Supplementary Information

Fluorocarbon Plasma Gas Passivation Enhances Performance of Porous Silicon for Desorption/Ionisation Mass Spectrometry

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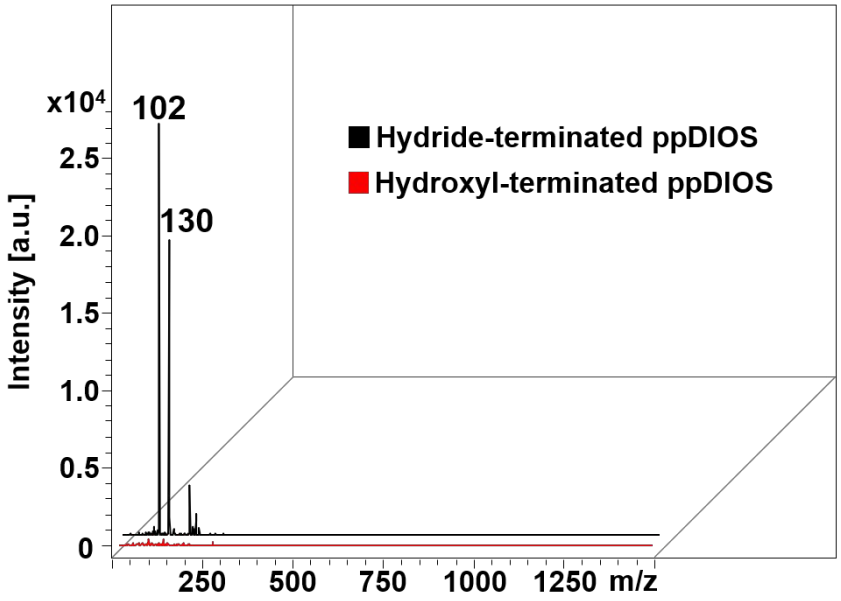

Figure S1: Background mass spectra for freshly etched (hydride-terminated) and ozone-oxidised (hydroxyl-terminated) ppDIOS surfaces. Background peaks are observed at *m/z* 102, 130, 198 and 212.

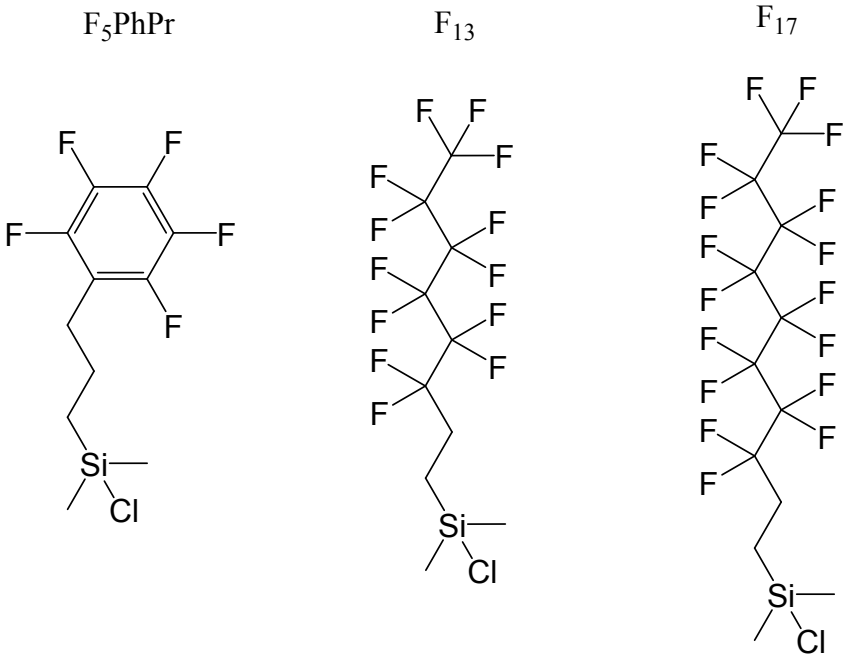

Figure S2. Chemical structures of F_5PhPr, F_{13} and F_{17}, common silanes used to functionalise DIOS surfaces.

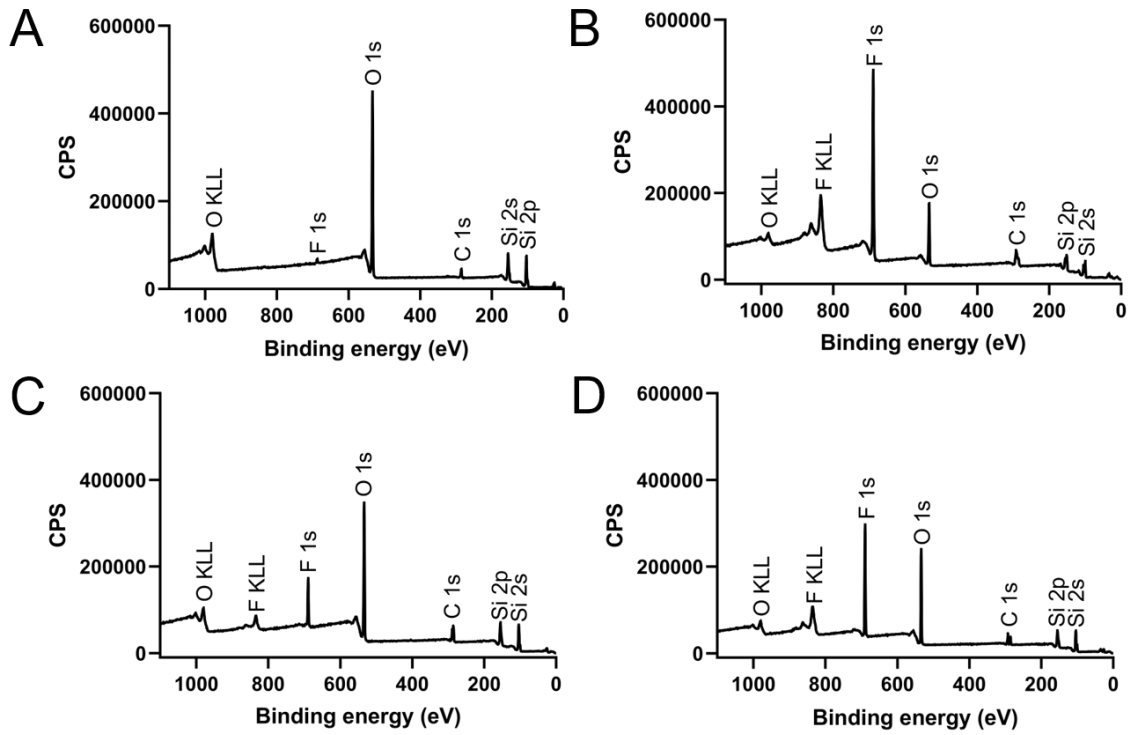

Figure S3: X-ray photoelectron spectroscopy (XPS) survey spectra for DIOS surfaces functionalised via A) ozone-oxidation, B) plasma polymerisation, C) F_5PhPr-silanisation and D) F_{13}-silanisation.

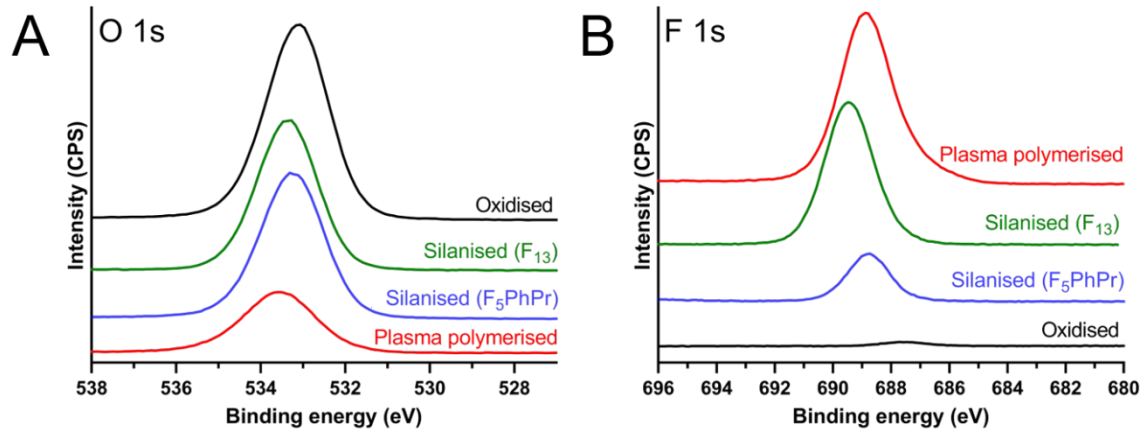

Figure S4: XPS analysis for functionalised DIOS surfaces showing A) high-resolution O 1s spectra and B) high-resolution F 1s spectra.

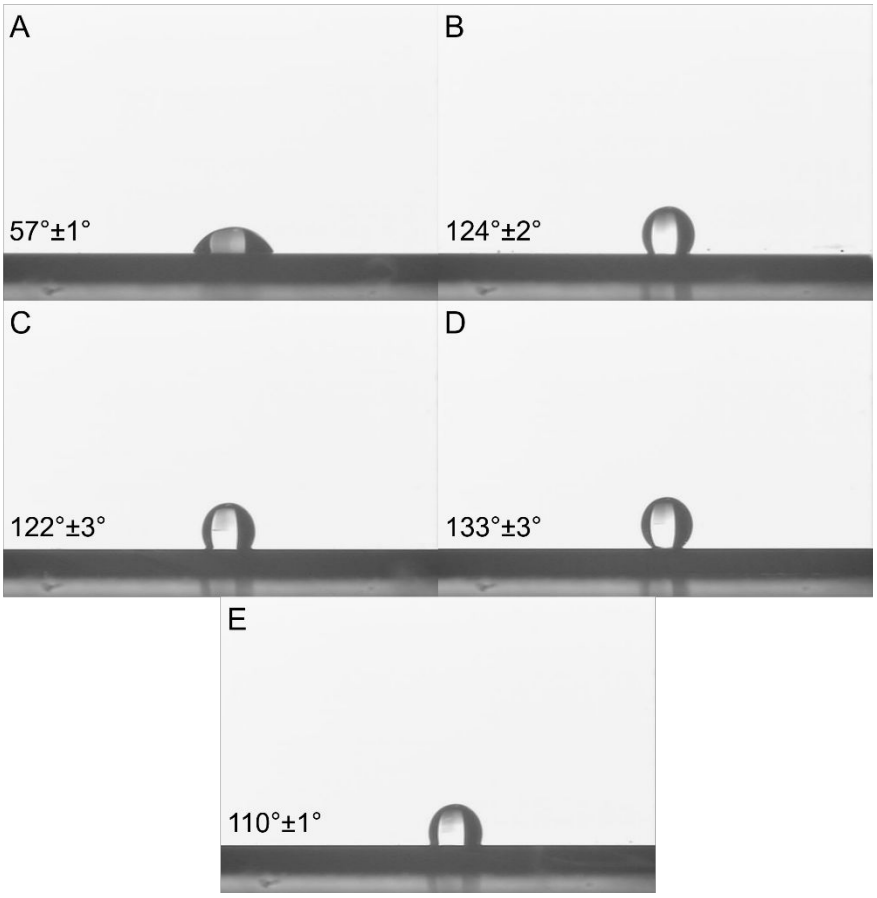

Figure S5: Water contact angle (WCA) measurements for DIOS substrates following A) ozone-oxidation, B) plasma polymerisation, C) F_5PhPr-silane functionalisation, D) F_{13}-silane functionalisation, and E) F_{17}-silane functionalisation. WCA was determined using 1 µL of water on a contact angle goniometer.

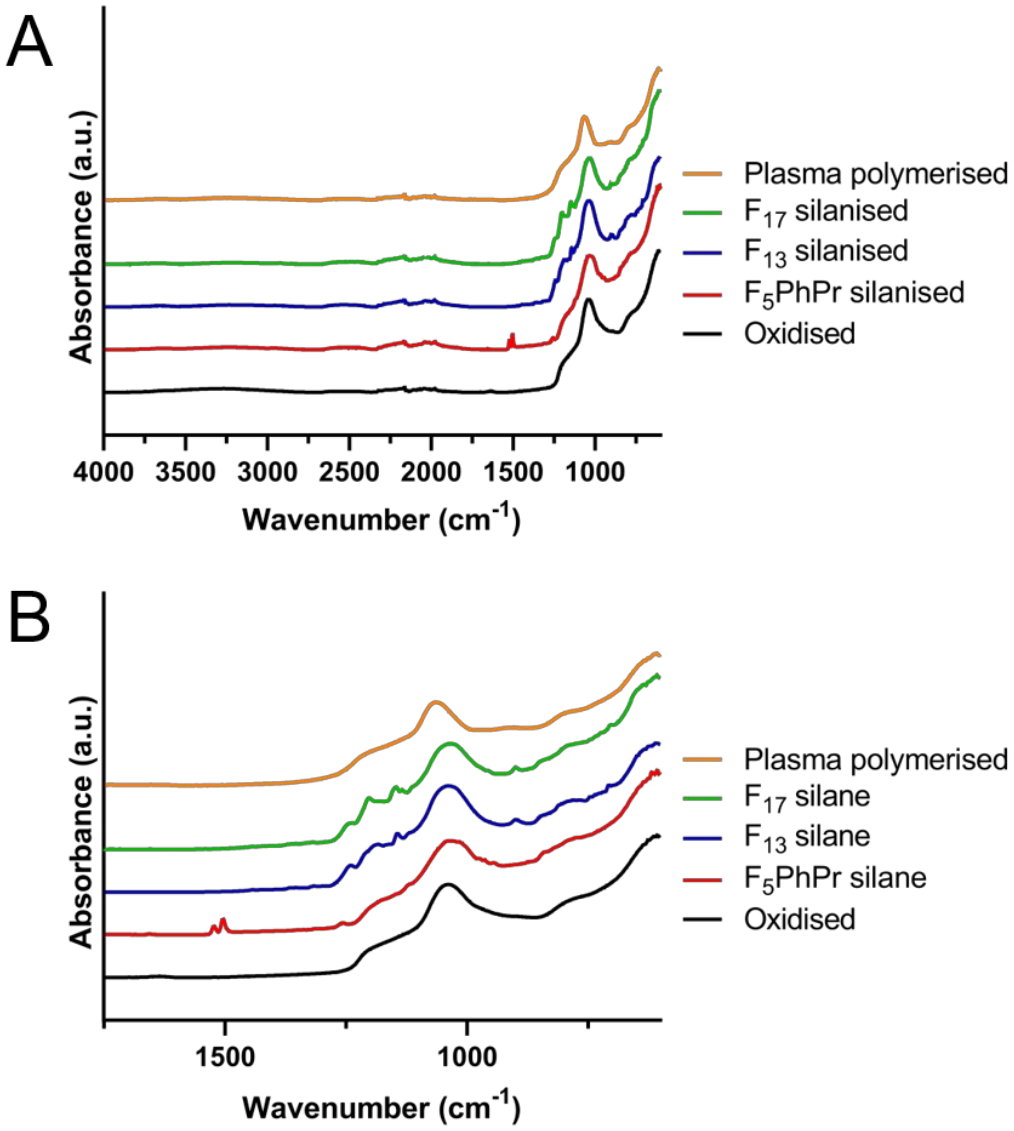

Figure S6. IR spectra overlays of oxidised, plasma polymerised and silanised DIOS surfaces between A) 4000-600 cm^{-1} and B) 1750-600 cm^{-1}.

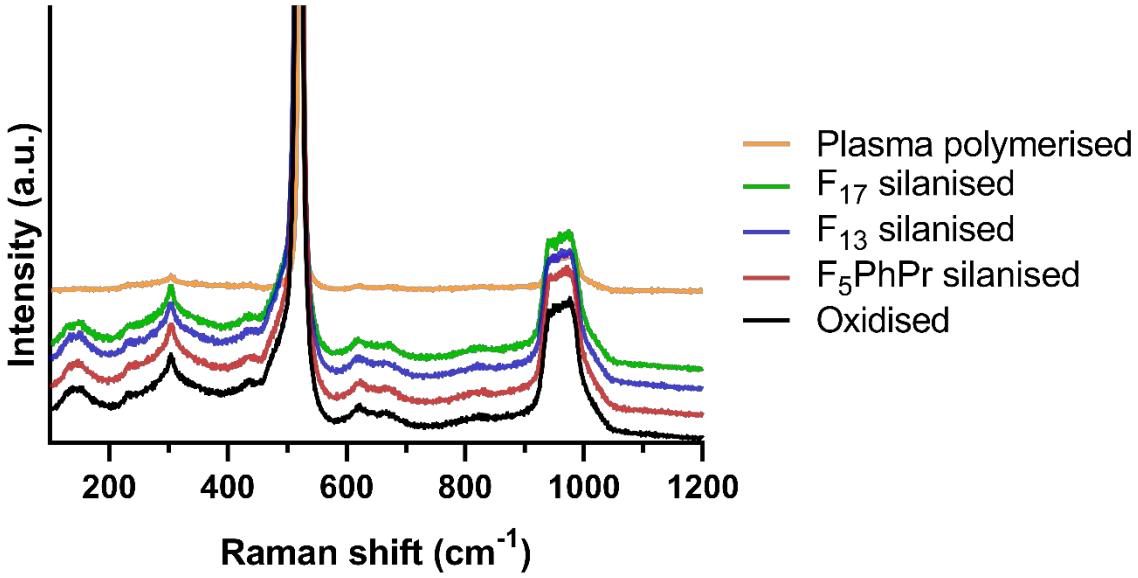

Figure S7. Raman spectra overlays of oxidised, plasma polymerised and silanised DIOS surfaces.

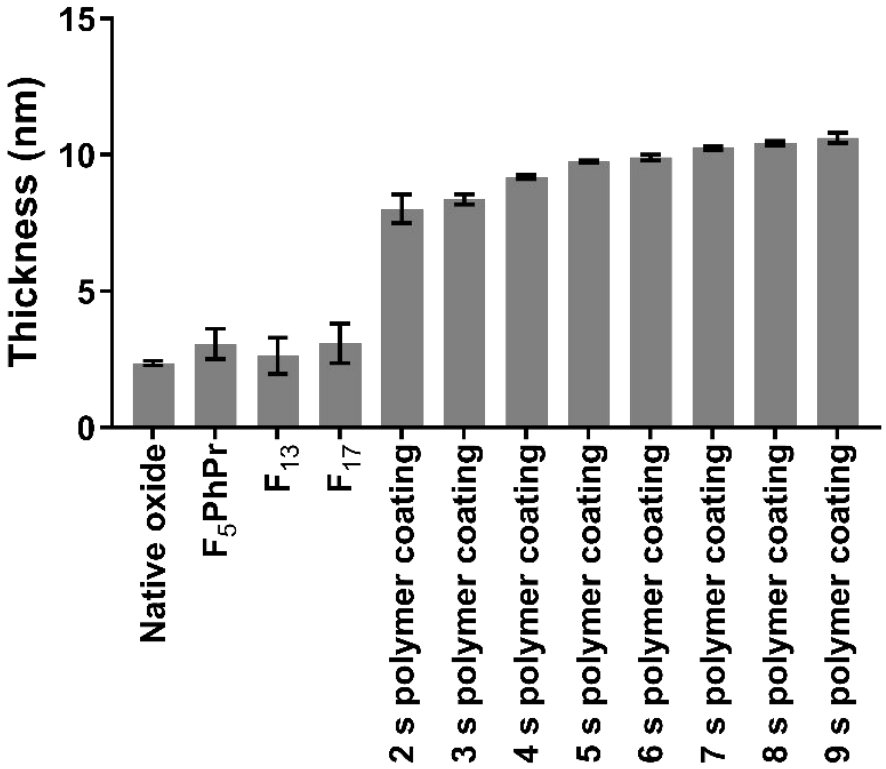

Figure S8: Average thickness of ppDIOS substrates following fluorocarbon gas passivation at various lengths of time. The native oxide layer present on the Si substrate, F_5PhPr, F_{13} and F_{17}-silanes, have been included for comparison. Error bars correspond to the standard deviation (n=3).

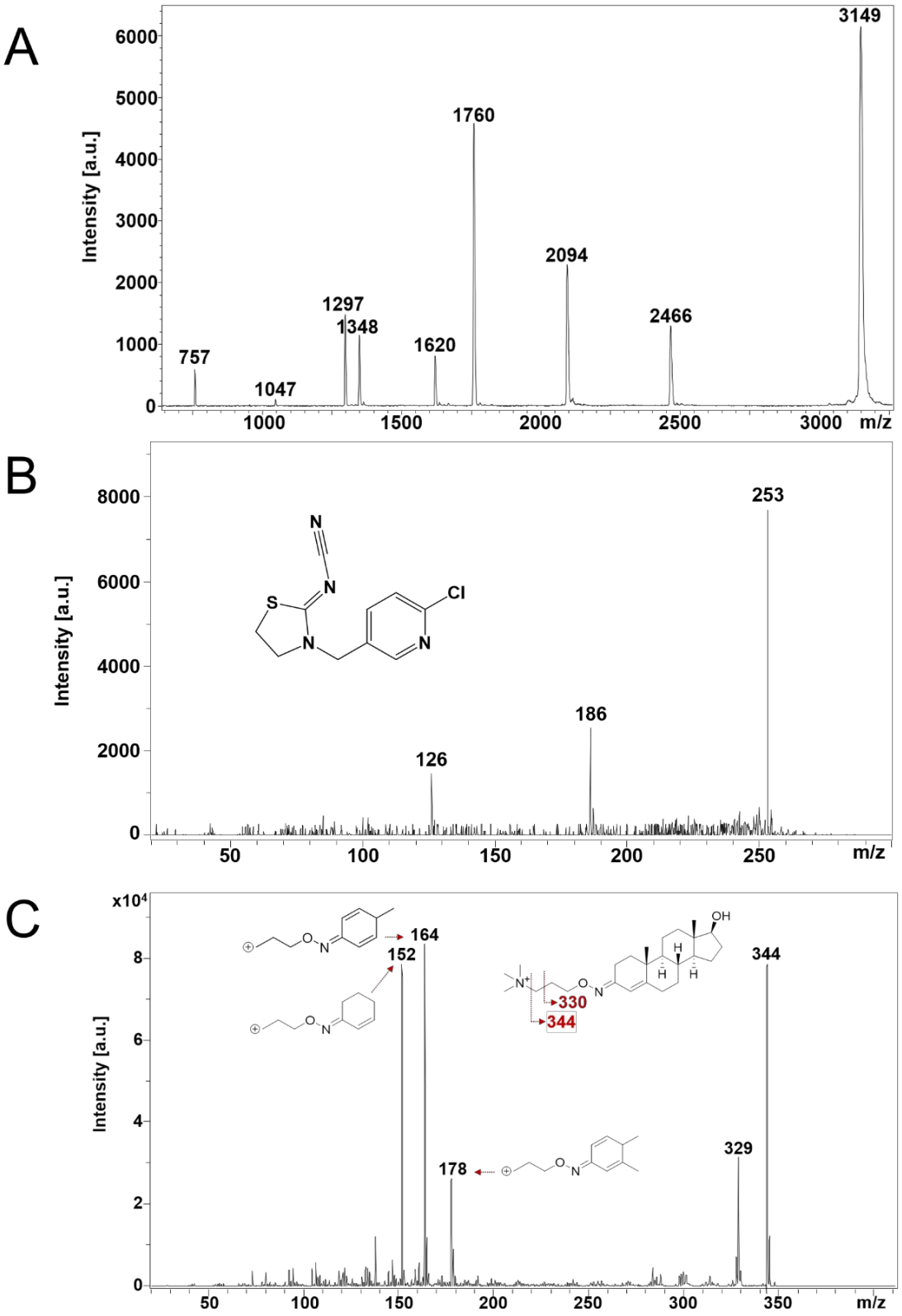

Figure S9. Mass spectra obtained using an F_{13}-silanised surface for A) a standard peptide mixture containing nine different peptides ranging from *m/z* 757 to *m/z* 3147; B) thiacloprid (*m/z* 253), at a concentration of 1 µg/mL, extracted directly from Surine; and C) quaternary aminooxy (QAO) derivatised testosterone, at a concentration of 100 ng/mL, extracted directly from Surine.

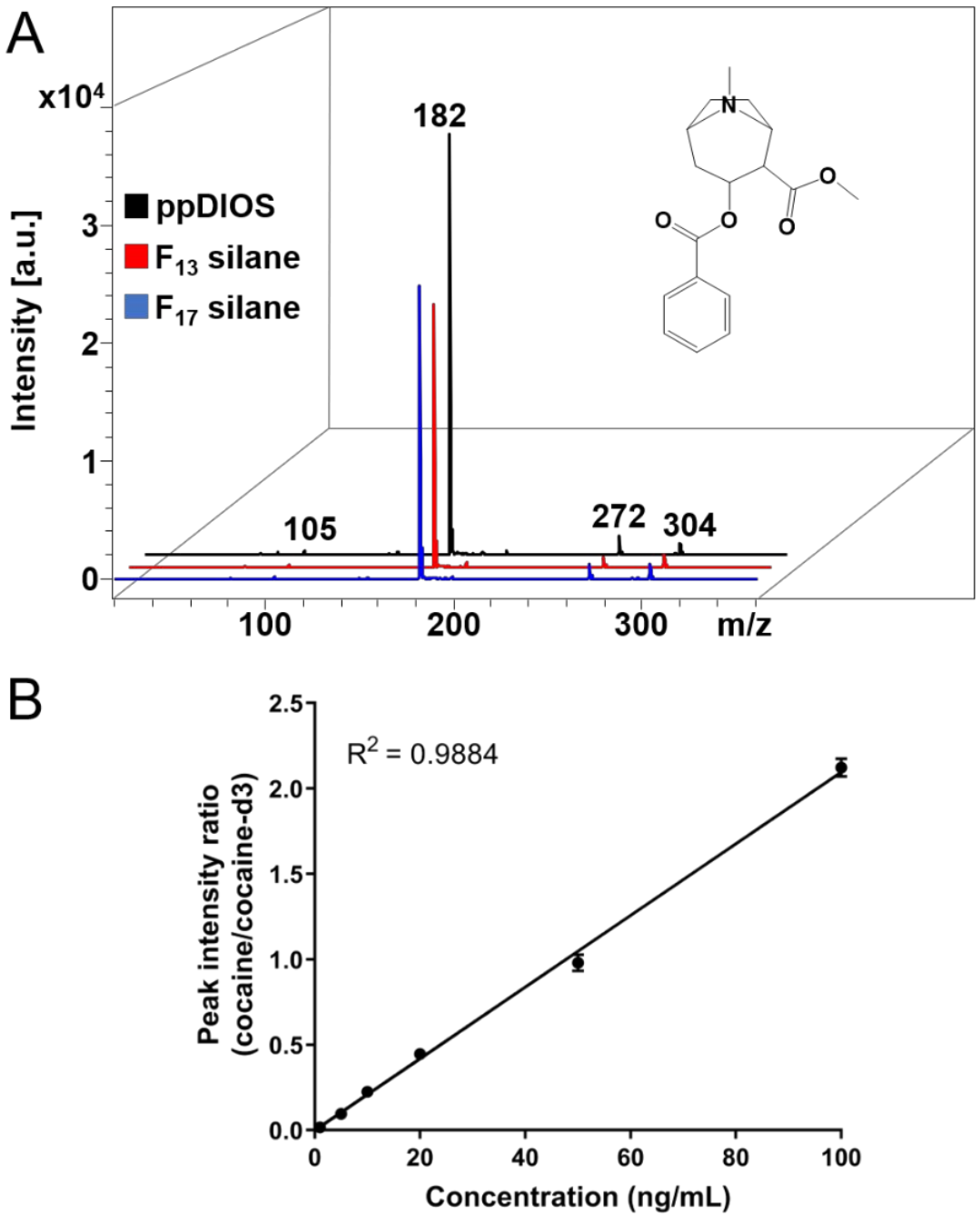

Figure S10. (A) Representative mass spectrum for cocaine (100 ng/mL, in water) at an ion of *m/z* 304, analysed using DIOS-MS on a ppDIOS surface. Fragment peaks are observed at *m/z* 105, *m/z* 182 and *m/z* 272. (B) Linear regression curve for cocaine in water for concentrations ranging from 1 to 100 ng/mL. Error bars correspond to the standard deviation (n=3).

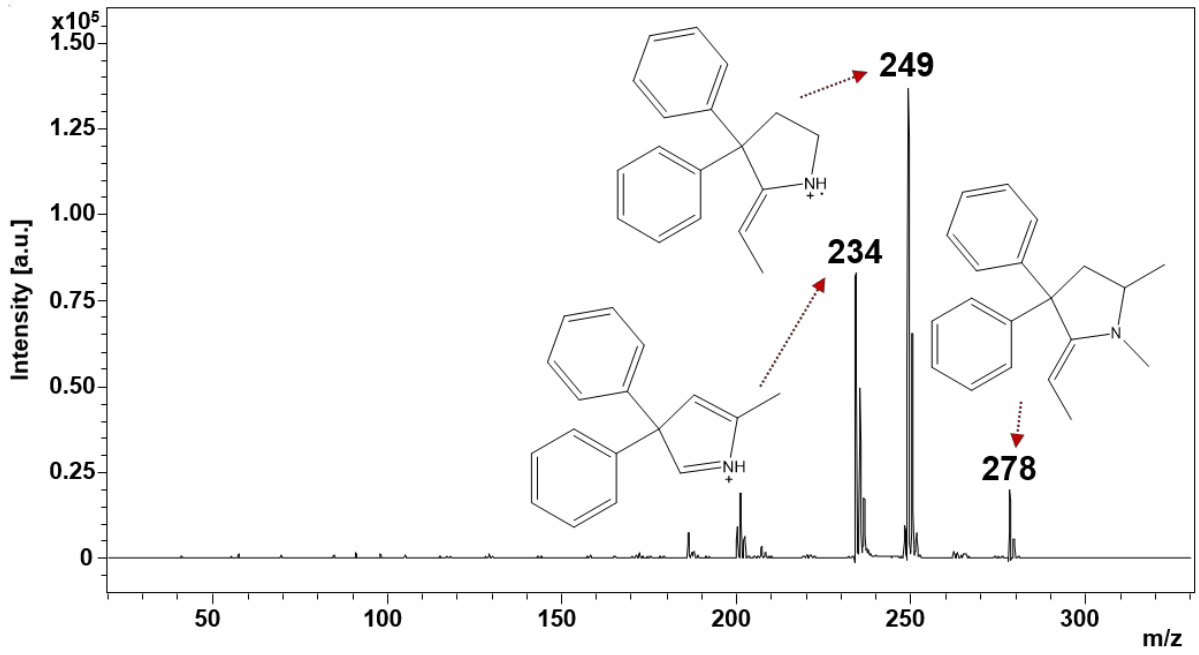

Figure S11. MS/MS mass spectrum for EDDP, a major urinary metabolite of methadone, at an ion of *m/z* 278, analysed using an F_{13}-silanised DIOS surface. Fragment peaks are observed at *m/z* 234 and *m/z* 249.

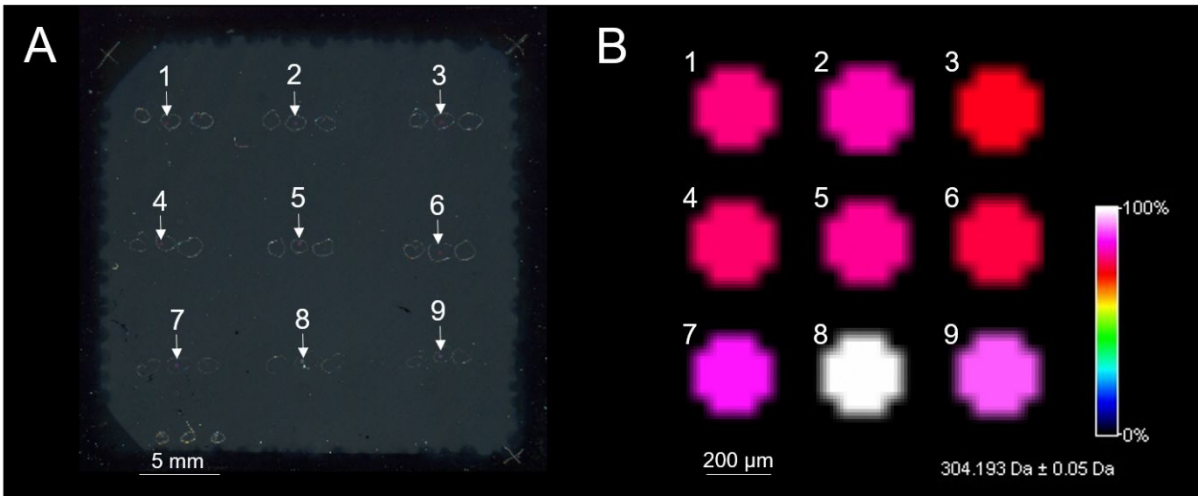

Figure S12: ppDIOS imaging of cocaine (100 ng/mL in chloroform) showing: A) a spot array where analysis was performed from nine different locations throughout the ppDIOS surface, and B) zoomed-in view of each of the imaged spots. The parent peak of cocaine was detected at *m/z* 304. An arbitrary colour scale detailing the relative intensity of each peak is displayed to the right.

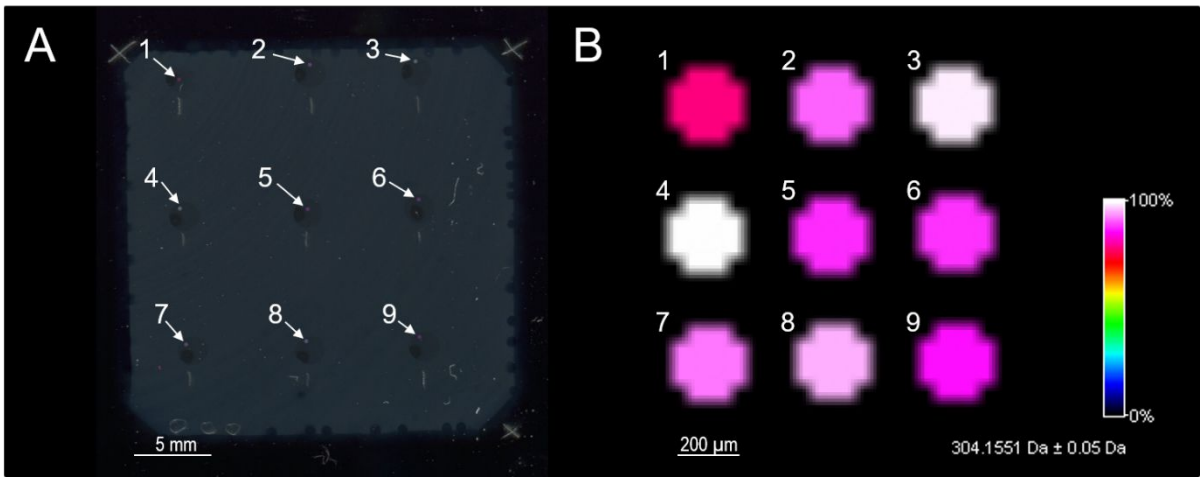

Figure S13: DIOS imaging of cocaine (100 ng/mL in chloroform) showing: A) a spot array where analysis was performed from nine different locations throughout the DIOS surface, and B) zoomed-in view of each of the imaged spots. The parent peak of cocaine was detected at *m/z* 304. An arbitrary colour scale detailing the relative intensity of each peak is displayed to the right. Reprinted with permission from ([1]). Copyright (2020) American Chemical Society.

References

1. Minhas, R. S.; Rudd, D. A.; Al Hmoud, H. Z.; Guinan, T. M.; Kirkbride, K. P.; Voelcker, N. H., Rapid Detection of Anabolic and Narcotic Doping Agents in Saliva and Urine By Means of Nanostructured Silicon SALDI Mass Spectrometry. *ACS Applied Materials & Interfaces* **2020,** *12* (28), 31195-31204.