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Recoveries of trace pseudoephedrine and methamphetamine residues from impermeable household surfaces: Implications for sampling methods used during remediation of clandestine methamphetamine laboratories

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ABSTRACT

Evaluation of the risk posed by contaminants present during and after decontamination of clandestine methamphetamine laboratories requires a connection between the levels of contaminants measured and those actually present at the scene. The recoveries of pseudoephedrine and methamphetamine from glass, stainless steel, and a range of impermeable surfaces likely to be found in a clandestine laboratory were examined, using GC-MS of derivatized samples as the analytical method. When surfaces had been cleaned prior to drug deposition, wiping with water-dampened filter paper can recover 60–80% of pseudoephedrine immediately after deposition, and at least 50% of the pseudoephedrine still present on a surface after 2 days when deposited at a surface concentration of 2.5 μg/100 cm^2. Wiping with methanol-dampened filter paper could recover 60–90% of the methamphetamine immediately after deposition, and could recover at least 50–60% of the methamphetamine still present after 2 days when 0.6 μg/100 cm^2 was initially deposited on the surface. Recoveries were lower for surfaces that had not been pre-cleaned. Methamphetamine and pseudoephedrine showed significant volatility in both the free base and hydrochloride forms, with experiments in an enclosed format showing up to half the recovered drug being present on a glass plate held about 4 mm above a substrate contaminated with one of the drugs at the above surface concentrations after 2 days. It is therefore important to remove any visible bulk contaminants and remove obvious pseudoephedrine or methamphetamine-contaminated surfaces prior to heating, ventilation or sealing of a clandestine laboratory to avoid redistribution of material around the site. A revised method for pseudoephedrine analysis was developed that could also detect the pseudoephedrine–formaldehyde adduct that can form from trace pseudoephedrine present at clandestine laboratories.

1. Introduction

Clandestine methamphetamine laboratories have been recognised as a significant risk to public health [1]. Since many clandestine laboratory operations are performed using inappropriate makeshift apparatus, and are done by non-chemists, contamination of the immediate surroundings and complete structures can occur. These contaminants present immediate and long term exposure hazards for clandestine laboratory operators ("cooks") and residents. Even after a laboratory has been dismantled, residual contamination can be present. The risks posed by such contamination are still being evaluated [1,2] and agencies are still determining appropriate methods for decontamination and measuring the extent of residual contaminants [3–5].

Remediation of a clandestine laboratory generally begins with a preliminary assessment, followed by the actual remediation, and final post-cleanup evaluation. Most current decontamination strategies for a clandestine methamphetamine laboratory follow the surrogate approach, aiming at decreasing methamphetamine surface contamination levels down to 0.1 μg/100 cm^2 which has been reported to be acceptable and practical level based on current knowledge and expertise, although a recent health-based evaluation has suggested a level of 1.5 μg/100 cm^2 [3]. A major issue is that these guidelines give values for analysed contaminants (such as methamphetamine or pseudoephedrine), rather than the amount actually present on a given surface. There are also uncertainties about the longevity of low-level contamination, and the amount of redistribution that can occur after deposition. The effects of volatility and surface chemistry on retention of contaminants are well-known in the more general indoor air quality literature [6].

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Pseudoephedrine is the most common starting material for clandestine methamphetamine synthesis via the red phosphorus method [7]. The present study aimed to determine how much pseudoephedrine or methamphetamine can be recovered from impermeable surfaces immediately after deposition, as well as after a defined duration on covered and uncovered glass, stainless steel, and some common household surfaces. During this study we found that trace pseudoephedrine samples were sometimes contaminated with a formaldehyde derivative (4S,5S)-3,4-dimethyl-5-phenyloxazolidine. We therefore report a method that is able to determine both pseudoephedrine and its oxazolidine derivative.

2. Materials and methods

2.1. Reagents and materials

All the solvents used were of at least either analytical or HPLC grade. Cyclohexanone was redistilled. The non-restricted chemicals were obtained from Aldrich, Scharlau and Supelco, and were of 98% purity or better. (+)-Pseudoephedrine hydrochloride (99% purity), (+)-pseudoephedrine free base (99% purity) and methamphetamine hydrochloride (>98% purity, Australian Government National Measurement Institute) were obtained from the Institute of Environmental Science and Research Ltd. (ESR).

2.2. GC-MS parameters

GC-MS analysis was carried out on a HP 6890 GC equipped with a HP 5973 mass selective detector (MSD), HP 7683B automatic sampler, and HP-5MS capillary column (30.0 m × 0.25 mm × 0.25 μm film thickness, Agilent). Helium was used as a carrier gas and the flow rate was 1 mL/min. The injector temperature was set at 185 and 250 °C for pseudoephedrine and methamphetamine analysis, respectively. The interface temperature was set at 280 °C. The oven temperature was programmed as follows: an initial temperature of 100 °C (pseudoephedrine) or 70 °C (methamphetamine) was held for 2 min, followed by an increase of 20 °C/min to 280 °C which was held for 2 min. Mass spectra were acquired in scan mode from m/z 41 to 500. The quantities of pseudoephedrine and methamphetamine were determined using ratios of the peak areas of the analytes to those for the internal standard peak (octadecane, "C-18", for derivatized pseudoephedrine, and tetradecane, "C-14", for derivatized methamphetamine).

2.3. Experimental details

Pseudoephedrine free base, pseudoephedrine hydrochloride, and methamphetamine hydrochloride were obtained as 1.0 mg/mL (concentration on a free base basis) solutions in methanol from ESR Ltd. and working solutions of 20 and 100 μg/mL were prepared by dilution with HPLC grade methanol or dichloromethane. The concentrations of the working solutions for pseudoephedrine hydrochloride and methamphetamine hydrochloride are expressed on a free base basis.

Methamphetamine free base was prepared from the methamphetamine hydrochloride stock solution. Methamphetamine hydrochloride aqueous solution (5 mL, of 1 mg/mL as methamphetamine free base) was made basic with 1 mL of 4% NaOH solution and was extracted thrice with three portions of 3 mL HPLC grade dichloromethane. The combined extracts were dried with anhydrous sodium sulfate, then the solution was made up to 10 mL to give 0.5 mg/mL metamphetamine free base in dichloromethane. Methamphetamine free base working solutions (20 and 2 μg/mL) were prepared by diluting a portion of this solution with HPLC grade methanol. The extracted methamphetamine free base solution showed a similar GC-MS response to that for an equivalent concentration of methamphetamine hydrochloride, indicating that the extraction was nearly 100% efficient. All working solutions were capped, labeled and kept at 4 °C.

Filter papers (Sartorius 1388, 110 mm in diameter) were sonicated in 5% Decon 90 solution for 15 min then soaked for 3 h before being rinsed thoroughly with milli-Q water, dried at 50 °C, and wrapped with aluminum foil until use as surface wipes. Glass and stainless steel plates were used as substrates to investigate the recovery of low levels of pseudoephedrine and methamphetamine, in both free base and hydrochloride forms. Prior to use, the plates were soaked in 5% Decon-90 overnight, then rinsed with milli-Q water thoroughly. Glass plates were then soaked in 5% nitric acid overnight followed by milli-Q water rinsing. Preliminary experiments showed poor recovery of pseudoephedrine from glass plates that had not been acid-soaked. Glass and stainless steel plates were dried at 100 °C, after which the plates were cooled and then stored wrapped with aluminum foil.

Substrates other than glass and stainless steel were washed with 5% Decon-90, rinsed thoroughly with milli-Q water and dried at 35 °C overnight, then were kept wrapped in aluminum foil. These substrates were adhesive vinyl laminate, engineered stone benchtop (quartz–polyester resin composite), and varnished floor wood (all from Kitchen Place, Auckland), painted metal sheet (PPG Industrial NZ Ltd.), and varnished benchtop wood (The University of Auckland).

Nitrile O-rings were used as the separator between two parallel surfaces ("enclosed surfaces") in part of the study. Prior to use, the O-rings were washed with 5% Decon-90 and rinsed thoroughly with milli-Q water before being dried at room temperature.

2.4. Deposition of samples

Methanolic pseudoephedrine or methamphetamine solutions (in free base or hydrochloride salt forms) were deposited onto the selected surfaces using a 100 μL syringe. The solution was spread over an area of about 80 cm^2 by slowly releasing the solution while moving the syringe needle within the defined area. The methanol was then allowed to evaporate.

2.5. Unenclosed aging experiment

After deposition of the drugs, the contaminated substrates were left on a bench at about 20 °C (range 19–23 °C) such that they were away from direct airflow. Samples were either taken immediately after solvent evaporation or after 2 days.

2.6. 2 days enclosed aging experiment

In order to enclose and contain any pseudoephedrine or methamphetamine that might volatilize, a second plate was held parallel a small distance (ca. 4 mm) above the substrate coated with the trace drug. This required a separator that would provide a good seal and would not cause contamination of the samples. Nitrile O-rings of 10 cm diameter were found to be most suitable. Drug-contaminated substrates were prepared as for the unenclosed experiment. When the solvent had dried, the substrate was covered with a plate (either glass or stainless steel) and then was placed in an incubator at 26 ± 1 °C for 2 days. To ensure a good seal of the O-rings, a 1 kg mass was placed on top of the plates.

2.7. Sample wiping protocol

Two pieces of clean filter paper were dampened with milli-Q water (for pseudoephedrine wipes) or with HPLC grade methanol

(for methamphetamine wipes). Two wipes were performed with each filter paper, in such a way that a 100 cm^2 area including the 80 cm^2 where solution had been deposited was sampled.

Wiping started in an outer corner of the area, and followed a concentric pattern, ending in the centre of the area. The filter paper was then folded with the wiped area facing in, and the area was again wiped from the opposite direction. The filter paper was then folded again with the exposed side in, and was stored in a capped, labeled 22.5 mL glass vial.

2.8. Extraction of sample from filter papers

An aliquot (4 mL) of 4% (m/v) sodium hydroxide solution was added to the sample vial containing the filter papers, and the filter papers were submerged completely into the sodium hydroxide solution prior to a 5 min ultrasonication. The filter papers were transferred into a 5 mL glass syringe using tweezers, then all the solution in the vial was placed into the syringe. The syringe plunger was depressed to force as much solution as possible into a 10 cm culture tube. The filter papers were then removed from the syringe and replaced into the initial sample vial. Additional 4% sodium hydroxide solution (2 mL) was added, and the extraction steps were repeated. The volume of the combined sodium hydroxide solution extract was about 6 mL.

A control experiment in which a solution containing 5 μg of pseudoephedrine free base was deposited on two pieces of filter paper as used in the previous section, with the filter papers being extracted as described above immediately after the solvent had evaporated and then derivatized with cyclohexanone as described in the next section and then GCMS analysis gave recoveries of 84.0 ± 1.4% (n = 3). A similar experiment with 0.1 μg methamphetamine hydrochloride deposited on the filter papers gave recoveries of 91.5% and 94.8% for duplicate experiments after derivatization with trifluoroacetic anhydride and GCMS analysis, while a repeat of this experiment with 0.5 μg methamphetamine hydrochloride deposited on the filter papers gave recoveries of 87.0% and 85.1% for duplicate experiments.

2.9. Sample preparation

The basic pseudoephedrine or methamphetamine solution was extracted twice with two portions of 3 mL HPLC grade dichloromethane. The dichloromethane solution was then dried by passage through anhydrous sodium sulfate before evaporation to about 200 μL using a gentle nitrogen flow and a heating block set at 26 °C, then the solution was transferred to a GC vial. About 200 μL of dichloromethane was then used to rinse the culture tube, and the solutions were combined in the GC vial.

Pseudoephedrine samples were evaporated to about 50 μL, then 25 μL of octadecane (10 μg/mL in n-heptane) was added followed by 1 mL of cyclohexanone:n-heptane (1:1). The vial was then capped and kept at room temperature for at least 24 h prior to GC-MS analysis. A control experiment for the evaporation and derivatization steps starting with 2.5 μg pseudoephedrine in 5 mL dichloromethane gave recoveries of 93.3 ± 2.0% (n = 3) upon derivatization with cyclohexanone and GC-MS analysis.

Methamphetamine samples were evaporated to about 100 μL, then 100 μL of ethyl acetate was added followed by 50 μL of trifluoroacetic acid anhydride (TFAA). The vial was tightly capped, shaken, and incubated at 38 °C for 1 h. The solvents and excess TFAA were carefully evaporated using a stream of nitrogen, then 20 μL of n-tetradecane (20 μL/mL in n-heptane) solution was added followed by 1.0 mL of ethyl acetate. The vial was flushed with nitrogen, capped, and shaken well prior to GC-MS analysis. Such samples remained stable for over a week at 25 °C.

3. Results and discussion

3.1. Analysis of underivatized pseudoephedrine and methamphetamine

The lowest concentration of underivatized pseudoephedrine that gave a discernable peak on the GC-MS was 0.39 μg/mL in n-heptane for a 1 μL injection volume using scan mode. The linear range was 3.12–25.0 μg/mL. The lowest concentration of underivatized methamphetamine that gave a discernable peak by GC-MS was 0.09 μg/mL for a 1.0 μL injection using scan mode. The linear range for underivatized methamphetamine hydrochloride in dichloromethane was 0.78–12.5 μg/mL. In both cases, these linear ranges are too high to allow monitoring of trace contamination.

An additional problem for pseudoephedrine was the formation of adducts in the presence of certain carbonyl-containing compounds. When low concentrations of pseudoephedrine in dichloromethane, chloroform, methanol or n-heptane were analysed by GC-MS, the peak at the retention time where pseudoephedrine eluted showed a base ion at m/z 71 rather than the m/z 58 expected for pseudoephedrine. This problem was also observed when filter paper was used to wipe pseudoephedrine from surface. This altered GC-MS behaviour was previously reported by Lambert [8] to have led to the misidentification of ephedrine as phenmetrazine, while Lewis suggested that the presence of formaldehyde in solvents or specimens during pseudoephedrine urinalysis can lead to oxazolidine formation [9].

Methanol is often used for standard solution preparation or as solvent for GC-MS introduction due to its universal solubility properties. However, oxazolidine formation was observed when low concentrations of pseudoephedrine in methanol were analysed by GC-MS. Thus, when pseudoephedrine free base (10 μg/mL) in HPLC grade methanol was analysed by GC-MS, the response for pseudoephedrine depended on the injection port temperature. A symmetric peak was observed for samples analysed at 250 and 185 °C, while an asymmetric tailing peak was observed at the lower temperatures 165 and 150 °C. The ion at m/z 58, characteristic of pseudoephedrine, decreased as the injector temperature increases, until it was nearly absent when methanolic pseudoephedrine was analysed using an injector temperature of 250 °C. Instead the ion at m/z 71 became dominant.

Koppel et al. have suggested that high injector temperatures in the injector port can dehydrogenate methanol to formaldehyde [10], and that this can affect drug analysis (although they did not include pseudoephedrine or ephedrine in their study). This formaldehyde may react with pseudoephedrine to form an oxazolidine in the injector port. This is consistent with the observations of increased adduct formation at higher injector port temperatures.

Formaldehyde is present as an airborne contaminant in many indoor environments, and it can react with pseudoephedrine at room temperature. It is also present in sampling media such as filter paper or cotton wipes. Soaking filter paper in dilute Decon-90 solution prior to use and storage isolated from atmosphere greatly reduced the formaldehyde content of the sampling media. Even so, at the trace levels being studied here, some pseudoephedrine was converted to the formaldehyde adduct.

3.2. Derivatization of pseudoephedrine

In our hands, TFAA derivatization of trace-level pseudoephedrine presented difficulties. In particular, if the pseudoephedrine–formaldehyde adduct was present, TFAA derivatization (38 °C, 1 h) lead to a variable amount of N,O-bis(trifluoroacetyl)ephedrine being formed as well as N,O-bis-(trifluoroacetyl)pseudoephedrine and N-trifluoroacetylpseudoephedrine, indicating some epimerization was occurring

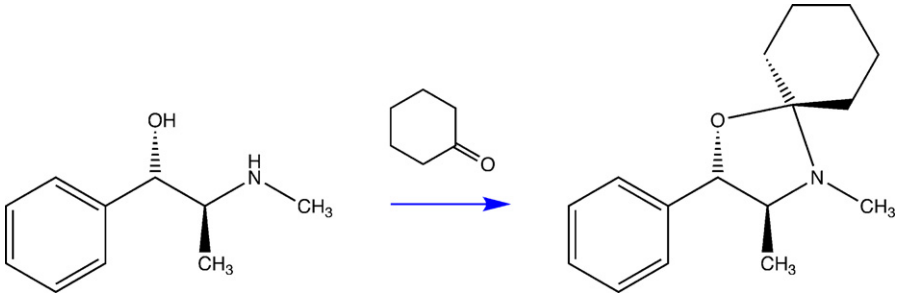

Fig. 1. Formation of the 1,3-oxazolidine derivative from pseudoephedrine and cyclohexanone [12].

during the process [11]. Therefore, an alternative derivatization strategy was developed for pseudoephedrine based on the in situ derivatization with cyclohexanone reported by El-Haj et al. [12]. Although this is not a standard method, the conclusions from the wipe sampling and sample preparation strategies will be applicable to any other derivatization and analysis strategy. El-Haj et al. proposed injecting pseudoephedrine in cyclohexanone to give in situ derivatization [12]. We found that the best derivatization yields were obtained if pseudoephedrine was left in a solution of 1:1 cyclohexanone:n-heptane at room temperature for 1 day.

A mixture of cyclohexanone:n-heptane (1:1) lead to a pseudoephedrine derivative with a symmetric GC peak for the pseudoephedrine derivative whereas a distorted GC-MS response was observed if neat cyclohexanone was used. The pseudoephedrine–cyclohexanone derivative (PSE-CYH) eluted at 8.99 min, after the internal standard C-18 peak at 8.76 min. The base peak of the mass spectrum was at *m*/*z* 202, with an ion at *m*/*z* 245 (M, the molecular ion) present in relatively large abundance. These mass spectral peaks match those reported previously [12,13] for this compound. The PSE-CYH derivative is stable for over 3 months at room temperature. The limit of detection for pseudoephedrine derivatized with cyclohexanone:n-heptane (1:1) for a 1 μL injection using scan mode was 48 ng/mL with a linear range of 97 ng/mL to 12.5 μg/mL (Figs. 1 and 2).

The cyclohexanone does not need to be removed following derivatization since it also serves as part of the sample solvent. However, the solvent delay on the GC-MS needs to be increased to 5 min to allow for elution of the cyclohexanone. This method detects the combined concentrations of both pseudoephedrine and the pseudoephedrine–formaldehyde derivative present in a sample, since the latter is converted to the pseudoephedrine-cyclohexanone derivative during the 24 h incubation time.

3.3. Surface recovery of pseudoephedrine

All reported recoveries are comparisons to standards of pseudoephedrine or methamphetamine at low concentrations that underwent the same derivatization steps as the samples. Thus, incomplete but reproducible derivatization will not affect the results. The extraction of pseudoephedrine or methamphetamine from the filter paper wipes led to small losses (7–16%, see Section 2.3), and the reported recoveries have not been corrected for such losses.

All deposition experiments were performed with the contamination spread over a circular region of 80 cm^2. However, surface concentration results in the text have been converted to μg/100 cm^2 for compatability with common sampling analysis protocols. When 2.5 μg/100 cm^2 of methanolic pseudoephedrine free base or pseudoephedrine hydrochloride is deposited onto clean glass or stainless steel and the surface is wiped with water-dampened filter papers immediately after the solvent has evaporated, 75% of the pseudoephedrine can be recovered. Similar high recoveries were obtained from other smooth surfaces, i.e. coated wall paper, stainless steel bench, and painted metal. For slightly rougher surfaces (varnished wood, Formica, or Melteca benchtop) about 60–65% of pseudoephedrine free base or pseudoephedrine hydrochloride were recovered from a 2.5 μg/100 cm^2 deposited sample, Table 1. This slightly lower recovery indicates that pseudoephedrine recovery is affected by the surface texture.

When pseudoephedrine free base or pseudoephedrine hydrochloride were deposited at concentrations of 2.5 μg/100 cm^2 on glass and stainless steel and then exposed in a thermostated room at approximately 20 °C for 2 days, less than 20% of the pseudoephedrine free base could be recovered, with only slightly higher recoveries (ca. 30%) for pseudoephedrine hydrochloride.

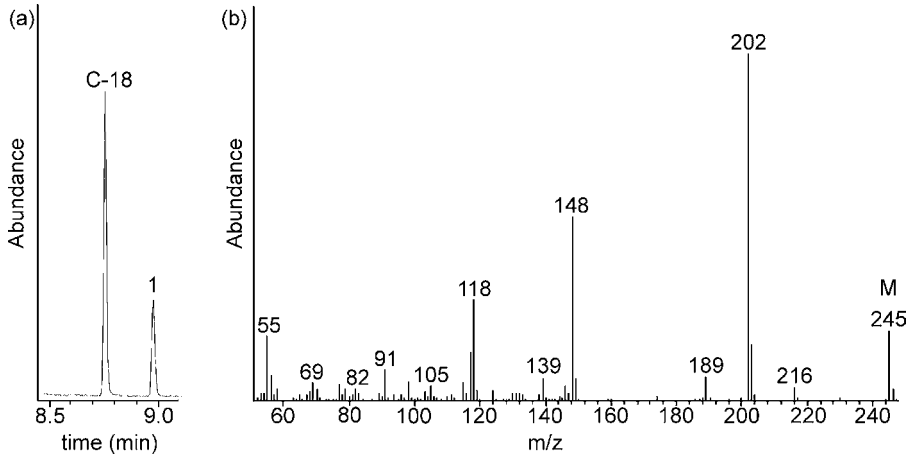

Fig. 2. (a) GC-MS chromatogram showing peak due to the pseudoephedrine–cyclohexanone derivative (1) at 8.99 min (peak at 8.76 min is the octadecane internal standard), and (b) the mass spectrum of PSE-CYH with *m*/*z* at 202 as the base peak and molecular ion at *m*/*z* 245.

Table 1
Recovery of pseudoephedrine free base and pseudoephedrine hydrochloride (2.0 μg/80 cm^2) from various clean impermeable surfaces immediately after deposition.

	Pseudoephedrine free base	Pseudoephedrine hydrochloride
Filter paper	80.7 ± 1.8	80.6 ± 3.7
Stainless steel	76.9 ± 0.4	75.1 ± 2.0
Painted metal	77.6 ± 0.4	74.6 ± 1.1
Composite benchtop	73.3 ± 1.5	67.3 ± 0.8
Vinyl laminate	76.0 ± 2.3	80.2 ± 1.9
Clean steel bench	73.8 ± 1.8	78.5 ± 1.4
Formica sheet	60.4 ± 0.5	57.7 ± 0.4
Varnished wood	60.8 ± 2.7	55.4 ± 2.1
Wood flooring	61.6 ± 0.3	60.4 ± 1.0
Clean Melteca bench	66.2 ± 2.3	66.8 ± 1.3

The observed sample loss could have happened via physical loss of small pseudoephedrine particles, or via revolatization of the pseudoephedrine. Irreversible adsorption or absorption of pseudoephedrine on the surface is unlikely, particularly on the glass, since these surfaces are relatively inert and smooth, and had been cleaned and acid-soaked. Since the importance of these loss mechanisms for trace-level drugs on contaminated surfaces is not well characterized, we performed experiments in which the treated surface was enclosed by another surface held about 4 mm above it, with an O-ring preventing sample loss to the external atmosphere.

When the substrate was enclosed, the total recoveries for both pseudoephedrine free base and pseudoephedrine hydrochloride deposited at a concentration of 2.5 μg/100 cm^2 were about 50% after 2 days at 26 °C, Table 2. The experimental design does not allow us to determine whether the observed loss is due to irreversible adsorption onto the glass, stainless steel or O-ring, or loss past the O-ring seal. However, control experiments showed that no pseudoephedrine could be extracted from the O-ring after exposure. In addition, experiments using a soft copper gasket instead of a nitrile O-ring did not give increased recoveries. Since the recovery from pseudoephedrine deposited directly onto filter paper was about 80%, these results suggest that about 60% of the pseudoephedrine is being transferred from the surface to the filter paper from the 2.5 μg/100 cm^2 sample left for 2 days. This is clearly in marked contrast to the open samples where less than 16% (free base) and less than 30% (hydrochloride) were recovered after 2 days.

Table 3
Recoveries of 2 μg pseudoephedrine free base and pseudoephedrine hydrochloride from selected surfaces covered with glass plates positioned ca. 4 mm above the surface (each surface area = 80 cm^2) after 2 days at 26 °C (±range/2).

Surfaces	Position	% recovery (n = 2, except *single sample)	
		Pseudoephedrine (2.0 μg)	
		Free base	Hydrochloride
Glass / Glass	Top	20.5*	14.6*
	Bottom	35.5*	49.5*
	Total	56.0*	64.1*
Glass / Painted metal	Top	5.2 ± 0.8	4.5 ± 0.4
	Bottom	5.2 ± 0.3	8.1 ± 0.8
	Total	10.4 ± 0.6	12.1 ± 1.7
Glass / Composite benchtop	Top	5.3 ± 0.4	5.5 ± 0.8
	Bottom	35.6 ± 0.9	36.7 ± 2.3
	Total	40.9 ± 2.3	42.2 ± 1.5
Glass / Vinyl laminate	Top	6.0 ± 0.2	5.3 ± 1.3
	Bottom	45.3 ± 4.3	43.6 ± 0.3
	Total	51.3 ± 4.5	48.9 ± 1.6
Glass / Varnished wood	Top	4.6 ± 0.7	5.2 ± 0.4
	Bottom	41.0 ± 3.1	38.8 ± 0.2
	Total	45.6 ± 2.4	44.0 ± 0.2
Glass / Wood flooring	Top	7.3 ± 1.9	3.9 ± 0.0
	Bottom	34.6 ± 0.5	35.3 ± 0.6
	Total	41.9 ± 2.4	39.2 ± 0.6

In the enclosed format, the household surfaces of wall paper, painted metal, kitchen top tile, varnished wood, and floor wood were all covered with a glass plate to increase the comparability of the results. A total of 40–55% of the deposited pseudoephedrine free base and pseudoephedrine hydrochloride could be recovered from most of the surfaces after 2 days, with the highest recovery being observed from a wall paper which was non-porous and smooth, Table 3. However, the recovery of pseudoephedrine from painted surfaces was very low. It is possible that the pseudoephedrine has a strong physical interaction with the paint (perhaps with the carbonyl group) or it may have reacted. This result shows that some smooth surfaces can retain pseudoephedrine so that surface wiping does not provide a good estimation of the amount of the material actually present. It should also be noted that the pseudoephedrine could be recovered in high yields (ca. 75%) from these painted surfaces immediately after deposition showing that the loss of recoverable pseudoephedrine was not immediate.

Table 2
Recoveries of pseudoephedrine free base and pseudoephedrine hydrochloride from enclosed glass and stainless steel at different concentrations (all masses deposited over 80 cm^2). Top plate was positioned ca. 4 mm above bottom plate, with O-ring spacer.

Pairs	Position	% recovery (n = 5, except in *n = 4, **n = 3)					
		10 μg pseudoephedrine		2 μg pseudoephedrine		1 μg pseudoephedrine	
		Free base	Hydrochloride	Free base	Hydrochloride	Free base	Hydrochloride
Glass / Glass	Top	22.5 ± 6.5	11.8 ± 3.8	23.9 ± 2.9	20.2 ± 3.4	20.9 ± 3.2	17.4 ± 1.7
	Bottom	23.4 ± 3.4	56.9 ± 4.3	23.0 ± 4.5	38.2 ± 4.7	31.2 ± 4.0	35.5 ± 2.9
	Total	45.9 ± 4.4	68.7 ± 2.4	46.9 ± 4.5	58.5 ± 2.8	52.1 ± 2.4	52.9 ± 2.3
Stainless steel / Stainless steel	Top	20.5 ± 2.6	12.7 ± 2.1	18.3 ± 2.4	14.6 ± 1.3	13.1 ± 1.5	17.0 ± 2.5
	Bottom	24.5 ± 3.2	61.6 ± 2.9	29.6 ± 3.1	40.8 ± 4.9	38.1 ± 2.4	35.2 ± 3.8
	Total	45.0 ± 3.6	74.3 ± 1.9	47.9 ± 2.8	55.4 ± 4.0	51.2 ± 1.7	52.2 ± 2.8
Glass / Stainless steel	Top	19.6 ± 3.1	9.2 ± 2.0	20.0 ± 2.3	16.8 ± 2.4	17.3 ± 1.7	13.5 ± 2.9
	Bottom	32.6 ± 2.2	67.4 ± 4.2	35.5 ± 4.4	40.0 ± 2.5	36.7 ± 5.0	43.8 ± 3.2
	Total	52.2 ± 1.4	76.7 ± 2.5	55.5 ± 6.3	56.8 ± 3.6	54.3 ± 4.5	57.3 ± 2.7
Stainless steel / Glass	Top	35.9 ± 4.0	14.0 ± 1.9	29.0 ± 2.4	30.1 ± 4.7*	29.5 ± 4.4	21.5 ± 6.2
	Bottom	20.9 ± 1.7	61.7 ± 2.8	24.3 ± 5.0	24.5 ± 5.5*	28.0 ± 6.5	38.7 ± 6.9**
	Total	56.8 ± 4.1	75.7 ± 2.3	53.5 ± 3.2	54.6 ± 2.7*	57.5 ± 6.5	58.4 ± 4.0**

Table 4
Recovery of methamphetamine free base and methamphetamine hydrochloride (0.5 μg/80 cm^2) from various clean, impermeable surfaces immediately after deposition (±range/2 for n = 2; ±std dev for n = 3).

Surfaces	% recovery (0.5 μg)	
	Methamphetamine free base (n = 2)	Methamphetamine hydrochloride (n = 3)
Painted metal	81.4 ± 0.1	77.9 ± 7.9
Composite benchtop	71.8 ± 1.0	79.5 ± 4.4
Vinyl laminate	85.1 ± 1.7	80.4 ± 0.6
Formica sheet	71.3 ± 0.0	80.3 ± 2.9
Varnished wood	63.5 ± 3.4	59.5 ± 8.1
Wood flooring	73.7 ± 3.3	71.9 ± 4.8

3.4. Surface recovery of methamphetamine

Samples containing trace levels of methamphetamine were derivatized with TFAA, since this led to improved chromatographic behaviour and limits of detection compared to underivatized methamphetamine, with a linear range of 31 ng/mL to 2 μg/mL and a limit of detection of 10 ng/mL.

Surface wipe sampling of methamphetamine hydrochloride from glass or stainless steel immediately after deposition gave a high recovery of about 90% of the sample at the three concentrations used, 0.12, 0.6 and 1.2 μg over 100 cm^2. A slightly lower recovery, 83–85%, was observed for methamphetamine free base at concentrations of 0.6 and 1.2 μg/100 cm^2. The slight decrease in recovery may be due to the higher volatility of methamphetamine free base compared to its salt form.

For common smooth, impermeable household surfaces (coated wall paper, ceramic tile, and painted metal), the averaged results show a high mean recovery (>70%) of methamphetamine free base and methamphetamine hydrochloride immediately after deposition, Table 4. These high recoveries immediately after deposition of methamphetamine are similar to those reported recently using isopropanol wipes [14]. For the more textured wood samples, a reasonably good recovery (60–70%) of both methamphetamine free base and methamphetamine hydrochloride was also observed immediately after deposition.

In a similar manner to the pseudoephedrine experiments, methamphetamine-contaminated surfaces were initially left exposed to the room atmosphere at ca. 20 °C. Methamphetamine free base (0.5 μg) and methamphetamine hydrochloride (2.0 and 0.5 μg) were deposited onto clean glass and stainless steel surfaces (ca. 80 cm^2) to represent low level methamphetamine contamination. Under these conditions, less than 30% of the methamphetamine could be recovered after 2 days.

Table 6
Recoveries of 0.5 μg methamphetamine free base and methamphetamine hydrochloride from selected clean impermeable surfaces sandwiched with a glass plate (surface area = 80 cm^2) after 2 days at 26 °C.

Surfaces	Position	% recovery	
		Methamphetamine (0.5 μg)	
		Free base (n = 4)	Hydrochloride (n = 3)
Glass / Painted metal	Top	20.4 ± 7.0	24.2 ± 3.7
	Bottom	60.4 ± 5.1	34.9 ± 5.9
	Total	80.8 ± 1.2	69.1 ± 2.3
Glass / Composite benchtop	Top	21.7 ± 6.7	5.3 ± 0.6
	Bottom	50.3 ± 5.3	54.7 ± 1.7
	Total	72.0 ± 7.1	60.0 ± 2.2
Glass / Vinyl laminate	Top	17.3 ± 4.3	14.9 ± 1.5
	Bottom	56.3 ± 4.7	44.7 ± 3.8
	Total	73.6 ± 2.5	59.6 ± 3.6
Glass / Varnished wood	Top	9.3 ± 0.5	9.7 ± 8.3
	Bottom	53.2 ± 0.9	45.8 ± 5.3
	Total	62.5 ± 1.2	55.5 ± 6.0
Glass / Wood flooring	Top	13.7 ± 4.3	6.5 ± 1.6
	Bottom	50.2 ± 0.7	48.9 ± 1.0
	Total	63.9 ± 5.0	55.4 ± 0.6

Once again, experiments using an enclosed format gave much higher recoveries, with significant amounts of methamphetamine being present on the cover plate. The overall recovery of methamphetamine free base and methamphetamine hydrochloride across the different surface pairs, glass–glass, stainless steel–stainless steel, glass–stainless steel, and stainless steel–glass was in the range of 70–80% with the highest recovery being observed for the glass pairs, Table 5. There was no obvious recovery difference between methamphetamine free base and methamphetamine hydrochloride and little difference between the substrates used. Almost all the experiments showed similar methamphetamine levels on the top and bottom plates, showing that redistribution due to volatilization is very important for methamphetamine at these surface concentrations.

When a glass plate was used to cover each of the surfaces of wall paper, painted metal, ceramic tile, varnished wood, and floor wood, 55–80% of the deposited methamphetamine free base could be recovered from the various surfaces or the cover plate, Table 6. The smooth surfaces (painted metal, ceramic tile and wall paper)

Table 5
Recoveries of methamphetamine free base and methamphetamine hydrochloride from enclosed glass and stainless steel surfaces at different concentrations (all masses deposited over 80 cm^2) (±range/2 for n = 2; ±std dev for n = 4).

Pairs	Position	% recovery (n = 2 except for 0.1 μg where n = 4)					
		1.0 μg methamphetamine		0.5 μg methamphetamine		0.1 μg methamphetamine	
		Free base	Hydrochloride	Free base	Hydrochloride	Free base	Hydrochloride
Glass / Glass	Top	39.7 ± 1.2	34.7 ± 2.1	37.4 ± 3.3	30.1 ± 3.3	–	31.6 ± 2.9
	Bottom	42.0 ± 0.3	47.3 ± 3.0	46.0 ± 4.6	49.8 ± 3.5	–	37.2 ± 5.2
	Total	81.7 ± 1.0	82.0 ± 1.0	83.4 ± 1.3	79.9 ± 0.3	–	68.8 ± 3.3
Stainless steel / Stainless steel	Top	33.0 ± 2.3	28.0 ± 0.4	26.7 ± 0.9	31.3 ± 2.5	–	30.7 ± 4.0
	Bottom	41.6 ± 0.4	48.0 ± 1.7	52.9 ± 0.5	43.7 ± 0.6	–	43.6 ± 3.0
	Total	74.6 ± 1.9	76.0 ± 1.3	79.6 ± 0.4	75.0 ± 3.1	–	74.3 ± 6.8
Glass / Stainless steel	Top	35.1 ± 0.9	17.5 ± 0.4	34.0 ± 2.3	17.7 ± 1.3	–	–
	Bottom	37.1 ± 1.9	56.8 ± 1.8	40.8 ± 4.4	54.0 ± 2.2	–	–
	Total	72.2 ± 1.1	74.3 ± 1.3	74.8 ± 2.2	71.7 ± 0.9	–	–
Stainless steel / Glass	Top	36.0 ± 3.3	38.3 ± 2.7	38.5 ± 3.9	32.9 ± 0.8	–	–
	Bottom	34.9 ± 2.5	32.0 ± 2.6	36.7 ± 6.7	39.0 ± 2.2	–	–
	Total	70.9 ± 0.8	70.3 ± 0.1	75.2 ± 2.8	71.9 ± 1.4	–	–

showed a high recovery (more than 70%) with about 20% of the deposited free base being recovered from the top cover (glass). The rougher surfaces (floor wood and varnish wood) showed a slightly lower total recovery (less than 65%), with less than 15% of the methamphetamine being recovered from the top cover. Whereas only trace amounts of pseudoephedrine could be recovered from a painted metal surface after 2 days at 26 °C, 70–80% of methamphetamine free base and methamphetamine hydrochloride could be recovered from this surface, indicating less interaction of methamphetamine with paint material.

4. Conclusion

Experiments where pseudoephedrine or methamphetamine was recovered immediately after the solvent had evaporated showed relatively high recoveries (for example, more than 70% for a surface concentration of 0.63 μg/100 cm^2 of methamphetamine free base or methamphetamine hydrochloride from the smooth surfaces) with overall recoveries being 5–10% less than those obtained when the drugs were applied directly to the filter paper wipes. This showed that little pseudoephedrine or methamphetamine was irreversibly bound or was lost as vapour or particulates on this short time scale.

When pseuodoephedrine- or methamphetamine-contaminated surfaces were studied in an enclosed format, significant amounts of pseudoephedrine free base, pseudoephedrine hydrochloride, methamphetamine free base, or methamphetamine hydrochloride were found on a glass plate positioned 4 mm above the contaminated surface, under conditions where physical transport of particulates is unlikely to have occurred. This shows that these compounds have sufficient vapour pressures that volatilization is a significant loss mechanism particularly at low surface concentrations on smooth surfaces such as glass or stainless steel. This volatility of pseudoephedrine has been noted previously [15].

Our data supports the use of methamphetamine as a surrogate to represent both methamphetamine and pseudoephedrine on household surfaces during clandestine laboratory remediation due to its high surface recovery and similar sample redistribution upon deposition to that seen for pseudoephedrine. Nonetheless, it must be ensured that methamphetamine sampling is representative because different surfaces have different retentions for methamphetamine as seen in the enclosed format experiments. Thus, collecting wipes from up to four different locations and combining these wipes into one composite sample as suggested in some guidelines [16] should be avoided if the wipe samples are taken from different surface materials. Ideally, samples should be discretely analysed for each type of surface material. Post-remediation sampling of a room should take into account the volatility of methamphetamine and pseudoephedrine. Finally, the cleanup level for methamphetamine and pseudoephedrine to 0.1 μg/100 cm^2 should be interpreted carefully because recovery from wipes is dependent on surface material and texture. Thus, the observed value may be only a fraction of that actually present on the surface. However, our results show that for many clean impermeable substrates, at least 50–60% of the material still present is recovered using these described wiping and analysis protocols. This means that the sampling combined with GC-MS underestimates the actual methamphetamine present by at most a factor of two for clean impermeable surfaces similar to those used in this study.

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