Electronic Supplementary Material (ESI) for Analytical Methods.

Direct Analysis in Real Time (DART) and Solid-Phase Microextraction (SPME) Transmission Mode (TM): A Suitable Platform for Analysis of Prohibited Substances in Small Volumes

Tijana Vasiljevic[a] and Janusz Pawliszyn[a*]

[a] Department of Chemistry, University of Waterloo, Waterloo, ON, Canada N2L 3G1

*Corresponding author: Tel.: +1 519 888 4567 x 35123, Fax: +1 519 888 4348

Email: janusz@uwaterloo.ca

Electronic supplementary information

Summary:

This document contains information pertaining to: (1) The mass-spectrometric conditions used on the TSQ-Vantage for the analysis of selected drugs; (2) Extraction time plots for selected analytes in oral fluid; (3) Measurement of nicotine in oral fluid obtained from 2 volunteers; (4) Extraction time plots for selected analytes in blood; (5) Skeletonization effect on the mesh's surface; and (6) SEM surface examination after blood extraction and DART desorption on SPME-TM meshes.

(1) Mass-spectrometric conditions used on the TSQ-Vantage for the analysis of selected drugs.

Analyte	Precursor m/z	Product m/z	S-lens	Collision energy (CE)
Cocaine	304.1	182.1	91	19
Cocaine-d3	307.1	185.1	116	18
Methamphetamine	150	91.1	63	20
Methamphetamine-d5	155.1	92.1	72	18
Methadone	310.2	265.1	93	14
Methadone-d3	313.1	268.1	93	13
Morphine	286.1	152.1	121	59
Morphine-d3	289.5	152.2	125	58
Heroin	370.1	165	165	29
Heroin-d9	379.2	272.1	171	46
Oxycodone	316.1	241.1	124	28
Oxycodone-d3	319.1	244.1	117	28
Codeine	300	152.1	120	60
Codeine-d3	303.1	152	125	68
LSD	324	223	118	23
LSD-d3	327	226	116	23
Benzoylecgonine	290.1	168.1	11	18
Benzoylecgonine-d3	293.1	171.1	98	18
Fentanyl	337.1	188	101	22
Fentanyl-d5	342	188	124	22
Nicotine	163.1	117	75	28
Nicotine-d4	167.1	121.1	71	28
Cocaethylene	318.1	195.7	78	20

Cocaethylene-d3	321.1	198.7	120	20
EDDP	278.1	233.9	78	31
EDDP-d3	281.1	233.9	140	31

Table S1. Details relating to the analytes used, their internal standards, and their measured parent and product m/z values. TSQ-Vantage parameters (S-lens and CE value) are also included.

(2) Extraction time plots for selected analytes in oral fluid.

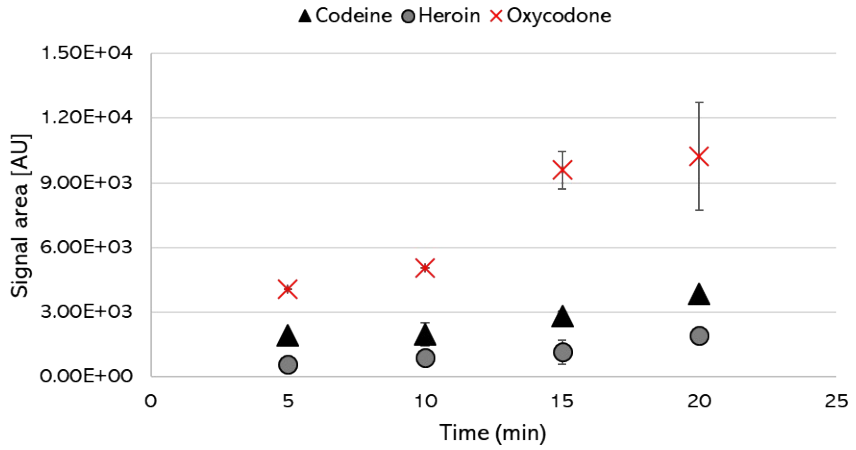

Figure S1. Extraction time plots for selected analytes spiked to 15 µL of oral fluid and analysed via DART-MS/MS with as source temperature of 450 °C and rail speed of 0.2 mm sec^{-1}.

	S/N Ratios		
Extraction time (min)	Codeine	Heroin	Oxycodone
5	3.7	13.4	18.1
10	3.8	19.7	22.4
15	5.4	25.4	42.6
20	7.3	41.8	45.5

Table S2. S/N ratios obtained for the time points examined in Figure S1.

(3) Measurement of nicotine in oral fluid obtained from of 2 volunteers

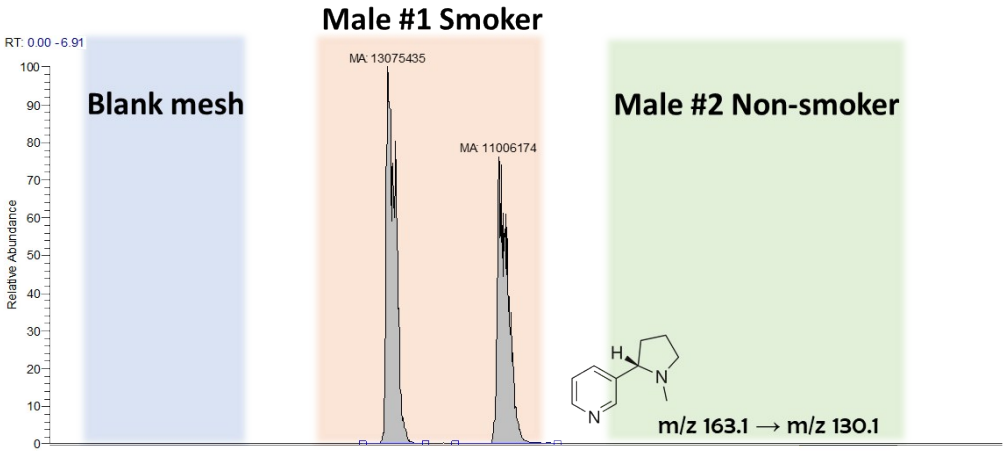

Figure S2. Ion chronogram obtained for measurements of nicotine signal in blank mesh and oral fluid samples from a male smoker and a male non-smoker male (n=2, for all).

(4) Extraction time plots for selected analytes in blood.

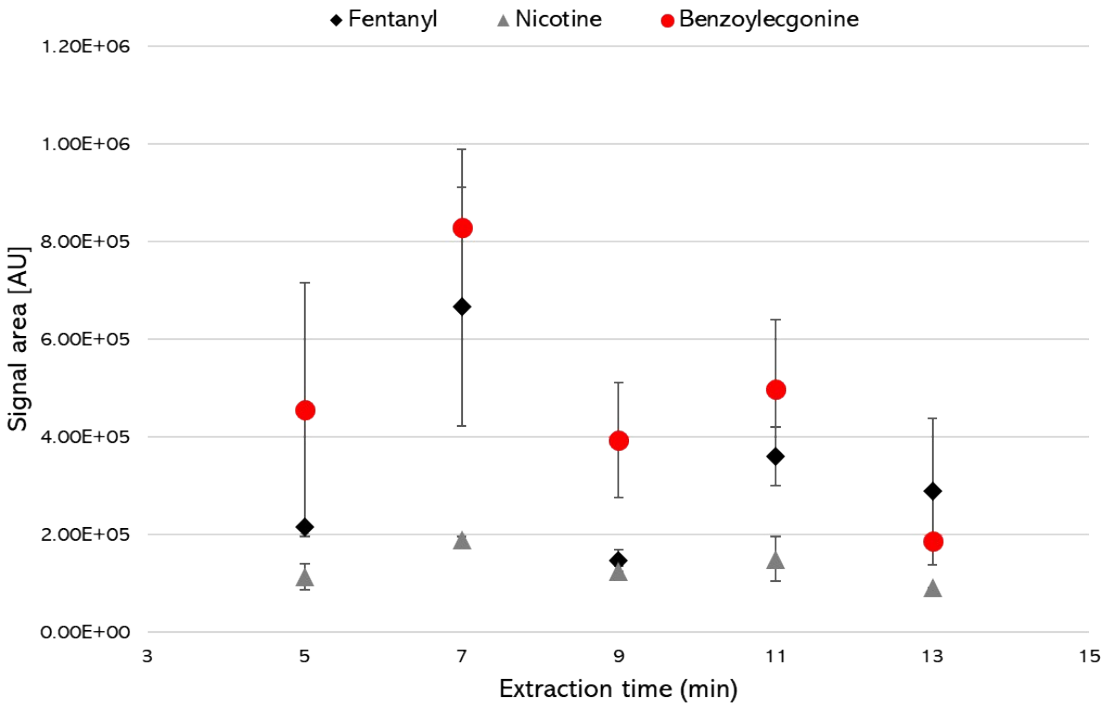

Figure S3. Extraction time plots for selected analytes (25 ng mL^{-1}) spiked to 25 µL of blood and analysed via DART-MS/MS with a source temperature of 450 °C and a rail speed of 0.2 mm sec^{-1}.

	S/N Ratios		
Extraction time (min)	Fentanyl	Nicotine	Benzoylecgonine
5	274.3	8.0	6.6
7	851.5	13.2	11.9
9	186.0	8.6	5.7
11	460.8	10.4	7.2
13	368.3	6.3	2.7

Table S3. S/N ratios obtained for time points examined in Figure S3.

(5) Skeletonization effect on mesh surface.

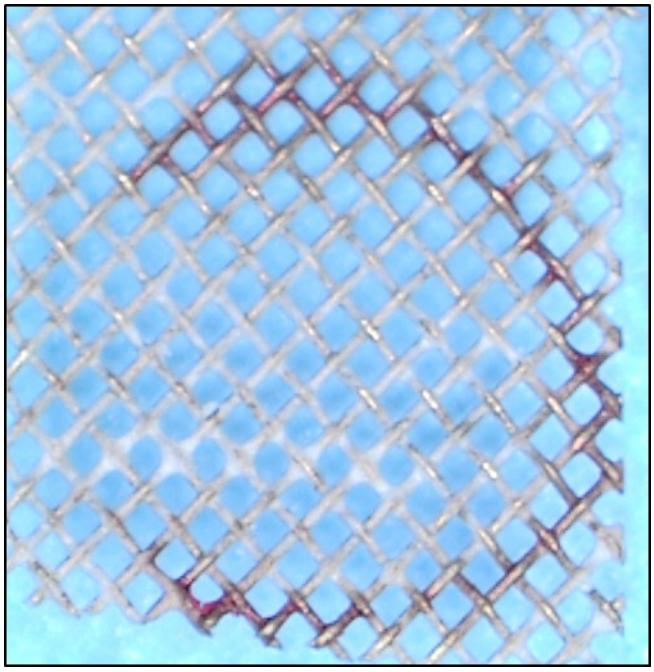

Figure S4. Formation of a “blood ring” or “skeletonization effect” on a dummy-mesh occurring in extractions exceeding 10 minutes.

(6) SEM surface examination after blood extraction on SPME-TM meshes.

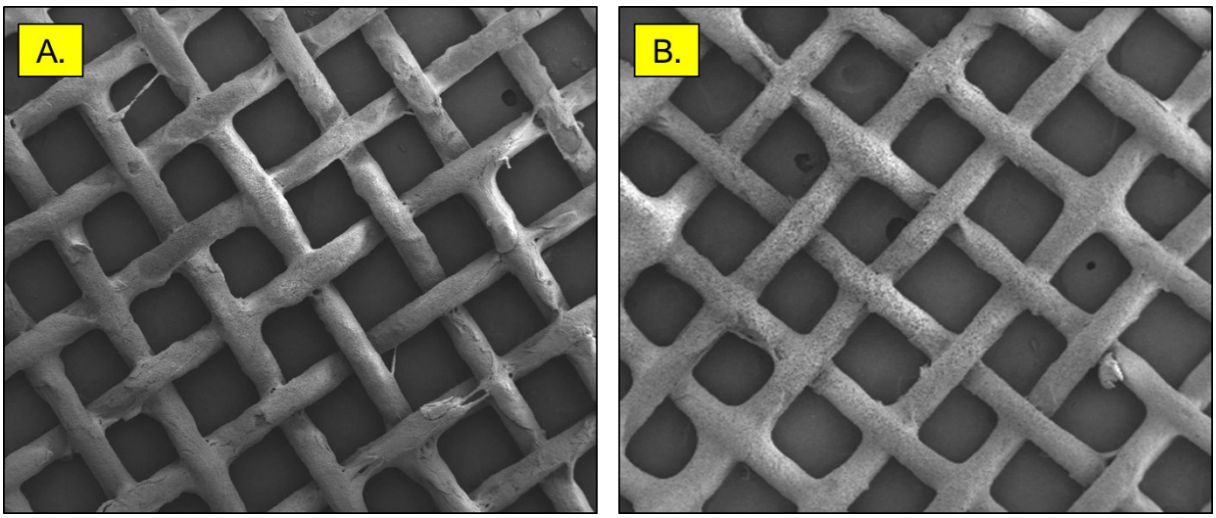

Figure S5. A. SEM image of a never-used HLB-coated mesh; B. image of a mesh used for a 7-minute blood extraction. Both images depict the mesh after the application of a wash step and DART desorption.