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Capillary microextraction: a new method for sampling methamphetamine vapour

Abstract

Clandestine laboratories pose a serious health risk to first responders, investigators, decontamination companies, and the public who may be inadvertently exposed to methamphetamine and other chemicals used in its manufacture. Therefore there is an urgent need for reliable methods to detect and measure methamphetamine at such sites. The most common method for determining methamphetamine contamination at former clandestine laboratory sites is selected surface wipe sampling, followed by analysis with gas chromatography – mass spectroscopy (GC-MS). We are investigating the use of sampling for methamphetamine vapour to complement such wipe sampling. In this study, we report the use of capillary microextraction (CME) devices for sampling airborne methamphetamine, and compare their sampling efficiency with a previously reported dynamic SPME method. The CME devices consisted of PDMS-coated glass filter strips inside a glass tube. The devices were used to dynamically sample methamphetamine vapour in the range of 0.42-4.2 μg m^{-3}, generated by a custom-built vapour dosing system, for 1-15 minutes, and methamphetamine was analysed using a GC-MS fitted with a ChromatoProbe thermal desorption unit. The devices showed good reproducibility (RSD< 15%), and a curvilinear pre-equilibrium relationship between sampling times and peak area, which can be utilised for calibration. Under identical sampling conditions, the CME devices were approximately 30 times more sensitive than the dynamic SPME method.

The CME devices could be stored for up to 3 days after sampling prior to analysis. Consecutive sampling of methamphetamine and its isotopic substitute, d-9 methamphetamine showed no competitive displacement. This suggests that CME devices,

pre-loaded with an internal standard, could be a feasible method for sampling airborne methamphetamine at former clandestine laboratories.

Keywords: Methamphetamine; Dynamic SPME; Capillary Microextraction; Gas chromatography - mass spectrometry (GC-MS); Vapor sampling; Chromatoprobe

Introduction

The clandestine manufacture of methamphetamine, especially in residential properties, is a significant concern in New Zealand and countries around the world, and represents a serious public health issue. While the precise nature of the dangers of passive exposure to contaminants at a former methamphetamine clandestine laboratory are not currently known, there have been reports of ill-health among first responders as well as residents in clandestine laboratories[1-3]. Burgess et al. reported that a large number of law enforcement personnel showed symptoms, mostly headaches and mucous membrane or respiratory irritation, while at a clandestine laboratory site, despite the use of a respirator.[4] Children are often present at these sites, and have a higher risk for toxic exposure, due to a number of factors such as their larger lung surface area relative to body mass, increased respiratory rates, hand-to-mouth behaviour and diminished understanding of risk.[5, 6] A number of studies[7-10] have reported the potential for methamphetamine absorption through dermal, oral and other routes, and it has been demonstrated that regular activities such as walking or vacuuming can re-suspend airborne methamphetamine at a contaminated site[11].

The recognition of this problem has led to the creation of guidelines by New Zealand[12], Australia[13], Canada[14] and a number of states in the US[15], that provide recommendations for testing, maximum permissible surface concentrations and remediation methods. Among other recommendations the “Guidelines for the

Remediation of Methamphetamine Clandestine Laboratory Sites" released by the NZ Ministry of Health in 2010, suggest a maximum methamphetamine surface concentration of 0.5 μg/ 100 cm-^{2}, and the NIOSH 9106 wipe sampling method, which involves the use of methanol-wetted gauze wipes or filter paper to wipe 100 cm^2 areas of suspected contaminated surfaces.[12, 16] The wipes are then transported to a laboratory, where the analytes are extracted by liquid-liquid extraction (using hexane and dichloromethane), or by Solid Phase Extraction (SPE), and then analysed by GC-MS.

None of the guidelines [12-15] have recommendations for the sampling and analysis of airborne methamphetamine. However, several studies have shown that particulate and/or vapour-phase methamphetamine is present at clandestine laboratory sites, and could accumulate on skin, fabric, porous and non-porous surfaces, and even permeate through paint and plasterboard, over time.[17-19] McKenzie et al. reported a dynamic Solid Phase Microextraction (SPME) sampling method combined with gas chromatography – mass spectroscopy (GC-MS) analysis that was designed to act as a supplementary method for the detection of methamphetamine at former clandestine laboratories, and were successfully able to detect methamphetamine at actual sites.[20] However, they found that the method could only detect methamphetamine at sites where at least one surface wipe sample exceeded 40 μg / 100 cm^2, and their study highlighted the need to develop a more sensitive sampling method that was still sufficiently rapid and robust to be practical for sampling in the field. In addition, McKenzie et al. only calibrated their SPME method under zero humidity conditions and SPME devices have been reported to show diminished sorption capacities under humid conditions [21].

Recently, Guerra et al. reported the design of a planar SPME device based on a glass fibre filter with a sol-gel siloxane coating, which addresses a primary limitation of SPME- the

limited surface area for sorption of analytes. The planar SPME device was reported to have a greater than 100 fold increase in surface area compared to a standard 100 μm PDMS SPME fiber, and this resulted in an increased sorption capacity.[22] The planar SPME device was used for headspace sampling of explosives[23, 24] and drugs[25], which were analysed using Ion Mobility Spectrometry (IMS). Based on this design, Fan and Almirall developed a method they called capillary microextraction of volatiles (CMV), for dynamic headspace sampling of volatiles with analysis by GC-MS which they successfully used to sample and analyse volatile organic compounds in military explosives and gunshot residue from shooters' hands.[26, 27]

The rapid sampling capability and sensitivity of this planar SPME should lead to improved dynamic sampling of airborne methamphetamine compared to the earlier reports using dynamic SPME. We have therefore prepared capillary microextraction (CME) devices and report the use of these CME devices in the sampling of methamphetamine vapour, generated using a custom-built vapour generation system. The methamphetamine vapour concentration (4.2 μg m^{-3}) used in the current study is the same as used in our prior SPME study[20] and is consistent with reported ranges at simulated[11] or former[28] clandestine laboratories. We also report the potential for pre-loading the CME devices with a deuterated internal standard, as a means of quantifying sorbed analytes.

Materials and Methods

CME device fabrication:

Glass fiber filters (Sartorius Stedium Biotech, 4.7 cm dia) were placed in a petri dish containing piranha solution (2:1 mixture of conc. H_2SO_4 (J.T. Baker, 95-98%) and H_2O_2 (Univar, 30%)) for a few minutes, dried in an oven at 90° C, rinsed with Type I water

98 (Sartorius Arium), then soaked in 1 M NaOH (ECP, 97.0% assay) for 1h to expose the
99 silanols on the surface. The filters were rinsed thoroughly with Type I water, and dried
100 in an oven at 120° C for 12 h. The sol-gel PDMS solution was prepared by mixing 2.060 g
101 vt-polydimethylsiloxane (Sigma Aldrich, mw~25,000) and 0.535 g
102 polymethylhydrosilane (Sigma Aldrich, mw~1700-3200) in 8 mL dichloromethane
103 (Scharlau 99.9%), and adding 1.10 mL methyltrimethoxysilane (Sigma Aldrich, 98%) and
104 0.875 mL 95% aq. trifluoroacetic acid (Applichem, 99.5%). The solution was vortexed
105 and stored in a Teflon-capped glass test-tube for 30 min before use.
106 The pre-cleaned filters were placed on a silicon wafer held on the chuck of a spin coater
107 (Laurell WS650- MZ-23NPP), and 1 mL of the polymer solution was deposited in the
108 centre of the filter, after which the filter was spun at 1000 rpm for 20 s. The filters were
109 dried in a desiccator for 12 h, soaked in dichloromethane for 1.5 h and then dried in an
110 oven at 40° C for 12 h. Finally, the filters were placed in a muffle furnace, with nitrogen
111 flowing through, set at 120° C for 1 h, 240° C for 1 h and 300° C for 3 h, and then slowly
112 cooled to room temperature.
113 The PDMS-coated and uncoated filters were characterised using a benchtop Scanning
114 Electron Microscope (JEOL JCM-6000 Neoscope) after they had been sputter coated with
115 gold.
116 Glass NMR tubes (Norell Inc.) with i.d. 2.4 mm were cut to 2 cm lengths, and cleaned by
117 sonication in isopropanol, and then air-dried. Using a razor blade, the polymer-coated
118 filters were cut into 2 cm x 2 mm strips and, using a pair of tweezers, 7 strips were stacked
119 and inserted into each glass tube section to form the CME device. The tubes were weighed
120 using an analytical balance, before and after the strips were inserted, to determine the
121 mass of the PDMS-coated filters in each device. Prior to use, the CME devices were

122 conditioned for an hour at 260° C in the inlet of a gas chromatograph equipped with a
123 ChromatoProbe.
124

Vapour generation system modifications:

The methamphetamine vapour generation system reported earlier[20] was modified to allow control of humidity (refer to Supplementary Material). The modified vapour dosing system was first characterised using a 0.1 mg/mL solution of tetradecane in heptane, injected to provide a final concentration of 4.2 μg m^{-3}. A stream of nitrogen, controlled by a mass flow controller (Alicat Scientific), flowed through an injection block placed on a hot plate at 90° C, into which a 0.1 mg/mL solution of tetradecane in heptane was injected, using a 50 μL gas tight syringe (SGE Analytical) at the rate of 10 μL h^{-1}, using a syringe pump (New Era Systems). Another stream of nitrogen, controlled separately by a rotameter, flowed through two bubblers containing Type I water and placed in a water bath at 20° C, and was connected to the tetradecane vapour stream, downstream of the injection block, by means of a ⅝ in Swagelok® tee. The combined streams of nitrogen were allowed to mix well inside a 500 mL Silcosteel™ canister, with a glass funnel at the outlet into which the sampler inlet could be placed. The flow rates of the two streams were controlled so that the combined flow rate was 2 L min^{-1}, and this was intermittently monitored independently, using a gas flow meter (TSI Inc.). The concentration of tetradecane was monitored using a photoionisation detector (PID; Baseline®-MOCON® Inc., Lyons), and measurements were taken at 0%, 30%, 50% and 70% relative humidity (RH). The relative humidity and temperature at the outlet were also monitored using a humidity meter (USBtenki, Dracal Tech., Longueuil).

Methamphetamine vapour sampling and analysis:

A 0.1 mg/mL methamphetamine free base solution was prepared in acetonitrile, using the following method: 1 mL of standard 1 mg / mL methamphetamine hydrochloride (99.9%, Cerilliant) in methanol was mixed with 1 mL of 4% aqueous NaOH and 1 mL of dichloromethane in a glass screw-cap test tube (Kimax), vortexed on high for 3 minutes

and centrifuged at 990 rpm for 5 min. The organic layer was passed through anhydrous Na_2SO_4 and collected in a GC vial. The extraction process was repeated with the aqueous layer, the organic layers were combined, evaporated to ~1 mL in a dry bath at 26° C under nitrogen, and made up to 10 mL with acetonitrile, in a volumetric flask. A 0.1 mg/mL d9-methamphetamine solution was prepared in the same manner, from a standard solution of 1 mg mL^{-1} d9-methamphetamine in methanol (99%, Cerilliant). Liquid injection gas chromatography-mass spectrometry (GC-MS) was carried out, in triplicate, to confirm that the extraction was quantitative.

For methamphetamine vapour generation, the 0.1 mg/mL solution was injected into the injection block, which was held at 185 C, at the rate of 5 µL h^{-1}, using a 50 µL or a 250 µL gas-tight syringe. Two separate but identical vapour dosing systems from the methamphetamine introduction point to the outlet funnel were used for the generation of methamphetamine and d9-methamphetamine vapour, in order to prevent any carry-over between the two analytes. Methamphetamine vapour was allowed to flow through the system for ~5 h before sampling was undertaken, in order to allow the system to come to steady state.

The dynamic SPME sampler reported by McKenzie et al.[18] was used for all SPME samples. For CME sampling, the CME devices were partially inserted into one end of a length of perfluoroalkoxy alkane (PFA) tubing with an i.d. ~2 mm and the other end of the tubing was connected to an air sampling pump (SKC Inc.). The connection between the CME device and the tubing was made air-tight by fitting another short piece of larger diameter PFA tubing around the junction. The dynamic SPME sampler or the CME device was placed into the mouth of the funnel at the outlet of the vapour generation system, without fully occluding it, sampled at a rate of 1 L min^{-1}, and sampling times were

recorded using a digital stop-watch. The CME devices were handled using tweezers at all times, and were wrapped individually in aluminium foil and placed in closed glass vials during storage.

The analytes collected by the CME devices were desorbed in a ChromatoProbe (Aviv Analytical Ltd.) attached to the inlet of an Agilent 7890 GC coupled to an Agilent 5975 C XL Mass Spectrometer. The GC-MS parameters used for the CME devices, SPME fibres and liquid injections are shown in Table 1.

Table 1: GC-MS parameters for CME devices, SPME and liquid injection

	CME	SPME	Liquid
Injection	Manual, ChromatoProbe	Manual	Auto, ALS
Inlet liner	Agilent 2 mm ultra-inert split/splitless gooseneck	Supelco 0.75 mm direct SPME liner	Agilent 2 mm ultra-inert split/splitless gooseneck
Inlet temp	260° C	250° C	250° C
Carrier gas	Helium	Helium	Helium
Pressure	14.49 psi	7.06 psi	7.06 psi
Average velocity	49.76 cm/sec	36.28 cm/sec	36.28 cm/sec
Injection volume	N/A	N/A	0.2 µL
Column	Restek RX1- 5MS 30 m x 250 µm x 0.25 µm	Restek RX1- 5MS 30 m x 250 µm x 0.25 µm	Restek RX1- 5MS 30 m x 250 µm x 0.25 µm
Oven temp	30° C, 2.5 min, 40° C/min, 260° C, 2.5 min	40° C, 2.5 min, 40° C/min, 300° C, 3 min	40° C, 2.5 min, 40° C/min, 300° C, 3 min
Ionisation mode	EI mode	EI mode	EI mode
Source temp	230° C	230° C	230° C
	280° C	280° C	280° C

Transfer line temp			
Mass range	38-280 amu	38-280 amu	38-280 amu
Acquisition	Scan mode	Scan mode	Scan mode

Blanks were run between samples to ensure complete desorption of analytes from the CME or SPME samplers. The initial high ending temperature for the SPME and liquid injections was to ensure that all the compounds were eluted from the column. However, it was determined that all the compounds of interest eluted early, and so the final column temperature was reduced to 260° C in later studies to extend the lifetime of the column. The ions m/z 58 and 91 and m/z 65 and 93 were used to identify methamphetamine and d9 methamphetamine respectively, and the default integration parameters for the GC/MSDChemStation software (Agilent Technologies) were used to determine peak areas in each extracted ion chromatogram (EIC).

The time for which a CME device could be stored after sampling was determined as follows: Three CME devices were used to sample the same concentration of methamphetamine (4.2 μg m^{-3}) for 10 min, after which each device was wrapped in aluminium foil, placed inside a sealed glass vial and stored at room temperature for zero, three and five days. Immediately prior to analysis, the CME devices were unwrapped and used to sample isotopically substituted methamphetamine (4.2 μg m^{-3}, 10 min), before being placed into the Chromatoprobe inlet for analysis by GCMS.

Results

Characterisation:

A comparison of the SEM images of the piranha etched and unetched filters (see Supplementary Material) showed that the piranha etching disturbed the arrangement of the fibres and made the individual fibres more accessible to subsequent processing. The subsequent siloxane coating completely penetrated the filters and coated fibres throughout the filter uniformly. On average, the coated filters were ~18 µm thicker than the uncoated ones (thickness of filters= 228.8 µm ± 4.3 µm). The average area density of PDMS on the PDMS coated filters was 2.78 x 10^{-3} g cm^{-2} (±1.12%), so that the assembled CME devices contain approximately 7.8 mg of PDMS. The CME devices were conditioned and blanks run until a low and reproducible background was obtained, (see SI) typically for an hour. The devices were found to be relatively sturdy and could withstand the high temperature of the GC inlet without cracking or disintegrating. Handling the CME devices with bare hands or with nitrile gloves resulted in large fatty acid and phthalate contaminant peaks that were difficult to eliminate and required re-conditioning, therefore the CME devices were only handled using clean stainless steel tweezers, or while wrapped in aluminium foil.

Control of humidity:

The modifications to the vapour dosing system allowed it to produce required humidity values precisely (relative standard deviation (RSD) < 1%) and the Silcosteel™ canister allowed for adequate mixing of the vapour stream and resulted in a vapour temperature of ~20° C at the outlet of the funnel. Initial experiments using tetradecane showed no variation in the PID signal with changes in the relative humidity, indicating that the vapour dosing system was working consistently.

Initial experiments with methamphetamine and d9 methamphetamine:

A key objective of the present study was to investigate whether the recently-reported CME sampling devices could provide enhanced sampling capability compared to our recently-reported dynamic SPME sampling method. For this reason we used identical experimental factors, including methamphetamine vapour concentrations volumetric flow rates and sampling times, to those reported in that earlier work. Gas chromatograms of the methamphetamine free base and d9-methamphetamine solutions in acetonitrile, via liquid injections, showed quantitative extraction and recovery from the original methanolic solutions. A comparison of the extracted ion chromatograms for m/z 58 and m/z 65 for methamphetamine and d9-methamphetamine respectively (Figure 1), showed a temporal overlap between the two peaks. The ratio between the two peak areas was 1: 1.1 (m/z 58:91), which was identical to the findings reported by McKenzie.[29]

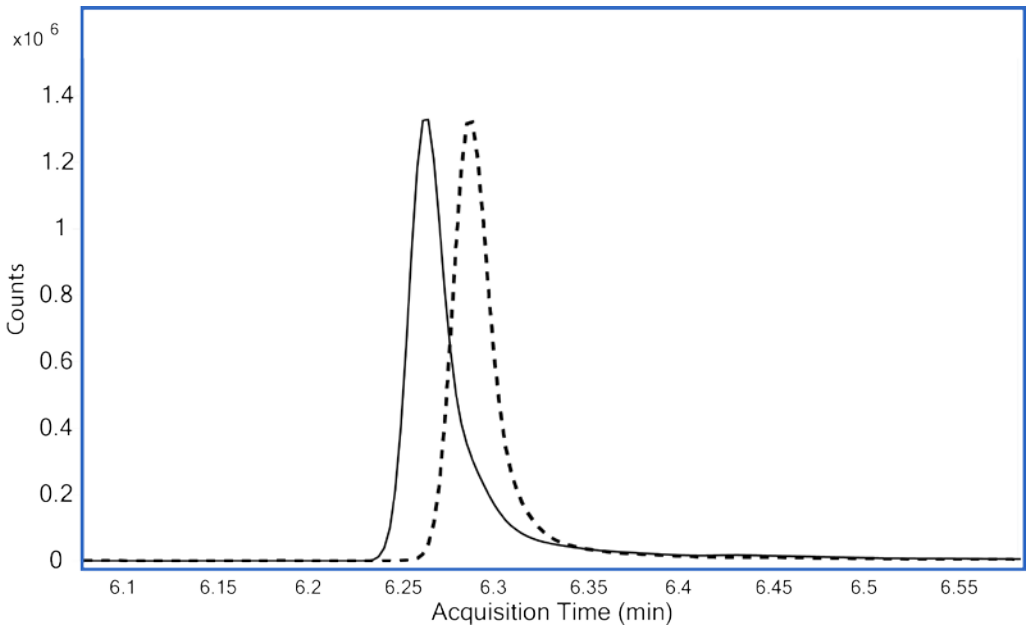


Figure 1: The extracted ion chromatograms for liquid injection of a solution containing both 0.01 mg/mL methamphetamine and 0.01 mg/mL d9-methamphetamine, showing ions m/z 65 (solid) and m/z 58 (dotted)

240 The methamphetamine vapour generation system was designed to minimise adsorption
241 of analytes such as methamphetamine, with most components after the
242 methamphetamine introduction point being either Teflon or Silcosteel. However, despite
243 these precautions, McKenzie et al[20] reported that a small amount of methamphetamine
244 was still retained within the vapour dosing system, and so suitable equilibration times of
245 12 h (initial) and 5 h (subsequent) were implemented prior to measurements being taken
246 to ensure steady state vapour concentrations were achieved. In addtion, separate vapour
247 dosing systems were used to generate methamphetamine and d9-methamphetamine
248 vapour.

249 **GC Method Development:**

250 The GC inlet was held at 260° C in splitless mode for Chromatoprobe sample introduction
251 to ensure that the methamphetamine was rapidly and completely desorbed from the CME
252 device and transferred onto the column, which was initially held at 30° C to allow the
253 analytes to preconcentrate at the head of the column. A higher initial carrier gas flow rate
254 of 1.9 mL min^{-1} was also used with the ChromatoProbe, as compared to the SPME and
255 liquid injections which had a flow rate 1 mL min^{-1}, to facilitate complete transfer onto the
256 column. The manual introduction of samples into the heated ChromatoProbe inlet caused
257 slight variations in the reported retention time and the observed peak areas and these
258 variations are incorporated in the observed reproducibility of the method. It was
259 ensured, however, that the time lapse between sample introduction and the start of the
260 GC run was always less than 1 s.

261 **Sampling and analysis:**

262 The reproducibility of methamphetamine vapour sample collection using the CME
263 devices was investigated by dynamically sampling 4.2 μg m^{-3} methamphetamine vapour

264 at a sampling flow rate of 1 L min^{-1} for a period of 10 min followed by immediate GC-MS
265 analysis. Blanks using the same CME device were analysed between samples. Repeated
266 sampling was carried out over several days, using multiple CME devices, at 0%, 30%, 50%
267 and 70% relative humidity, in a randomized order, with each CME device being analysed
268 immediately after exposure to methamphetamine vapour. Dynamic SPME sampling of
269 methamphetamine vapour was also performed under the same dosing and sampling
270 conditions to allow direct comparison of the two sampling techniques. The extracted ion
271 peak areas for methamphetamine (m/z 58) and d9-methamphetamine (m/z 65) from the
272 GCMS chromatograms were used to characterise the behaviour of the vapour generator
273 and sampling devices. CME sampling was found to result in approximately 30 times
274 larger peak areas in the GCMS chromatograpms than dynamic SPME sampling (Figure 2),
275 and the two methods showed similar repeatability (RSD=12 %). At a tenfold lower
276 methamphetamine vapour concentration of 0.42 μg m^{-3}, sampling for 10 min with the
277 CME devices resulted in a proportionately lower response in the GCMS chromatograms,
278 while no integrable peaks were observed upon sampling with dynamic SPME for 10 min.

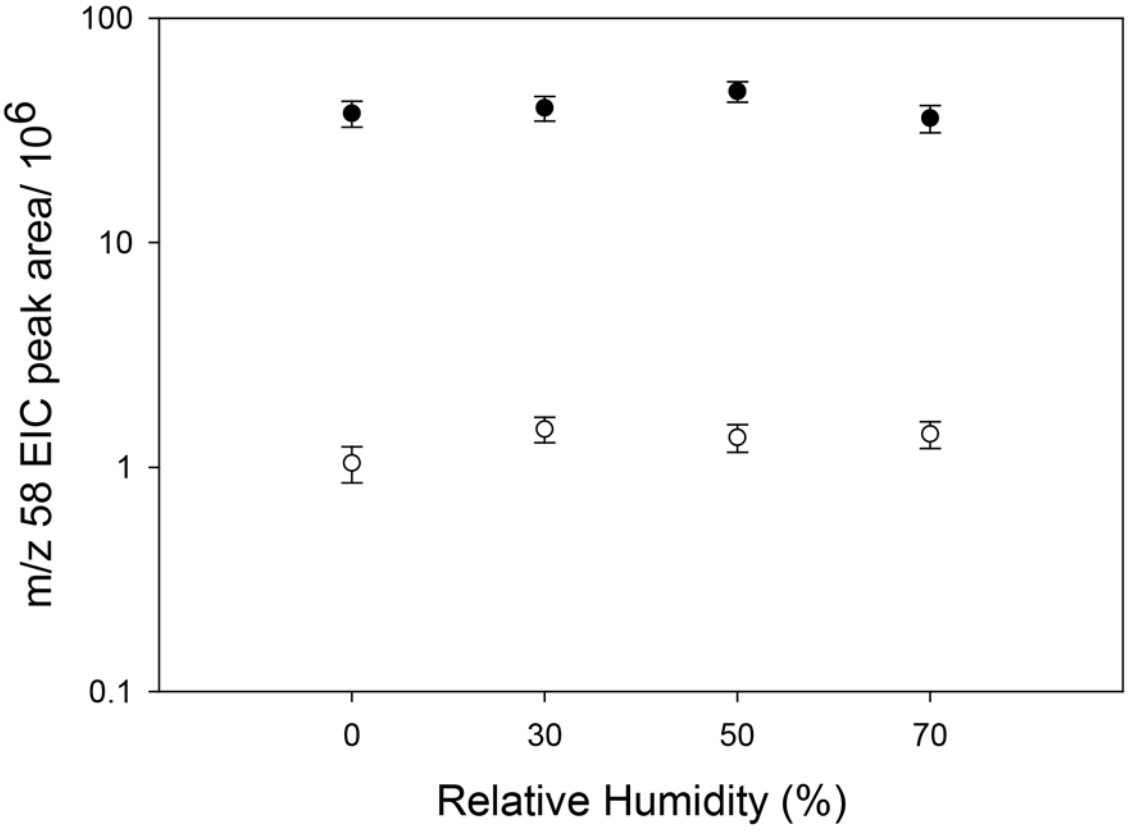
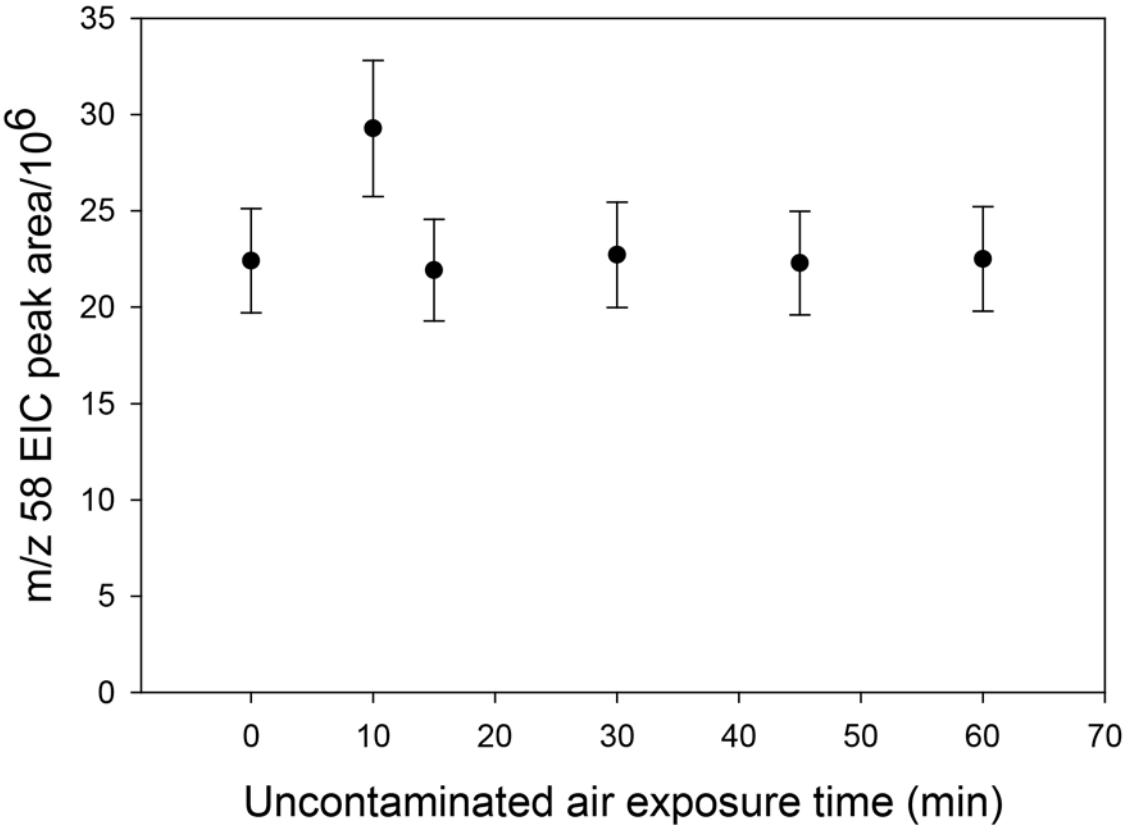


Figure 2: Comparison of m/z 58 peak areas in GCMS chromatograms for CME sampling (filled) and dynamic SPME sampling (unfilled) of 4.2 µg m^{-3} methamphetamine, sampled for 10 minutes at 0%, 30%, 50% and 70% relative humidity, n=6 for each parameter combination. Error bars show one standard deviation from the mean value.

The retention of methamphetamine that had already been sorbed onto a CME device during subsequent active sampling of clean air or upon passive storage in static conditions, was also investigated. The CME devices were used to sample methamphetamine vapour at 4.2 µg m^{-3} for 10 minutes, after which the CME device and air pump were moved to an adjacent laboratory where clean air was drawn through the CME devices for different lengths of time prior to GCMS analysis. As shown in Figure 3, drawing air through the CME device at 1 L min^{-1} for periods of less than one hour did not reduce the amount of methamphetamine retained on the device. The experiments using the shortest time of exposure to clean air (10 min) showed a significantly higher signal than the 0 time or longer exposure to clean air. Due to the experimental design these 10

294 min measurements were performed first in the analytical runs while all others were
295 performed in a random order, and this may have introduced a small systematic error for
296 those results. The results for the 15 min to 60 min exposure to clean air are very
297 consistent and show that methamphetamine is retained on the CME device for periods of
298 up to one hour even when air is being drawn through the device.



299

300 **Figure 3: Observed m/z 58 peak areas when 4.2 µg m^{-3} methamphetamine was sampled for 10 min**
301 **with CME devices which were then used to dynamically sample uncontaminated air for the times**
302 **shown prior to GCMS analysis, n=6. Error bars are one standard deviation**

303

304 The amount of sorbed methamphetamine on the CME devices did not reach steady state
305 for sampling times up to 30 min, when they were exposed to methamphetamine at 4.2 µg
306 m^{-3} (longer exposure times were not investigated), so that the relationship between
307 methamphetamine GCMS peak area and exposure time was curvilinear (Figure 4). All

samples were collected in a random order. It was also noted that while the CME devices were reusable, they had a limited life-span and showed a drop in sensitivity over time, and so the use of each device was limited to a total of 50 samples.

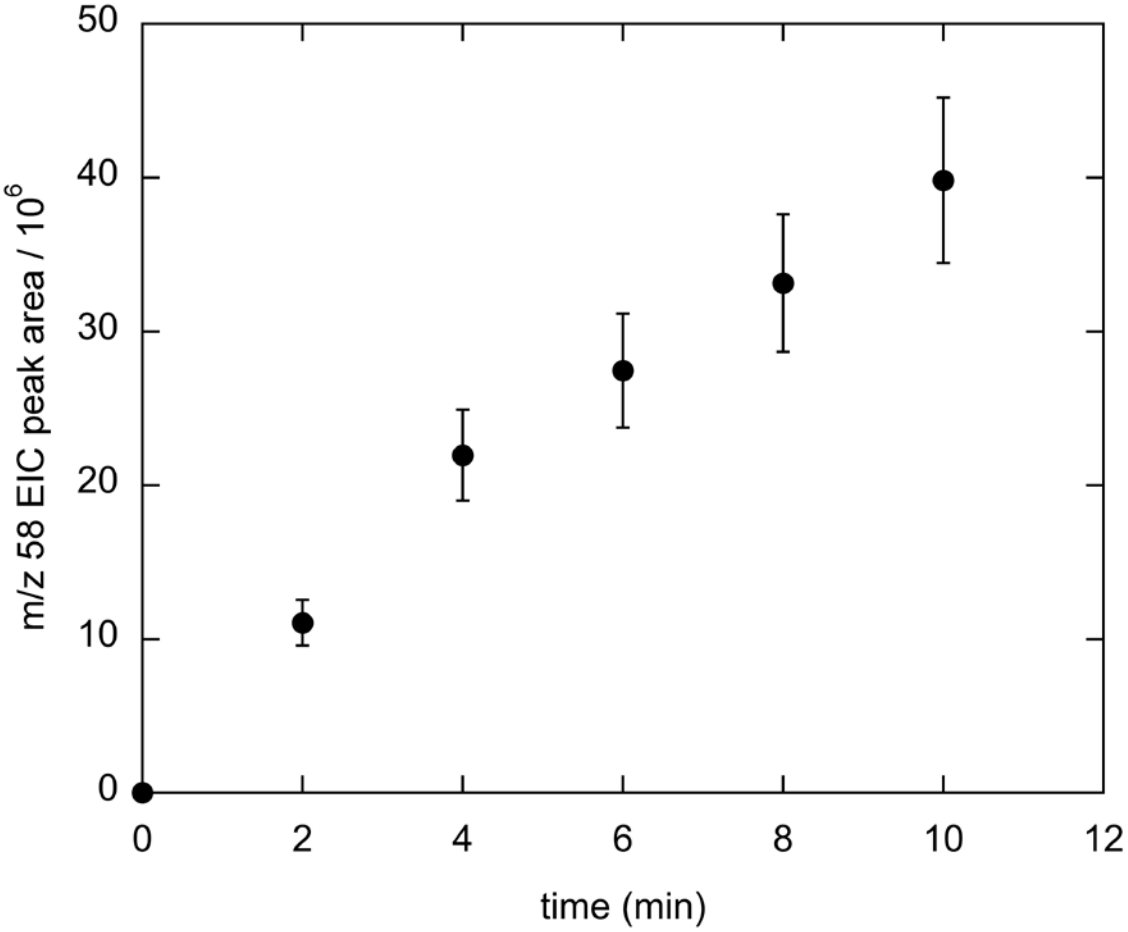


Figure 4: Observed m/z 58 GCMS peak area for methamphetamine as a function of CME sampling time for 4.2 µg m^{-3} methamphetamine vapour, n=6, r^2= 0.995.

The slight variability in construction of the CME devices combined with the observed decrease in sensitivity for the CME devices when they were re-used multiple times highlighted the need for an internal standard. For comparability with our earlier dynamic SPME sampling study d9-methamphetamine was used as the internal standard. Thus, CME devices were exposed to d9-methamphetamine vapour (4.2 µg m^{-3}, 10 min) using the dosing system, and then were wrapped in clean foil and stored. The same CME devices were then used to sample methamphetamine at 4.2 µg m^{-3} for the same exposure time

(10 min), and then they were analysed immediately by GC-MS. The results (Figure 5) showed that the deuterated methamphetamine was not displaced by methamphetamine, and the GCMS peak areas showed the same ratio for m/z 58: m/z 65, as for the liquid injections. When the experiment was repeated with the dosing in reverse order, with methamphetamine sampled first, the same results were obtained, Figure 5, demonstrating that the CME devices can be pre-loaded with an internal standard prior to sampling and analysis. The internal standard approach was shown to improve the reproducibility of the analyses, with the relative standard deviation of the m/z 58:m/z 65 ratio being 4.2%.

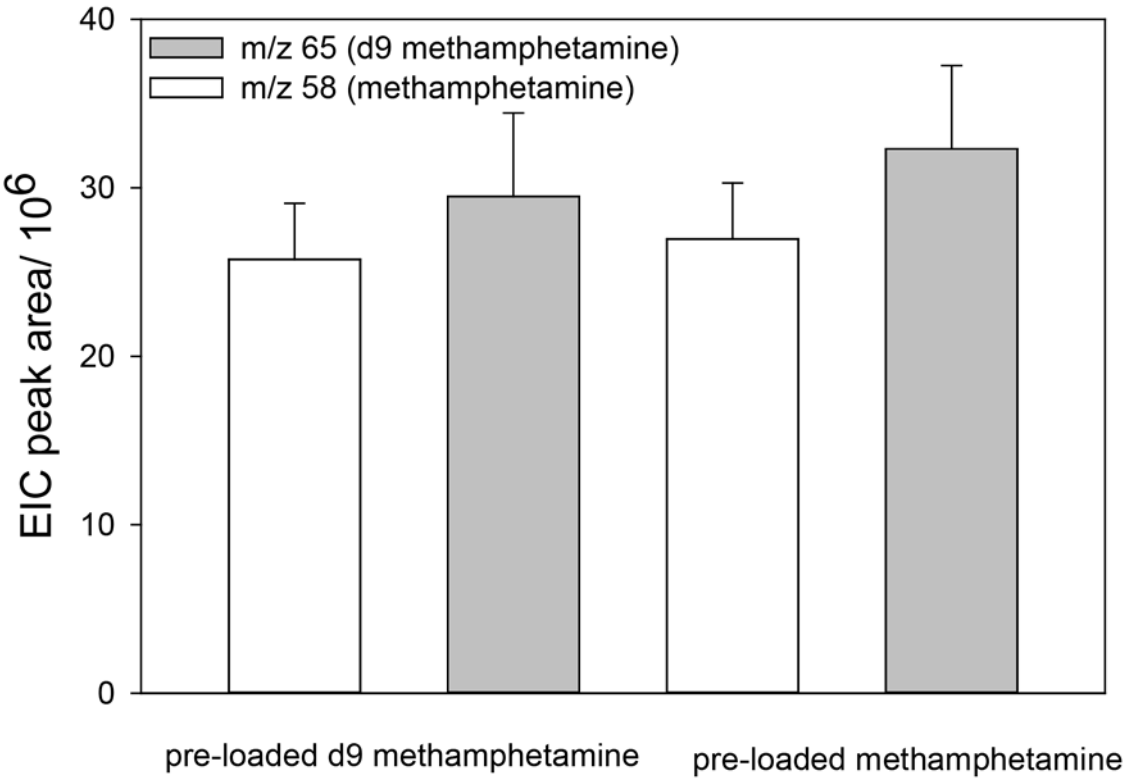


Figure 5: Observed GCMS peak areas for methamphetamine (m/z 58) and d9-methamphetamine (m/z 65) when CME devices were preloaded with methamphetamine and then used to sample d9-methamphetamine or vice versa. n = 6

Finally, we determined the time that the CME devices could be stored at room temperature after sampling, prior to analysis. Three CME devices were first used to sample methamphetamine vapour (4.2 μg m^{-3}) for 10 min, then were demounted from the sample pump, wrapped in foil and placed in a vial. They were then reconnected to the sample pump and used to sample isotopically substituted d9-methamphetamine vapour for 10 min then analysed. The experiment was then repeated with the same three CME devices, but with storage times in the vials of 3 and 5 days. The results (Figure 6) show that there is very little decrease in the m/z 58 signal characteristic of methamphetamine after 3 days storage, but that about half the methamphetamine has been lost after 5 days. This ability to retain methamphetamine is significantly better than for SPME fibres, which showed some loss of analyte after ~3 h of storage. However, if the CME devices were left in the open after sampling, a decrease in the amount of sorbed analyte was observed in as little as 4 h post-sampling.

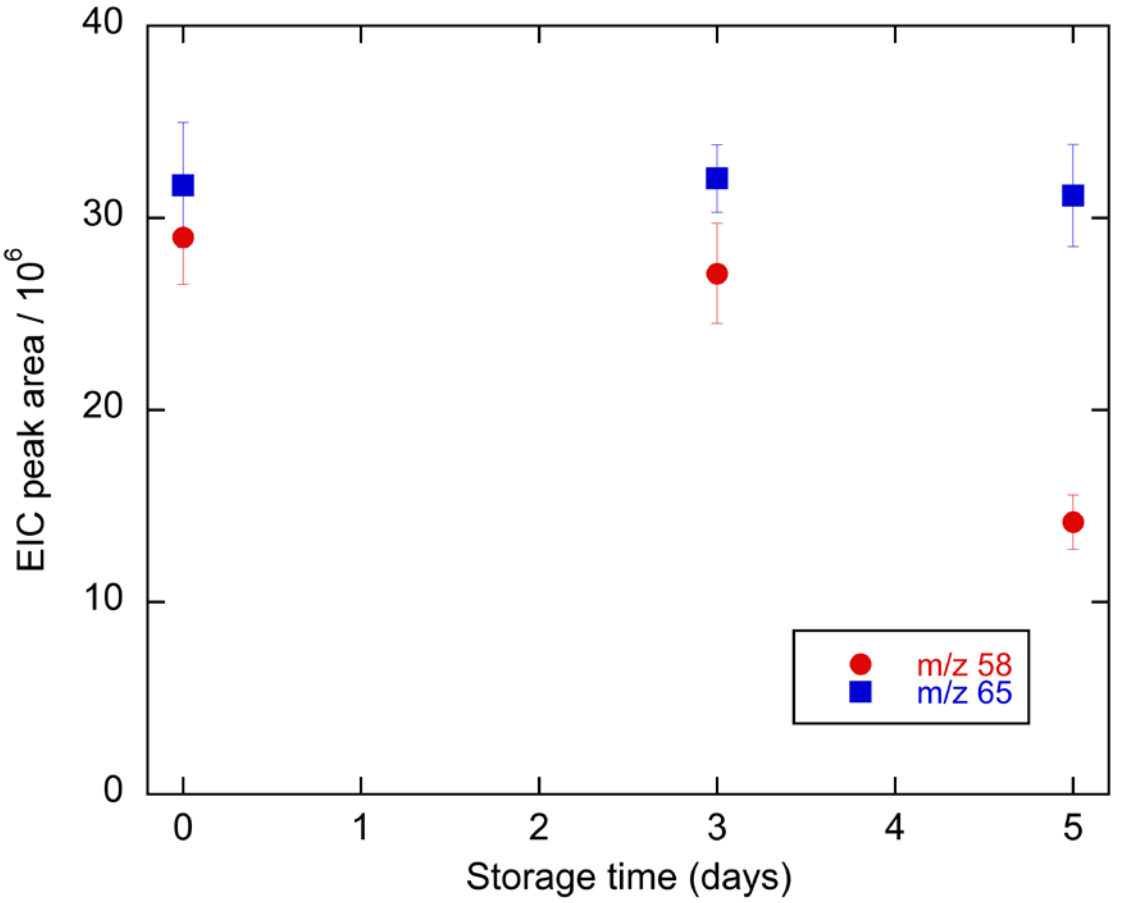


Figure 6 Observed peak areas when methamphetamine (4.2 µg m^{-3}) was sampled for 10 min on CME devices which were then stored for the times shown at room temperature wrapped in aluminium foil in capped glass vials prior to vapour sampling of d9-methamphetamine (4.2 µg m^{-3}) for 10 min and then analysis by GCMS. Each point corresponds to a three measurements using separate CME devices.

Conclusion

Several groups have been investigating the use of high surface area SPME devices [30-33], in order to increase the sensitivity and selectivity of the sampling prior to instrumental analysis. We considered the use of such devices as a complementary method to wipe sampling for determining the extent of methamphetamine contamination at a former clandestine laboratory site. The current implementation allows rapid and reliable sampling at the site but does require analysis of the CME device at a laboratory. However, the sampling strategy is compatible with a portable GC-MS with a direct sample

362 introduction system and so could be adapted so that samples could be analysed on-site,
363 to provide information to professionals such as first-responders or decontamination
364 contractors.
365 This study provides external validation of the CME design proposed by the Almirall
366 group, based on PDMS sol-gel modification of glass fibre filters[26, 27]. We have
367 successfully demonstrated the practicality of the capillary microextraction device for
368 methamphetamine vapour analysis and have shown that it can collect approximately 30
369 times more methamphetamine than commercial SPME fibres under similar dynamic
370 sampling conditions[18, 20]. This improved sensitivity implies that this method should
371 now be able to detect airborne methamphetamine in houses with moderate
372 methamphetamine contamination, whereas the dynamic SPME method only detected
373 airborne methamphetamine when accompanying surface wipe samples showed
374 concentrations greater than 40 μg / 100 cm^2[18]. We have also shown that both SPME
375 and CME devices can be used to detect and measure methamphetamine vapour under a
376 wide range of humidity conditions (0 – 70%), despite reports that some SPME analyses
377 are affected by humidity.[21]
378 In conclusion, dynamic sampling with the CME devices combined with Chromatoprobe
379 desorption and GCMS analysis showed a substantial increase in sensitivity over the
380 dynamic SPME method for sampling airborne methamphetamine, but with very similar
381 time and minimal additional equipment requirements. Our current implementation of
382 the CME devices has a materials cost of approximately U.S. $2. 80 for each device, so that
383 costs are not excessive if a laboratory has a GCMS equipped with a Chromatoprobe or
384 similar sample introduction device. The rapid sampling time, relative ease of use and

385 ability to retain analytes over extended time periods make CME devices attractive for
386 sampling in the field.
387

Supplementary Material

The revised design of the vapour dosing system to allow variations in the relative humidity of the vapour stream and SEM images characterising the stages of CME device preparation are given in the Supplementary Material. Supplementary data associated with this article can be found in the online version.

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