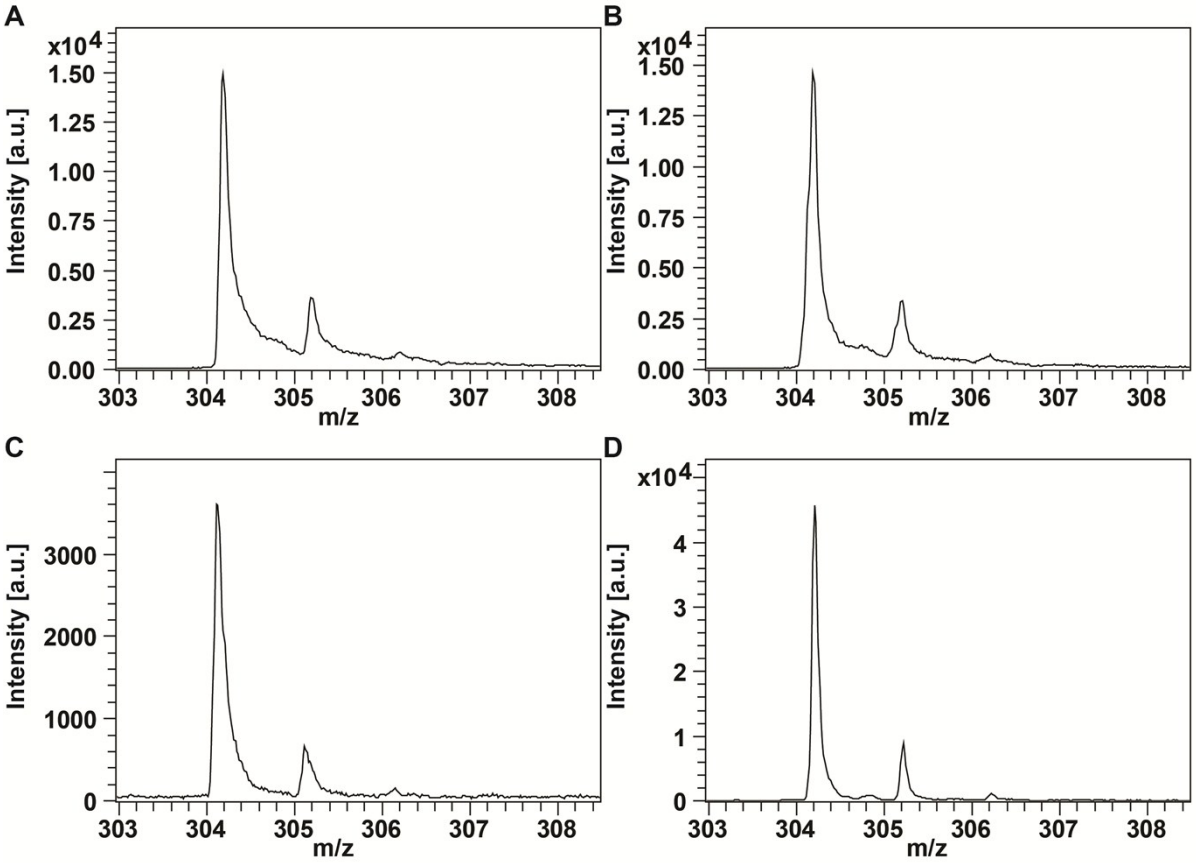

Fig. S4. SALDI mass spectra for cocaine on A) 85.0 ± 17.2 µm, B) 56.1 ± 8.3 µm, C) 35.2 ± 7.2 µm and D) 19.2 ± 2.4 µm pSi-MPs functionalized with F_{13}.

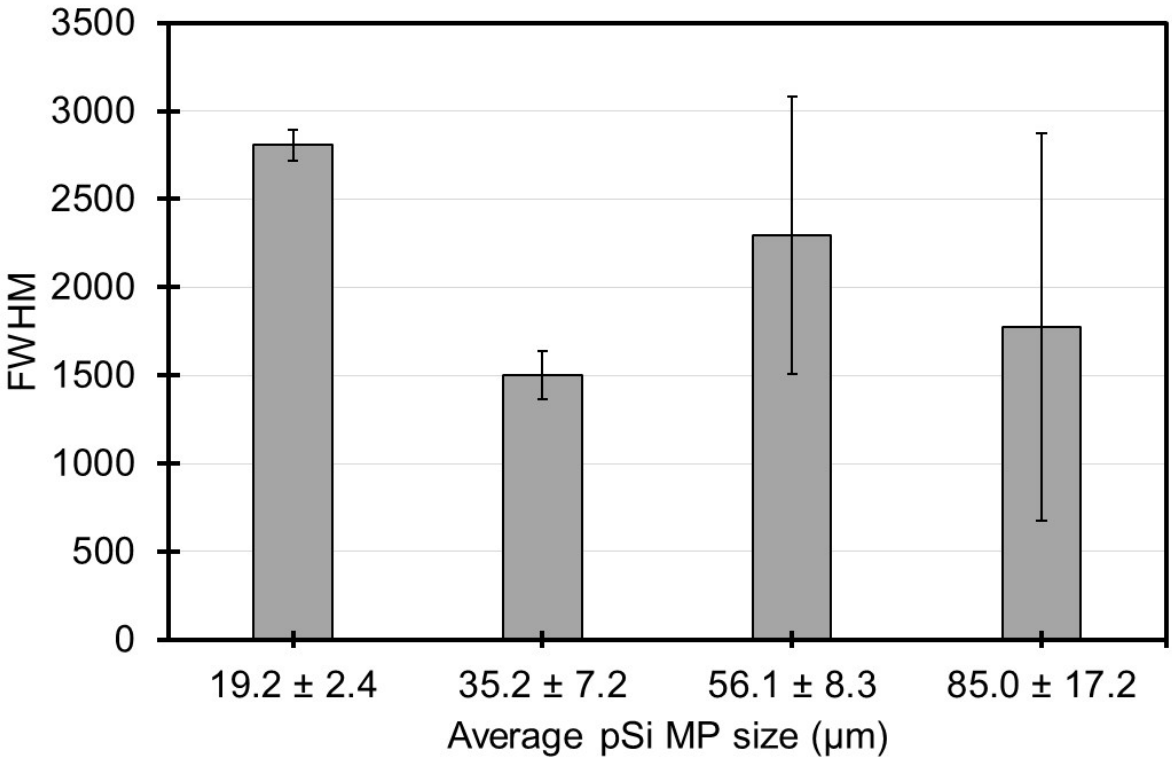

Fig. S5. Full width half maximum (FWHM) values for sieved pSi-MPs corresponding to average S/N observed for the detection of cocaine on 19.2 ± 2.4 µm, 35.2 ± 7.2 µm, 56.1 ± 8.3 µm and 85.0 ± 17.2 µm. FWHM was calculated using flexAnalysis software. Error bars correspond to standard deviation (n=3).

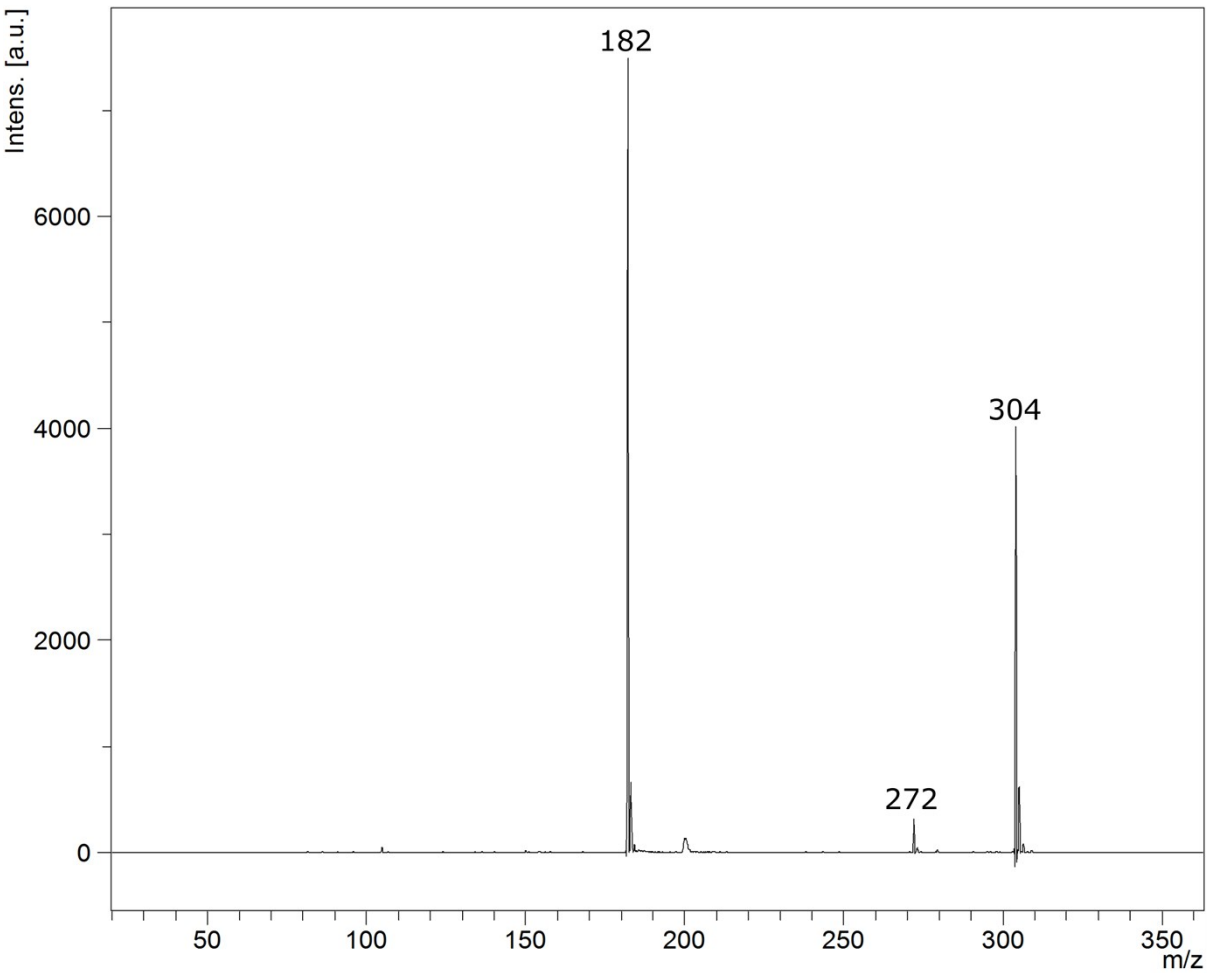

Fig. S6. Representative SALDI-MS/MS spectrum observed for cocaine in water. Characteristic fragment peaks were observed at m/z 272 and 182.

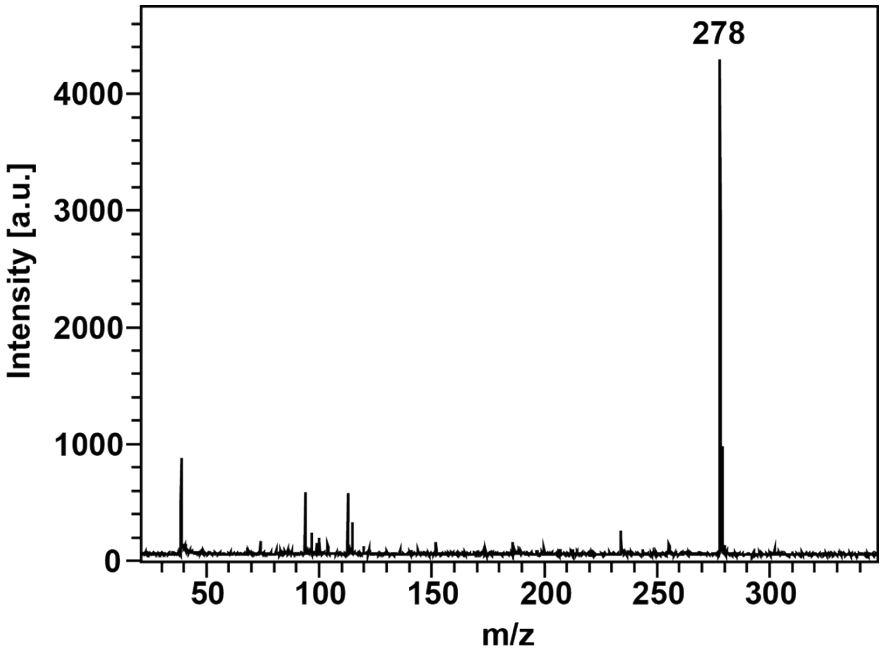

Fig. S7. Representative SALDI mass spectrum observed for a urine sample analyzed on F_{13} functionalized pSi-MP showing the presence of EDDP (MH^+ 278).

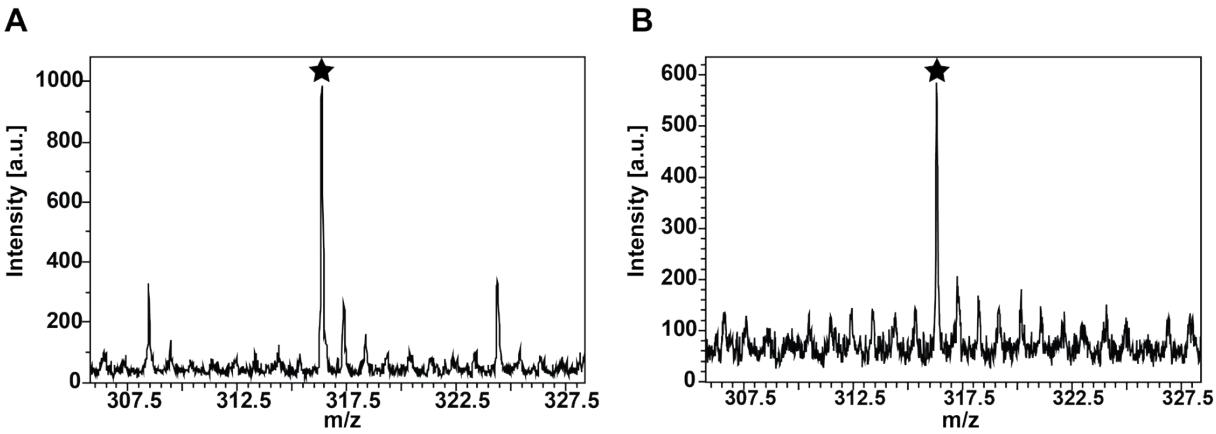

Fig. S8. SALDI mass spectra on F_{13} functionalized pSi-MP for oxycodone in A) plasma (20.4 ng/mL) and B) saliva 2 h post dose. Star represents the detection of oxycodone (MH^+ 316).