Supplementary Material

Derivatization of amphetamine to allow its electrochemical detection in illicit drug seizures

Marc Parrilla,[a,b] Noelia Felipe Montiel,[a,b] Filip Van Durme,[c] Karolien De Wael*[,a,b]

[a]AXES Research Group, Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.

[b] NANOlab Center of Excellence, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.

[c] Drugs and Toxicology Department, National Institute for Criminalistics and Criminology (NICC), Vilvoordsesteenweg 100, 1120, Brussels, Belgium.

*Corresponding author: Karolien De Wael (karolien.dewael@uantwerpen.be)

Table of contents

Tables

Table S1. Composition of the real samples analyzed by the forensic laboratory (i.e., gas chromatography-mass spectrometry and gas chromatography/flame ionization detection) and comparison of the analysis with the electrochemical portable device.

Sample	Code	GC-MS	GC-FID / wt.%	EF / AMP wt.%	Accuracy / %
1	6.62	**Amphetamine** Caffeine	- -	**44.2**	**-**
2	6.63	**Amphetamine** Caffeine **3-Fluoroamphetamine**	**35.8** 27.8 **24.9**	**58.3 ±4.9**	**96.0**
3	6.64	**Amphetamine** Caffeine **3-Fluoroamphetamine**	**68.1** 29 **0.3**	**69.9**	**102.2**
4	3.61	**Amphetamine** Methamphetamine	- -	**80.1**	**-**
5	510	**Amphetamine**	25.8	**21.4**	**83.0**
6	597	**Amphetamine** Caffeine	52.2 29.2	**55.7**	**106.6**
7	598	**Amphetamine**	75.3	**66.8**	**88.8**
8	955.1	**Amphetamine** Caffeine	4.9 41.6	**4.3**	**87.2**
9	955.5	**Amphetamine** Caffeine	6.1 51.5	**5.3**	**87.0**
10	102.9.2	**Amphetamine** Caffeine MDMA **3-Fluoroamphetamine**	6.6 13.3 1.4 1.8	**7.7**	**97.3**
11	270.6	**Amphetamine** Caffeine	20.9 48.4	**11.8***	**56.6***
12	898.1	**Amphetamine** Caffeine	47.9 41.8	**47.2**	**98.6**
13	897.3	**Amphetamine** Caffeine	57.6 31.2	**52.3**	**90.8**
14	911	**Amphetamine** Caffeine	22.6 16.0	**20.9**	**92.6**
15	359	**Amphetamine** Caffeine	67.7 20.7	**59.0**	**87.1**
16	741	**Amphetamine**	100.3	**110.9**	**110.6**
17	824.2.3.2	**Amphetamine** Caffeine	36.4 1.3	**32.0**	**87.7**
18	855.2	**Amphetamine** Caffeine	77.8 13.4	**86.6**	**111.3**
19	127.1.6	**Amphetamine**	62.1	**70.2**	**113.1**
20	127.1.7.1	**Amphetamine**	94.9	**107.8**	**113.6**

***This sample exhibited issues during sample preparation.

Figures

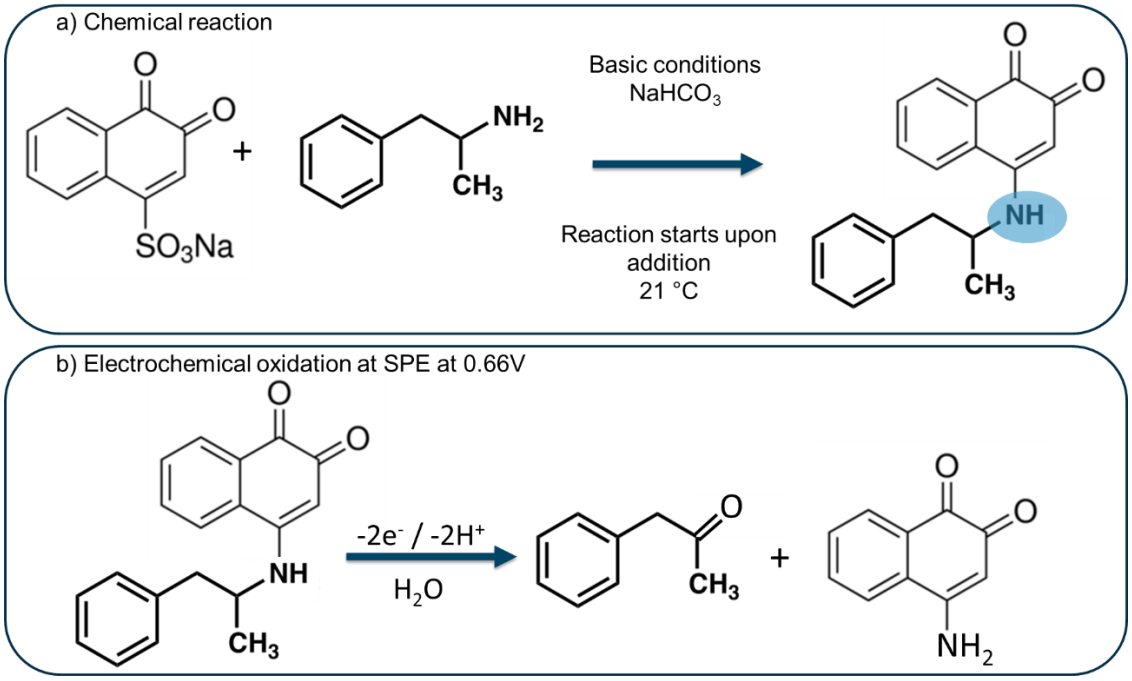

Fig. S1. Illustration of the suggested reactions: a) chemical reaction occurring during the mixture of AMP with a primary amine group and NQS with the sulfonate group in carbonate buffer pH 10 at room temperature. The electroactive group is highlighted in light blue. b) suggested electrochemical oxidation of the product of the chemical reaction at a SPE after applying 0.66V.

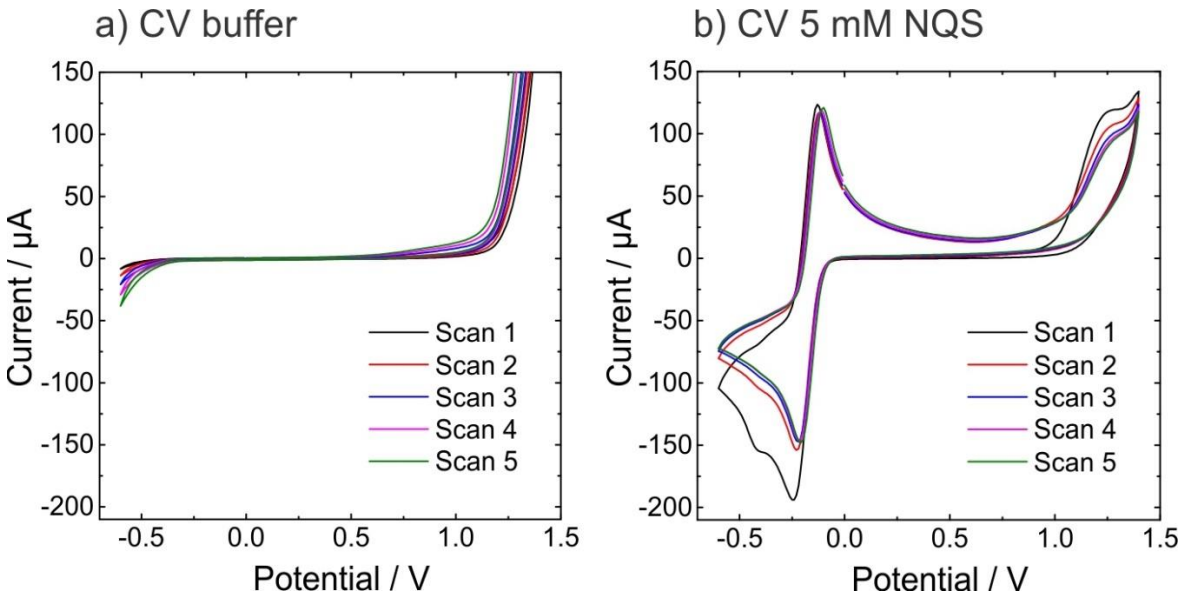

Fig. S2. Cyclic voltammograms of 5 consecutive scans on the SPE using 20 mM carbonate buffer pH 10 with 100 mM KCl: a) blank (buffer only), b) 5 mM NQS.

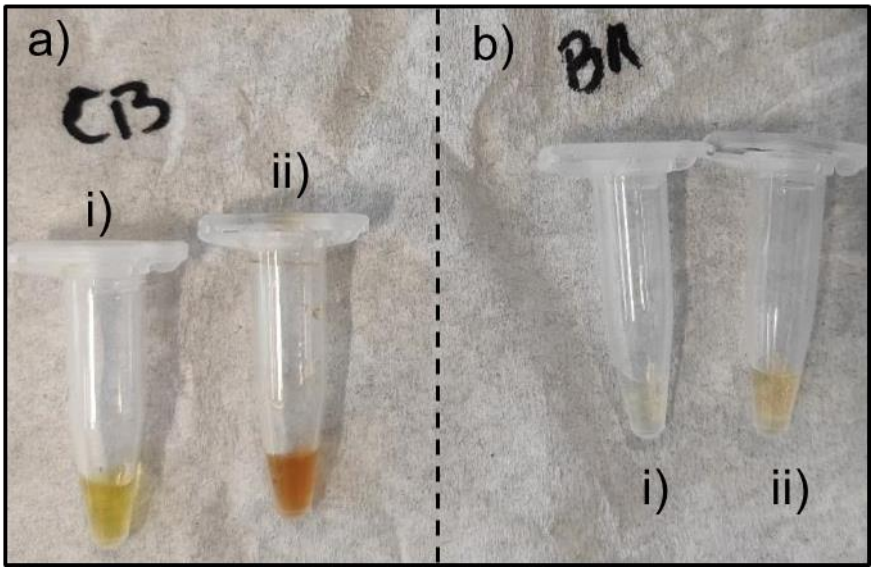

Fig. S3. Image of 1.5 mL tubes showing the chemical reactions: a) using carbonate buffer pH 10, i) containing 1 mM NQS and ii) containing 1 mM NQS + 0.5 mM AMP; b) using Britton-Robinson buffer pH 10, i) containing 1 mM NQS and ii) containing 1 mM NQS + 0.5 mM AMP.

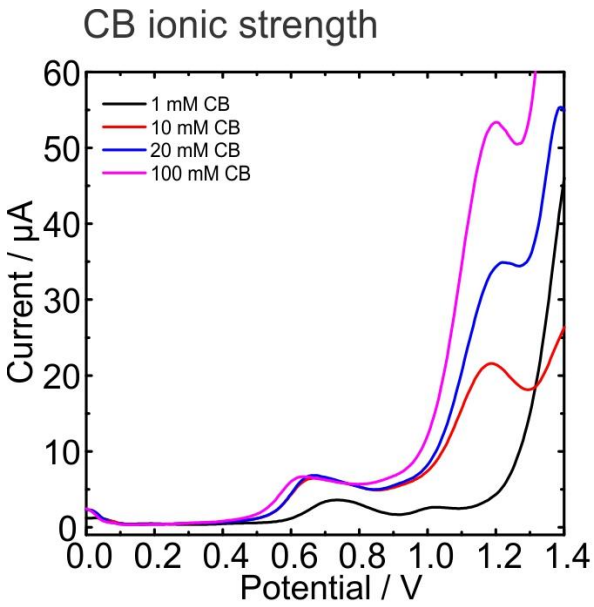

Fig. S4. Raw square wave voltammograms obtained from the influence study of the ionic strength of carbonate buffer (1, 10, 20 and 100 mM) on the analytical response of 0.5 mM AMP + 5 mM NQS after 2.5 min reaction time.

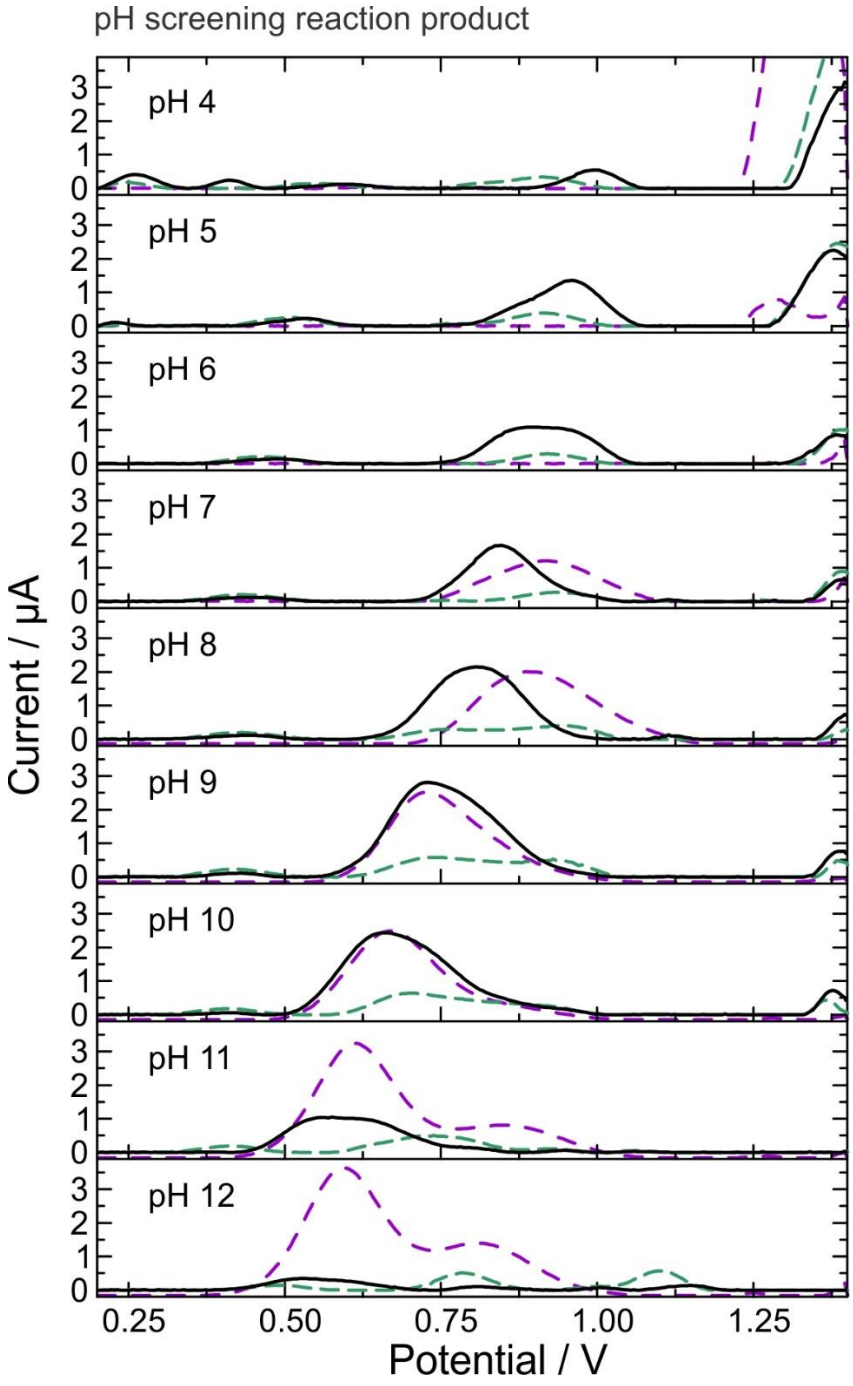

Fig. S5. pH screening of the product of the reaction (previous batch employing bicarbonate buffer after 1h reaction) between 1 mM AMP and 5 mM NQS (**black straight line**) and control experiment with 5 mM NQS (**green dashed line**). An aliquot of the reaction product was added into the corresponding Britton-Robinson buffer (from pH 4 to pH 12) to reach a 100 µM solution and interrogated by SWV. Additionally, a molecule containing a tertiary amine group, i.e. N-N-dimethylcyclohexylamine, (**purple dashed line**) was tested for comparison purposes.

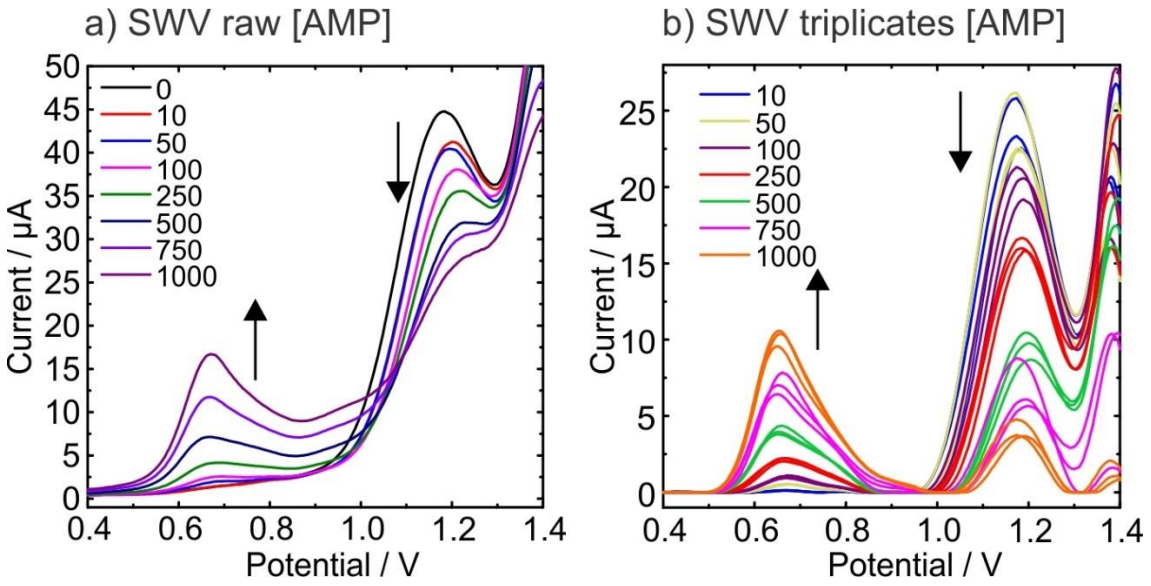

Fig. S6. SWV of increasing concentrations of AMP after the chemical reaction with 5 mM NQS during 2.5 min in 20 mM CB pH 10: a) SWV raw data corresponding to Figure 3a; b) Baseline-corrected SWV of triplicates at each concentration (i.e. 10, 50, 100, 250, 500, 750 and 1000 µM), peak potential at 0.66V was employed for the construction of the calibration curve in Figure 4b.

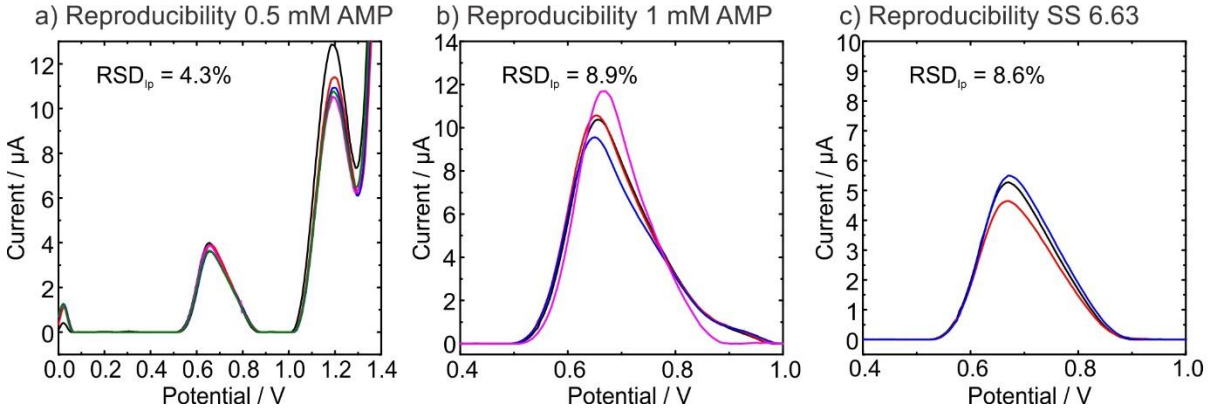

Fig. S7. Intraday reproducibility studies by SWV of AMP with 5 mM NQS after 2.5 min reaction at SPE CB pH 10: a) 0.5 mM AMP (n=5), b) 1 mM AMP (n=4), c) street sample (SS) 6.63 (n=3).