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Detection of illicit drugs on surfaces using direct analysis in real time (DART) time-of-flight mass spectrometry†

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Methamphetamine (meth) from meth syntheses or habitual meth smoking deposited on household surfaces poses human health hazards. The U.S. State Departments of Health require decontamination of sites where meth was synthesized (meth labs) before they are sold. National Institute for Occupational Safety and Health (NIOSH) methods for meth analysis require wipe sampling, extraction, clean-up, solvent exchange, derivatization, and/or mass spectral analysis using selected ion monitoring. Rapid and inexpensive analyses could screen for drug-contamination within structures with greater spatial resolution, provide real-time analyses during decontamination, and provide thorough documentation of successful clean ups. Herein an autosampler/open-air ion source time-of-flight mass spectrometric technique is described that required only direct sampling using cotton-swab wipes. Each wipe sample collection required 2 min and data acquisition required only 13 s per sample. Optimum collision-induced dissociation voltages, desorption gas temperatures, and wipe sample solvents were determined for 11 drugs. Peaks were observed in analyte-ion traces for 0.025 μg/100 cm^2 of meth and seven other drugs. This level is half the detection limit of NIOSH methods and one-fourth of the lowest U.S. state decontamination limit for meth. Dynamic ranges of 100 in concentration were demonstrated for eight drugs, which is sufficient for a screening technique. The volatilities of 11 drugs deposited on glass were determined. The pick up of the drugs by solvent-soaked cotton-swab wipes from glass relative to acrylic latex paint was also compared. Published in 2011 by John Wiley & Sons, Ltd.

In 2010 alone, 10 247 methamphetamine (meth) lab incidents were reported by the U.S. Drug Enforcement Administration.[1] Meth syntheses that use the red phosphorus or anhydrous ammonia methods produce meth vapor, aerosols, and particulates that contaminate floors, walls, ceilings, and objects.[2] Meth contamination is found immediately and long after meth syntheses, at levels well above U.S. state clean-up standards.[2,3] These standards can also be exceeded by meth residues produced by habitual meth users.[4] Gauze pad wipe samples analyzed by National Institute for Occupational Safety and Health (NIOSH) mass spectrometric methods[5–9] have detection limits of 0.05 or 0.1 μg/100 cm^2. Based primarily on NIOSH method detection limits, 15 U.S. states[10] have set decontamination standards of 0.1–0.5 μg /100 cm^2.

To quantify meth retrievable from surfaces, the gas chromatography/mass spectrometry (GC/MS)[5,6,8] and liquid gas chromatography/mass spectrometry (LC/MS) methods[7,9] require wipe sampling, extraction, clean-up, solvent exchange, and/or mass spectral analysis using selected ion monitoring. Derivatization is also required for the GC/MS methods. The expense of these methods limits the thoroughness with which meth labs can be screened for drug contamination. Biased sampling or judgmental sampling plans are recommended by the U.S. Environmental Protection Agency (EPA).[11] In either case, meticulous focus on a sampling plan is necessary due to the limited number of samples collected. A simple, specific, sensitive, inexpensive, and high-throughput, screening technique with a meth detection limit of 0.1 μg/100 cm^2 or less would enable collection of more wipe samples to screen for meth contamination before and after decontamination.

The popularity of specific illegal drugs changes over time, and new designer drugs can become common. A new screening technique should be capable of identifying and detecting numerous smoked or spilled illicit-drug residues on surfaces. Interpretation of the mass spectra obtained using an inexpensive and broadly applicable screening technique based on the analysis of wipe samples could assure a perspective buyer of a property that gross contamination by numerous illegal drugs, including those listed in Table 1, is absent. A simple kit could enable wipe sample collection by people with no prior field sampling experience.

Our laboratory has performed direct analyses of wipe samples for analytes on insoluble surfaces using an open-air ion source coupled to a mass spectrometer.[12–16] Similar analyses of wipe samples of smoke condensed on surfaces or spilled drugs should be possible. Nine drugs were investigated that are used illicitly, including several that are commonly smoked, along with nicotine found in tobacco smoke and pseudoephedrine, which is used to produce methamphetamine. Their chemical structures are shown in Fig. 1.

Factors which are important to wipe sample pick up of drugs and the persistence of drug residues are the impermeability and inertness of surfaces, the tendency of drugs to adhere to or penetrate a surface, and the volatility of drugs. Several experiments investigated these factors.

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Table 1. Optimum values for three variables and observable peak limits for 11 drugs

Analyte	Analyte ion m/z $[M+H]^+$	CIDV (V)[a] (% RCPA)[b]	Temperature (°C) setting (% RCPA)[c]	Pick up solvent (% RCPA)[d]	OPL[e] (μg/(100 cm^2))
Amphetamine	136.1121	50 (81,100,95)	200 (89,100,64)	IPA (72,100,31)	0.025[f]
Pseudoephedrine HCl	148.1121[g]	70 (81,100,94)	200 (69,100,84)	IPA (46,100,14)	0.025[f]
Methamphetamine	150.1277	45 (82,100,87)	200 (80,100,91)	IPA (41,100,40)	0.025[f]
Nicotine	163.1230	45 (67,100,83)	150 (100,84,54)	IPA (22,100,15)	0.1
Ketamine HCl	238.0993	45 (91,100,75)	200 (87,100,98)	IPA (43,100,18)	0.025[f]
PCP	244.2060	30 (88,100,83)	200 (0,100,63)	IPA (44,100,16)	0.025[f]
Morphine	286.1438	80 (74,100,88)	300 (58,100,70)	IPA (11,100,3)	0.1
Cocaine	304.1543	45 (93,100,95)	250 (92,100,91)	IPA (62,100,20)	0.025[f]
THC	315.2318	40 (69,100,81)	250 (85,100,100)	IPA (73,100,1)	0.1
Fentanyl	337.2274	50 (78,100,86)	250 (71,100,78)	IPA (32,100,15)	0.025[f]
Heroin	370.1649	80 (73,100,89)	250 (100,100,98)	IPA (28,100,17)	0.025[f]

[a]The voltage applied to the cone orifice leading into the mass spectrometer (CID voltage).
[b]The numbers in parentheses are the average (N = 3) % relative chromatographic peak areas (% RCPAs) compared with that obtained for the optimum CID voltage (100%). 5 V increments in the CID voltage below and above the optimum correspond to the lesser % RCPAs.
[c]The helium stream temperature was set between 150 and 350°C in 50°C increments for each analyte. The numbers in parentheses are the % RCPAs corresponding to temperatures different from the optimum by –50, 0, and +50°C, except for nicotine for which 150°C was the optimum temperature.
[d]The testing order for the solvents was MeOH, IPA, and water. The numbers in parentheses are the corresponding % RCPAs.
[e]Observable peak limit.
[f]Lowest level tested.
[g]A product ion, $[M+H-H_2O]^+$, was the quantitation ion for pseudoephedrine.

EXPERIMENTAL

Instrumentation

A Direct Analysis in Real Time (DART®) ion source (IonSense, Saugus, MA, USA) interfaced to a JEOL AccuTOF® 100 time-of-flight (TOF) mass spectrometer (JEOL USA, Peabody, MA, USA) was used to acquire all the mass spectra. A Vapur® evacuated flange was located between the DART ion source and the mass spectrometer.

DART-TOFMS parameters

The following instrument settings were those recommended by the manufacturer. The DART settings were: positive ion mode; needle voltage, 3.5 kV; electrode 1 voltage, 150 V; and electrode 2 voltage, 250 V.

The mass spectrometer settings included: ring lens voltage, 10 V; orifice 2 voltage, 5 V; cone temperature, 120°C; peak voltage, 600 V (to observe ions down to m/z 60); bias voltage, 28 V; focus voltage, –120 V; reflectron voltage, 800 V; pusher voltage, 778 V; pulling voltage, –778 V; suppression voltage, 0.20 V; flight tube voltage, –7000 V; and detector voltage, 2300 V. The mass range acquired was m/z 60–600 and the scan rate was 8/s. The optimum orifice 1 voltage settings were analyte-specific as discussed below.

The ion abundance was maximized for a helium flow rate of 7.0 L/min (nearly the maximum available) and a setting of 15 for the throttle valve located along the vacuum line between the Vapur flange and the membrane pump (IonSense). The high helium flow rate subjected the cotton-swab wipe samples to more heat at a given helium temperature, and more gas was directed into the ceramic tube leading into the Vapur flange. The high-throughput autosampler minimized helium consumption for large sets of swabs. The optimum helium temperature was analyte-specific as discussed later.

Autosampler

An autosampler fabricated from N-scale model railroad flatcars (flatbed wagons), track, and a transformer (±15 VDC power supply); a small variable-speed DC motor; several pulleys; and other readily available and inexpensive components[12,13] transported the heads of the cotton-swab wipe samples sequentially through the open-air ionizing region of the DART ion source. To maximize simplicity and speed when screening for drugs, water-soaked swab heads were not placed between analyte swabs to mitigate carry over,[15] which is a problem when high levels of analyte are present. If carry over were a significant problem, copious quantities of the analyte would obviously be present and decontamination would be required. Effective removal of drugs below or near the decontamination limit would eliminate the carry over.

Field sample carrier

A field sample carrier that contained the core element of the autosampler, a 3-feet long, ¼-inch square aluminum bar with 76 holes along its length to support cotton-swab heads, was used when collecting wipe samples from household surfaces.[14] The head of each 6-inch swab was covered by an inverted 1.8-mL, wide-mouth, glass vial held in place by a linear cell assembly that encased the bar before and after a wipe sample was taken. After collecting a wipe sample, the swab stick was clipped off at the base of the cell assembly to avoid acquiring multiple

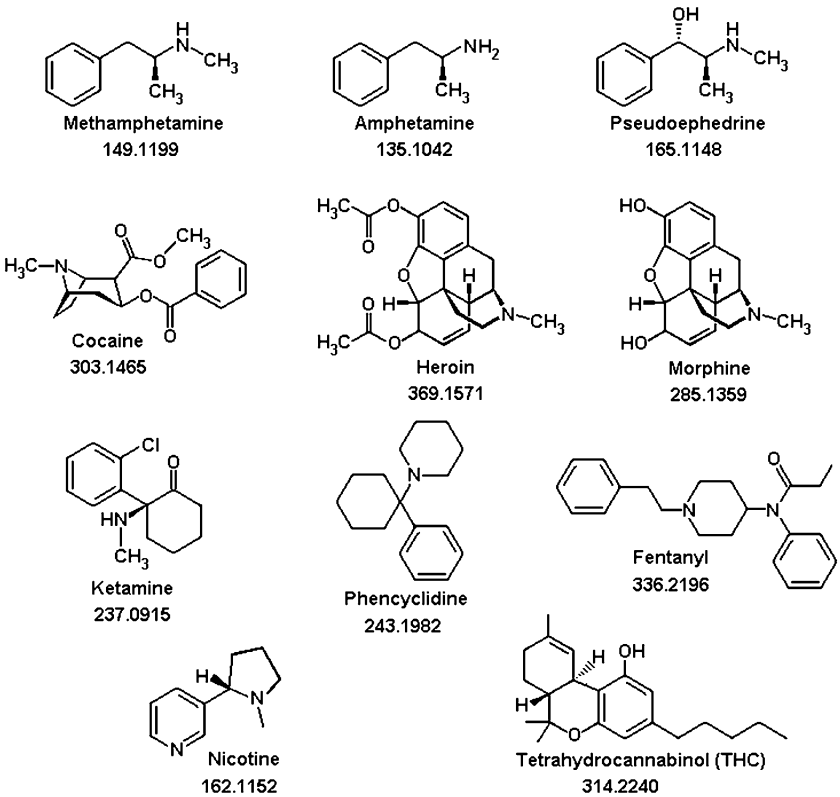

Figure 1. Structures and monoisotopic masses of nine illicitly smoked drugs, nicotine, and pseudoephedrine.

samples with the same swab and to make the swab ready for analysis. Before analysis, the cell assembly and vials were quickly removed and the support bar with wipe samples was loaded onto the flat cars of the autosampler.

Analytes

Eleven standards containing 1 mg of one of the test drugs listed in Table 1 in 1 mL of methanol were purchased from Cerilliant (Round Rock, TX, USA). The standards were refrigerated. Distilled water was used for serial dilutions immediately prior to depositing analytes on surfaces.

A time-release, cold-remedy tablet (Target, Minneapolis, MN, USA) provided 120 mg of pseudoephedrine for preliminary experiments and for a drug pick up study from household surfaces.

Paint

For some experiments two coats of Lowe's (Mooresville, NC, USA) acrylic latex paint (Extra Premium Valspar, interior flat) were applied with a paint brush to a mirror to simulate a painted wall or ceiling.

Wipe sample solvents

Methanol (GR, EM Science, Gibbstown, NJ, USA), 99% isopropanol (IPA), and distilled water were each tested as wipe sample solvents for picking up the 11 drugs from a mirror. Only IPA and water were compared for picking up the drugs from acrylic latex paint. Distilled water and IPA were purchased from supermarkets to minimize the cost of analyses.

Laboratory surfaces

A mirror provided an impermeable, smooth, insoluble, and easily cleaned surface. The mirror was wiped twice with distilled water on paper towels between experiments, and this yielded non-detectable drug levels. Because paint could not be removed from drywall between experiments, two coats of acrylic latex paint were brushed across the mirror at least 2 h apart to provide a painted surface. The paint was allowed to cure for at least 1 week (the time specified on the label) before the paint would survive washing with a mild soap solution. Each paint surface was sampled only once except for the recovery experiments. A razor blade was used to remove paint from the mirror between experiments.

Cotton swabs

While small pieces of walls, ceilings, or floors could be chiseled free and small pieces of furniture, drapes, or clothing could be cut free for analysis, a non-destructive and more reproducible sampling technique with solvent-soaked cotton swabs was preferred, although detection limits might be higher. An area of 100 cm^2 was wipe-sampled to provide a more representative sample than a chip or piece of fabric, which would require alignment so that the helium beam grazed the original surface.

Sampling such a large area would increase the likelihood of finding small localized regions of drug residues. Use of cotton swabs also provided compact samples with similar shapes that enable automated, high-throughput, direct analyses.[12] Cotton swabs with 6-inch wooden sticks (REF 867-WC, Puritan, Guilford, ME, USA), which contained no glue to affix the cotton to the stick, were used to acquire the wipe samples.

For laboratory experiments, solvent-soaked cotton-swabs were used to acquire wipe samples, air-dried, and analyzed 0.75 to 3 h later to minimize volatilization of the analyte from the swabs before analysis. The household surface wipe samples were analyzed within 24 h.

Analyte deposition

Martyny *et al.*[4] burned meth to provide deposition on surfaces similar to that expected from smoking the drug. Our focus was the applicability of our analytical system for the detection of smoked drugs. More convenient depositions consisted of ejecting 25, 50, or 100 μL of aqueous drug solutions from a 100-μL syringe while guiding the syringe back and forth from top to bottom onto horizontal, 10 × 10-cm surfaces, or by spraying 0.14 mL of an aqueous solution with a small bottle equipped with a manually depressed spray nozzle. At least 1 h and 3 h were allowed for the solutions to dry on glass and paint, respectively, before wipe sampling.

Sampling technique

Analytes deposited within 100-cm^2 areas delineated by a fishing line on the mirror or painted mirror were wipe-sampled using the head of a 6-inch-long cotton swab that had been dipped for 5 s into methanol, IPA, or water in a scintillation vial. To measure an average solvent volume on swabs, 10 swabs were dipped into a 10-mL graduated cylinder containing one of the solvents. The average volumes were 0.17, 0.18, and 0.17 mL for methanol, IPA, and water, respectively. The solvent-soaked swab head was rolled right-to-left and back until the entire 100 cm^2 was sampled. The swab was rotated 90° and the rolling procedure was repeated to ensure a uniform distribution of the analyte along the swab head and around its circumference. This was important, since the leading and trailing edges of the swab are preferentially sampled as it passes through the helium stream. For water, the cotton compacted during sampling and no fibers stuck out from the swab head. After wipe sampling with methanol or IPA, however, such fibers were evident. The swab was rolled nearly parallel to the surface sampled until all the cotton was compacted and the entire swab head was aligned with the stick. This practice pushed fibers sticking out from the swab back into the swab head and minimized any effect on measured ion abundances that the fibers and slight shape differences of the swab heads might cause.

The solvent was allowed to dry in air to simplify ion-molecule chemistry,[16,17] to simulate real-world wipe samples which would be dry before reaching the instrument, and to avoid having different amounts of solvent present on the swabs during analysis, which would consume heat from the helium stream to evaporate solvent rather than to desorb analyte and thus lower the sensitivity. Unless stated otherwise, triplicate wipe samples were acquired for each level of analyte from all surfaces.

RESULTS AND DISCUSSION

Area calculations for paired chromatographic peaks

A peak is observed as the helium stream grazes the leading edge and again when it grazes the trailing edge of the swab. When the swab blocks the ceramic tube into the Vapur flange, the signal sometimes approaches 0, as shown in Fig. 2. The signal for each swab is the sum of the areas for the pair of chromatographic peaks arising from the swab. Figure 2(a) shows the area integrations provided by the data system. The region between the two peaks was used as the baseline after the first peak and before the second peak. Using this region to establish a baseline inflates the calculated peak areas, because an artificially low chemical-noise baseline is observed when background contaminants are not continuously analyzed.

A simple integration procedure was written in the Lotus 123 macro language to provide the integrated areas shown in Fig. 2 (b). The ion abundances versus time for the full scan data acquisition were imported into an ancillary PC. Five-point averages were calculated to smooth the data. The baseline was taken as the minimum abundance within 30 scans prior to the first peak maximum. All abundances above the minimum were added until either: (1) the abundance at least 20 scans after the second peak was less than the minimum or (2) the abundances at least 40 scans after the second peak were greater for the next three scans than for the scan being considered. This algorithm included carry over in the area when large amounts of analyte were present.

Optimum conditions for 11 drugs

Table 1 provides the optimum conditions of collision-induced dissociation voltage (CIDV), temperature, and solvent determined for 2.5 μg of 11 individual drugs deposited on 10-cm squares of the mirror.

The CIDV was varied over a wide range to find the maximum analyte ion abundance for each analyte. The voltage and precursor or product ion that provided the greatest

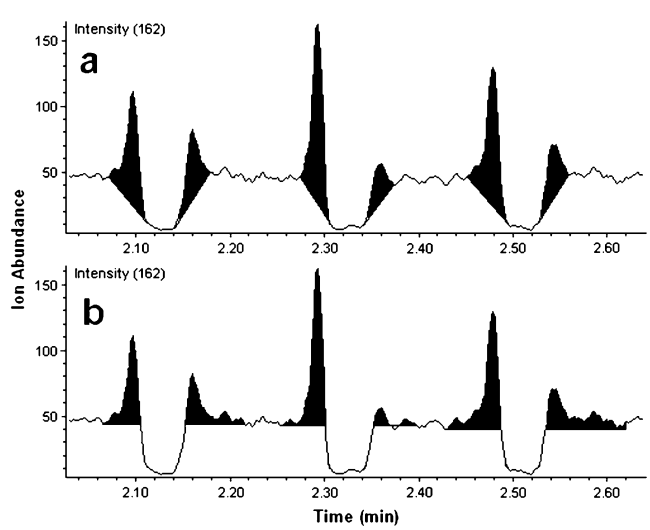

Figure 2. (a) Areas calculated by the data system for the chromatographic peaks from three swabs and (b) the area calculation provided by the Lotus 123 macro.

ion abundance with minimal interference from interfering ions were chosen to detect that analyte.

Higher CIDVs induce more fragmentation, while pulling more ions into the mass spectrometer. The $[M+H]^+$ ion provided the greatest ion abundance for 10 drugs, but pseudoephedrine lost a water molecule so easily that the maximum abundance was found for the *m/z* 148 product ion $[M+H–H_2O]^+$. Phencyclidine (PCP) easily fragmented at low CIDV to yield ions at *m/z* 159 ($[C_{12}H_{15}]^+$; a benzonium ion having lost the five-membered ring containing a nitrogen atom) and *m/z* 86 ($[C_5H_{12}N]^+$; the protonated N-containing ring), while heroin and morphine required higher CIDVs to provide their largest $[M+H]^+$ ion abundances, since product ion formation was minimal. The optimum CIDVs for the other eight drugs were between 40 and 50 V. The CIDVs shown in Table 1 were –5 V, 0 V, and +5 V different from the optimum values. The average RSD (n = 3) for the CIDV determinations was 14%. The average –5 V and +5 V paired peak areas relative to the optimum CIDV were 80% and 87%, respectively. Hence, broad maxima were observed for optimizing the CIDV. The maxima can be shifted by accumulated material on the inner surface of the ceramic tube of the Vapur flange and on the entrance cone into the mass spectrometer.

Helium temperature settings of 150°C to 350°C with 50°C increments were used to find the optimum desorption temperatures. In general, higher molecular mass drugs yielded higher optimum desorption temperatures than lower mass drugs. Excluding nicotine and PCP, the average paired peak area obtained at 50°C below the optimum temperature was 81% of the area obtained for the optimum value. The corresponding value for all 11 drugs when data were acquired at 50°C above the optimum temperature was 84%. Generally, broad maxima were also observed for the temperature setting.

The three solvents used to pick up drugs from the mirror were methanol, IPA, and distilled water. In all cases, IPA was the best solvent for picking up drugs from the glass surface. The average relative paired peak areas for all 11 drugs using methanol, IPA, and water were 43%, 100%, and 17%, respectively. The choice of solvent is more critical for optimizing drug pick up from glass (and presumably other impermeable surfaces) than off-optimum settings in the CIDV and temperature.

Observable peak limits from glass

The detection limit provided by NIOSH methods 9101 and 9106 for methamphetamine is 0.05 µg/100 cm^2. Because 12 U.S. states have a minimum decontamination target for meth of 0.1 µg/100 cm^2, analyte peaks observed for a concentration of 0.025 µg/100 cm^2, one-fourth of the lowest decontamination standard and one-half of the NIOSH detection limit, would provide adequate sensitivity for a screening technique.

Distilled water for blanks, and eight aqueous solutions to provide 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, and 5 µg of the individual drugs, were each deposited on three 10 × 10-cm mirror squares. An IPA-soaked swab was rolled across each square after the water had evaporated. All 27 swabs for each drug were mounted on the same support bar, and spectra for all swabs were recorded during a single data acquisition. Figure 3 shows the ion chromatogram recorded for meth.

A signal trace that provides observable peaks at the decontamination limit is required for an acceptable screening technique. In Fig. 4, portions of ion traces for 10 drugs are shown. For all three wipe samples the analyte level chosen for display for each drug provided chromatographic peaks well above the baseline or any small peaks observed for the three blank wipe samples. Visual inspection established that the height of the leading or trailing edge peak for each analyte swab was at least three times the peak-to-peak noise of the surrounding baseline.

Peaks were observed for 0.025 µg/100 cm^2 of amphetamine, meth, pseudoephedrine, ketamine, PCP, heroin, cocaine, and fentanyl. Morphine, tetrahydrocannabinol (THC), and nicotine (not shown) were observable at the 0.1 µg/100 cm^2 level. These observable peak thresholds are listed in Table 1. The appearance of the ion chromatograms suggests that for several drugs, peaks would be observed if lower levels were tested.

Based on the maximum ion abundances and appearance of the ion traces in Fig. 4, the sensitivity of the DART-TOFMS analysis decreases according to the sequence: ketamine > cocaine > amphetamine ≈ pseudoephedrine ≈ meth ≈ PCP > fentanyl > heroin > THC > morphine.

All 11 drugs can be detected from a smooth impermeable surface at the lowest U.S. state decontamination limit for meth of 0.1 µg/100 cm^2. For any drug of interest, acquiring wipe samples of a standard deposited at its decontamination

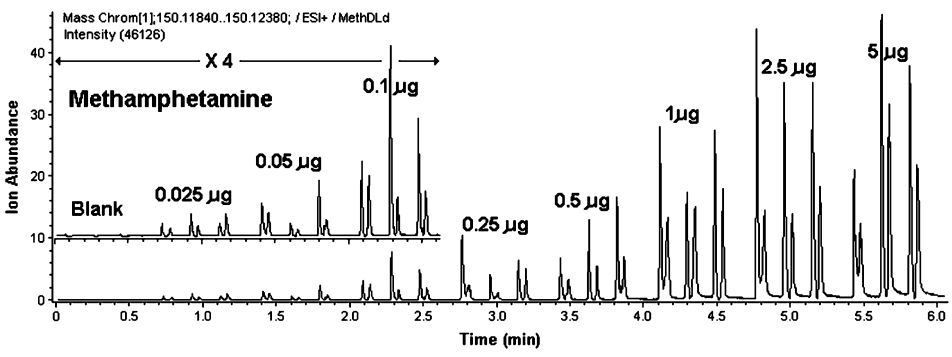

Figure 3. *m/z* 150 ion chromatogram for triplicate IPA-soaked wipe samples for no methamphetamine and eight levels of methamphetamine deposited on 10 × 10-cm mirror squares.

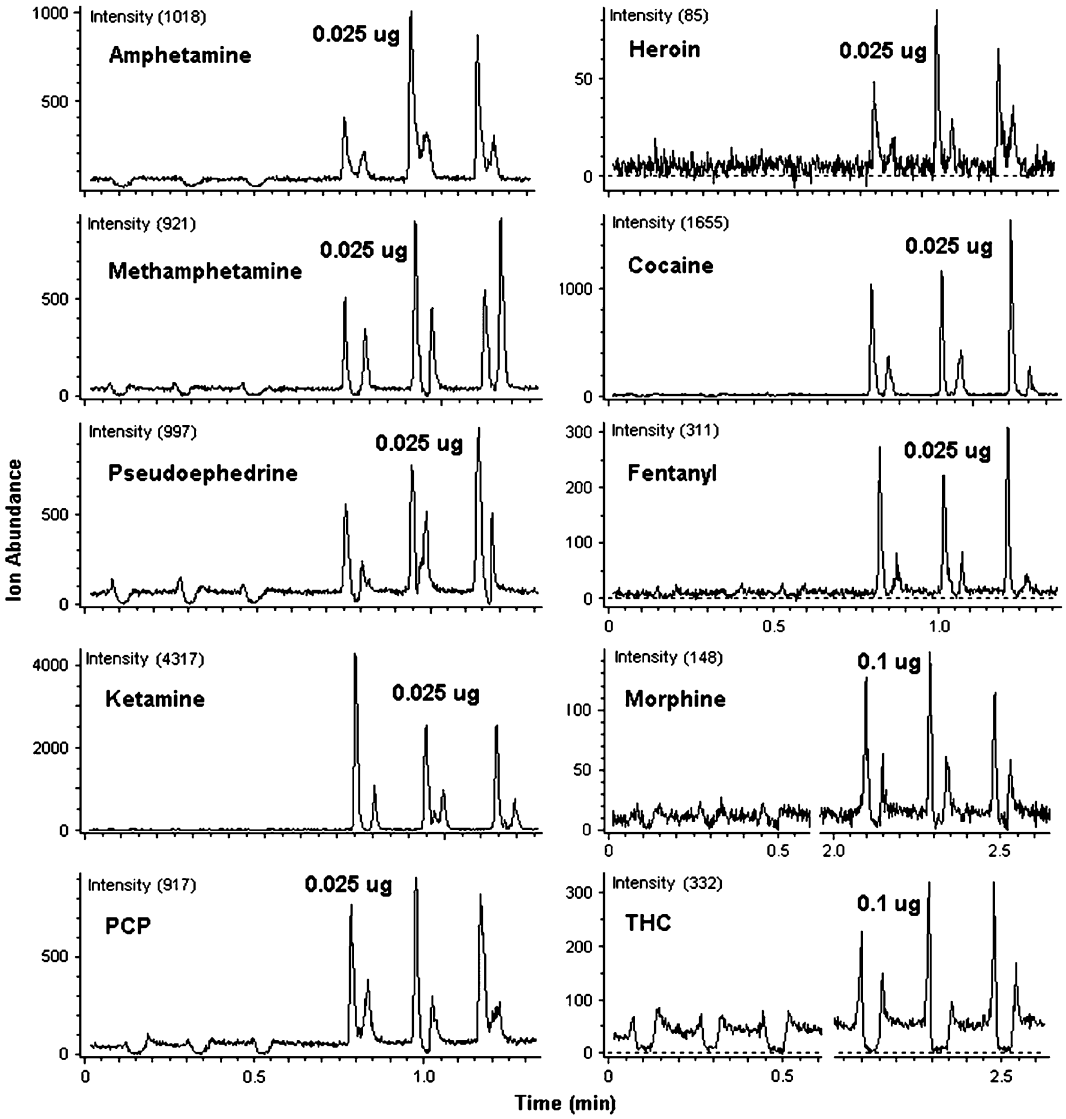

Figure 4. Analyte-ion traces for three blank wipe samples and for triplicate wipe samples at the lowest amount of analyte tested for which chromatographic peaks were visually obvious.

limit onto clean glass with a hand-held mechanical sprayer would provide an ion chromatogram to document adequate sensitivity and to compare with those obtained for wipe samples from interior surfaces. Product ion spectra acquired at three CIDVs for the standard and suspected drug should also be compared to confirm the identity of the drug.

Screening for multiple drugs

If multiple drugs are present on a swab, ion signals will be observed from each one, because full scan spectra are acquired. Figure 5 was obtained for wipe samples of 2.5 µg each of meth, cocaine, and THC, perhaps the three most commonly abused drugs, and for a mixture of 2.5 µg of each drug. Each drug was readily detected in the presence of the others.

Mass interferences

It was important for lowering the observable peak limits for two drugs that the analyte ion could be distinguished from isobaric mass interferences. Figure 6 shows the analyte ion and interferences for nicotine and THC. The resolving powers measured from the mass peaks at half height were 4600 and 5400 for nicotine and THC, respectively. The best signal-to-interference ratio was obtained at *m/z* values corresponding to the vertical lines in Fig. 6.

Based on its exact mass, the *m/z* 163 interference for nicotine was due to a compound with the composition $C_6H_{10}O_5$, probably a sugar unit from the cellulose of the cotton-swabs. The level of the interference varied greatly among swab blanks. The *m/z* 315 interference for THC was present at a level that was nearly constant during each data acquisition.

Partial dynamic ranges

Figure 7 displays log-log plots of the average paired chromatographic peak areas for each set of three swabs versus the amount (µg) of analyte on the mirror squares for all drugs tested except nicotine. The plots illustrate a dynamic range of at least 100 for eight drugs. A wider dynamic range is

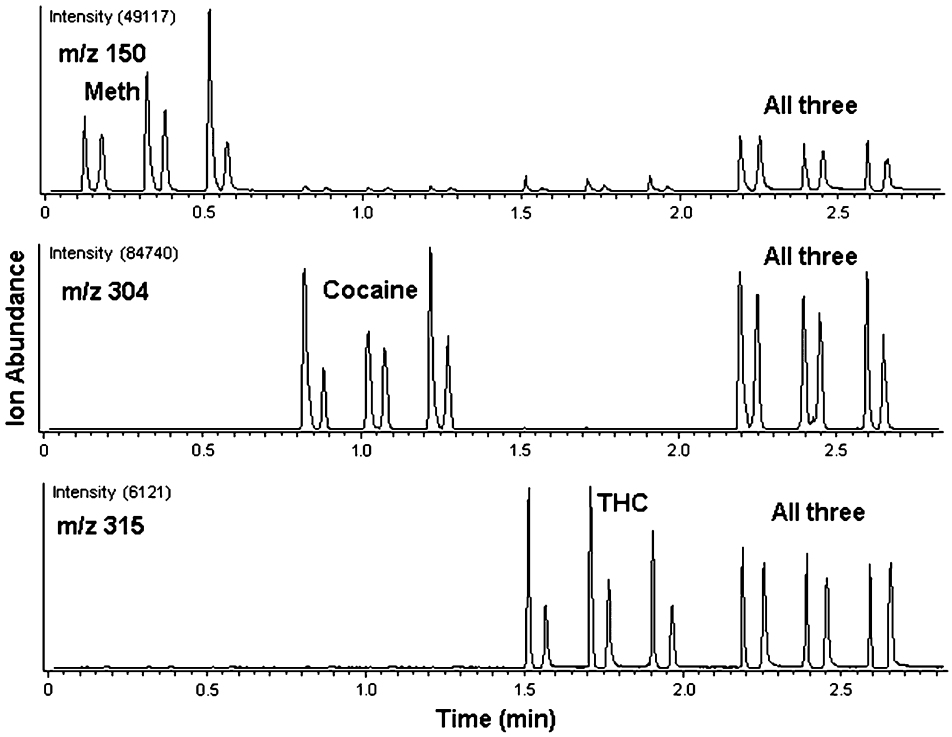

Figure 5. Analyte-ion chromatograms for methamphetamine, cocaine, and THC for triplicate wipe samples collected from glass of 2.5 µg each of methamphetamine, cocaine, THC, and 2.5 µg of each in a mixture of all three drugs. The CIDV was 45 V, the temperature was 250 °C, and the solvent was IPA.

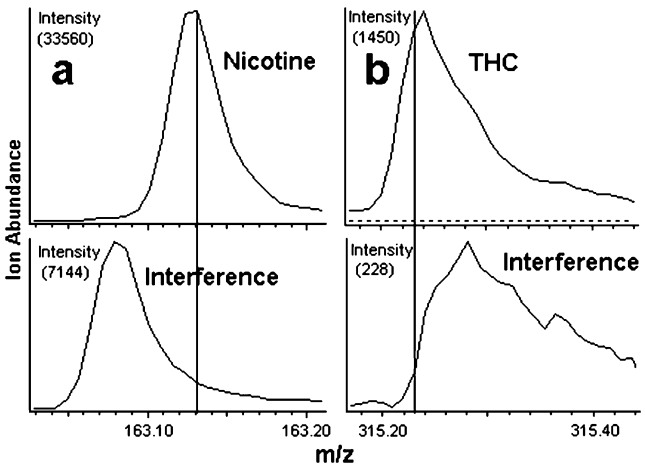

Figure 6. Peak profiles (a) for the analyte ion for nicotine (top) and an interference and (b) for the analyte ion for THC and an interference.

likely for many of the drugs, but, for screening of levels near a remediation limit, these dynamic ranges are adequate. The average RSD (n = 3) for the plotted points was 24%.

Volatility of drugs from glass

How long drug residues posing health risks remain on impermeable surfaces will depend on the amount initially present and the volatility of the drug. Abdullah and Miskelly[18] studied the loss of meth by volatilization from various impermeable surfaces in both free base and hydrochloride forms and found that the volatilities were similar. In this study, the losses of the 11 drugs from glass after 1 week were determined. Wipe samples were acquired on the same day for 2.5 µg of each drug that had been deposited on six mirror squares, 1 h and 1 week earlier. A single data acquisition recorded the data for all 12 swabs. Major differences in the remaining amount of drug were found, as listed in Table 2. The volatility of the drugs increased in the sequence: heroin < cocaine < ketamine < pseudoephedrine ≈ nicotine < fentanyl < morphine ≈ amphetamine < meth < PCP ≈ THC. These results suggest that many drugs on impermeable surfaces will volatilize and condense elsewhere or be transported outside if windows are open for long periods, but drugs that condensed on permeable surfaces could strongly adhere to the surfaces or be absorbed into the bulk material and remain indefinitely. Meth labs that had been shut down for months were found to still have high levels of the drug on many surfaces or within materials.[2] The average RSDs (n = 6) for the wipe samples of the 11 drugs deposited 1 h and 1 week earlier were 22% and 26%, respectively.

Pick up and drug retention by paint

Pick up of drugs provides a measure of risk exposure. If a drug is not easily removed from a surface or bulk material, it may pose a minimal risk when touched, relative to the amount of drug present. Painted surfaces, which might not be impermeable and inert, often comprise most of the surface area within meth labs. If a drug adhered strongly to paint, IPA would be expected to pick up more drug than water, because IPA picked up more drug from glass. However, if most of a drug is absorbed into the paint and the paint was

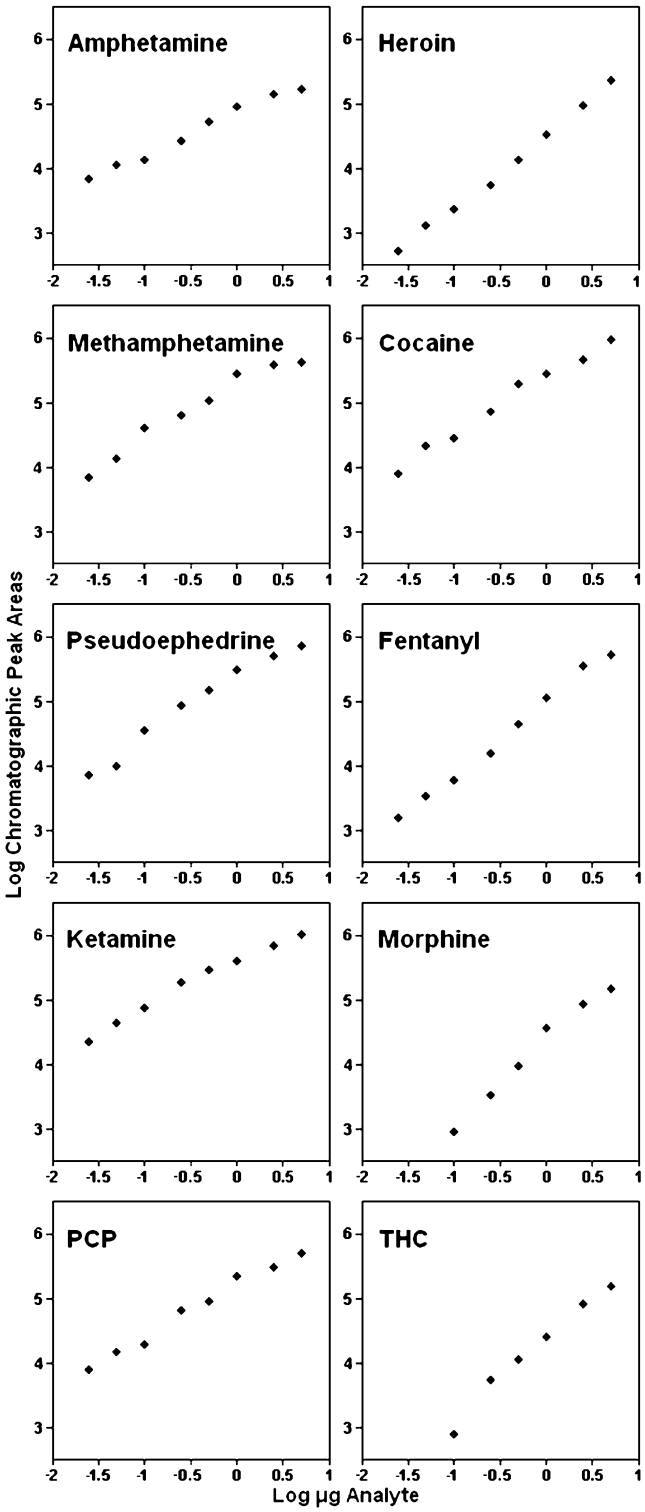

Figure 7. For 10 drugs, the log of average chromatographic peak areas from three swabs vs. the log of µg of analyte deposited on the mirror squares.

soluble or formed a suspension in water to a greater extent than in organic solvents, pick up by water would improve relative to IPA for the drug due to collection of a layer of paint. Gaynor *et al.* have shown that meth can be absorbed into paint.[2]

Table 2. Volatility from glass, relative recoveries of IPA and water from paint, and pick up ratios from glass vs. paint

Analyte	% After 1 week from glass (%)	IPA, water from paint	Glass/ Paint
Amphetamine	7	100,12	14
Pseudoephedrine HCl	19	48,100	55
Methamphetamine HCl	4	50,100	17
Nicotine	19	100,45	20
Ketamine HCl	27	46,100	12
PCP	2	34,100	11
Morphine	8	n.d.*	—
Cocaine	69	52,100	111
THC	1	n.d.	—
Fentanyl	10	38,100	61
Heroin	91	41,100	655

*Not detected from paint.

To compare paint removal using three solvents, mass spectra were examined for blank wipe samples from week-old paint. Low levels of *m/z* 90 ($C_4H_{12}NO^+$) and 104 ($C_5H_{14}NO^+$) ions from paint additives, probably from 2-(dimethylamino)-ethanol and/or 2-amino-2-methyl-1-propanol[19] and 1-(dimethylamino)propan-2-ol,[20] were evident. The relative abundances for the *m/z* 104 ion were 40%, 45%, and 100% for methanol-, IPA-, and water-soaked swabs, respectively. When, after sampling, a still wet, water-soaked cotton swab was rolled across clean glass, a film of paint appeared on the glass. These observations confirm that a layer of week-old paint is picked up by the cotton swabs, especially when water is the solvent.

Three IPA-soaked swab, wipe samples were collected from glass, and three IPA-and water-soaked wipe samples were each collected from 1-week old acrylic latex paint onto which 10 µg of each of the 11 drugs had been deposited. With this data, drug pick up from glass using IPA was compared with pick up from week-old paint using both IPA and water and between IPA- and water-soaked swabs from the paint. The analyte-ion trace for the nine swabs was collected during a single data acquisition. The 'IPA, water from paint' column in Table 2 lists the % relative pick ups for the two solvents from paint. These relative pick ups indicated that absorption for nine drugs decreased in the sequence: PCP > fentanyl ≈ heroin > ketamine ≈ pseudoephedrine ≈ meth ≈ cocaine >> nicotine > amphetamine. Repeating the experiment with 50 µg of morphine or THC still did not provide peaks in the analyte-ion traces for the paint.

For meth on glass from Table 1, water picked up 40% as much meth as IPA did. For meth on week-old paint from Table 2, IPA picked up 50% as much meth as water did. The superior ability of water to strip the paint provided a 5-fold enhancement in pick up for water relative to IPA between sampling glass and paint.

Using the same data, the average signal from the solvent that provided the greater pick up for paint was compared with that obtained for IPA wipe samples from glass, as shown in the 'Glass/Paint' column in Table 2. The pick ups of the drugs from paint were more than an order of magnitude less than from

glass. For week-old paint, adsorption and/or absorption were important for all 11 drugs, and the drugs were less available for pick up by solvent-soaked swabs. The order of drug availability for paint relative to glass decreased in the order: PCP ~ ketamine ~ amphetamine ~ meth ~ nicotine < pseudoephedrine ~ fentanyl < cocaine < heroin < morphine ~ THC.

Drug recoveries from surfaces

Not all the drug within the 100-cm^2 area sampled is picked up. To obtain a measure of what fraction remains behind, wipe samples were taken repeatedly from the same glass and painted squares.

For glass, absorption was not an issue. Three successive triplicate samplings with water of 2.5 µg of meth from the same three glass squares provided relative summed peak areas of 100%, 12%, and 2%. For IPA, four successive triplicate samplings of 2.5 µg of meth from glass provided relative summed peak areas of 100%, 69%, 40%, and 21%. One might conclude that the recovery using water was greater than that for IPA, because it appears that less meth was left behind for successive samplings using water.

However, it can be seen from Table 1 that the first samplings using water provided only 40% as much signal as the first samplings using IPA. In addition, sampling three mirror squares with 10 µg of meth using water-soaked swabs and then the same three squares with IPA-soaked swabs provided 55% as much signal for the first-collected, water-soaked swabs as for the IPA-soaked swabs. Much less meth is picked up by water-soaked swabs, especially for repeated samplings.

The amount of meth in a drop of solution might be much more than sufficient to occupy the adsorptive sites under the drop, and the bulk of the meth could then be more available for pick up. After the meth left behind has been redistributed by the wet swab throughout the 100-cm^2 area while collecting the first wipe sample, most of the meth could occupy adsorptive sites and become more difficult to pick up. IPA was the better solvent for picking up meth adsorbed on the glass, and a greater fraction of the adsorbed meth was picked up in successive wipe samplings.

The amount of meth picked up by the last three of the four wipe samples was 1.3 times that picked up by the first wipe sample. Hence, the first IPA-soaked swabs recovered less than half of the meth from glass.

For paint, adsorption was an issue. The reduction in signal for successive samplings for both IPA and water from the paint was less than the reductions from glass. For water-soaked swabs, successive samplings provided relative ion abundances of 100%, 51%, 32%, and 29%. These results also indicate that absorption occurs and that paint is removed by the swabs, although less pressure is applied by rolling swabs than by rubbing with cotton gauze pads[5–9] or filter paper.[18]

Paint variation

The composition, thickness, and age of the paint and analyte deposition method could all influence the amount of meth or other drugs that absorb into the paint and the amount that is picked up by solvent-soaked swabs. Similar low pick ups using IPA and water to wipe sample for pseudoephedrine were obtained from 9-year-old paint from a different vendor that was applied with a roller within a home, and the *m/z* 90 and 104 ions were not observed. Either the older paint had never contained the additives or they had out-gassed over time. Water might not always provide an advantage over IPA for pseudoephedrine, meth, or other drugs, because real-world painted surfaces are likely to be much older than 1 week.

Using methanol-soaked, 12-ply, 3-inch-square, cotton gauze pads, Chin[8] obtained recoveries for 0.6 µg of meth deposited on flat paint surfaces of 51% and 74% for meth applied as a solution by a syringe (wet deposition) and for meth dried on a Teflon sheet that was then rubbed onto the paint surface (dry deposition), respectively. The lower recovery for wet deposition supports the hypothesis that meth more easily infiltrates the paint from solutions. Deposition of combustion products that include water would probably provide a recovery within this range using Chin's cotton-gauze square, wipe-sampling technique. Recoveries from latex paint for wipe samples acquired by rolling IPA-soaked cotton-swab heads across the paint were lower. Presumably, rubbing dissolves and collects more latex paint containing the meth than does rolling with pressure insufficient to break the 6-inch-long wooden stick.

Pick up of pseudoephedrine from household surfaces

Glass and paint are only two of the many surfaces found in structures. Figure 8 displays a chromatogram for the *m/z* 148 ion from pseudoephedrine collected from seven household surfaces. Triplicate wipe samples using IPA-soaked swabs were collected within a 100-cm^2 template from a glass table, a floor tile, a kitchen table with a vinyl veneer surface, a varnished Philippine mahogany door, 9-year-old latex paint applied with a roller, a cloth quilt, and a medium pile nylon carpet. Pseudoephedrine (10 µg) had been sprayed onto each 10-cm square with a small manual sprayer, which delivered 0.14 mL within a 3-cm circle, when the nozzle was positioned about 5 cm above the surface by a fixture. Considerably more pseudoephedrine was picked up from the impermeable surfaces. The thick cloth quilt absorbed both the analyte solution and the IPA from the swab, so that very little analyte was recovered. The nylon rug was less absorbent, and more analyte was picked up. The latex paint also retained the analyte, and little was retrieved by the IPA-soaked swab. Using water as the solvent in an earlier experiment made little difference in analyte recovery from the household paint. The low level for the wipe sample from the first 100-cm^2 area of the door may be due to wearing away of the thin varnish coating. The door was positioned horizontally, having served as a desk for about 20 years, and items were dragged across one section most often. The soft wood that was exposed absorbed more analyte than the varnish.

Fast, low cost, and green analyses

The method described herein requires no sample extraction, sample clean-up, solvent exchange, or derivatization, which can require 2–3 h for mixing steps alone for a modified version of NIOSH method 9106.[8] Batch processes probably reduce the time per sample before a 25-min GC program required for each final extract is run to acquire mass spectra.[8] Up to 57 mL of various solvents and solutions including methylene chloride were used for each sample.[8] For NIOSH method 9111, sample extraction required 30 mL of 0.2 N sulfuric acid, mixing for 30 min, and clean up using an ion chromatography column prior to injection onto an LC column. The LC program required 25 min.[9]

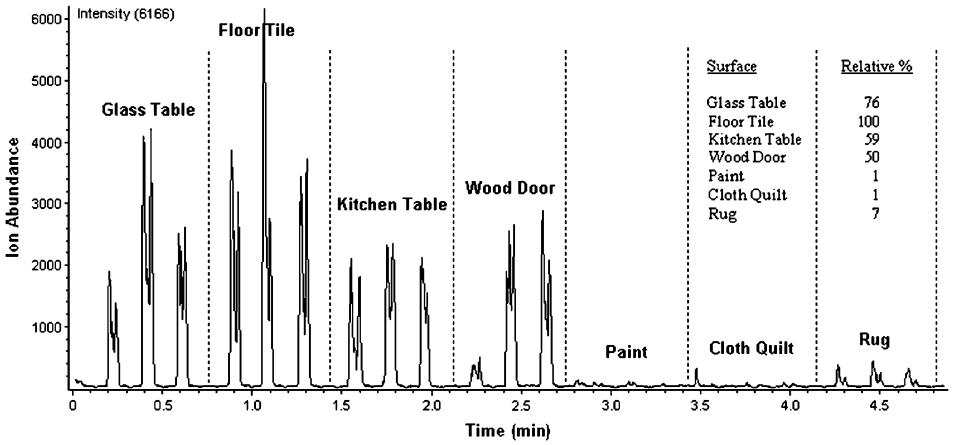

Figure 8. Analyte-ion chromatogram (*m/z* 148) for pseudoephedrine from triplicate sets of cotton-swab wipe samples acquired from household surfaces after depositing 10 µg of the drug onto 100-cm^2 areas.

The time axis in Fig. 3 illustrates that 27 wipe samples were analyzed in about 6 min (13 s/swab) with a single gap between swabs within a triplicate set and with two gaps to separate the sets to allow the user (and Lotus macro) to easily correlate leading and trailing edge peaks with individual swabs and swabs with wipe samples. The time required to collect a wipe sample was 2 min, perhaps twice the time required to collect a cotton gauze or filter paper wipe sample. Each 6-inch cotton swab cost about 3 cents. Additional costs were power, nitrogen, and helium. About 0.2 mL of solvent was required to wet each swab before collecting a sample from a dry surface. No solvent waste was generated. Hence, each analysis was faster, cheaper, and greener than conventional GC/MS or LC/MS analyses.

CONCLUSIONS

A single-stage, time-of-flight mass spectrometer with modest resolving power provided adequate specificity to resolve analyte ion profiles from mass interferences for 11 drugs. This capability was most useful for the *m/z* 315 ion from THC and the *m/z* 163 ion from nicotine.

The minimum decontamination level specified by 12 U.S. states is 0.1 µg/100 cm^2. The sensitivity was adequate for detecting 0.025 µg/100 cm^2, one-fourth of this level, for meth, amphetamine, pseudoephedrine, ketamine, PCP, heroin, cocaine, and fentanyl for each wipe sample acquired in triplicate. For morphine, THC, and nicotine, 0.1 µg/100 cm^2 was detected. An average RSD of 24% (n = 3) was obtained for eight levels of eight drugs and six levels of two drugs.

The use of cotton-swab wipe samples, field sample carrier, and autosampler minimized the time per analysis, greatly increasing the throughput of the technique. Devising complex sampling strategies to mitigate the disadvantage of acquiring few samples due to analysis costs would no longer be necessary. Inexpensive and rapid screening for drug residues in clandestine drug labs or building interiors prior to property transactions would reveal which rooms, if any, required decontamination. The sensitivity, speed, and precision of this screening technique are adequate for real-time monitoring of decontamination and thorough documentation of successful clean ups.

Direct analysis of solvent-soaked, cotton-swab, wipe samples required only 0.2 mL per sample and generated none of the waste associated with sample extraction, clean-up, derivatization, and/or chromatography required by conventional mass spectrometric methods. IPA provided the best solvent for impermeable surfaces, while water picked up more of seven drugs from week-old paint. Overall, IPA was the best solvent. Ultra-pure solvents are not required, and both IPA and distilled water could be purchased from a supermarket in the field.

Nine illicitly used drugs and two legal drugs were considered in this study. This technique could also be applied to detect other smoked drugs from surfaces and spilled drugs from carpeted floors, especially drugs with structures that contain a non-aromatic N atom. Numerous wipe samples of surfaces and carpets could be collected and analyzed prior to property transactions to screen for many drugs.

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REFERENCES

[1] Drug Enforcement Administration. Maps of Methamphetamine Lab Incidents, **2010**. Available: http://www.usdoj.gov/dea/concern/map_lab_seizures.html.
[2] K. Gaynor, M. Bevan, S. Lee, P. Swedenborg. Wipe sampling, results, and cleaning former meth labs: Minnesota Studies' Impact on Meth Lab Cleanup Guidance. Minnesota Pollution Control Agency, **2007**. Available: http://www.pca.state.mn.us/index.php/view-document.html?gid=2831.
[3] J. W. Martyny, S. L. Arbuckle, C. S. McCammon Jr, E. J. Esswein, N. Erb, M. Van Dyke. Chemical concentrations and contamination associated with clandestine methamphetamine laboratories. *J. Chem. Health & Safety* **2007**, July/Aug, 40.

[4] J. W. Martyny, S. L. Arbuckle, C. S. McCammon Jr, M. Van Dyke. Methamphetamine contamination on environmental surfaces caused by simulated smoking of methamphetamine. *J. Chem. Health & Safety* **2008**, Sept/Oct, 25.

[5] NIOSH Method 9106, NIOSH Manual of Analytical Methods, (5th edn), (draft). Available: http://www.cdc.gov/niosh/review/public/176/pdfs/NIOSH9106FINAL03.pdf.

[6] NIOSH Method 9109, NIOSH Manual of Analytical Methods, (5th edn.), (draft). Available: http://www.cdc.gov/niosh/review/public/177/pdfs/NIOSH9109Final.pdf.

[7] NIOSH Method 9111, NIOSH Manual of Analytical Methods, (5th edn.), (draft). Available: http://www.cdc.gov/niosh/review/public/178/pdfs/NIOSH9111MethodFinal.pdf.

[8] R. Chin. Analysis of methamphetamine on wipes by GC/MS-SIM mode or GC/MS/MS spectrometry. Environmental Chemistry Laboratory, Southern California; California Dept. of Toxic Substances Control, **2009**. Available: http://www.dtsc.ca.gov/AssessingRisk/ECL/upload/ECL-Report_Meth-Wipes.pdf.

[9] D. C. Wickman, M. C. Siso, J. M. Reynolds, J. B. Perkins. Methamphetamine on cotton gauze wipes by LC-MS-SIM. Data Chem Laboratories, Inc. NIOSH 9111, Issue 1, Backup Data Report, **2005**. Available: http://www.cdc.gov/niosh/review/public/178/pdfs/9111MethamphetaminebackupReport12-8-05pcs.pdf.

[10] Utah Department of Health. Methamphetamine clandestine lab cleanup regulations by state, January, **2008**. Available: http://health.utah.gov/meth/docs/PDFs/Statebystatefinal.pdf.

[11] US EPA Voluntary guidelines for methamphetamine laboratory cleanup, August, **2009**. p. 10. Available: http://www.epa.gov/oem/meth_lab_guidelines.pdf.

[12] A. H. Grange. An inexpensive autosampler to maximize throughput for an ion source that samples surfaces in open air. *Environ. Forensics* **2008**, *9*, 127.

[13] A. H. Grange. An autosampler and field sample carrier for maximizing throughput using an open-air, surface sampling ion source for MS. *Am. Lab.* **2008**, *40*, 11.

[14] A. H. Grange. An integrated wipe sample transport/autosampler to maximize throughput for a DART®/oa-TOFMS. *Environ. Forensics* **2008**, *9*, 137.

[15] A. H. Grange. Rapid semi-quantitative surface mapping of airborne-dispersed chemicals using mass spectrometry. *Environ. Forensics* **2009**, *10*, 183.

[16] A. H. Grange, G. W. Sovocool. Automated determination of precursor ion, product ion, and neutral loss compositions and deconvolution of composite mass spectra using ion correlation based on exact masses and relative isotopic abundances. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 2375.

[17] L. Song, S. C. Gibson, D. Bhandari, K. D. Cook, J. E. Bartmess. Ionization mechanism of positive-ion direct analysis in real time: a transient microenvironment concept. *Anal. Chem.* **2009**, *81*, 10080.

[18] A. F. Lim Abdullah, G. M. Miskelly. Recoveries of trace pseudoephedrine and methamphetamine residues from impermeable household surfaces: implications for sampling methods used during drug remediation of clandestine methamphetamine laboratories. *Talanta* **2010**, *81*, 455.

[19] G. W. Harris, J. N. Pitts. Rates of reaction of hydroxyl radicals with 2-(dimethylamino)ethanol and 2-amino-2-methyl-1-propanol in the gas phase at 300 ± 2 K. *Environ. Sci. Technol.* **1983**, *17*, 50.

[20] Bisomer Amine 700™. Emulsion coating performance test results. Cognis. Available: http://www.cognis.com/NR/rdonlyres/DCBB975A-A54C-44A7-AEC9-CB02F4115BE7/0/A_Multipurpose_Performance_Additive.pdf.