SUPPORTING INFORMATION

Detection of Opioids on Mail/Packages using Open Port Interface Mass Spectrometry (OPI-MS)

Haidy Metwally[1], Prashant Agrawal[1], Rachael Smith[1], Chang Liu[2], Yves LeBlanc[2]

Thomas R. Covey [2], and Richard Oleschuk[1*]

[1]*Department of Chemistry, Queen's University, Kingston, Ontario,*

K7L 3N6, Canada.

[2]*SCIEX, 71 Four Valley Drive, Concord, Ontario L4K 4 V8, Canada*

* Corresponding author: Richard Oleschuk

E-mail address of the corresponding author: richard.oleschuk@chem.queensu.ca

This file contains:

Materials and Methods

Supporting Figures

Materials and Methods

Materials. All solvents used (methanol, acetonitrile, and formic acid) were purchased from Fischer Scientific (Ottawa, ON). Ziploc bags™ were purchased locally and manufactured by S.C. Johnson and son (Brantford, ON). Coffee used in the surrogate experiment was obtained from a local coffee shop at Queen's University, house blend.

Mass Spectrometry.

An OPI was externally connected via PEEK tubing (1/16" OD*0.01" ID, IDEX, NY, USA) to an API 3200 triple quadrupole mass spectrometer (Sciex, Concord, ON) and its electrospray ionization source (ESI). The ESI probe was maintained at a voltage of +5.5 kV, with ion source nitrogen gas settings GS1 = 45 psi, GS2 = 20 psi, curtain gas = 50 psi and heated nebulizer temperature = 300 °C. The OPI is connected to an external syringe pump for solvent delivery. The flow rate of solvent (50% methanol or acetonitrile: 49.9% water: 0.1% formic acid) was controlled by the aspiration force induced by GS1 (nebulizing gas) to achieve a constant dome-shaped sampling surface without over-spilling. Tandem mass spectrometry (MS/MS) conditions were declustering potential (DP) =45 V, entrance potential (EP)=10 V, collision energy(CE)=32 V, collision cell exit potential (CXP)=10.

Data Analysis. All of the curve fitting calculations were done using Sigmaplot 11.0 while the limits of mass detection (LOD_{mass}) were computed in excel by employing linear regression method:

$$LOD_{mass} = \frac{3S}{b}$$

S: is the standard deviation of the response, while b *is* the slope of the calibration curve. [1]

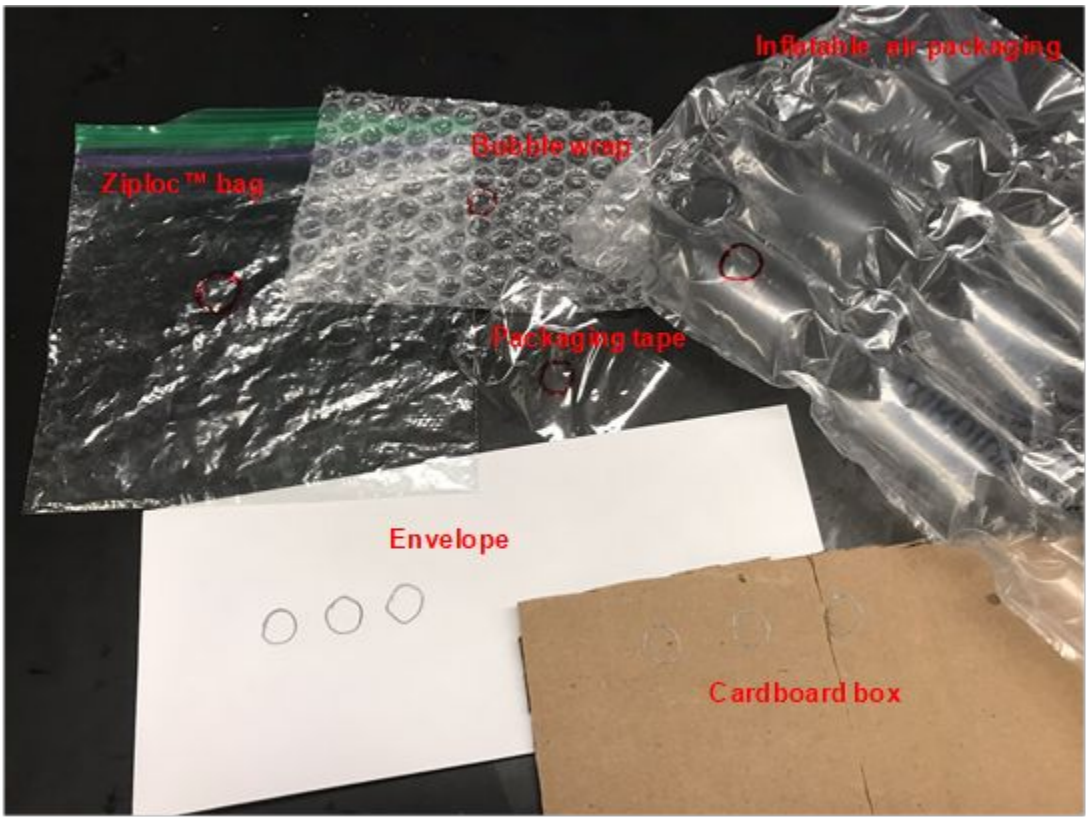

Figure S1. A photograph of different mail packages used in this study. Envelope and cardboard box represent porous materials while Ziploc bag™, bubble wrap, and inflatable air packaging are nonporous materials. Pencil/Sharpie™ rings mark the position of deposited/dried calibrants on different packaging materials. The area within the circles swiped with OPI source.

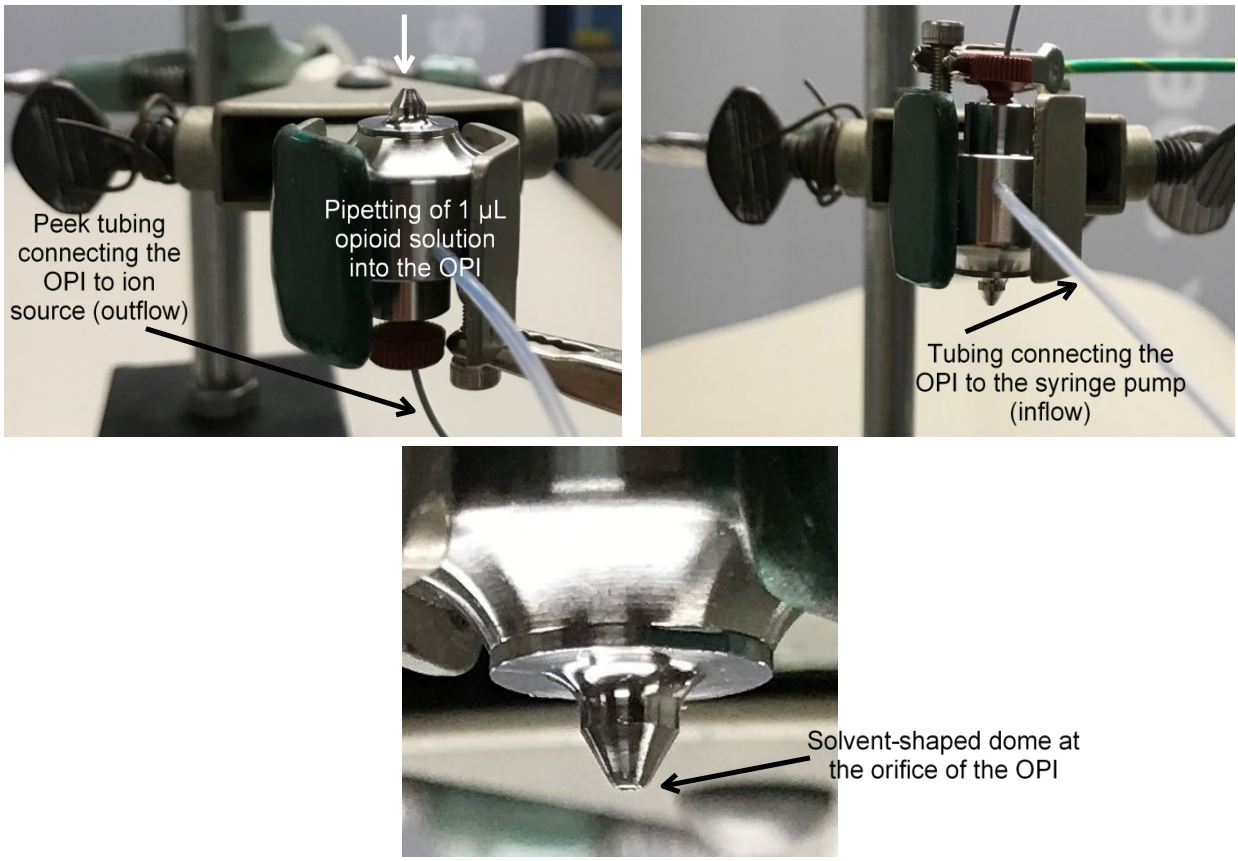

Figure S2. The OPI, upward-facing (left), where a liquid can be pipetted directly into the orifice of OPI. While the OPI, downward-facing (right) at which the solvent-shaped dome (continuously flushing) is swiped across a potentially contaminated surface. Magnified photo of the OPI showing the solvent-shaped dome (lower right).

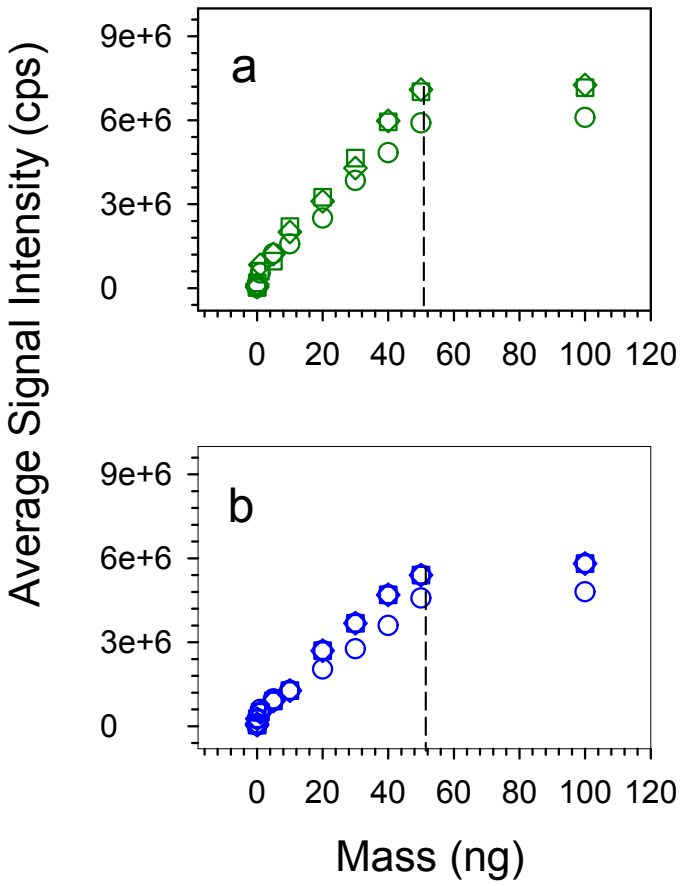

Figure S3. Average signal intensities from different deposited masses are showing that beyond 50 ng, the response is no longer linear (plateau) (a) Packaging tape and (b) Bubble wrap. The dashed line corresponds to 50 ng.

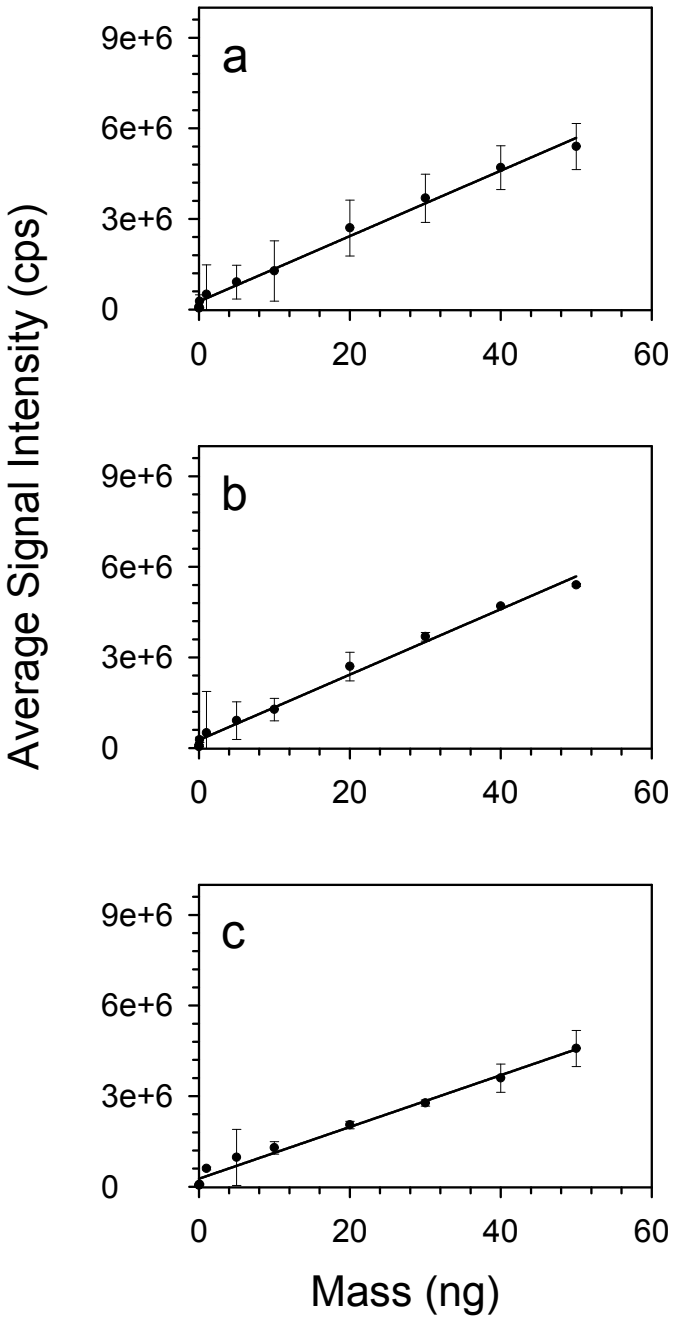

Figure S4. Quantitative analysis of different calibrants from bubble wrap. (a) Fentanyl (LOD_{mass} = 2.5 ng). (b) Heroin (LOD_{mass} = 2.6 ng). (c) Oxycodone (LOD_{mass} =3.2 ng). Error bars represent the standard deviation of three replicates.

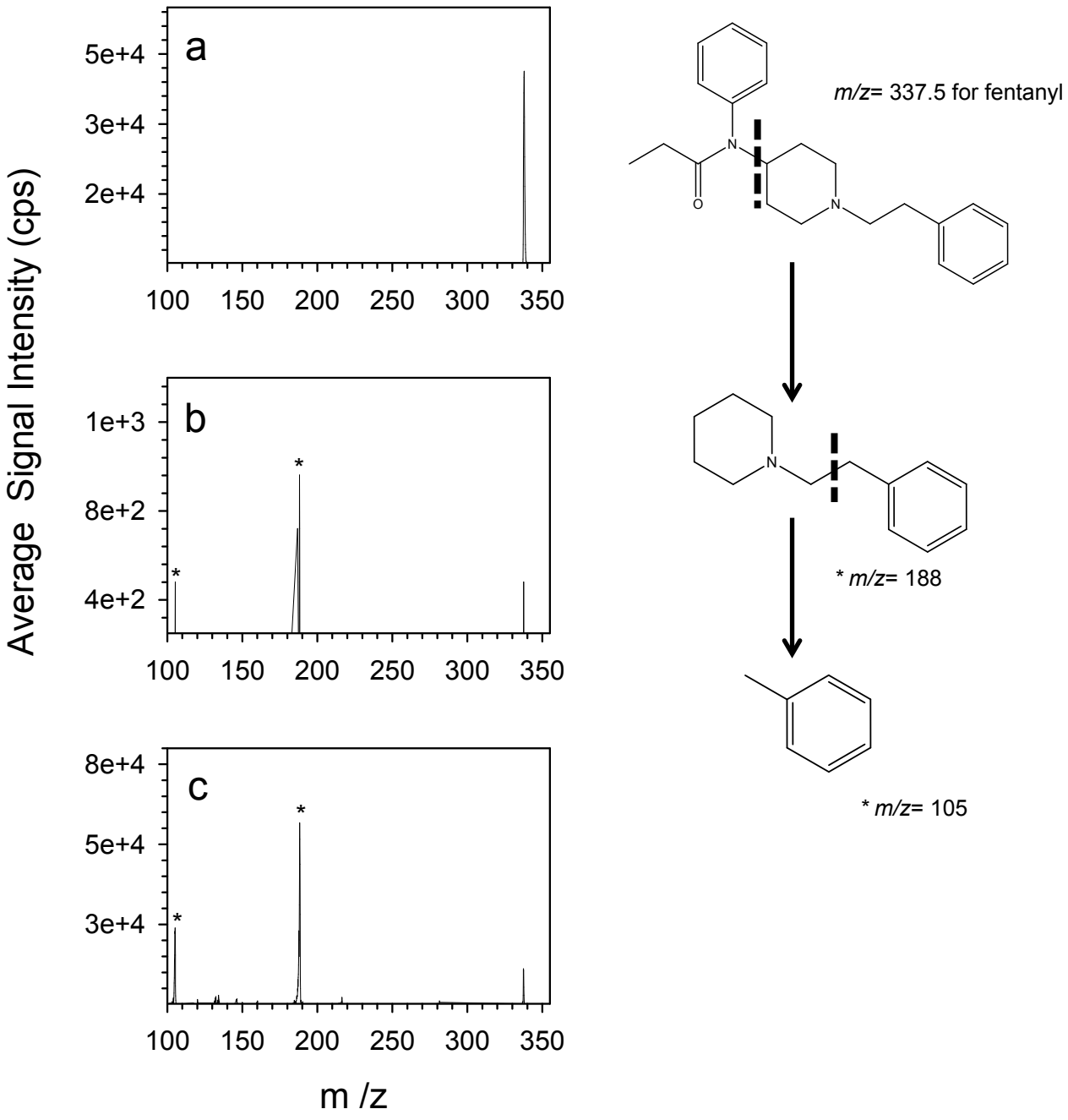

Figure S5. Mass spectra showing MS/MS fragmentation of fentanyl (precursor-ion) using collision energy (32 V) applied to the second quadrupole. (a) The precursor-ion of fentanyl having *m/z* 337.5 shown at very low collision energy (5 V). (b) A mass of 1pg from an envelope underwent tandem mass spectrometry showing the two main fragments of *m/z* 188 (*) and *m/z* 105(*). (c) A mass of 1 ng from an envelope showing the two main fragments. [2]

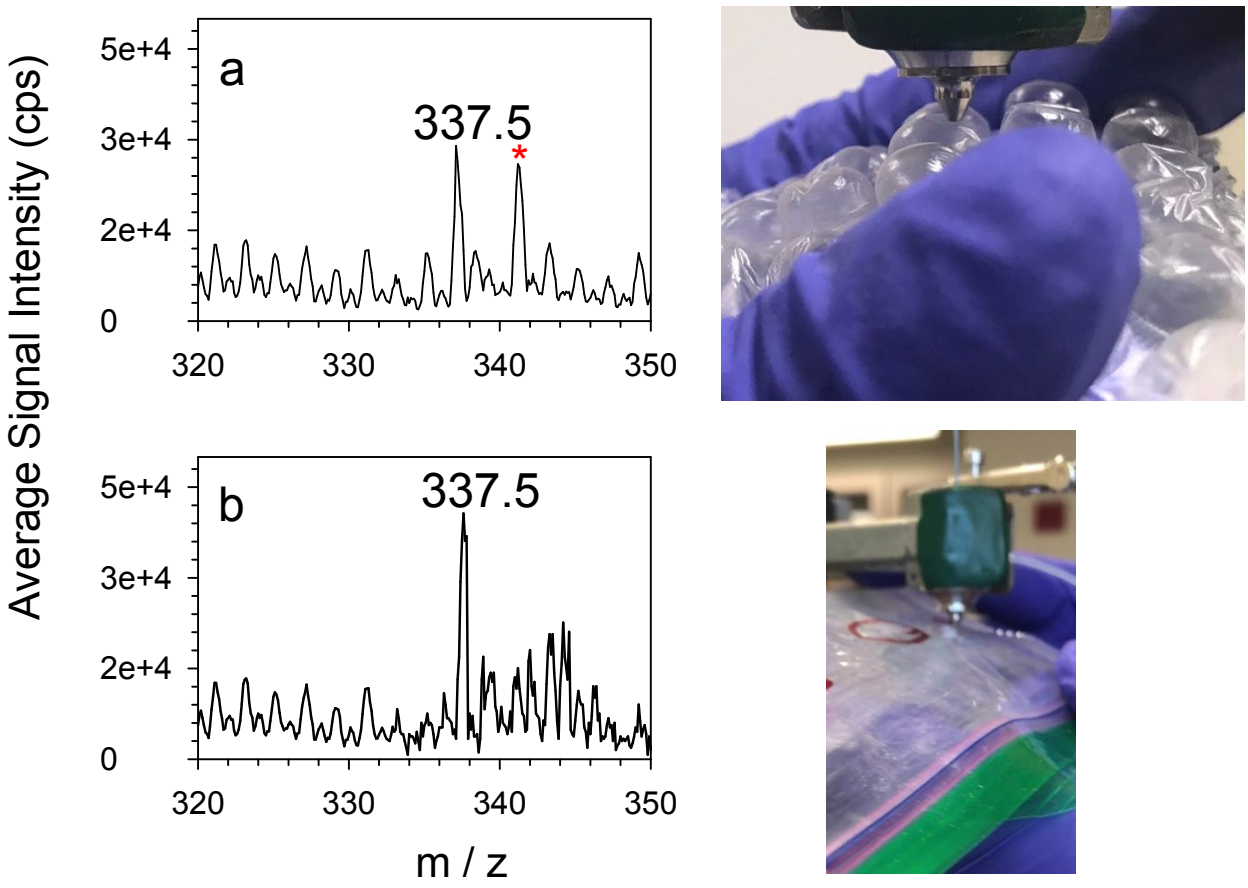

Figure S6. Non-invasive detection of opioids from (a) Bubble wrap and (b) Ziploc bag ™. With bubble wrap, 1 ng/µL of fentanyl solution was injected inside the bubble, and the outer surface of the bubble was swiped across the OPI, showing a peak at *m/z* 337.5 for the singly protonated fentanyl. For the Ziploc bag™, a fentanyl solution (1 ng/µL) was pipetted inside the bag, and the OPI was swiped on the outer surface. The asterisk (*) represents an unknown contaminant associated with the bubble wrap.

References

(1) Shrivastava, A.; Gupta, V. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron. Young Sci.* **2011,** *2*, 21-25.

(2) Day, J.; Slawson, M.; Lugo, R. A.; Wilkins, D. Analysis of Fentanyl and Norfentanyl in Human Plasma by Liquid Chromatography-Tandem Mass Spectrometry Using Electrospray Ionization. *J. Anal. Toxicol.* **2003,** *27*, 513-516.