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Enhancement in sample collection for the detection of MDMA using a novel planar SPME (PSPME) device coupled to ion mobility spectrometry (IMS)

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Trace detection of illicit drugs challenges the scientific community to develop improved sensitivity and selectivity in sampling and detection techniques. Ion mobility spectrometry (IMS) is one of the prominent trace detectors for illicit drugs and explosives, mostly due to its portability, high sensitivity and fast analysis. Current sampling methods for IMS rely on wiping suspected surfaces or withdrawing air through filters to collect particulates. These methods depend greatly on the particulates being bound onto surfaces or having sufficient vapour pressure to be airborne. Many of these compounds are not readily available in the headspace due to their low vapour pressure. This research presents a novel SPME device for enhanced air sampling and shows the use of optimized IMS by genetic algorithms to target volatile markers and/or odour signatures of illicit substances. The sampling method was based on unique static samplers, planar substrates coated with sol-gel polydimethyl siloxane (PDMS) nanoparticles, also known as planar solid-phase microextraction (PSPME). Due to its surface chemistry, high surface area and capacity, PSPME provides significant increases in sensitivity over conventional fibre SPME. The results show a 50–400 times increase in the detection capacity for piperonal, the odour signature of 3,4-methylenedioxymethamphetamine (MDMA). The PSPME-IMS technique was able to detect 600 ng of piperonal in a 30 s extraction from a quart-sized can containing 5 MDMA tablets, while detection using fibre SPME-IMS was not attainable.

In a blind study of six cases suspected to contain varying amounts of MDMA in the tablets, PSPME-IMS successfully detected five positive cases and also produced no false positives or false negatives. One positive case had minimal amounts of MDMA resulting in a false negative response for fibre SPME-IMS.

Keywords: illicit drugs; ion mobility spectrometry; 3,4-methylenedioxymethamphetamine (MDMA); odour signatures; planar solid phase microextraction

Introduction

Sensitive methods for the fast detection of illicit drugs that can be made in the field by non-scientific personnel would benefit the areas of homeland security and justice science. The very low vapour pressure of many illicit drugs such as amphetamines, cannabis, LSD, cocaine, heroin and their related compounds, requires liquid extraction methods accompanied by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) analysis techniques.[1] Solid phase microextraction (SPME) has become an important and widespread sampling and extraction method that is integrated directly or through an interface with the injection ports of GC and LC instruments. This technique, first introduced by Pawliszyn in 1990, is now an essential sampling tool for a wide variety of applications including many within forensic chemistry.[2] The SPME technique relies on cylindrical geometry fibres coated with an extraction phase consisting of cross-linked polymers. The fibres are used to isolate and concentrate analytes from aqueous and gas-phase matrices in two principal modes: direct immersion (DI) and headspace (HS) configurations. Both modes are based on equilibrium distributions of the analyte compounds between the fibre, the sampling matrix and the sample itself, in the case of HS sampling.

Extensive research has been devoted to the investigation of sensitive analysis of illicit drugs from body fluids such as urine, serum, saliva and sweat using DI SPME. Commercial fibres and pre-treated chemically derivatized fibres were immersed inside the suspected medium for efficient extraction.[3,4,5,6]

A headspace SPME (HS-SPME) configuration has been reported for the detection of illicit drugs from hair samples by Musshoff *et al*. who developed a fully automated procedure for the determination of cannabinoids and amphetamines from this matrix.[7,8] This method included four steps: (1) pre-treatment wash and alkaline hydrolysis of hair samples, (2) HS-SPME sampling of the emitted vapours, (3) on-fibre derivatization, (4) SPME-GC/MS analyses. Cannabinoids were also analysed by Rodrigues *et al*. using HS-SPME for the extraction of vapours emitted following the basic extraction of pre-treated head hair samples, using GC/MS-single ion monitoring (SIM) analysis without further derivatization.[9]

The HS-SPME technique has proven to be an efficient and sensitive pre-concentration sampling method, mainly because it avoids the need for organic solvents, and has been applied for drug sampling from suspected evidence, and has been used for drug sampling from suspected evidence. Methamphetamine and its

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impurities from south-east Asian methamphetamine tablets were better extracted by HS-SPME than by different liquid extractions, as was demonstrated by Koester *et al*.[10] Brown *et al*. converted the amine salt of amphetamine-type drugs into their volatile free bases using triethylamine. For improved chromatographic performance, the headspace above the drug was sampled by a SPME fibre that had been previously derivatized with alkylchloroformates.[11] Lorenzo *et al*. used SPME-GC/MS to characterize the headspace fingerprint of 2,4,6-trinitrotoluene (TNT), Compostion-4 (C4), (3,4-methylenedioxymethamphetamine) MDMA and cocaine, explosives and illicit drugs to aid in the investigation and understanding of canine odour detection.[12,13]

Instruments based on ion mobility spectrometry (IMS) have become some of the most prominent explosive trace detectors with more than 10 000 commercial and 50 000 military instruments already installed. This is due to their excellent sensitivity, high-speed detection (less than 10 s), ease of use with simplified data interpretation and relatively low cost. The current sample collection technique relies on pumping or wiping suspected surfaces for residues or particulates of drugs or explosives using a filter or swab, respectively.[14]

Perr *et al*. developed a novel interface, designed as an add-on accessory, which enables an alternative sample to be introduced into IMS instruments using SPME fibres.[15] Introduction of SPME fibres into the IMS instrument allowed for the analysis of vapours rather than particles, the original application of this technique. A combination of both techniques, SPME-IMS, allowed for significant improvements in both detection sensitivities and analysis time. The performance of the combined techniques was demonstrated with explosives.

Recently, Lai *et al*. reported, for the first time, the applicability of SPME-IMS to the detection of illicit drugs from actual cases,[16] by demonstrating the extraction of methyl benzoate (MB), piperonal, α-pinene and β-pinene, and limonene, the well-known odour signatures of cocaine,[17] MDMA,[18] and marijuana[18] respectively, from evidence in drug seizure cases. Since the compounds mentioned above are not detectable under the default operating conditions provided by the IMS manufacturers, a genetic algorithm (GA) IMS optimization technique was employed, yielding sensitivity with limits of detection (LODs) in the low nanogram range for each compound. The method was tested in the presence of different volatile interferences emanating from goods typically transported in enclosed spaces such as cargo. Findings from the above studies demonstrated that SPME-IMS is a very promising technique for rapid field detection of drugs.[19]

More recently, Guerra *et al*. developed a novel device based on the HS-SPME.[20] The device is based on a planar glass substrate of rectangular geometry, 3.8 × 2.5 cm to accommodate introduction into an IMS inlet, coated with polydimethyl siloxane (PDMS) film or alternatively with sol-gel PDMS nanoparticles. Both modes of planar SPME (PSPME) devices were used for the sampling of explosives and compared with commercial PDMS SPME fibres under the same experimental conditions. The analysis of the desorbed vapours sampled by the different SPME devices, the fibre and both planar geometries, was conducted using an IMS as a detector. Better capacities, LOD's and extraction efficiencies were achieved using both PSPME devices compared to SPME fibres for the target compounds. Moreover, the sol-gel PDMS device yielded better results due to its higher surface area, compared to the PDMS film.

Since the late 1990s, the proportion of street Ecstasy drug tablets containing MDMA as an active compound (chemical structure shown in Figure 1a) has increased to around 80–90%.[21] The high polarity and the low vapour pressure of MDMA, like most amphetamine-type amine salt drugs, made direct headspace (HS-SPME) detection of MDMA tablets ineffective. However, piperonal (Figure 1b), a common starting material in MDMA synthesis, has been previously reported to be one of the dominant characteristic volatile compounds of MDMA tablets.[16,22] Although piperonal has a high vapour pressure (1.0 mmHg at 87 °C), sensitive detection and consequently shorter sampling times are still considered essential for field applications.

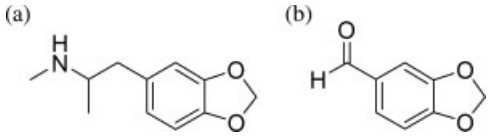

Figure 1. 3,4 methylenedioxymethamphetamine (MDMA) (a) and piperonal (b) molecular structures.

Detection of vapours emanating from hidden illicit drugs in large open or closed spaces has been a challenging task. The detection of trace levels of target compounds in a complex and high-throughput environment requires a highly sensitive and selective analytical technique as well as a fast sampling device. The research described here is aimed at overcoming this challenge by combining the planar sol-gel nanoparticle-based sampling device, PSPME, to an optimized IMS (GA) analysis technique. The utility of the PSPME-IMS-(GA) method was demonstrated in the detection of piperonal as a selective odour signature confirming the presence of MDMA drug, using standard solutions and suspected tablets from actual cases.

Experimental

Chemicals

Dichloromethane (DCM) 99.9% and HPLC-grade acetonitrile (ACN) were obtained from Fisher Scientific (Fair Lawn, NJ), piperonal 99% was obtained from Sigma-Aldrich (St Louis, MO) and drug case samples containing MDMA and/or other drugs, were sampled at the Miami Dade Police Department – Crime Laboratory Bureau (MDPD-CLB), while maintaining a strict chain of custody. Concentrated sulfuric acid, 96%, hydrogen peroxide, 30% and solid sodium hydroxide (NaOH) were purchased from Fisher Scientific. Vinyl-terminated PDMS (vt-PDMS) was purchased from Gelest (Morrisville, PA), methyltrimethoxysilane (MTMOS) (≥98%) from Fluka (Steinheim, Germany), poly (methylhydrosiloxane) (PMHS) from Sigma–Aldrich and trifluoroacetic acid (TFA) 99% from Acros (St. Louis, MO).

Instrumentation

An Itemiser 2 IMS (GE Securities, Wilmington, MA) was used for analysis of the MDMA target compound, piperonal, directly introduced by liquid spikes and following extraction by the planar SPME device and SPME fibre (100 µm, PDMS) from Supelco (Bellefonte, PA), from standard spikes and real drug case samples. An SPME-IMS interface[15] was made in-house (patent pending) and used for desorption of the SPME fibres. The operating conditions for the IMS and SPME-IMS interface are listed in Table 1. For piperonal detection, it was necessary to change the operating parameters on the IMS in order to achieve a response. The IMS variables were systematically optimized to cover a wide range of conditions

Table 1. Operating conditions in IMS and SPME-IMS interface

GE Itemiser 2 Operating Conditions	Piperonal
Ko ($cm^2/V \times s$)	1.51
Desorber temperature (°C)	215
Drift tube temperature (°C)	80
Sample flow (mL min^{-1})	500
Detector flow (mL min^{-1})	350
Polarity	+
Reagent gas	Nicotinamide
SPME-IMS interface operating conditions	
Interface temperature (°C)	260 ± 1
Warm-up time (h)	1

quickly and reliably using a systematic approach using a genetic algorithm (GA). Details on the GA approach and its advantages over a grid search and a random search approach have been previously reported.[16] To perform the optimization, the following parameters were varied: the drift tube temperature was varied between 40–90 °C at 10 °C increments, the drift gas flow rate (50–350 mL min^{-1} at 100 mL min^{-1} interval), the sample gas flow rate (500–3500 mL min^{-1} at 1000 mL min^{-1} interval), and dopant gases were air, nicotinamide, ammonia, and dichloromethane, tested in both positive and negative operating modes. The drift tube temperature was varied between 40–90 °C at 10 °C increments, the drift gas flow rate (50–350 mL min^{-1} at 100 mL min^{-1} interval), the sample gas flow rate (500–3500 mL min^{-1} at 1000 mL min^{-1} interval) and dopant gases were air, nicotinamide, ammonia and dichloromethane, tested in both positive and negative operating modes . The optimization results show that the detection of piperonal was possible at drift tube temperatures between 40 °C and 110 °C using air or nicotinamide in positive mode with little influence of the gas flow rates on the signal response. Nevertheless, the optimal response for piperonal was achieved under the operating conditions listed in Table 1.

Response curves resulting from IMS analysis of target compounds

The piperonal standard solutions were made from a stock solution of 1000 µg mL^{-1} piperonal in DCM. A volume of 2 µL each of 1, 2, 5, 8, and 10 µg mL^{-1} concentrations of piperonal was spiked onto filters (Smiths Detection, Mississauga, ON, Canada) and the piperonal monomer was analysed by the IMS. Piperonal has been reported to produce a proton-bound dimer at high concentrations, so realizing the extraction capabilities of PSPME, a second response curve was generated for this ion species, with the lowest concentration being the first observance of dimer formation. A volume of 2 µL each of 30, 40, 50, 100, 130 and 150 µg mL^{-1} of piperonal, diluted from the 1000 µg mL^{-1} stock, was also spiked onto filters and analysed by IMS. Triplicate analyses of each concentration were conducted and a response curve was generated by plotting mass (typically in the ng range) versus the cumulative signal output. From the equation of the best fit line, the mass detected by IMS following sampling using the fibre SPME and the PSPME was calculated.

Preparation of the PSPME device

The preparation of the sol-gel PSPME devices used in this study is detailed elsewhere.[20] Pre-cleaned microscope slides (Chase Scientific Glass, Vineland, NJ), 1 mm thick, were cut into 3.81 cm × 2.54 cm rectangular pieces. This glass substrate was immersed in a 2 : 1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide and placed in an oven for 20 min at 90 °C. The glass slides were rinsed with deionized water following removal of the cleaning solution and dipped in 1 M NaOH for 1 h and again rinsed with deionized water. The glass slides were dried in an oven at 120 °C for 12 h. The coating solution was prepared as follows: 6.40 g of vt-PDMS was dissolved in 8 mL of DCM then 3.42 mL MTMOS and 1.67 g PMHS were added to the mixture. Then 2.73 mL of TFA (5% water v/v) was added and the solution was mixed using a vortex mixer. The coating solution remained untouched for 30 min and each prepared glass was dipped in the coating solution for 1 h. The newly prepared extraction device was placed in a desiccator for 12 h, then dipped for 6 h in DCM. Gelation occurred for 12 h in an oven at 40 °C. The planar SPME device was conditioned in an oven under a nitrogen atmosphere for 1 h at 120 °C, 1 h at 240 °C and 3 h at 300 °C.

Sampling by PSPME was conducted by suspending the device above the headspace of gallon and quart-sized cans (All American Containers, Miami, FL), spiking the compounds with known concentrations, and immediately sealing the lid with a rubber mallet. These cans were preconditioned in an oven at 150 °C for over 24 hours to remove any volatiles from the cans themselves that could interfere with the extraction and analysis. Alternatively sampling by the SPME fibre was achieved by creating a hole in the lid of the can where an 11 mm stopper sleeve (Wheaton, Millville, NJ) could fit snugly and through which the fibre SPME was inserted and exposed for sampling immediately after the sample had been spiked and the can sealed.

The determination of equilibrium extraction times for the PSPME device and SPME fibre was as follows: 100 µL of 100 µg mL^{-1} piperonal solution was spiked into gallon cans and sampled at different time intervals from 3 to 10 min. Once each sampling was complete, the PSPME device was removed and introduced into the IMS via the sample desorber. The PSPME was conditioned in a GC oven at 150 °C and a blank of the PSPME device was obtained prior to each sampling. After sampling with the fibre, it was removed and the analytes were introduced into the IMS by thermal desorption via the SPME-IMS interface.[15] The fibre was conditioned in the injection port of the GC at 250 °C and a blank of the fibre was obtained prior to each sampling.

A comparison of the extraction efficiency of piperonal by both SPME types was conducted under strict experimental conditions by sampling for only 6 min at a sampling distance of 20 cm from the emitting source, 2 and 5 µg spikes (100 µL spikes each of 20 and 50 µg mL^{-1} piperonal, respectively, in a volatile solvent) within a metal gallon can of 0.12 m^2 surface area.

Sampling of seized drugs

Five tablets known to contain MDMA were placed in quart-sized cans, sealed and allowed to stand for 48 hours to ensure equilibrium extraction conditions. Then PSPME devices were used to sample the headspace for the following time intervals: 0.5, 1, 3, 5, 8.5, 9.5, 11, and 12 min. In a separate experiment, the extraction efficiency of both the PSPME and the fibre SPME were tested in relation to the number of tablets in the can. Cans containing 1, 3, 5 and 10 MDMA tablets were sampled by both SPME and PSPME for 15 min, allowing for 30 min equilibration between the sample and the headspace between analyses. This experiment was conducted in triplicate for the PSPME device and in duplicate for

the fibre. The results from these two experiments dictated the best sampling parameters for further blind tests involving suspected MDMA cases. For the final on-site experiment, six actual drug cases were selected. Some contained MDMA (confirmed by GC/MS) and others did not contain the drug. Five tablets of each suspected drug case were allowed to equilibrate inside a quart-sized can overnight, followed by 15 min extraction time and IMS analysis. The composition of the drug cases was revealed only after the SPME-IMS and PSPME-IMS results were reported.

Discussion

The PSPME-IMS method performance was tested using piperonal standard solutions and with actual cases containing MDMA tablets. The performance was evaluated and compared with the commercial PDMS SPME fibre and the amounts of piperonal detected by both devices were quantified using response curves of standard solutions.

Response curves

Piperonal detected by IMS following absorption on each device matrix, SPME fibres and PSPME was quantified through the use of response curves obtained by adding freshly prepared standard solutions onto filters followed by IMS analysis. In this study two separate complementary response curves, each for a different product ion, monomer and dimer, served for quantification of the detected piperonal under the same IMS operating conditions. As the vapour concentration of the analyte increases in the IMS ion source, a protonated monomer product ion first appears, with a corresponding loss in the reactant ion intensity. With further increase in the analyte concentration, a second product ion (protonated dimer) appears through a stepwise clustering phenomenon at the expense of both the reactant ions and the monomer product ions.[23] The monomer response curve (Figure 2a) exhibited linear regression in the range of 2–20 ng for piperonal with a limit of detection (LOD) of 2 ng mainly due to high background level. The ionization of gaseous molecules is facilitated in positive mode and in low temperature IMS operation. The precision of the monomer analysis method varied from 50% for close to the LOD concentrations to 2% for the highest concentration in this dynamic range.

The response curve for the dimer product ions was also determined for use in the quantification of the total detected piperonal amounts emitted from the MDMA tablets. The response curve obtained for the dimer exhibited a logarithmic regression curve in the 60–300 ng range for piperonal (Figure 2b). The intensity response is expressed in logarithmic format and was previously demonstrated by Eiceman *et al*. for better categorization of different molecule classes, mainly in low-temperature drift-tube analyses.[24]

Evaluation of PSPME-IMS method performance using standard solutions

Both devices, PSPME and SPME fibre, were introduced into gallon-sized cans, spiked with 100 µL of a high concentration piperonal solution, 1000 µg/ml (100 µg piperonal), for a 10 min extraction time, and analysed immediately by IMS. The plasmagrams shown in Figure 3 demonstrate the results obtained from headspace sampling using both devices. The monomer ion peak for piperonal is found at a drift time of 8.3 ± 0.05 ms and the reduced mobility

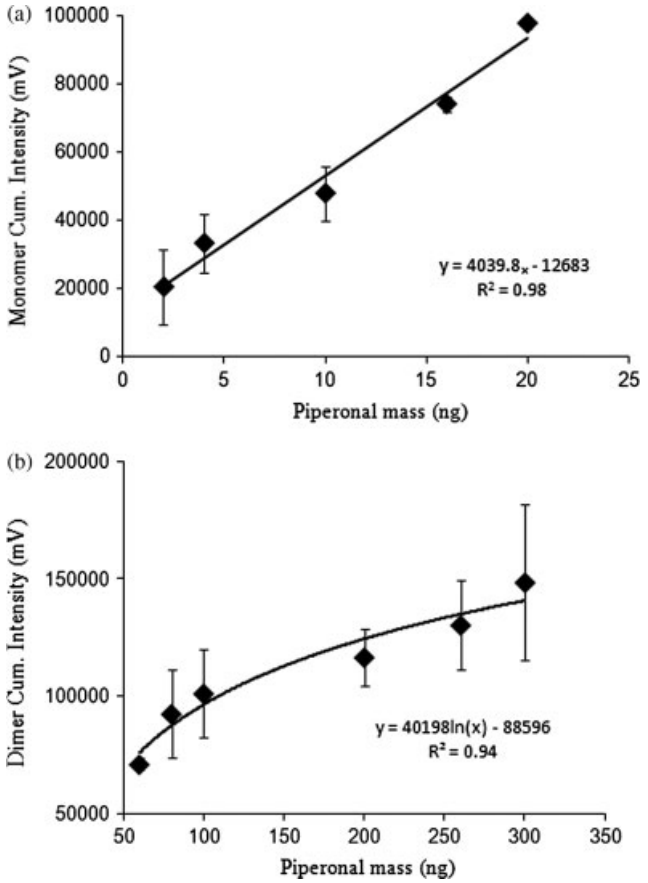

Figure 2. Piperonal monomer (a) and dimer (b) product ion calibration curves.

value of the product ion is $K_0 = 1.51\ cm^2\ V^{-1}\ s^{-1}$.[20] As the monomer ions formed, the reactant ion peak (RIP) intensity decreased as expected. A significantly higher cumulative intensity is observed for all the scans of the piperonal peak as well as for the highest signal peak when sampling the headspace using PSPME in comparison to the SPME fibre. At higher concentrations, the observed decrease in peak intensity for the monomer shown for PSPME corresponds with the formation of a proton-bound dimer ion. Both the higher monomer response as well as the formation of a dimer measured by the PSPME device confirms the higher piperonal extraction efficiency over the SPME fibre.

Ideally, spiking a known mass of analyte dissolved in a volatile solvent inside a closed container can produce a headspace with the maximum concentration being the mass of the spiked compound divided by volume of the headspace but, in practice, lower concentrations should be expected. Uncontrolled processes of unspecific adsorption/absorption to surfaces are expected to decrease the available amount of the spike. The experimental parameters can influence the distribution coefficient of the analyte fraction absorbed or remaining in the vapour. A SPME sampling of the headspace created by spiking standard mixtures (including a solvent) will probably result in the solvent molecules adsorbing/absorbing into the fibre. The volatility of both, the target compound and solvent, the sampling time and/or the sampling temperature may also result in some displacement of the target compounds by solvent molecules thus decreasing the extraction efficiency of a specific target analyte. When considering the capacity of the specific SPME device,[25] greater solvents effects are encountered when

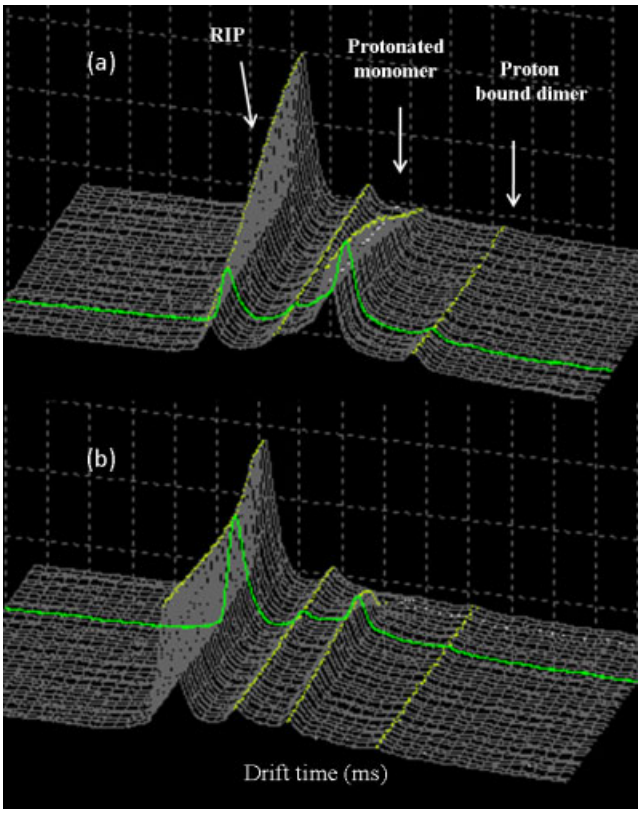

Figure 3. Plasmagrams of piperonal intensities response obtained by PSPME device (a) and SPME fibre (b).

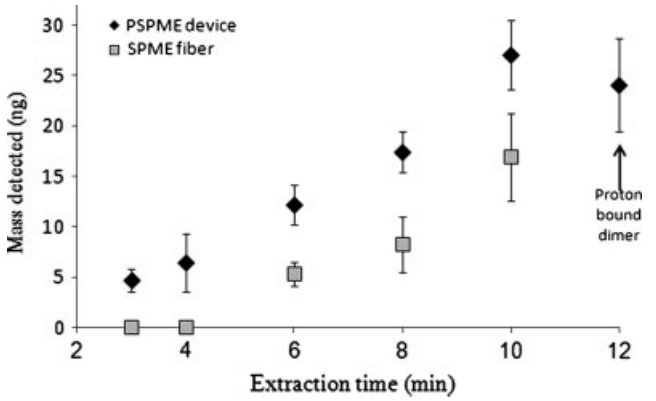

Figure 4. Extraction curves for PSPME device versus SPME fibre from gallon-sized cans spiked with 10 μg of piperonal.

Table 2. Extraction efficiencies measured by PSPME device and SPME fibre inside gallon-sized cans containing 2 μg and 5 μg of piperonal

	PSPME device		SPME fibre	
Mass of piperonal spiked (μg)	2	5	2	5
Mass of piperonal detected (ng)	1.5 ± 1.1	4 ± 0.4	ND*	ND*

* ND – not detectable

sampling with the fibre compared to the PSPME device. When sampling MDMA tablets from an actual case with the PSPME device, solvent effects can be minimized in comparison with sampling dilute standard solutions of piperonal, but may be replaced by other overwhelming volatile components emitted from the MDMA tablets depending on manufacturing procedures for the illicit drug.

The mass detected by IMS versus extraction time was tested and evaluated by sampling lower concentrations of piperonal, 100 μL of a 100 μg mL^{-1} solution (10 μg piperonal), using both devices. The devices were allowed to sample the vapours for different extraction times immediately following the spike of piperonal into the can that ranged from 3 to 10 min. The results are shown in Figure 4 and represent the equilibrium curve for piperonal. Overall, a consistent increase in the intensity response was measured with both devices along the complete time range tested for extraction. The increasing trend in responses with time can be explained either by built-up vapour concentration inside the cans and/or gradual vapour absorption onto the devices. However, at all times tested, the PSPME device resulted in higher cumulative response intensity in comparison with the SPME fibres. Using the experimental conditions described above, in the shortest extraction time (3–4 min), the detection of piperonal was only achieved when the PSPME device was used. Identical measurements with a SPME fibre yielded no response, indicating lower extraction capability of the SPME fibre. The signal measured on PSPME at extraction times longer than 10 minutes was outside the linear dynamic range for the monomer product ion. The decrease in the response peak at 12 minutes extraction time was accompanied by the formation of the dimer product ion peak. The increase in the response intensity using both devices showed similar slope at the extraction time range of 4 min to 10 min. These results suggest similar profile adsorption kinetics on both devices under these experimental conditions. The overall amounts of piperonal detected were very low with maximum recovery of 0.3% of the original mass spiked for a 10 min PSPME extraction.

Considering an equilibrium process with SPME and the volatility of piperonal, this outcome is not surprising and could be attributed to one or more of the following: (1) high affinity of the piperonal molecules to the PSPME coating followed by an inefficient desorption stage at the IMS inlet; (2) displacement of the piperonal molecules from the coating by solvent molecules; (3) non-specific adsorption of piperonal onto the container surface; (4) tendency of piperonal molecules to remain in the headspace rather than partition into the coating – in other words, piperonal may have a small K_{fh} (partition coefficient between the SPME phase and the headspace phase) in this experimental setup. With regard to assumption (1), it has been our experience that piperonal samples extracted by the PSPME device produce a signal even at the second thermal desorption, although smaller than the first, while the piperonal on the fibre is completely desorbed after the first introduction into the IMS inlet. This is attributed to the higher mass loadings on the PSPME device as compared with the fibre SPME. The amounts of piperonal detected for the second desorption are not demonstrated in Figure 4 because the evaluation of PSPME device as a PSPME-IMS coupled method was planned to follow the recommended operating procedure of the instrument with one desorption only.

Table 2 lists the mass detected by IMS after extraction using both devices when sampling very low concentrations of piperonal close to IMS detection limits. A volume of 100 μL of 50 μg mL^{-1} and 20 μg mL^{-1} of piperonal solution (5 μg and 2 μg piperonal) were spiked into gallon-sized cans for 6 minutes of extraction time. Under these conditions, no piperonal alert could be achieved using the SPME fibres for sampling for either concentration tested. In

contrast, using PSPME devices recorded positive piperonal alerts for all measurements. An average amount of 4 ng piperonal was detected following absorption onto the PSPME phase in a 6 minute extraction for a 5 μg spike of the compound of interest. The absorbed average amount (N = 3) was found to be twice the amount of the method LODs. This result is also correlated to the absorbed average amount, 4.7 ng, measured for 10 μg piperonal in a 3 minute extraction, as presented in Figure 4. Similar average amounts measured in both experiments demonstrates that the equilibrium concentration had been reached in less than 3 minutes, leaving the extraction time as the dominant parameter for increased recovery.

The amount detected under the same conditions, following absorption from a 2 μg spike of piperonal, was slightly below that detected by the LOD analysis method. Extrapolated quantification at this concentration range yielded an average sampled amount of only 1.5 ng piperonal on the PSPME phase. Nevertheless, this amount generated a signal significantly greater than the PSPME blank samples, mainly due to lower background levels attained for the PSPME device than for IMS filters that were used for piperonal response curves. The repeatability between the three replicated experiments was found to be low, as expected, in correlation with the measured deviation determined for the LOD concentration of the IMS analysis method.

Theoretically, from the complete evaporation of a spike without any kind of unspecific adsorption processes, the maximum piperonal concentration inside of a gallon-volume container can be calculated. In practice, the vapour concentration is expected to be much lower. Applying this conservative calculation, the LODs for PSPME-IMS and SPME-IMS could both be estimated from the minimal theoretical concentration that could be measured by each device. A calculated LOD of 2.5 μg L^{-1} was obtained for the SPME-IMS complete method, while a significantly lower LOD of 0.5 μg L^{-1} was obtained for the PSPME-IMS novel method. Both LODs were determined by the 6 min extraction time measurements.

In all stages, the PSPME-IMS coupled technique showed a strong advantage over SPME-IMS in terms of enhanced capacity and higher sensitivity.

Evaluation of PSPME-IMS method performance on MDMA tablets

The PSPME-IMS method was applied to detect presumptively MDMA tablets from real cases using piperonal as the target odour signature for detection. In the headspace above MDMA tablets, although no additional solvents were used in the dilution, other possible volatiles interferences, as well as trace amounts of processing solvents, may still have been present following synthesis. In contrast with the finite source of piperonal vapours generated from diluted solutions of the analyte in volatile solvent, MDMA tablets can be considered as an infinite continuous vapour source of piperonal during timed experiment measurements.

A preliminary experiment with MDMA tablets aimed to determine the minimum extraction time which is required to approach equilibrium extraction conditions. This experiment was conducted by sealing five MDMA tablets (~1.5 g) originating from the same case, in quart cans for 48 h to equilibrate. The results are illustrated in Figure 5. The *x*-axis displays the extraction times, from 30 seconds up to 15 minutes and the *y*-axis demonstrates the cumulative amount detected by the IMS. Two peaks had been analysed for piperonal under these experiment conditions at all extraction times. The earlier peak, at 8.3 ± 0.05 ms drift

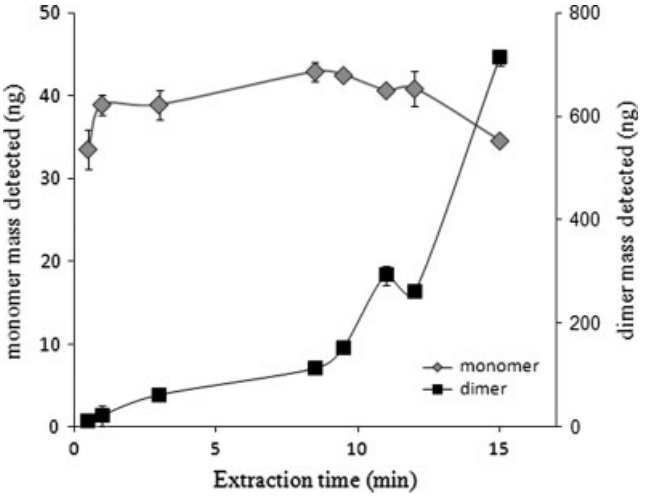

Figure 5. Equilibrium time curve of piperonal vapours emitted from MDMA tablets.

time, is determined to be the monomer product ions and the delayed peak, at 9.8 ± 0.05 ms drift time, represents the dimer product ion. Consistent detection of the dimer product ions at all extraction time points signalled high extraction efficiency for these conditions. The steep short increase from 30 s to 1 min stabilized at a constant response for the monomer product ions for all extraction time measurements, from 1 min up to 12 min, indicating its saturated detection level. At 15 minutes extraction time a small reduction in efficiency was measured. However, the initial small dimer product ions detected at only 30 seconds were followed by consistent increases with longer extraction times, yielding for 15 minutes the highest response. It can be assumed that extraction times longer than 15 minutes will yield higher extraction efficiencies. It was nevertheless decided in advance to apply an extraction time of 15 minutes for all MDMA tablets experiments to enable large-scale measurements in a reasonable time period.

The extraction efficiency of the PSPME device was evaluated using various quantities of tablets. Different quantities of MDMA tablets (ten, five, three and one tablets), all originating from the same case, were added to the quart cans and sealed for 24 h to equilibrate. The headspace generated inside was sampled by suspending the PSPME devices, and the SPME fibres for comparison, for 15 minute extraction times. The results are illustrated in Figure 6. Detectable levels of piperonal from the headspace generated by only 1 tablet were achieved by extracting with either device, with higher amounts detected from higher quantities of tablets. Both PSPME and SPME produced high responses for both the monomer and dimer product ions. However, overall, consistently higher extraction efficiencies were measured with the PSPME device than with the SPME fibres under all experimental conditions, both for the monomer and dimer product ions.

Saturated levels of monomer product ions were analysed following absorption by PSPME device by sampling the headspace generated from only 1 tablet while, with SPME fibres, saturated monomer product ion levels were observed with five MDMA tablets under the same experimental conditions.

Furthermore, the continuous increase in PSPME dimer product ion signal with additional MDMA tablets demonstrates the device's high capacity for absorption. Under the same SPME fibre conditions, the increased response detected for the dimer product ions from one to five tablets continued with significant decrease

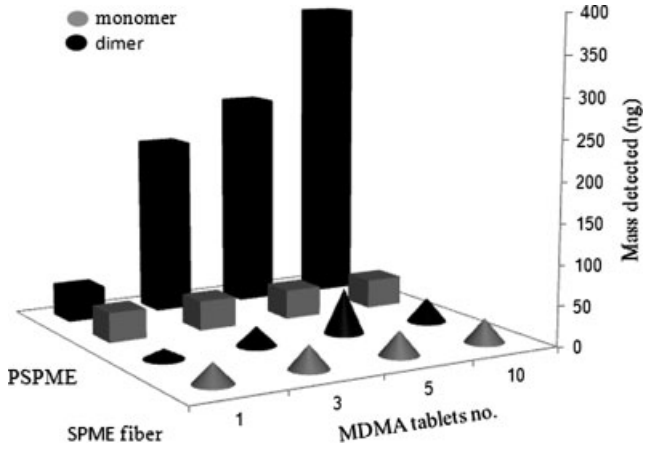

Figure 6. The PSPME device and SPME fibre extraction efficiencies versus MDMA tablets number.

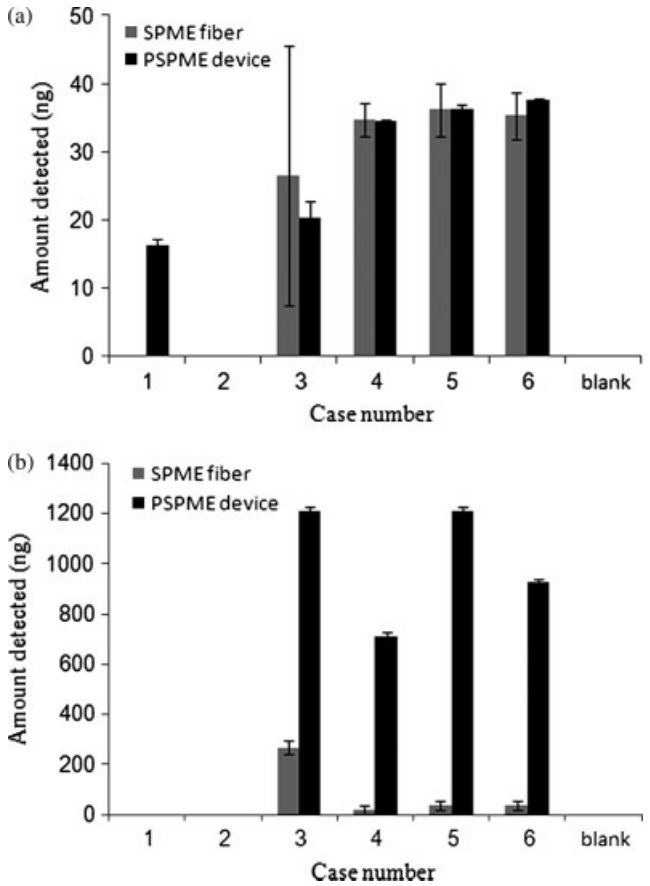

Figure 7. Detection of monomer (a) and dimer (b) product ions of piperonal above the headspace of suspected MDMA tablets from real case scenarios.

in sampling the headspace generated from 10 tablets. Despite the high concentration measured for one and three tablets here, it was decided to use five tablets in each can for further experiments, in case the emitting source would contain lower amounts of MDMA or aged samples would be tested.

The novel PSPME-IMS method was tested for analysis of suspected MDMA tablets, with evidence seized from six different real cases scenarios at the MDPD-CLB. The results obtained by both devices for each suspected case are illustrated in Figure 7. Sampling and IMS analysis of the headspace generated inside the cans, each from a different suspected case, using PSPME and SPME fibres, both indicated positive for MDMA tablets for cases 3, 4, 5 and 6. Even though high responses of monomer and dimer product ions were detected by both devices for these cases, even higher response for the dimer product ions were obtained with the PSPME devices than with the fibres, demonstrating their higher extraction capacity. Moreover, the PSPME devices gave more replicable results for all cases than the commercial SPME fibres.

No piperonal vapours were detected in the headspace generated from case 2, using either device for sampling. This was later confirmed by the forensic examiner from GC/MS data as a case negative for MDMA. No piperonal vapours were extracted from the headspace generated from case 1 tablets when only using SPME fibres as the sampling device. Following these SPME fibre results, the suspected tablets of case 1 might have been considered as a negative MDMA case. However, sampling case 1 under the same conditions as the fibre using the novel PSPME device enabled piperonal vapours to be detected clearly. Even though lower amounts were detected in this case than in the other four positive cases, clear, consistent peaks of the monomer product ions were analysed, confirming these tablets as a positive case for MDMA. The detections performed by the PSPME-IMS method for all tested cases correspond with the MDPD-CLB GC-MS data in this blind study test. Sample preparation followed by GC-MS analysis, according to MDPD-CLB protocols, confirmed the suspected tablets from all the cases, excluding case 2, to be positive MDMA-based tablets. Case 2 was the only case confirmed as negative for MDMA by the MDPD-CLB. According to GC-MS analysis, case 1 had a significantly lower concentrations of MDMA in the tablet analyzed compared to tablets from the positive cases 3 to 6. This is significant because, although SPME-IMS (GA) is a proven sensitive method for the detection of piperonal, if sampling had only been carried out with the fibre then case 1 would have been incorrectly deemed negative. This highlights the capabilities of the PSPME device in even the most difficult of cases.

Conclusions

An activated glass slide coated with sol-gel PDMS nanoparticles (PSPME device) was used to sample and pre-concentrate vapours emitted from a representative illicit drug, MDMA. The results obtained show that the novel device coupled to IMS exhibited significant improvement over the fibre SPME-IMS method in detection of piperonal vapours using standards as well as real case samples. Positive detection was achieved using PSPME-IMS within seconds of sampling time as well as in the case where a minimal MDMA sample was present. Under the same sampling conditions, the fibre SPME-IMS method failed to detect the presence of the drug. Moreover, the PSPME has an operational advantage over the fibre SPME because PSPME can be inserted directly into the desorber of a commercial IMS for analysis without the need for an interface or modification to the front end of the analyser. The geometry of the novel device makes it applicable to the numerous IMS instruments already deployed in the field and in forensic laboratories. However, the method requires the IMS setting to be configured at the optimal conditions for the target analytes, previously determined using a GA for a group of volatiles found in the headspace of drugs.

This work has reported, for the first time, the utility and effectiveness of the PSPME-IMS method in the sampling and detection of the MDMA odour signature, piperonal. It is expected that the application of PSPME-IMS will be successfully expanded to the analysis of other illicit substances (drugs and explosives) that are currently of much interest to the law enforcement and homeland security communities.

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