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Forensic electrochemistry: simultaneous voltammetric detection of MDMA and its fatal counterpart “Dr Death” (PMA)†

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The simultaneous detection of substances present in drugs of abuse is increasingly important since some materials are known for their high mortality rate. One drug that received considerable attention is *para*-methoxyamphetamine (PMA), commonly known as ‘Dr Death’ – this substance is linked with several deaths internationally and can often be found together with 3,4-methylenedioxymethamphetamine (MDMA) in drugs sold under the alias “ecstasy”, a very popular drug of abuse. This work reports for the first time the detection and quantification of MDMA and PMA simultaneously through an electrochemical technique using screen-printed graphite electrodes (SPEs). The electroanalytical sensing of MDMA/PMA, MDMA and PMA are explored directly at bare unmodified SPEs yielding a detection limit (3σ) corresponding to $0.25 \mu\text{g mL}^{-1}/0.14 \mu\text{g mL}^{-1}$ for MDMA/PMA, $0.04 \mu\text{g mL}^{-1}$ MDMA and $0.03 \mu\text{g mL}^{-1}$ PMA. Raman spectroscopy and presumptive colour tests were also performed on MDMA/PMA, MDMA and PMA using the Marquis, Mandelin, Simon’s and Robadope tests but were found to not be able discriminate when PMA and MDMA are both present in the same samples. We report a novel electrochemical protocol for the sensing of PMA and MDMA which is independently validated in a synthetic (MDMA/PMA) sample with HPLC.

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Introduction

3,4-Methylenedioxymethamphetamine (MDMA, Scheme 1) is a synthetic entactogen which shares a structural similarity to methamphetamine and acts as a central nervous system (CNS) stimulant producing mood enhancement, increased energy and other empathetic effects by increasing the intra-synaptic concentrations of the key neurotransmitters serotonin, dopamine and norepinephrine.^{1–5} MDMA was first synthesised by Merck in 1912 as a potential appetite suppressant, and over the next seventy years, a number of researchers explored the psychedelic properties of MDMA with little success.⁶ During the 1970s and 80s MDMA surfaced on the recreational drugs market, its widespread abuse and potential long-term health effects led many countries to prohibit its possession, supply and manufacture. Currently in the UK, MDMA (or “ecstasy”) is controlled as a Class A, Schedule 1 substance due to its illicit

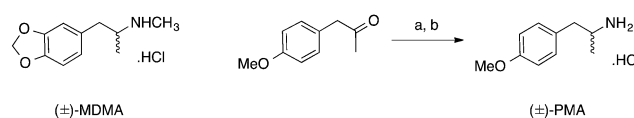
use as a recreational drug and its implication in a number of highly publicized fatalities.^{7–13} It is usually found in tableted form (containing 60–70 mg MDMA) with each batch being stamped with a particular motif, e.g. a Mitsubishi™ logo, smiley faces or letters.

Since the global prohibition of MDMA and its precursors (*i.e.* 3,4-methylenedioxyphenyl-2-propanone, piperonal, safrole and isosafrole) a wide range of structurally-related phenethylamines have appeared on the recreational drugs market, including the designer drug, 4-methoxyamphetamine (PMA, Scheme 1). As a synthetic entactogen, PMA acts on the CNS producing mood enhancement, heightened sexual arousal and increased energy by increasing the release of intra-synaptic concentration serotonin and also inhibiting its reuptake.¹⁴ Animal models suggest that PMA is more toxic, than MDMA, resulting in hyperthermia (*i.e.* serotonin syndrome) due to the enhancement of serotonin release and the delayed onset of action.^{15,16} It is believed that

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Scheme 1 The structure of (±)-3,4-methylenedioxyamphetamine hydrochloride (MDMA) and the synthesis of (±)-4-methoxyamphetamine hydrochloride (PMA).



working and counter electrodes, was screen-printed onto a polyester (Autostat, 250 micron thickness) flexible film. After curing the screen-printed carbon layer in a fan oven at 60 degrees Celsius for 30 minutes, next a silver/silver chloride reference electrode was included by screen-printing Ag/AgCl paste (Product Code: C2040308D2; Gwent Electronic Materials Ltd, UK) onto the polyester substrates, which was subsequently cured once more in a fan oven at 60 degrees for 30 minutes. Finally, a dielectric paste (Product Code: D2070423D5; Gwent Electronic Materials Ltd, UK) was then printed onto the polyester substrate to cover the connections and define the active electrode areas, including that of the working electrode (3 mm diameter). After curing at 60 degrees for 30 minutes the SPEs are ready to be used. The reproducibility and repeatability of the fabricated batches of electrodes were explored through comparison of cyclic voltammetric responses using $\text{Ru}(\text{NH}_3)_2^{2+/3+}$ redox probe in 1 M KCl. Analysis of the voltammetric data revealed the % relative standard deviation (%RSD) to correspond to no greater than 0.82% ($n = 20$) and 0.76% ($n = 3$) for the reproducibility and repeatability of the fabricated GSPEs (for use in electroanalysis). For each electrochemical experiment/scan, a new screen-printed graphite electrode was used. All differential pulse voltammograms were baseline corrected.

Raman

Raman Spectroscopy was performed using a 'Renishaw InVia' spectrometer with a confocal microscope $\times 50$ objective,

spectrometer with an argon laser of 514.3 nm excitation. Spectra were recorded using a 10 s exposure time for 1 accumulation. Three spectra were recorded and an average representation is presented within the manuscript.

Analysis of synthetic sample: "ecstasy synthetic"

For the electrochemical determination of MDMA/PMA solutions were prepared using carefully weighed samples of "synthetic ecstasy" in PBS (pH 7). Subsequently, the solution was sonicated for 3 minutes for homogenization and filtered to remove remaining undesirable insoluble materials. A total of five seized ecstasy tablets were analysed *via* HPLC and the presence of PMA was not detected in either tablet, so a sample containing the two substances was created. PMA is a lethal substance when administered in substantial quantities, but produces similar effects to MDMA. As it is a cheaper substance, it is occasionally added to MDMA in ecstasy tablets to lower the cost of the drug.

Results and discussion

Electrochemical detection of MDMA and PMA

First, cyclic voltammetric measurements were performed using screen-printed graphite electrodes (SPEs) in solutions containing PMA, MDMA and MDMA/PMA in phosphate buffer (pH 7). Fig. 1A shows the cyclic voltammograms of SPE in the presence ($500 \mu\text{g mL}^{-1}$) and absence of PMA. In the case of PMA a well-defined oxidation peak is observed at +1.162 V. Fig. 1B shows the cyclic voltammograms in the presence ($250 \mu\text{g mL}^{-1}$) and

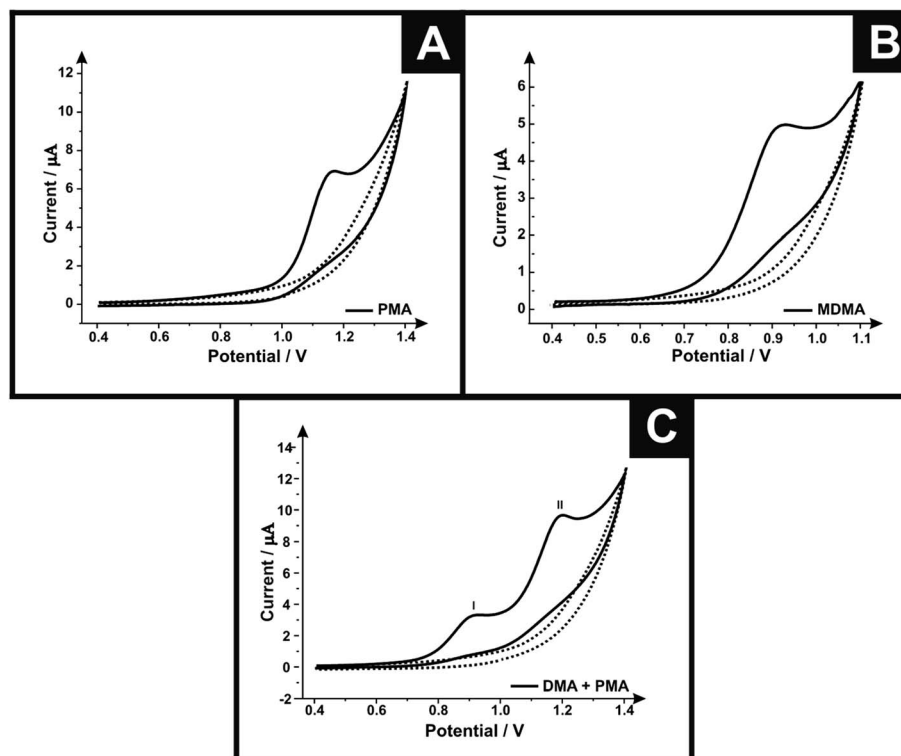


Fig. 1 Cyclic voltammograms of SPE (A) in presence ($500 \mu\text{g mL}^{-1}$) and absence of PMA, (B) in presence ($250 \mu\text{g mL}^{-1}$) and absence of MDMA and (C) in presence ($250 \mu\text{g mL}^{-1}$)/($500 \mu\text{g mL}^{-1}$) and absence of MDMA/PMA in PBS (pH 7) (scan rate: 100 mV s^{-1}).



absence of MDMA using the SPEs. The cyclic voltammogram in the presence of MDMA shows the oxidation peaked in +0.924 V. Fig. 1C shows the cyclic voltammograms in the presence of (250 $\mu\text{g mL}^{-1}$)/(500 $\mu\text{g mL}^{-1}$) and absence of MDMA/PMA where two oxidation peaks can be observed; peak I at +0.92 V due to oxidation of MDMA and peak II at +1.20 V is due to oxidation of PMA. The sole presence of an oxidation peak for all the analytes suggests an electrochemically irreversible reaction.

Different electrodes were explored towards the electrochemical oxidation of the target analytes to provide a direct comparison with the response obtained using the screen-printed graphite electrode. Fig. SI-1† shows the electrochemical response of the SPE, boron doped diamond (BDD) and glassy carbon (GC). For the target analyte MDMA, the SPE shows an optimal response with the electrochemical oxidation occurring at the lowest overpotential (+0.99 V) with the highest current density (145.42 $\mu\text{A cm}^{-2}$) when compared with the BDD (+1.19 V and 127.44 $\mu\text{A cm}^{-2}$) and GC (+1.15 V and 137.77 $\mu\text{A cm}^{-2}$). The current densities were calculated using the geometric area of the electrode surfaces. For PMA, the GC (+1.28 V) and SPE (+1.29 V) show the potential response similar, but the GC show the highest current density (376.22 $\mu\text{A cm}^{-2}$) when compared with the BDD (229.70 $\mu\text{A cm}^{-2}$) and SPE (252.37 $\mu\text{A cm}^{-2}$). The difference of current density of the GC and SPE does not make the GC advantageous because this electrode needs to go through a pre-treatment step each time it is used, which is not necessary for the SPE because after each use the electrode is disposed thereby gaining time. In the case of the MDMA/PMA, the SPE exhibits the optimal voltammetric response (88.99 $\mu\text{A cm}^{-2}$ MDMA/89.97 $\mu\text{A cm}^{-2}$ PMA) and lowest overpotential (+0.97 V MDMA/+1.26 V PMA) when compared with the BDD (+1.15 V and 71.65 $\mu\text{A cm}^{-2}$ MDMA/+1.45 V and 82.80 $\mu\text{A cm}^{-2}$

PMA) and GC (+1.18 V and 77.75 $\mu\text{A cm}^{-2}$ MDMA/+1.51 V and 83.34 $\mu\text{A cm}^{-2}$ PMA). The SPE was chosen since it exhibits the best electrochemical response, being an electrode for easy handling, low cost and high reproducibility.

Next, the effect of scan rate upon the electrochemical oxidation were explored for the target analytes in PBS (pH 7). A plot of peak height against the square-root of scan rate was constructed for PMA ($I_p/A = 7.10 \times 10^{-5} \text{ A (V s}^{-1})^{-0.5} + 1.21 \times 10^{-6} \text{ A}$, $R^2 = 0.997$), MDMA ($I_p/A = 3.05 \times 10^{-5} \text{ A (V s}^{-1})^{-0.5} + 1.17 \times 10^{-6} \text{ A}$, $R^2 = 0.993$) and MDMA/PMA ($I_p/A = 2.87 \times 10^{-5} \text{ A (V s}^{-1})^{-0.5} + 6.61 \times 10^{-8} \text{ A}$, $R^2 = 0.996$)/ $I_p/A = 3.49 \times 10^{-5} \text{ A (V s}^{-1})^{-0.5} - 7.10 \times 10^{-7} \text{ A}$, $R^2 = 0.990$) and found to be linear in all cases indicating a diffusional electrochemical process. The effect of the pH on the voltammetric response (differential pulse voltammetry) were also explored for the target analytes PMA, MDMA and MDMA/PMA in various buffers. Fig. SI-2† shows the voltammograms for the SPE in (A) 500 $\mu\text{g mL}^{-1}$ PMA/PBS, (B) 500 $\mu\text{g mL}^{-1}$ MDMA/PBS and (C) 500 $\mu\text{g mL}^{-1}$ PMA + 250 $\mu\text{g mL}^{-1}$ MDMA/PBS (pH 7) over a range of pH (2–12). It can be seen that the oxidative peak exhibits a potential at more negative offset to regions with increasing pH (acid to basic) and a fall in current values of the oxidative peak at basic pH with a linear relationship for PMA of ($E_p/V = -0.03 \text{ V per pH} + 1.27 \text{ V}$; $R^2 = 0.945$) with a gradient of 28.30 mV per pH that value is close to that expected for a 1 proton and 2 electron process (30 mV per pH unit at 25 °C), for MDMA to ($E_p/V = -0.02 \text{ V per pH} + 1.00 \text{ V}$; $R^2 = 0.988$) with a gradient of 20.50 mV per pH which is close to that expected for a 1 proton and 3 electron process (20 mV per pH unit at 25 °C) and MDMA/PMA ($E_p/V = -0.02 \text{ V per pH} + 1.01 \text{ V}$; $R^2 = 0.978$)/($E_p/V = -0.03 \text{ V per pH} + 1.34 \text{ V}$; $R^2 = 0.993$) sustaining the response of individually analysed analytes. The appearance of one new peak (between +0.6 and +0.7 V) above pH

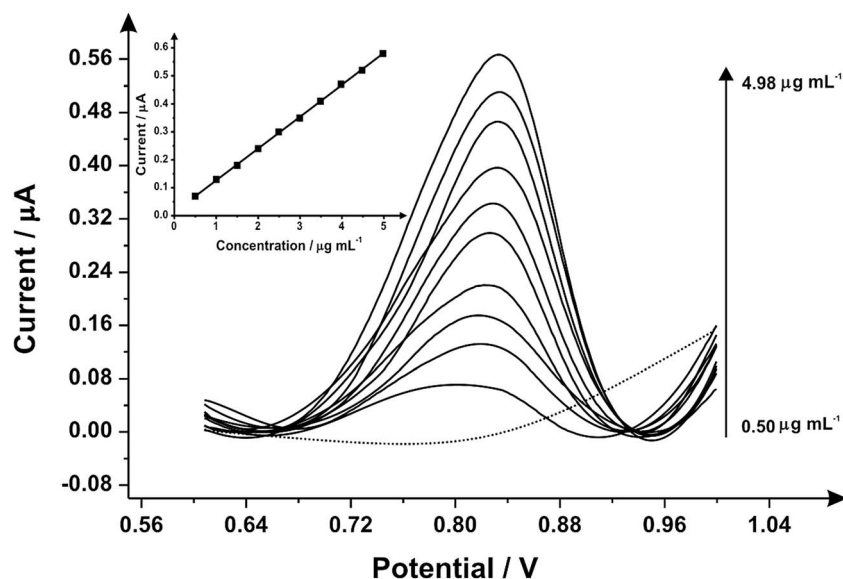


Fig. 2 Differential pulse voltammograms obtained utilizing the screen-printed graphite electrodes by adding aliquots of MDMA (pH 7.0) at concentrations in the range of 0.50–4.98 $\mu\text{g mL}^{-1}$ (in phosphate buffer supporting electrolyte); the dotted line represents a blank. (inset) An analytical curve corresponding to the anodic peak for the oxidation of MDMA over the concentration range (E -step: 0.002 V; E -pulse: 0.1 V; t -pulse: 0.05 s; scan rate: 0.005 V s^{-1} ; t -eq. 1 s).



9 is related with the acid–base properties of the MDMA and is probably due to the existence of an electron lone-pair.³⁵ The pH of 7 was chosen due to the good electrochemical responses compared with other pHs.

Differential pulse voltammetry was next utilised to explore the electroanalytical efficiency of the proposed protocol through utilising the SPEs by adding aliquots of MDMA (pH 7.0) at concentrations over the range of 0.50–4.98 $\mu\text{g mL}^{-1}$ into a pH 7 phosphate buffer; Fig. 2 shows the voltammetry. Through the additions of MDMA there is an increase in the current intensity of the oxidation peak and a small displacement of potential into positive regions. The insert graph shows the linear calibration curve obtained from the differential pulse voltammograms ($I_p/\mu\text{A} = 0.11 \text{ A mL g}^{-1} [\mu\text{g mL}^{-1}] + 0.01 \mu\text{A}$; $R^2 = 0.999$ and $N = 3$) with a limit of detection (3σ) found to correspond to 0.04 $\mu\text{g mL}^{-1}$ and a relative standard deviation (%RSD) of 2.14%. Again note that each additions is made with a new SPE. Various methods have been used before in the detection and quantification of MDMA^{45–48} and Table 1 summarises these with the results of this work also presented and compared demonstrating our approach is competitive.

Fig. 3 illustrates the voltammetric behaviour of the SPEs through the addition of aliquots of PMA (in phosphate buffer pH 7.0) at concentrations over the range of 0.50–4.98 $\mu\text{g mL}^{-1}$. The linear calibration curve of the anodic current of oxidation peak as a function of PMA concentration is presented in the insert of Fig. 3 ($I_p/\mu\text{A} = 0.21 \text{ A mL g}^{-1} [\mu\text{g mL}^{-1}] + 0.07 \mu\text{A}$, $R^2 = 0.999$ and $N = 3$) with a limit of detection (3σ) found to correspond to 0.03 $\mu\text{g mL}^{-1}$ and relative standard deviation (%RSD) of 4.3. Last, the analytical performance of MDMA/PMA using SPEs were explored (see Fig. 4) with additions made over the range of 2.00–19.60 $\mu\text{g mL}^{-1}$ for MDMA ($I_p/\mu\text{A} = 0.09 \text{ A mL g}^{-1} [\mu\text{g mL}^{-1}] + 0.08 \mu\text{A}$; $R^2 = 0.999$; $N = 3$) and 2.00–19.60 $\mu\text{g mL}^{-1}$ for PMA ($I_p/\mu\text{A} = 0.18 \text{ A mL g}^{-1} [\mu\text{g mL}^{-1}] + 0.03 \mu\text{A}$; $R^2 = 0.999$; $N = 3$). The limit of detection (3σ) was found to correspond to 0.14 $\mu\text{g mL}^{-1}$ for PMA (Fig. 4 inset) and 0.25 $\mu\text{g mL}^{-1}$ for MDMA (Fig. 4 inset) and relative standard deviations (%RSD) of 3.2% MDMA and 3.8% for PMA. Table 1 summarises these electro-analytical results and benchmarks these against the current literature demonstrating our work is highly competitive.

Alternative approaches for the sensing of MDMA/PMA

Raman spectroscopic. Raman spectroscopy is commonly utilised for rapid and reliable characterisation in the literature. Raman spectra of MDMA, PMA and a MDMA/PMA mixture are presented in Fig. SI-3.† The MDMA spectrum shows a response similar that reported in the literature.^{49,50} The Raman spectrum of PMA is not found in the literature, but it is possible to identify peaks similar to the spectra of amphetamine which is expected since PMA is an amphetamine analogue differing only by the ether group attached to the aromatic ring. The application of Raman spectroscopy towards the MDMA and PMA mixture (see Fig. SI-3B†), however does not give a satisfactory response because of poor resolution between the two signals suggesting that utilization of Raman spectroscopy towards the simultaneous detection of MDMA and PMA is not practicable.

Table 1 Analytical methods currently reported in the literature for the detection of the target analytes

Analyte	Analytical method	Matrix	Analytical linear range	Limit of detection	Reference
PMA	Gas chromatography equipped with a nitrogen phosphorus detector	Peripheral and heart blood	0.125 mg L ⁻¹ to 1.0 mg L ⁻¹	N/A	51
MDMA	Square wave voltammetry	Supporting electrolyte	8–45 μM	1.2 μM	35
		Human serum	12–45 μM	2.4 μM	
PMA	Capillary electrophoresis with diode array	Plasma	50–5000 ng mL ⁻¹	20.92 ng mL ⁻¹	52
		Urine		24.26 ng mL ⁻¹	
MDMA	Turn-on fluorogenic probe	Water	N/A – not disclosed	0.13 μM	53
MDMA	Thin layer chromatography/fluorescence	Urine	N/A – not disclosed	50 ng	54
MDMA	HPLC–chemiluminescence	Plasma	0.01–1.0 ng mL ⁻¹	3 ng mL ⁻¹	55
		Hair root	0.10–10 ng mL ⁻¹	17 ng mL ⁻¹	
		Hair shaft	0.10–10 ng mL ⁻¹	14 ng mL ⁻¹	
MDMA	Cyclic voltammetry – dip coating/spin coating	KCl (0.1 mol L ⁻¹)	4.2–48 $\mu\text{mol L}^{-1}$	3.5/2.7 $\mu\text{mol L}^{-1}$	56
MDMA	This work	Phosphate buffer	0.50–4.98 $\mu\text{g mL}^{-1}$	0.04 $\mu\text{g mL}^{-1}$	N/A
PMA			0.50–4.98 $\mu\text{g mL}^{-1}$	0.03 $\mu\text{g mL}^{-1}$	
MDMA/PMA (simultaneous)			2.00–19.60 $\mu\text{g mL}^{-1}$ (for both)	0.25 μM/0.14 $\mu\text{g mL}^{-1}$	



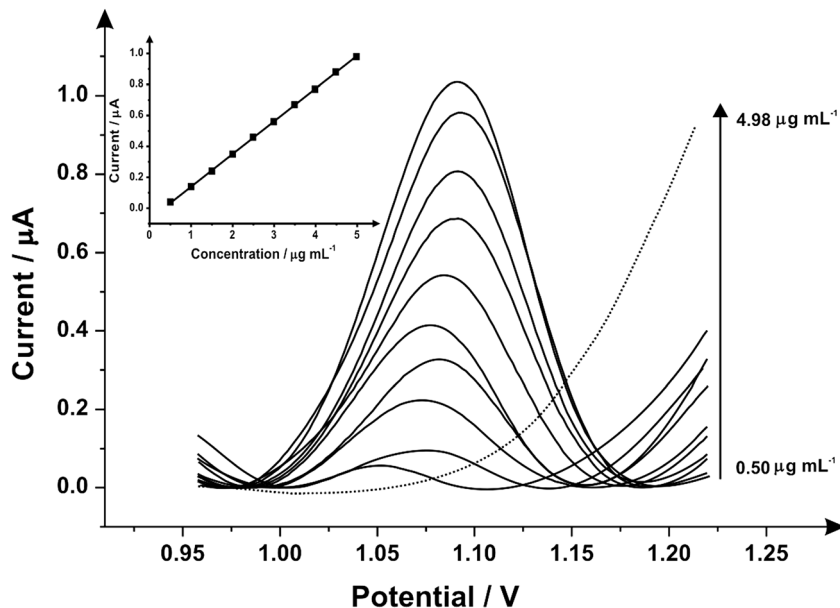


Fig. 3 Differential pulse voltammograms of the screen-printed graphite electrode by adding aliquots of PMA (in phosphate buffer pH 7.0) at concentrations in the range of 0.50–4.98 $\mu\text{g mL}^{-1}$ (in phosphate buffer supporting electrolyte); the dotted line represents a blank. (inset) An analytical curve corresponding to the anodic peak for the oxidation of PMA over the concentration range (E -step: 0.002 V; E -pulse: 0.1 V; t -pulse: 0.05 s; scan rate: 0.005 V s^{-1} ; t -eq. 1 s).

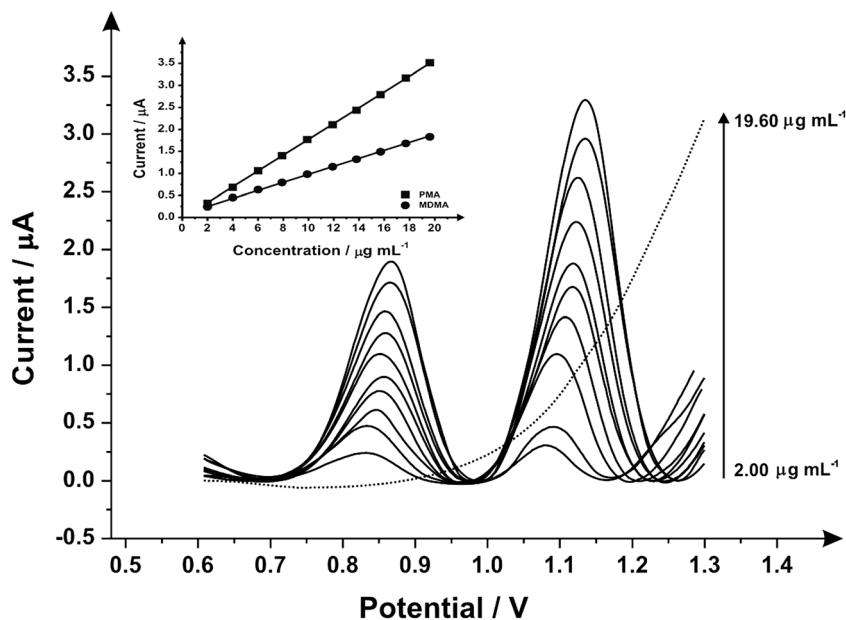


Fig. 4 Differential pulse voltammograms obtained utilizing the screen-printed graphite electrodes by adding aliquots of MDMA/PMA (in phosphate buffer pH 7.0) at concentrations in the range of 2.00–19.60 $\mu\text{g mL}^{-1}$ (in phosphate buffer supporting electrolyte); the dotted line represents a blank. (inset) An analytical curve corresponding to the anodic peak for the oxidation of PMA and MDMA over the concentration range (E -step: 0.002 V; E -pulse: 0.1 V; t -pulse: 0.05 s; scan rate: 0.005 V s^{-1} ; t -eq. 1 s).

Presumptive colour tests. Presumptive colour tests for the two analytes were carried out according to the United Nations recommended guidelines.³⁹ The following standard presumptive tests were applied in this study: (i) Marquis test; (ii) Mandelin test; (iii) Simon's test and (iv) Robadope test. The preparation of the reagents and test procedure is detailed in the Experimental section. A solution of each reference standard (10

mg mL^{-1}) was prepared in methanol and 1–2 drops placed into a dimple well of a spotting tile. The required presumptive test reagent (1–2 drops) was then added and any colour change or other noticeable effect occurring immediately on addition of the reagents was noted and observations were made again after 5 min. The results (see ESI, SI-4[†]) indicated that the secondary amine, MDMA, gave a positive reaction with Marquis, Mandelin



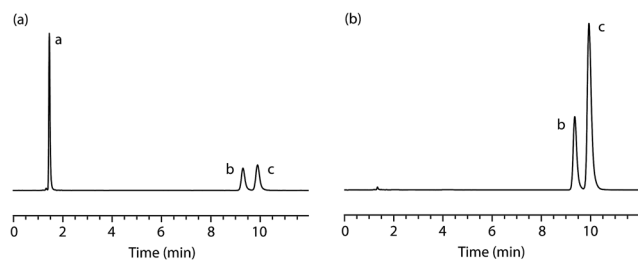


Fig. 5 (a) Representative chromatogram of a solution containing PMA ($10 \mu\text{g mL}^{-1}$, peak b) and MDMA ($10 \mu\text{g mL}^{-1}$, peak c) obtained using an ACE 3 C18 column ($150 \text{ mm} \times 4.6 \text{ mm i.d.}$, particle size: $3 \mu\text{m}$); flow-rate: 1.2 mL min^{-1} ; mobile phase: aqueous potassium dihydrogen phosphate buffer (0.05 M , $\text{pH } 3.2 \pm 0.02$) : acetonitrile ($90 : 10\% \text{ v/v}$); detector wavelength (UV): 210 nm ; (b) representative chromatogram of test mixture ($10 \mu\text{g mL}^{-1}$) containing PMA and MDMA ($30 : 70\% \text{ w/w}$) obtained using an ACE 3 C18 column ($150 \text{ mm} \times 4.6 \text{ mm i.d.}$, particle size: $3 \mu\text{m}$); flow-rate: 1.2 mL min^{-1} ; mobile phase: aqueous potassium dihydrogen phosphate buffer (0.05 M , $\text{pH } 3.2 \pm 0.02$) : acetonitrile ($90 : 10\% \text{ v/v}$); detector wavelength (UV): 210 nm . The t_0 was determined from the t_R of a solution of uracil ($10 \mu\text{g mL}^{-1}$, peak a).

and Simon's reagents, whilst the primary amine, PMA, gave a positive reaction with the Robadope reagents. Solutions containing $25 : 75\% \text{ v/v}$; $50 : 50\% \text{ v/v}$ and $75 : 25\% \text{ v/v}$ (PMA : MDMA) were prepared by mixing appropriate volumes of solutions (10 mg mL^{-1}) of the reference standards in methanol and screened against the standard tests. The data (see SI-5†) indicated that in all cases the test reagents (when compared to the pure standards) confirmed the presence of MDMA (even at concentrations *circa.* $25\% \text{ v/v}$), however, the presence of PMA (indicated by a positive reaction with Robadope reagent) was not as easy to discriminate using this method even when present at high concentrations (*circa.* $75\% \text{ v/v}$), demonstrating that the utilisation of this presumptive colour test in particular for products containing these two compounds is potentially problematic and cannot be relied upon in these cases. The simulated sample of MDMA adulterated with PMA ($30\% \text{ w/w}$), was screened against the standard tests and observed to give analogous results to the mixture containing $25 : 75\% \text{ w/w}$ (PMA : MDMA). The sample gave a positive reaction with

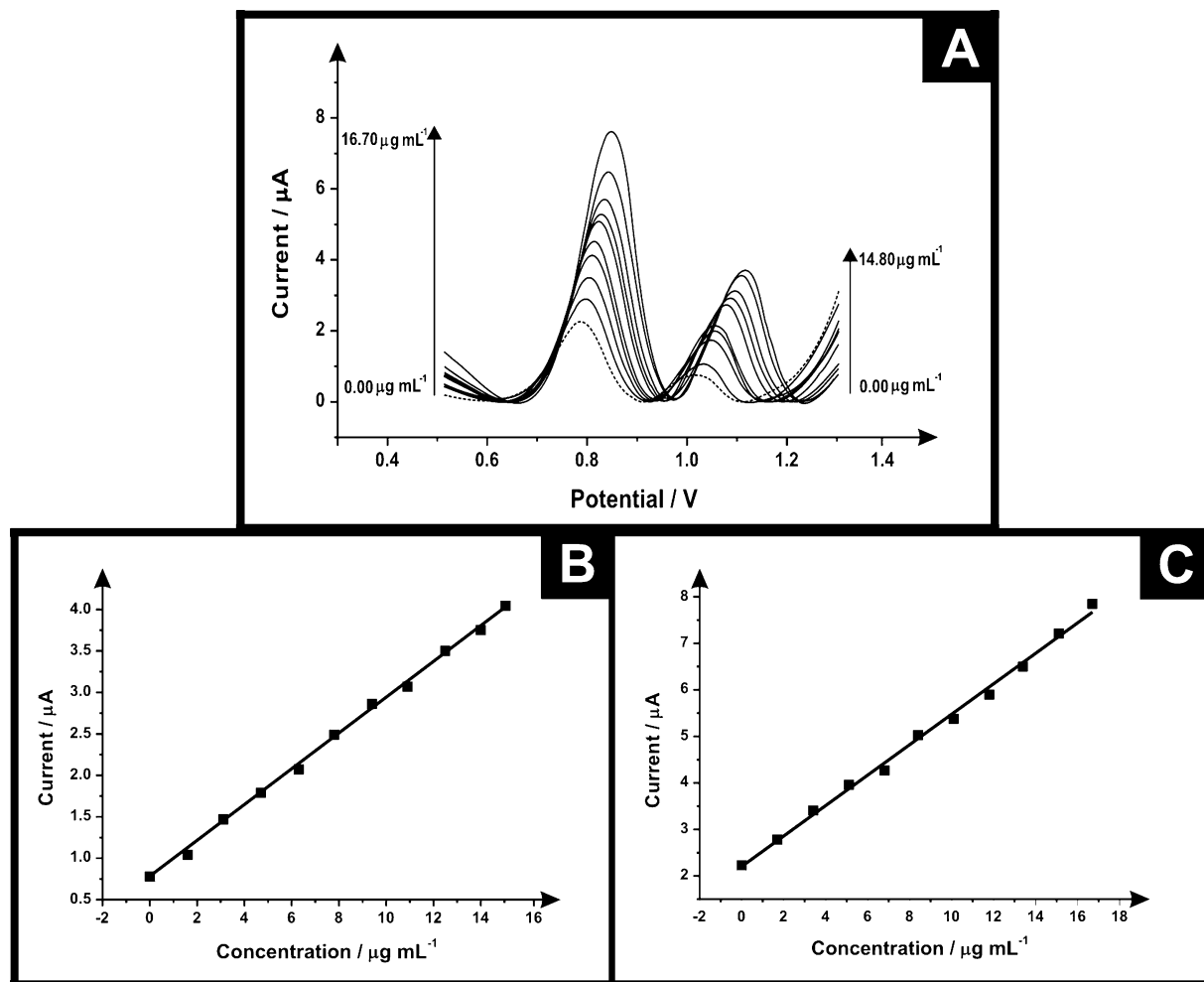


Fig. 6 Differential pulse voltammograms following a series of standard additions of "ecstasy" over the range $0.00\text{--}14.80 \mu\text{g mL}^{-1}$ and $0.00\text{--}16.70 \mu\text{g mL}^{-1}$ for PMA and MDMA respectively (in phosphate buffer supporting electrolyte); the dotted line represents a blank. (inset) An analytical curve corresponding to the anodic peak for the oxidation of (B) MDMA and (C) PMA over the concentration range ($E\text{-step}$: 0.002 V ; $E\text{-pulse}$: 0.1 V ; $t\text{-pulse}$: 0.05 s ; scan rate: 0.005 V s^{-1} ; $t\text{-eq.}$ 1 s).



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