1 # SUPPLEMENTARY INFORMATION

2 **Polydopamine coated hypodermic needles as a microextraction device for**

3 **the determination of tricyclic antidepressants in oral fluid by direct**

4 **infusion MS /MS**

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1. Multiple Reaction Monitoring (MRM) transitions for the direct infusion MS analysis.

Table S1. Multiple reaction monitoring parameters for MS analyses

Analyte	Precursor ion [M+H]+ (m/z)	Product ions (m/z)	Collision energy (V)	Fragmentor voltage (V)
Clomipramine	315.2	**86.1**	18	114
		58.2	50	
Trimipramine	295.2	**100.2**	20	125
		58.2	40	
Imipramine	281.2	**86.1**	18	96
		58.2	50	
Amitriptyline	278.2	233.1	20	140
		91.1	40	
Desipramine	267.1	**72.2**	15	145
		44.2	20	
Nortriptyline	264.2	105.1	22	96
		91.1	30	
Clomipramine-d3 (IS)	318.2	**89.2**	18	132
		61.2	46	
Desipramine-d3 (IS)	270.2	193.0	42	132
		75.2	18	
Nortriptyline-d3 (IS)	267.2	105.1	22	96
		91.1	30	

Quantitation transition in bold

2. Extraction procedure for the optimization of the pDA coating synthesis.

For the optimization of the pDA coating procedure, a simple extraction method using hypodermic needles synthesized under different conditions was used for the extraction of clomipramine (CLO), trimipramine (TRI), imipramine (IMI), amitriptyline (AMI),

21 desipramine (DES) and nortriptyline (NOR) from an aqueous solution (50 ng/mL) adjusted

22 to pH 10 using NH_4OH (1 M). The extraction was carried out using an orbital shaker (1000

23 rpm). For conditioning, needles were first immersed in methanol for 30 s and then in an

24 alkaline solution of ultrapure water adjusted to pH 10 with ammonia. Then, each needle was

25 immersed into 5 mL of an aqueous analyte solution (50 ng/mL) for 30 min. Two washing

26 steps were performed with ultrapure water (pH 10) prior to elution in 200 µL of methanol

27 into HPLC vials with insert. Finally, each vial was analysed by mass spectrometry. Take note

28 that this extraction procedure evaluates the pDA attached to both the outer and inner surfaces
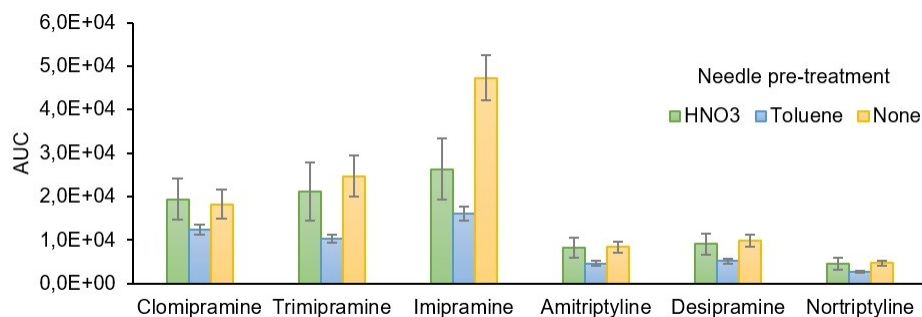
29 of the needle.

30 **3. Optimization of the needle coating**

31 The optimization of the pDA coating process considered three different variables, namely:

32 number of coating cycles, concentration of dopamine and needle surface pre-treatment.

33 Figure S1 and S2 shows the latter variables that are described and commented in the main

34 text.
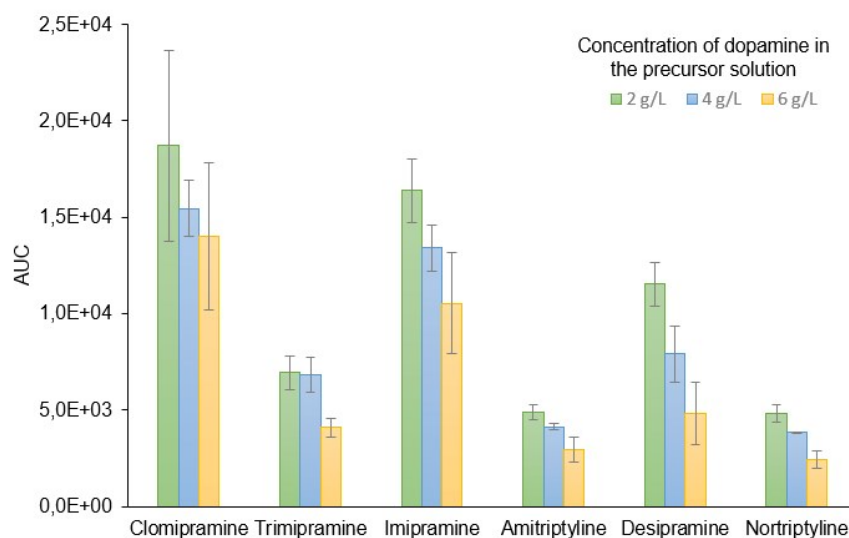
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36 *Figure S1. Extraction performance of needles synthesized using pDA precursor solutions with different*

37 *concentration (2, 4 and 6 g/L).*

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Figure S2. Study of the needle pre-treatment on the extraction capability of pDA coated needles. hypodermic

needles on a 50 ng/mL solution of tricyclic antidepressants.

4. Optimization of the microextraction procedure

The extraction performance was optimized considering the effect of three variables, namely:

ionic strength, sample loading cycles, and the number of elution strokes. Figure S3 presents

the effect of the ionic strength, expressed as salinity (mmho/cm), on the extraction of the

target compounds.

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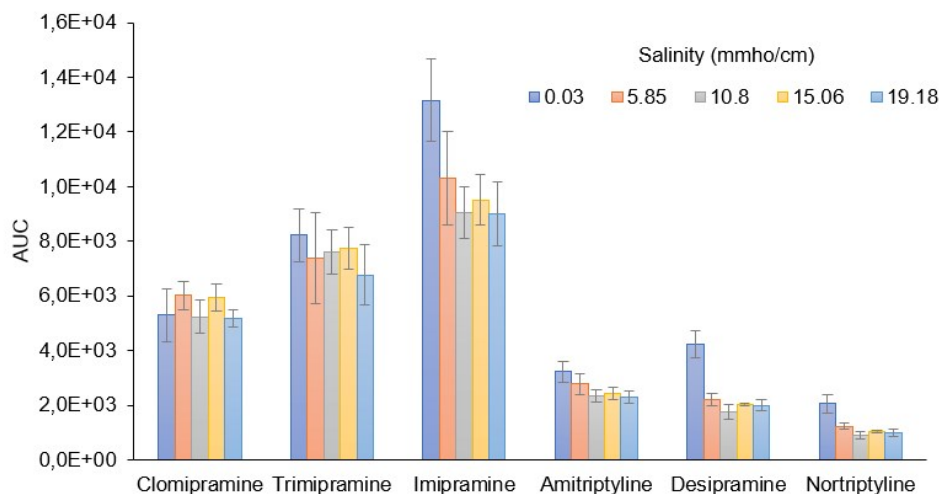
Figure S3. Study of the effect of ionic strength over the extraction efficiency of pDA-coated needles. The ionic

strength is expressed in salinity units (mmho/cm).

Finally, the number of elution strokes was evaluated. The results showed (Figure S4) that a

single stroke was enough to obtain an efficient elution of the TCAs for MS analysis.
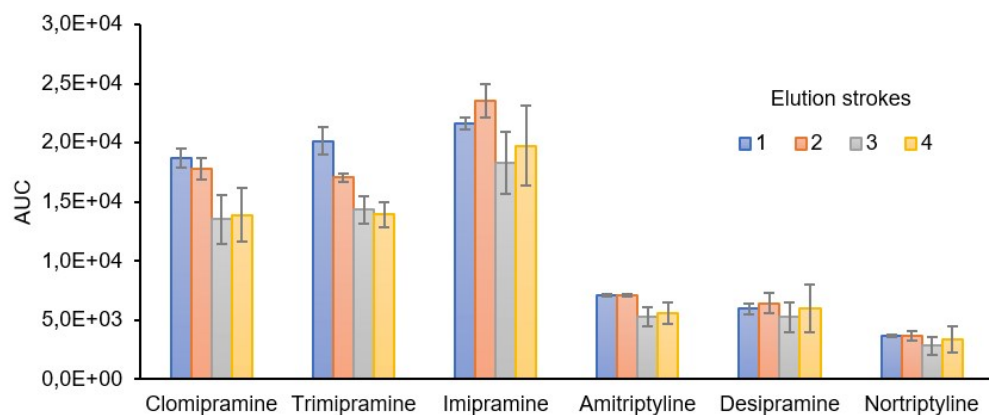
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52 **Figure S4**. *Study of the effect of elution strokes on the analytical signal.*

53 5. Calibration models

54 **Table S2**. Regression results obtained for each target analyte.

Analyte	Slope	Intercept	R^2
Clomipramine	0.0070	-0.0011	0.9997
Trimipramine	0.0107	-0.0090	0.9969
Imipramine	0.0106	0.0113	0.9983
Amitriptyline	0.0035	0.0036	0.9984
Desipramine	0.0039	0.0024	0.9966
Nortriptyline	0.0065	0.0019	0.9994

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