METHAMPHETAMINE and Illicit Drugs, Precursors, and Adulterants on Wipes by Solid Phase Extraction 9109

FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 9109, Issue 1 **EVALUATION: Partial** **Issue 1: 17 October 2011**

U.S. regulatory OELS
OSHA or MSHA: none for surfaces
Other published OELs and guidelines
NIOSH, ACGIH, or AIHA: none for surfaces
States: Table 2

PROPERTIES: Table 3

SYNONYMS: Table 4

SAMPLING

SAMPLER: Wipe

SAMPLE AREA: 100 cm^2 or 1000 cm^2

SHIPMENT: Ship refrigerated preferably, <6 °C

SAMPLE STABILITY: At least 30 days at <6 °C (See Table 5)

FIELD BLANKS: 2 to 10 blanks per sample set

MEASUREMENT ACCURACY

LEVEL STUDIED: 3.0 µg/sample

BIAS: Table 10 [1]

OVERALL PRECISION ($\hat{S}_{rT}$): Surface recovery not performed

ACCURACY: Table 8a and 8b [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY/MASS SPECTROMETRY

ANALYTES: Table 1

DESORPTION: 0.1 M sulfuric acid

CLEANUP/ EXTRACTION: Solid phase extraction

DERIVATIZATION: MSTFA and MBHFBA

INJECTION VOLUME: 2 µL Splitless

TEMPERATURE Injection: 255 °C.
Detector: 285 °C
Column: 90 °C (2 min), to 310 °C (10 °C/ min), hold 6 min

MASS SPECTROMETER: Scan mode (29 – 470 AMU), 2 scan/sec or selected ion monitoring (SIM) mode (Table 6)

CARRIER GAS: Helium, 1.5 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32 mm i.d., 0.5 µm film DB-5ms, or equivalent

CALIBRATION: Standards from spiked wipes with internal standard, See Table 7

RANGE: Table 8a and 8b [1].

ESTIMATED LOD: Table 5

PRECISION ($\bar{S}_r$): Table 8a and 8b [1]

APPLICABILITY: For methamphetamine the range is 0.05 to 60 µg/sample (sample = 100 cm^2 or 1000 cm^2). This method was developed for the analysis of selected drugs and precursors on surfaces in clandestine drug labs. [2, 3] Sampling methodology was tested using wipes on smooth, non-porous surfaces. The APPENDIX contains sampling information for other types of surfaces.

INTERFERENCES: No chromatographic interferences detected. Water, surfactants and polyols inhibit derivatization.

OTHER WIPE METHODS: NIOSH 9106 uses liquid-liquid extraction and gas chromatography/mass spectrometry (GC/MS) to measure multiple drugs [4]. NIOSH 9111 uses liquid chromatography/mass spectrometry (LC/MS) to measure methamphetamine [5].

REAGENTS:

NOTE: See APPENDIX A for special instructions on reagents.

1. Analytes listed in Table 1*
2. Internal standards from those listed in Table 9
3. Solvents, residue free analytical grades
   a. Isopropanol (IPA)*
   b. Methanol*
   c. Methylene chloride (CH_2Cl_2)*
   d. Acetonitrile*
4. Concentrated sulfuric and hydrochloric acids (AR or trace metals analysis grades)*
5. Ammonium hydroxide (NH_4OH), 28-30%, A.C.S. grade*
6. Bromothymol blue, ≥95%, A.C.S.; crystal violet (Gentian Violet), ≥95%, A.C.S.
7. Purified gases: helium for carrier gas, nitrogen for drying
8. MSTFA (N-methyl-N-trimethylsilyl-trifluoro-acetamide) derivatizing agent*
9. MBHFBA (N-methyl-N,N-bisheptafluorobutyramide) derivatizing agent*
10. 4,4'-Dibromooctafluorobiphenyl, 99%
11. Deionized water (ASTM type II)

SOLUTIONS:

NOTE: See APPENDIX A for special instructions on solutions.

1. Prepare solutions of analytes of interest (Table 1). Calculate concentrations as the free base. Keep solutions refrigerated (<6 °C). Protect solutions from light.
   a. Stock solutions are prepared at about 1-2 mg/mL in methanol.
   b. Analyte spiking solutions are prepared by diluting the stock solutions to about 200 µg/mL each in methanol.
2. Prepare internal standard spiking solution in methanol at about 200 µg/mL. NOTE: Add about 2 mg of crystal violet per 20 mL of internal standard spiking solution to help indicate which samples have been spiked.
3. Desorption solution: 0.1 M sulfuric acid. Add 22 mL conc. sulfuric acid to 4 liters deionized water.
4. Bromothymol blue pH indicator solution: 1 mg/mL in 4:1 isopropanol:deionized water.
5. Crystal violet indicator: 2-3 mg/mL in isopropanol.
6. Solid phase extraction (SPE) wash solution: Aqueous 0.1 M hydrochloric acid: Dilute 8.3 mL concentrated hydrochloric acid in about 800 mL water, dilute to 1 liter with ASTM Type II water.
7. SPE elution solution: 80:20:2 CH_2Cl_2:IPA:NH_4OH v/v. Prepare fresh daily.
8. 0.3 M hydrochloric acid in methanol: Dilute 2.5 mL conc. hydrochloric acid in about 80 mL methanol; dilute to 100 mL with methanol.
9. Derivatization diluent solvent: acetonitrile containing 4 µg/mL of 4,4'-dibromo-octafluorobiphenyl (optional).

* See SPECIAL PRECAUTIONS

EQUIPMENT:

NOTE: See APPENDIX B for special instructions on equipment.

1. Wipe, cotton gauze, (7.6 cm × 7.6 cm) 12-ply or equivalent.
2. Sample storage and shipping container: 50-mL polypropylene centrifuge tubes with PTFE-lined caps or equivalent.
3. Gas chromatograph/mass spectrometer detector, with column and integrator, See p. 9109-1.
4. Solid phase extraction (SPE) columns: Any of the following or other equivalent mixed phase cation exchange hydrophilic solid phase extraction columns:
   a. Waters Oasis® MCX, 60 mg/3 cc (Waters Corp. Milford, MA.)
   b. Clean Screen®, 300 mg/3 mL (United Chemical Technologies, Inc., Bristol, PA, Cat. no. #CSDAU303.)
   c. Speedisk® H2O-Philic SC-DVB (J.T.Baker, Center Valley, PA).
   d. BOND ELUT-CERTIFY®, 200 mg/3mL (Agilent Technologies, Santa Clara, CA).
5. Collection tubes and GC vials:
   a. Glass test tubes (13 mm x 100 mm) with PTFE-lined caps
   b. GC autosampler vials, 2-mL Limited-volume, 300-500 µL (amber vials recommended), and caps.
6. Volumetric flasks: 10-, 100-, and 250-mL.
7. Reagent bottle, 4-L .
8. Liquid Transfer:
   a. Syringes: 10-, 25-, and 100-µL.
   b. Mechanical pipette with disposable tips, 5-mL.
   c. Repeating dispensers: 1 to 5-mL.
   d. Syringe or repeating dispenser: 100-µL.
   e. Syringes: 250-µL.
9. Forceps.
10. Gloves: latex or nitrile. Avoid vinyl gloves (see 9109-3, Sampling, step 1, NOTE 2).
11. Rotating mixer capable of 10-30 rpm.
12. Vacuum manifold box with 12 to 36 vacuum ports, and adjustable flow rates.
13. Nitrogen blow-down apparatus with water bath capable of maintaining 35 °C.
14. Vortex mixer.
15. Pasteur pipettes.
16. pH paper.
17. Template: 10 cm x 10 cm (or 1 foot x 1 foot) opening made of relatively rigid disposable cardstock or sheet of PTFE.
18. Ice or other cold media for shipping.

SPECIAL PRECAUTIONS: The solvents are flammable and have associated adverse health effects. Phenethylamines target the nervous system at very low concentrations and are easily absorbed through the skin. Avoid breathing vapors. Avoid skin contact. Work should be performed in a hood with adequate ventilation. Analysts must wear proper eye and hand protection (e.g., latex gloves) to prevent absorption of even small amounts of amines through the skin as well as for protection from the solvents and other reagents. Dissolving concentrated hydrochloric or sulfuric acid in water is highly exothermic. Goggles must be worn. The derivatization reagents react violently with water.

Caution must also be exercised in the handling and analysis of samples. Clandestine drug labs may produce unknown and seriously toxic by-products. For example, in the manufacture of designer drugs (e.g., MPPP, a homolog of Alphaprodine), at least one very neurotoxic by-product, 1-methyl-4-phenyl-1,2,5,6-tetrahydropyridine (MPTP), has been identified that specifically and irreversibly causes Parkinson's disease [6, 7].

SAMPLING:

See APPENDIX C for special instructions on sampling.

1. Using a new pair of gloves, remove a gauze wipe from its protective package. Moisten the wipe with approximately 3 to 4 mL of methanol (or isopropanol).
   NOTE 1: Apply no more solvent than that needed to moisten approximately the central 80% of the area of the gauze wipe. Excess solvent may cause sample loss due to dripping from the wipe.
   NOTE 2: Do not use vinyl gloves due to the potential for leaching of phthalate plasticizers and contamination of the samples.
2. Place the template over the area to be sampled (may tape in place along outside edge of template). Wipe the surface to be sampled with firm pressure, using vertical S-strokes. Fold the exposed side of the pad in and wipe the area with horizontal S-strokes. Fold the pad once more and wipe the area again with vertical S-strokes.
3. Fold the pad, exposed side in, and place in shipping container and seal with cap.
   NOTE: Keep samples refrigerated (<6 °C). While methamphetamine and several related amines are stable on the recommended wipe media for at least 7 days at room temperature, refrigeration is recommended as soon as possible (see Table 5).
4. Either clean the template before use for the next sample or use a new disposable template.
5. Label each sample clearly with a unique sample identifier.
6. Prepare a minimum of two field blanks with one field blank for every ten samples.
   NOTE: In addition, include at least 3 media blanks for the analytical laboratory to use for their purposes. The wipes used for the media blanks should be from the same lot as the field samples.

SAMPLE PREPARATION:

See APPENDIX D for special instructions on sample preparation.

7. Desorption from media:
   a. Remove cap from shipping container.
      NOTE: Sample wipe should fit loosely in the container. If not, transfer sample to a larger container.
   b. Spike 60 µL of internal standard spiking solution onto each wipe sample.
   c. Add 30 mL desorption solution (0.1 M sulfuric acid).
      NOTE: If the samples were transferred to a larger container, rinse the original shipping container with the desorption solution, shake, and decant the rinsate into the larger container.

d. Cap securely and mix contents by inverting the tubes end over end on a rotary mixer or equivalent at 10-30 rpm for at least one hour.
e. Check the pH which should be about ≤ 4. If needed, adjust the pH with diluted (2.5 to 3 M) sulfuric acid drop-wise, mixing the contents by shaking or inversion a few times after each addition of acid before checking the pH.
f. After mixing, transfer 10 mL of supernatant to a 25-mL glass centrifuge tube.
NOTE: If extraction is to be performed on a subsequent day, store samples in a refrigerator. Analytes are stable in the desorption solution for at least one week refrigerated.

8. Solid phase extraction procedure:
a. Column selection: Select one of the SPE columns listed in the EQUIPMENT section. Each brand of column has a slightly different conditioning procedure and resistance to flow. Other brands of SPE columns may also work. Elution profiles of drugs to be analyzed need to be determined before use of columns other than those specified.
b. Setting up columns: Attach SPE columns to vacuum ports on the manifold. Attach vacuum line to vacuum pump capable of 25-30 psi vacuum.
c. Conditioning: Condition each column with 1 column volume (3 mL) of methanol followed by 1 column volume of Type II deionized water. For some brands (e.g., Speedisk®) the conditioning volume is 1/3 column volume. Check product literature.
d. Loading: Load each SPE column with 5 mL of the sample acid desorbate solution. Adjust vacuum so that the flow rate is about 1-2 mL/minute. The vacuum required to obtain that flow rate varies with brand of SPE column.
e. First wash: Wash each column with 1 column volume (3 mL) of 0.1 M aqueous hydrochloric acid. For some brands (e.g., Oasis® or Speedisk®) this volume may be decreased to 2 or 1 mL, respectively.
f. Second wash: Wash each column with 1 column volume of methanol. Add the methanol in 2 or 3 separate aliquots to ensure that the aqueous acid is flushed through. Discard all effluents.
g. Drying: Remove last traces of water in the SPE columns by pulling air through the columns under increased vacuum (e.g., 25 psi) for 5 minutes. Silica-based SPE columns or columns with high resistance to flow may require a longer time to reach dryness.
h. Elution: Position 13 x 100 mm collection tubes under each column. Elute analytes with 3 mL of elution solution (80:20:2 methylene chloride:isopropanol:concentrated ammonium hydroxide v/v, freshly prepared). Adjust vacuum so that the flow rate is 1 mL/minute or less. For some brands (e.g., Speedisk®) this flow rate may occur without applied vacuum. Most of the analytes (e.g., amphetamine, ephedrine, methamphetamine, etc.) are eluted in the first milliliter.

9. Evaporation: To each collection tube containing eluate, add about 5 µL crystal violet solution and 100 µL of 0.3 M hydrochloric acid in methanol. The samples are evaporated to dryness under gently blowing nitrogen at 25-35 °C. The samples should be removed from the evaporation bath within a few minutes after dryness. A mixed whitish and purple residue will remain. The purple color of the crystal violet helps to make the residue more visible when dried. The color of the crystal violet remains a constant blue to blue-violet during concentration and drying.
10. Derivatization: (Perform under the hood.) Add 100 µL of acetonitrile containing the optional dibromooctafluorobiphenyl secondary internal standard. Add 25 µL MSTFA and 25 µL MBHFBA in that order. Cap tubes between additions to prevent atmospheric humidity from affecting the reagents. (See note below. Have no more than 5 or 6 tubes uncapped at a time.) Vortex each tube about 4-5 seconds. Using Pasteur pipettes, transfer each mixture to low-volume (300-500 µL) amber autosampler vials and cap vials.
NOTE 1: Some derivatization takes place at room temperature, especially trimethylsilylation. Derivatization is completed on-column after injection. No prior heating is required or recommended.
NOTE 2: The color of the reconstituted solution should be deep blue to violet. If the color turns light blue or turquoise upon standing, moisture may be present (the vials may not have

been capped tightly enough). Such samples need to be reprocessed beginning at step 8 since the derivatives are not stable in the presence of moisture. If the vials are securely capped, the solutions will be stable for several days at room temperature and at least a week refrigerated. Protect vials from light (amber vials recommended.)

11. Analyze samples, standards, blanks, and QCs by GC-MS. (See MEASUREMENT, steps 15-17 and p. 9109-1.)

CALIBRATION AND QUALITY CONTROL:

12. Determine retention times for the derivatives of the analytes of interest using the column and chromatographic conditions specified on page 9109-1. Table 11 gives typical retention times for various drugs, precursors, and adulterants. Figure 1 shows a typical chromatogram.
13. Calibrate daily with at least six calibration standards and a blank selected from Table 7 to cover the analytical range.
    a. Prepare the analyte spiking solution as follows: Add known amounts of individual drug stock solutions to a volumetric flask and dilute to volume with methanol. A recommended final concentration for this solution is approximately 200 µg each per mL.
    b. Prepare calibration standards and media blanks in clean shipping containers (e.g., 50-mL polypropylene centrifuge tubes or equivalent).
       NOTE: Liquid standards (standards without added blank wipe media) may be prepared in lieu of media standards if cotton gauze was used for the samples.
    c. Add 3 mL methanol (or isopropanol if isopropanol was used with the samples in the field) to each calibration standard and media blank.
       NOTE: If two gauze wipes were routinely used for every sample, increase methanol (or isopropanol) to 4 mL. See Table 7, footnote 2.
    d. Spike a known volume of analyte spiking solution into each calibration standard by spiking directly onto the media or into solution. Use the spiking volumes suggested in Table 7 to cover the desired range.
    e. Process each of these through the desorption, solid phase extraction (SPE), drying, and derivatization steps (steps 7 through 11) along with the field samples.
    f. Analyze these along with the field samples. (See MEASUREMENT, steps 15-17.)
14. Prepare matrix-spiked and matrix-spiked duplicate (QC and QD) quality control samples.[8]
    a. Cotton gauze from the same lot used for taking samples in the field should be provided to the analytical laboratory to prepare these matrix-spiked quality control samples.
    b. The quality control samples (QC and QD) must be prepared independently at concentrations within the analytical range. (See Table 7 for applicable concentration ranges.)
    c. One quality control media blank (QB) must be included with each QC and QD pair.
    d. Spike QC and QD with a known amount of target analyte as suggested in Table 7.
       i. Transfer clean wipes to new shipping containers.
       ii. Add 3 mL of methanol (or isopropanol if isopropanol was used in wiping) to each wipe.
       iii. Spike QC and QD with a known amount of analyte as suggested in Table 7.
       NOTE: If two gauze wipes were used for the majority of samples in an analytical set, use two clean gauze wipes for each QB, QC, and QD, and increase isopropanol (or methanol) to 4 mL. See Table 7, footnote 2.
    e. Process quality control samples through the desorption, SPE, drying, and derivatization steps (steps 7 through 11) along with the calibration standards, blanks, and field samples.
    f. Analyze these along with the calibration standards, blanks, and field samples. (See MEASUREMENT, steps 15-17.)

MEASUREMENT:

See APPENDIX G for special instructions on measurement.

15. Analyze the calibration standards, quality control samples, blanks, a continuing calibration verification (CCV) standard consisting of one of the initial calibration standards, and samples by GC/MS.
    a. Set gas chromatograph according to manufacturer's recommendations and to conditions listed on page 9109-1.
    b. Set mass spectrometer conditions to manufacturer's specifications and those given on page 9109-1 for the scan mode or those in Table 6 for the SIM mode.
    c. Inject sample volume with autosampler or manually.
       NOTE: After the derivatives are prepared and just before analyzing any samples or standards, inject the highest concentrated standard several times in order to prime or deactivate the GC column and injection port. This will help minimize any drift in the instrument's response to target analytes relative to their internal standards.
    d. After analysis, the vials should be recapped promptly and refrigerated if further analysis is anticipated.
16. Using extracted ion current profiles for the primary (quantification) ions specific to each analyte, measure GC peak areas of analyte(s) and internal standard(s) and compute relative peak areas by dividing the peak area of the analyte by the area of the appropriate internal standard. Recommended primary (quantification) ions and internal standards are given in Tables 6, 8 and 9. Prepare calibration graph (relative peak area vs. µg analyte per sample).
17. Samples from initial investigations of clandestine laboratories are likely to include highly contaminated samples. If sample results exceed the upper range of the calibration curve, the sample in the GC vial may be diluted and reanalyzed or a smaller aliquot of the initial acid desorbate diluted, re-extracted, derivatized, and analyzed. Refer to APPENDIX H for instructions and limitations on making dilutions.

CALCULATIONS:

18. Determine the mass in µg/sample of respective analyte found in the wipe samples, and in the media blank from the calibration graph.
19. Calculate final concentration, C, of analyte in µg/sample:

$$C = c\frac{V_1}{V_2}\frac{V_3}{V_4} - b\frac{V_5}{V_2}$$

c = concentration in sample (in µg/sample determined from the calibration curve).

$\frac{V_1}{V_2}$ = volume correction factor (needed only when the volume of internal standard spiking solution used for spiking the samples - such as for composite samples requiring larger desorption solution volumes - is different from that used for spiking the calibration standards). (See Table 7, footnote 4).

V_1 = volume in µL of internal standard spiking solution used to spike samples.

V_2 = volume in µL of internal standard spiking solution used to spike the standards.

$\frac{V_3}{V_4}$ = dilution factor, if applicable.

V_3 = 5 mL (volume of desorbate normally taken for extraction in step 8d).

V_4 = volume in mL of desorbate actually taken for extraction and diluted to 5 mL with blank desorbing solution containing internal standard.

b = concentration in media blank (in µg/sample determined from the calibration curve).

$\frac{V_5}{V_2}$ = volume correction factor for the media blank (needed only if the volume of internal standard spiking solution used for spiking the media blank is different from that used for spiking the calibration standards).

V_5 = volume in µL of internal standard spiking solution used to spike media blank.

20. Report concentration, C′, in µg per total area wiped (in cm^2) as follows:

$$C' = \frac{C}{A}$$

C = µg/sample (step 19).
A = Total area wiped in cm^2 per sample.

NOTE: In general, if the area wiped was greater than or less than 100 cm^2, do not convert value to µg/100 cm^2 unless specifically required or allowed by agency having legal jurisdiction. For example, if the sample was a composite sample and the area was 400 cm^2, report results as µg/400 cm^2 and not averaged to µg/100 cm^2 since regulatory agencies might not allow averaging of composite results to 100 cm^2. To avoid confusion, report separately both µg/sample (C) and the total area wiped in cm^2 per sample (A) for both discrete and composite samples.

EVALUATION OF METHOD:

This method was developed according to the NIOSH sampling and analytical method development guidelines. [2] This method was evaluated for those analytes listed in Tables 8a and 8b over a range of approximately 0.1 µg/sample to 30 µg/sample for several types of sampling media. These concentration levels represent approximately the 1 through 300 times the limit of quantitation (LOQ) level for most of the analytes. Results are reported in the Backup Data Report [1].

The limits of detection (LOD and LOQ) were determined by preparing a series of liquid standards in desorption solution, processing by the SPE of NIOSH 9109, and analyzing in the scan mode. The LODs were estimated using the procedure of Burkart [9]. An LOD of 0.1 µg/sample for methamphetamine on wipes was achieved in the scan mode. The LOD was set at 0.1 µg/sample because that was the level of the lowest calibration standard in the LOD/LOQ study. Lower LODs (e.g., 0.02 µg/sample) have been achieved in practice by including calibration standards at lower concentration levels. The cleanliness and performance of the mass spectrometer must be maintained such that at 0.1 µg/sample a signal of at least 5 to 10 times the baseline noise is achievable. This is more easily accomplished in the SIM mode.

Six different wipe media were evaluated. These were 3″x3″ (7.5 cm x 7.5 cm) 12-ply cotton gauze, 4″x4″ (10 cm x 10 cm) AlphaWipe® (TX 1004), 4″x4″ (10 cm x 10 cm) 4-ply NU GAUZE®, 4″x4″ (10 cm x 10 cm) 4-ply MIRASORB®, 4″x4″ (10 cm x 10 cm) 6-ply SOF-WICK®, and 4″x4″ (10 cm x 10 cm) 4-ply TOPPER® sponges. Results are given in the Backup Data Report [2]. No synthetic media performed better than cotton gauze. Some media (NU GAUZE® and SOF-WICK®) gave inconsistent results.

Precision and accuracy were determined by analyzing 6 replicates at each of 6 concentration levels (nominally 0.1, 0.3, 1, 3, 10, and 30 µg/sample). Results are presented in Table 8a for cotton gauze and 8b for AlphaWipe®. The best precision and accuracies were dependent upon the use of carefully chosen internal standards, especially with steric hindrance of the amine (e.g., having N-ethyl and N-propyl groups). Long term sample storage stability was determined for periods up to 30 days under refrigeration (<6 °C) and for up to 7 days at room temperature (22-24 °C). Results are given in Table 5.

Chlorodifluoroacetic anhydride (CDFAA) and pentafluoro propionic anhydride (PFPA) were evaluated as derivatizing agents for the SPE eluates. These were not effective, probably due to the high level of ammonium chloride residues in the SPE column eluates. They were most effective with the liquid-liquid extraction procedure of NIOSH 9106 [4].

For SPE, the mixed silanization-acylation reagent, MSTFA and MBHFBA [10, 18], proved very effective. The derivatization mixture is transferred directly to amber mini-GC vials and direct-injected without prior heating.

Recovery of amphetamines from six different types of surfaces using cotton gauze was evaluated (see Table 10). The practice of serial wiping (wiping the same surface area a second time with a second gauze wipe and combining both wipes as a single sample) was evaluated. Four solvents for wetting the gauze were tested (distilled water, 5% distilled white vinegar, isopropanol, and methanol). Six replicates samples were taken on a latex painted wall. Recoveries and precisions are given in Table 10. The recoveries with 5% distilled white vinegar were better than for distilled water, but not as good as for isopropanol. Methanol is superior to isopropanol. Recoveries with isopropanol are greatly improved with a repeat (serial) wipe (11% improvement compared to only about 6% improvement with methanol). The study and results are reported in the Backup Data Report for NIOSH 9109 [1]. Additional research on surface sample recovery and solvent effectiveness has been reported by Martyny [10, 11].

REFERENCES:

[1] Reynolds JM, Siso MC, Perkins JB [2004]. Backup Data Report for NIOSH 9109, Methamphetamine and illicit drugs, precursors, and adulterants on wipes by solid phase extraction, Abridged. Unpublished. Prepared under NIOSH Contract 200-2001-0800.

[2] NIOSH [1995]. NIOSH Technical Report: Guidelines for air sampling and analytical method development and evaluation. By Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

[3] Martyny JW, Arbuckle SL, McCammon CS Jr., Esswein EJ, Erb N [2003]. Chemical exposures associated with clandestine methamphetamine laboratories [http://www.njc.org/pdf/chemical_exposures.pdf].

[4] NIOSH [2011]. Methamphetamine and illicit drugs, precursors, and adulterants on wipes by liquid-liquid extraction: Method 9106. In: Ashley KA, O'Connor PF, eds. NIOSH manual of analytical methods. 5th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, [www.cdc.gov/niosh/nmam/].

[5] NIOSH [2011]. Methamphetamine on wipes by liquid chromatography/mass spectrometry: Method 9111. In: Ashley KA, O'Connor PF, eds. NIOSH manual of analytical methods. 5th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, [www.cdc.gov/niosh/nmam/].

[6] Baum RM [1985]. New variety of street drugs poses growing problem. Chemical and Engineering News, 63(63):7-16.

[7] Buchanan JF, Brown CR [1988]. Designer drugs, a problem in clinical toxicology. Medical Toxicology 3:1-17.

[8] NIOSH [1994]. Chapter C: Quality Assurance. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113. [www.cdc.gov/niosh/nmam/].
[9] Burkart JA [1986]. General procedures for limit of detection calculations in the industrial hygiene chemistry laboratory. Applied Industrial Hygiene 1(3):153-155.
[10] Martyny JW. Decontamination of building materials contaminated with methamphetamine [http://health.utah.gov/meth/html/Decontamination/DecontaminationofBuildingMaterialsContaminatedwithMeth.pdf]. Date accessed: May, 2011.
[11] Martyny JW [2008]. Methamphetamine sampling variability on different surfaces using different solvents [http://health.utah.gov/meth/html/Decontamination/MethSamplingVariabilityonDifferentSurfaces.pdf]. Date accessed: May, 2011.
[12] Crockett DK, Frank EL, and Roberts WL [2002]. Rapid analysis of metanephrine and normetanephrine in urine by gas chromatography-mass spectrometry. Clinical Chemistry 48: 332-337.
[13] Budavari S, ed. [1989]. Merck Index, 11th ed. Rahway, New Jersey: Merck and Co.
[14] Sweet DV, ed. [1997]. Registry of toxic effects of chemical substances. DHHS (NIOSH) Publication No. 97-119. [http://www.cdc.gov/niosh/pdf/97-119.pdf].
[15] Sigma-Aldrich MSDS sheets [http://www.sigma-aldrich.com]. Date accessed: May 10, 2004.
[16] Cerilliant Analytical Reference Materials. 811 Paloma Drive, Suite A, Round Rock, Texas 78664 [www.cerilliant.com].
[17] Howard PH, Meylan WM [1997]. Handbook of physical properties of organic chemicals. Boca Raton, Florida: CRC/Lewis Publishers. See also Syracuse Research Corporation's website [http://www.syrres.com/esc/physdemo.htm] for demos and updates. Date accessed: May 10, 2004.
[18] Little JL [1999]. Artifacts in trimethylsilyl derivatization reactions and ways to avoid them. Journal of Chromatography. A, 844:1-22.
[19] Zhang JS, Tian Z, Lou ZC [1989]. Quality evaluation of twelve species of chinese ephedra (Ma Huang). Acta Pharmaceutic Sinica 24(11):865-871.
[20] Cui JF, Zhou TH, Zhang JS, and Lou ZC [1991]. Analysis of alkaloids in chinese ephedra species by gas chromatographic methods. Phytochemical Analysis 2:116-119.
[21] Andrews KM [1995]. Ephedra's role as a precursor in the clandestine manufacture of methamphetamine. Journal of Forensic Sciences 40(4):551-560.
[22] OSHA [2001]. Evaluation guidelines for surface sampling methods. Industrial Hygiene Chemistry Division, OSHA Salt Lake Technical Center, Salt Lake City, Utah. [http://www.osha.gov/dts/sltc/methods/surfacesampling/surfacesampling.pdf]. Date accessed: May 2011.

METHOD DEVELOPMENT BY:

John M. Reynolds, Maria Carolina Siso, and James B. Perkins, DataChem Laboratories, Inc., Salt Lake City, Utah under NIOSH Contract CDC 200-2001-0800.

Table 1. Formula and registry numbers of analytes

Compound (alphabetically)	MW[1] (Daltons) Free base	HCl salt	Hemisulfate salt	Structural Formula As free base	CAS #[2]	RTECS[6]
(DL)-Amphetamine	135.21	171.67	184.25	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH_2$	300-62-9[3] 60-13-9[5]	SH9450000 SI1750000
(D)-Amphetamine[7]	135.21	171.67	184.25	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH_2$	51-64-9[3] 51-63-8[5]	SI1400000
(L)-Amphetamine	135.21	171.67	184.25	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH_2$	156-34-3[3]	SH9050000
Caffeine	194.19			$(CH_3)_3{\cdot}[C_5HN_4O_2]$	58-08-2[3]	EV6475000
(DL)-Ephedrine	165.24	201.70	214.28	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	90-81-3[3] 134-71-4[4]	
(L)-Ephedrine[8]	165.24	201.70	214.28	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3)NH{\cdot}CH_3$	299-42-3[3] 50-98-6[4] 134-72-5[5]	KB0700000 KB1750000 KB2625000
(D)-Ephedrine	165.24	201.70	214.28	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3)NH{\cdot}CH_3$	321-98-2[3] 24221-86-1[4]	KB0600000 KB1925000
(±)-MDEA	207.27	243.73		$CH_2O_2C_6H_3{\cdot}CH_2{\cdot}CH(CH_3)NH{\cdot}C_2H_5$	82801-81-8[3] 116261-63-2[4]	
(±)-MDMA	193.24	229.71		$CH_2O_2C_6H_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	42542-10-9[3] 92279-84-0[4]	SH5700000
(+)-MDMA[7]	193.24	229.71		$CH_2O_2C_6H_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	64057-70-1[4]	SH5700000
(DL)-Methamphetamine	149.24	185.70	198.28	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	4846-07-5[3]	
(D)-Methamphetamine[7]	149.24	185.70	198.28	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	537-46-2[3] 51-57-0[4]	SH4910000 SH5455000
(L)-Methamphetamine	149.24	185.70	198.28	$C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	33817-09-3[3]	SH4905000
Phencyclidine	243.39	279.85		$C_6H_5{\cdot}C[C_5H_{10}]{\cdot}N[C_5H_{10}]$	77-10-1[3] 956-90-1[4]	TN2272600 TN2272600
Phentermine	149.24	185.70		$C_6H_5{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}NH_2$	122-09-8[3] 1197-21-3[4]	SH4950000
(DL)-Norephedrine	151.21	187.67	200.25	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH_2$	14838-15-4[3] 154-41-6[4]	RC2625000 DN4200000
1R,2S (-)-Norephedrine	151.21	187.67	200.25	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH_2$	492-41-1[3]	RC2275000
1S,2R (+)-Norephedrine	151.21	187.67	200.25	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH_2$	37577-28-9[3]	
1S,2S (+)-Norephedrine	151.21	187.67	200.25	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH_2$	36393-56-3 2153-98-2[4] 492-39-7[4]	RC9275000
(D)-Pseudoephedrine[8,9]	165.24	201.70	214.28	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NHCH_3$	90-82-4[3] 345-78-8[4]	UL5800000 UL5950000
(L)-Pseudoephedrine[10]	165.24	201.70	214.28	$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}NH{\cdot}CH_3$	321-97-1[3]	

(1) Molecular weights are calculated from the empirical formula using the 1987 IUPAC Atomic Weights of the Elements, Merck Index [10]. The molecular weight of the hemisulfate is ½ the weight of the 2:1 sulfate salt (2 moles amine + 1 mole H_2SO_4).
(2) CAS from various sources: Merck Index [13], NIOSH RTECS [14], MSDS sheets from Sigma/Aldrich [15], Cerilliant [16], and other sources [17].
(3) Free base form.
(4) Hydrochloride salt.
(5) 2:1 Sulfate salt (2 moles amine + 1 mole H_2SO_4.
(6) RTECS = NIOSH Registry of Toxic Effects of Chemical Substances [14].
(7) More active isomer.
(8) Naturally occurring isomer.
(9) The D form of pseudoephedrine is a decongestant.
(10) The L form of pseudoephedrine is a bronchodilator. Dehydroxylation forms the less active L-methamphetamine.

Table 2. Methamphetamine Regulations by State (Jan 2008)*

State	Standard	State	Standard
Alaska**	0.1 µg/100 cm^2	Minnesota	0.1 µg/100 cm^2 (meth labs), < 1.5 µg/100 cm^2 (meth use)
Arizona	0.1 µg/100 cm^2	Montana	0.5 µg/ft^2
Arkansas	0.1 µg/100 cm^2	New Mexico	1.0 µg/ft^2
California***	< 1.5 µg/100 cm^2	North Carolina	0.1 µg/100 cm^2
Colorado	0.5 µg/100 cm^2	Oregon	0.5 µg/ft^2
Connecticut	0.1 µg/100 cm^2	South Dakota	0.1 µg/100 cm^2
Hawaii	0.1 µg/100 cm^2	Tennessee	0.1 µg/100 cm^2
Idaho	0.1 µg/100 cm^2	Utah	0.1 µg/100 cm^2
Kentucky	0.1 µg/100 cm^2	Washington	<0.1 µg/100 cm^2

The following states have no standard: Alabama, Delaware, D.C., Florida, Georgia, Illinois, Indiana, Iowa, Kansas, Louisiana, Maine, Maryland, Massachusetts, Michigan, Mississippi, Missouri, Nebraska, Nevada, New Hampshire, New Jersey, New York, North Dakota, Ohio, Oklahoma, Pennsylvania, Rhode Island, South Carolina, Texas, Vermont, Virginia, West Virginia, Wisconsin, Wyoming.

* NIOSH has not established health-based or feasibility-based airborne Recommended Exposure Limits (RELs) or surface contamination guidelines for clandestine drug laboratories. State surface contamination limits are provided as an aid to those seeking additional information and does not constitute endorsement by NIOSH. The National Alliance for Model State Drug Laws (NAMSDL) website (http://www.namsdl.org/home.htm) periodically summarizes state feasibility-based decontamination limits and proposed state legislative requirements and guidelines. However, state information is subject to change, and specific state's surface contamination limits, and other state decontamination requirements and guidelines should be obtained directly from each state.

** Guidance and Standards for Cleanup of Illegal Drug-Manufacturing Sites Revision 1 April 19, 2007 Alaska Department of Environmental Conservation, Spill Prevention and Response Division, Prevention and Emergency Response Program. http://www.dec.alaska.gov/spar/perp/methlab/druglab_guidance.pdf

*** In Oct 2009 House Bill 1489 was passed into law to incorporate the new standard as the state limit. All other states: Data source: http://health.utah.gov/meth/html/Resources/OtherStates/Nationalcomparison (downloaded April 2011).

Table 3. Physical properties of analytes[1]

Compound (alphabetically)	CAS	m.p. (°C)	Vapor Pressure (mm Hg)	pK_a[4]	Log P[5]	Solubility in Water, g/100mL
(DL)-Amphetamine	300-62-9	—	—	10.1 @ 20 °C	1.76	2.8 @ 25 °C
(D)-Amphetamine	51-64-9	<25	—	9.9[6]	1.76	—
(D)-Amphetamine sulfate	51-63-8	>300	—	—	6.81	—
(L)-Amphetamine	156-34-3	—	0.201 @ 25 °C	10.1 @ 20 °C	1.76	2.8 @ 25 °C
Caffeine	58-08-2	238	15 @ 89 °C	10.4 @ 40 °C	-0.07	2.16 @ 25 °C
(DL)-Ephedrine	90-81-3	76.5	—	—	0.68	—
(L)-Ephedrine	299-42-3	34	0.00083 @ 25 °C	10.3 @ 0 °C	1.13	63.6 @ 30 °C
(L)-Ephedrine HCl	50-98-6	218	$2.04E^{-10}$ @ 25 °C	pH 5.9 @ 1/200 dil.[3]	-2.45	25[6]
MDEA	82801-81-8	—	—	—	—	—
MDMA HCl	42542-10-9	148-149[2]	—	—	—	—
(D)-Methamphetamine	537-46-2	—	0.163 @ 25 °C	9.87 @ 25 °C	2.07	1.33 @ 25 °C
(D)-Methamphetamine HCl	51-57-0	170-175[2]	—	—	—	—
Phencyclidine	77-10-1	46.5	—	8.29[6]	4.69	—
Phencyclidine HCl	956-90-1	233-235[2]	—	—	—	—
Phentermine	122-09-8	—	0.0961 @ 25°C	—	1.90	1.86 @ 25 °C
Phentermine HCl	1197-21-3	198[2]	—	—	—	—
(±) Phenylpropanolamine	14838-15-4	—	0.000867 @ 25 °C	9.44 @ 20 °C	0.67	14.9 @ 25 °C
(±) Phenylpropanolamine HCl	154-41-6	194	—	—	-2.75	—
(L)-Norephedrine	492-41-1	51-53[3]	—	—	—	—
1*S*,2*S* (+)-Norephedrine	36393-56-3	77.5-78	0.000867 @ 25 °C	9.44 @ 20 °C	0.83	14.9 @ 25 °C
1*S*,2*S* (+)-Norephedrine HCl	492-39-7	—	—	pH 5.9-6.1 in aq. soln.[3]	0.22	2 @ 25 °C
(D)-Pseudoephedrine	90-82-4	119	0.00083 @ 25 °C	10.3 @ 0 °C	0.89	10.6 @ 25 °C
(D)-Pseudoephedrine HCl	345-78-8	181-182[2]	—	pH 5.9 @ 1/200 dil.[3]	—	—

(1) Handbook of Physical Properties of Organic Chemicals unless otherwise noted [17].
(2) Merck Index [13].
(3) Sigma-Aldrich MSDS [15].
(4) Negative log of the acid dissociation constant for the amine in aqueous solution.
(5) Log P = octanol-water partition coefficient.
(6) Temperature not given in source.

Table 4. Synonyms of analytes

Generic names[1]	Trade and street names[2]	Additional names[3]
(DL)-Amphetamine; (±)-Amphetamine	Benzedrine; Phenedrine; bennies	(±)-α-Methylbenzeneethanamine[4]; dl-α-Methylphenethylamine[4]; dl-1-Phenyl-2-aminopropane; (±)-Desoxynorephedrine
(D)-Amphetamine; (+)-Amphetamine	Dextroamphetamine; Dexedrine; dexies	(S)-α-Methylbenzeneethanamine[4]; d-α-Methylphenethylamine[4]; d-1-phenyl-2-aminopropane; d-β-Phenylisopropylamine
(L)-Amphetamine; (-)-Amphetamine	Levoamphetamine; component of Adderall	(R)-α-Methylbenzeneethanamine[4]; l-α-Methylphenethylamine[4]; l-1-phenyl-2-aminopropane; (-)-1-phenyl-2-aminopropane
Caffeine	Component (with ephedrine) of cloud 9 and herbal XTC	3,7-Dihydro-1,3,7-trimethyl-1H-purine-2,6-dione[4]; 1,3,7-Trimethylxanthine
(DL)-Ephedrine; (±)-Ephedrine	Ephedral; Racephedrine; Sanedrine	(*R**,*S**)-(±)-alpha-[2-(Methylamino)ethyl]benzenemethanol; DL-alpha-[1-(Methylamino)ethyl] benzyl alcohol; *dl*-Ephedrine
(L)-Ephedrine; (-)-Ephedrine; (1*R*,2*S*)-(-)-Ephedrine; *l*-Ephedrine	Primatene; Xenadrine; Ma Huang (Ephedra sinica and other species[5]); (with caffeine) cloud 9 and herbal ecstasy	(*R*-(*R**,*S**))-*α*-(1-Methylaminoethyl)benzenemethanol; L-erythro-2-(Methylamino)-1-phenylpropan-1-ol; (1*R*,2*S*)-(-)-2-Methylamino-1-phenyl-1-propanol; (-)-alpha-(1-Methylamino-ethyl)-benzyl alcohol; (-)-1-hydroxy-2-methylamino-1-phenylpropane; L-(-)-Ephedrine
(D)-Ephedrine		(1*S*,2*R*)-(+)-2-Methylamino-1-phenyl-1-propanol; (+)-Ephedrine
MDEA	MDE; Eve	(±)-3,4-Methylenedioxy-N-ethylamphetamine; *N*-ethyl-alpha-methyl-1,3-benzodioxole-5-ethanamine
MDMA	Adam, ecstasy	*N*,*α*-Dimethyl-3,4-1,3-benzodioxole-5-ethanamine; 3,4-Methylenedioxymethamphetamine
(DL)-Methamphetamine; (±)-Methamphetamine		*N*,*α*-Dimethylbenzeneethanamine[4]; *N*,*α*-Dimethylphenethylamine; *dl*-Desoxyephedrine; N-methyl-*β*-phenylisopropylamine
(D)-Methamphetamine; (+)-Methamphetamine; *d*-Methamphetamine	Methedrine; Desoxyn; chalk; crank; crystal; glass; ice; meth; speed; upper	(*S*)-*N*,*α*-Dimethylbenzeneethanamine; (*S*)-(+)-*N*,*α*-Dimethyl-phenethylamine[4]; *d*-1-Phenyl-2-methylaminopropane; *d*-Desoxyephedrine; *d*-N-methyl-*β*-phenyl-isopropylamine
(L)-Methamphetamine; (-)-Methamphetamine	Component in decongestant vapor inhaler (Vick's brand)	(*R*)-(-)-*N*,*α*-Dimethylphenethylamine; (-)-Deoxyephedrine; (-)-2-(Methylamino)-1-phenylpropane
Phencyclidine	Sernylan; Sernyl; angel dust; PCP; peace pill	1-(1-Phenylcyclohexyl) piperidine[4]
Phentermine	Fastin; Normephentermine	*α*,*α*-Dimethylbenzeneethanamine[4]; *α*,*α*-Dimethylphenethylamine[4]; 1,1-Dimethyl-2-phenylethylamine; *α*-Benzylisopropylamine
(DL)-Norephedrine; (±)-Norephedrine	(±)-Phenylpropanolamine; Obestat; Phenedrine;	(*R**,*S**)-(±)-*α*-(1-Aminoethyl)benzenemethanol[4]; -(±)-*α*-(1-Amino-ethyl)benzyl alcohol[4]; (±)-2-Amino-1-phenyl-1-propanol
(L)-Norephedrine; (-)-Norephedrine	Natural form found in Ephedra sinica and other species[5]	(1*R*,2*S*)- 2-Amino-1-phenyl-1-propanol; (1*R*,2*S*)-Norephedrine; *l*-erythro-2-Amino-1-phenylpropan-1-ol
(D)-Norephedrine; (+)-Norephedrine	Metabolite of cathinone in urine of Khat users.	(1*S*,2*R*)- 2-Amino-1-phenyl-1-propanol; (1*S*,2*R*)-Norephedrine; *d*-erythro-2-Amino-1-phenylpropan-1-ol
(+)-Norpseudoephedrine; Cathine	Amorphan; Adiposettin; Reduform; found naturally in Khat plant	(*R**,*R**)-*α*-(1-Aminoethyl)benzenemethanol[4]; *d*-threo-*α*-2-Amino-1-hydroxy-1-phenylpropane; 1*S*,2*S*-(+)-Norpseudoephedrine
L-(+)-Pseudoephedrine; (+)-Pseudoephedrine; *d*-Pseudoephedrine	Afrinol; Novafed; Sinufed; Sudafed; natural form found in Ephedra sinica and other species[5]	(*S*-(*R**,*R**))- *α*-[1-(Methylamino)ethyl]benzenemethanol; (1*S*,2*S*)-(+)-2-Methylamino-1-phenylpropanol; *d*-(alpha-(1-Methylamino)-ethyl)benzyl alcohol; (1*S*,2*S*)-(+)-Pseudoephedrine; *d*-threo-2-Methylamino-1-phenylpropan-1-ol; (+)-*ψ*-Ephedrine
D-(-)-Pseudoephedrine; (-)-Pseudoephedrine		(1*R*,2*R*)-(-)-Pseudoephedrine; (-)-*ψ*-Ephedrine; *l*-threo-2-Methylamino-1-phenylpropan-1-ol; (+)-*ψ*-Ephedrine

(1) Common or generic names. Salts forms are not given for simplicity.

(2) Trade and street names are exemplary, not exhaustive. Street names change over time and by locality. Salts and free base forms are not distinguished.

(3) Other names from Merck Index [13], NIOSH Registry of Toxic Effects of Chemical Substances [14], and MSDS sheets [15, 16]. NOTE: For amphetamine and methamphetamine the prefixes R-, D-, d-, and (+)- , although they mean different things, are essentially synonymous for the dextrorotatory stereoisomer and S-, L-, l-, and (-)- are essentially synonymous for the levorotary stereoisomer. Many other synonyms exist.

(4) Uninverted CAS name as given in Merck Index [13].

(5) Extracts of Ephedra species contain various amounts of (+)-Norephedrine, (-)-N-methylephedrine, and (+)-N-methylpseudoephedrine. (+)-Norephedrine is reduced to amphetamine and N-methylephedrine and N-methylpseudoephedrine reduce to N,N-dimethylamphetamine [19, 20]. The presence of these latter two compounds in methamphetamine samples indicate that Ephedra spp. extracts may have been used in the synthesis [21].

Table 5. Limit of detection (LOD), method detection limit (MDL), and sample storage stability[1]

		Estimated LOD[3]		Estimated MDL[4]		Storage Stability[5]	
Compound	Int. std.[2]	µg/sample liq. stds[6]	µg/sample liq. stds[7]	µg/sample cotton gauze	µg/sample AlphaWipe®	30 days 4 °C	7 days 22 °C
(D)-Amphetamine	D11-Amp	0.1	0.1	0.02		100.5	94.5
	D14-Met	0.1	0.05	0.02	0.02	99.7	87.9
	NMPhen	0.1		0.04		-	-
Cocaine	D11-Amp	0.6		0.2[9]		99.3	98.8
	D14-Met	0.4		0.1[9]	0.1[9]	98.5	91.9
	NMPhen	0.4		0.1[9]		-	-
(L)-Ephedrine	D11-Amp	0.2	0.2	0.02		95.6	97.2
	D14-Met	0.1	0.1	0.02	0.02	94.8	90.5
	NMPhen	0.1		0.02		-	-
MDEA	N-PAmp	0.1		0.06	0.1	98.9	102.1
MDMA	D11-Amp	0.1		0.02		99.7	111.1
	D14-Met	0.1		0.02	0.04	98.9	103.2
	NMPhen	0.1		0.03		-	-
(D)-Methamphetamine	D11-Amp	0.2	0.07	0.02		98.7	100.6
	D14-Met	0.1	0.05	0.02	0.02	98.0	93.5
	NMPhen	0.1		0.02		-	-
Phencyclidine	D11-Amp	0.6		0.1[9]		103.7	105.2
	D14-Met	0.4		0.1[9]	0.5[9]	102.9	97.7
	NMPhen	0.4		0.1[9]		-	-
Phentermine	D11-Amp	0.2		0.03		102.0	101.5
	D14-Met	0.1		0.03	0.03	101.1	94.3
	NMPhen	0.1		0.04		-	-
(±)-Norephedrine[8]	D11-Amp	0.1	0.05	0.03		94.3	92.7
	D14-Met	0.1	0.05	0.03	0.03	93.6	86.2
	NMPhen	0.1		0.03		-	-
Pseudoephedrine	D11-Amp	0.2	0.2	0.02		100.4	97.9
	D14-Met	0.1	0.1	0.02	0.02	99.6	91.1
	NMPhen	0.1		0.02		-	-

(1) Backup Data Report [1].

(2) Internal standards: D11-Amp = Amphetamine-D_{11}, D14-Met = Methamphetamine-D_{14}, NMPhen = N-Methyl phenethylamine, N-PAmp = N-Propyl amphetamine.

(3) LODs vary according to individual GC columns, instrument conditions and cleanliness, media interferences, and internal standards used. LODs were calculated on liquid standards using the procedure of Burkart (LODs for linear calibration curves are calculated as 3 times the standard error of the lowest three standards analyzed in replicate divided by the slope of the calibration curve). [9]

(4) MDLs are provided to satisfy regulatory agencies requiring this expression of sensitivity. These MDLs are calculated as the standard deviation of six replicates on spiked media analyzed at the 0.1 µg/sample level (except as noted) times the Student's t value for 6 replicates (3.365). (Normally 7 replicates are required.)

(5) Cotton gauze samples were spiked at 3 µg/sample per analyte. Six samples were analyzed immediately after preparation. Six samples were stored at room temperature (about 22 °C) for 7 days and then analyzed. Eighteen samples were stored at >6 °C. Of the 18 samples stored at >6 °C, six each were analyzed at 7 and 21 days and three each were analyzed at 14 and 30 days. (Backup Data Report [1].) Apparent recoveries vary according to internal standard used.

(6) These LODs are conservative since the lowest calibration standard for these determinations was 0.1 µg/sample. Lower LODs are achievable with lower concentration calibration standards and operation of the mass spectrometer in the SIM mode.

(7) Typical LODs for a five point calibration curve with single standards at each concentration level. The lowest calibration standard for these determinations was 0.05 µg/sample.

(8) (±)-Norephedrine = (±)-phenylpropanolamine.

(9) MDLs for cocaine and phencyclidine were determined from the 0.3 µg/sample level because the GC peaks for the 0.1 µg/sample level were un-measurable. Precisions at the 0.3 µg/sample level were such that the MDLs calculated to 0.1 µg/sample anyway. This value may be realistic since the 0.1 µg/sample level samples had been stored for one month prior to analysis which may have affected stability.

Table 6. Example of mass spectrometer operation parameters for selected ion monitoring mode[1]

Heptafluorobutyryl-trimethyl-silyl derivatives	Scan window[2]	Acquisition ions (*m/z*) per group[3]									
Acquisition Group 1	8.20 to 10.20	104	118	128	132	210	213	240	244	254	261
Acquisition Group 2	10.20 to 13.20	179	240	254	282	296	456				
Acquisition Group 3	13.20 to 19.00	82	162	182	200	242	254	268			

GC Peak No.[4]	Target Analytes and Internal Standards	Retention Time[6](min)	Primary Ion (*m/z*)[7] (Quantification Ion)	Secondary ion and approximate relative abundance[8](relative to the Primary Ion)	
	Acquisition Group 1:				
13	Amphetamine-D_{11} (I$)[9]	8.46	244	128	70%
5	Amphetamine	8.54	240	118	70%
92	Phentermine	8.72	254	132	12%
81	N-Methyl phenethylamine (I$)[9]	8.54	240	104	100%
68	Methamphetamine-D_{14} (I$)[9]	9.86	261	213	30%
64	Methamphetamine	9.94	254	210	35%
	Acquisition Group 2:				
95	Phenylpropanolamine	10.49	179	240	18%
97	N-Propylamphetamine (I$)[9]	11.05	282	240	85%
36	Ephedrine	11.40	179	254	17%
98	Pseudoephedrine	11.68	179	254	15%
32	Dibromooctafluorobiphenyl[10]	12.82	296	456	100%
	Acquisition Group 3:				
59	MDMA	13.81	254	162	80%
57	MDEA	14.19	268	162	60%
86	Phencyclidine	15.62	200	242	35%
27	Cocaine	18.65	182	82	110%

(1) In this example, 10 analytes and 5 internal standards are grouped into 3 acquisition groups having no more than 10 primary and secondary ions per acquisition group. For 6 analytes and internal standards or less, one acquisition group may be sufficient.

(2) Scan window is in minutes. Actual times are dependent upon GC column and instrument conditions.

(3) Ions (*m/z*) in bold numbers are suggested primary (quantification) ions. For best signal to noise ratio, do not exceed 10 ions per acquisition group. Dwell time per ion (*m/z*) is 50 milliseconds.

(4) GC peak numbers are those in Figures 1 and 2 and Table 11.

(5) The list of analytes and internal standards shown is an example. Analyte(s) and internal standard(s) must be selected according to analytical objectives.

(6) Retention times are dependent upon GC column and instrument conditions.

(7) The better ions for quantification are usually the base peak or those with masses >100 *m/z* and relative abundances >50% of the base peak. These minimize interference from co-eluting hydrocarbons. The suggested primary ions are not necessarily the base peaks in the mass spectra of the analytes, especially if the base peaks are ions common to aromatics (e.g., *m/z* 91) and paraffinic or olefinic hydrocarbons (e.g., *m/z* 42, 57, and 58). Suggested ions for other analytes and internal standards are given in Tables 11 and 12.

(8) Secondary ions may be used for quantification if the primary ion encounters interference. Secondary ions improve qualitative identification for SIM analyses. The relative abundances given are approximate (±10 to 20%) and depend upon specific instrument tuning and conditions. They are relative to the primary ion and not necessarily to the base peak in the mass spectrum of each analyte. The relative abundance of secondary ions for each analyte needs to be determined from a mass spectrum acquired on the instrument to be used.

(9) (I$) = internal standard. Internal standards must be paired with the appropriate analytes. Tables 8a and 8b give precision and accuracy data for various pairings. Other potentially useful internal standards are given in Tables 9 and 11. Highly deuterated analogs of the target analytes are preferred, where available.

(10) Dibromooctafluorobiphenyl is an optional secondary internal standard useful for monitoring autosampler performance and instrument tuning. A shift in the mass axes or the relative abundance of *m/z* 296 to that of *m/z* 456 throughout an analytical sequence will help signal degraded tuning.

Table 7. Suggested spiking schedule for calibration standards and quality control samples

	Add the following to clean shipping containers (e.g., 50-mL polypropylene centrifuge tubes) in the following order.						
Name	Number of Wipes[1,2]	Volume[2] of Isopropanol or Methanol[3]	Volume[2] of Internal Standard Spiking Solution[4,5]	Volume of Target Analyte Spiking Solution[5,6]	Volume of Spiking Solution diluted 1/20[5,7]	Volume[2] of Desorption Solution[8]	Resulting µg/sample as Free Base[9]
Calibration Standards[10]							
CS0	0	3 mL	60 µL		0.0 µL	30 mL	0.00
CS1	0	3 mL	60 µL		2 µL	30 mL	0.02
CS2	0	3 mL	60 µL		5 µL	30 mL	0.05
CS3	0	3 mL	60 µL		10 µL	30 mL	0.1
CS4	0	3 mL	60 µL		20 µL	30 mL	0.2
CS5	0	3 mL	60 µL		60 µL	30 mL	0.6
CS6	0	3 mL	60 µL	10 µL		30 mL	2.0
CS7	0	3 mL	60 µL	30 µL		30 mL	6.0
CS8	0	3 mL	60 µL	100 µL		30 mL	20
CS9	0	3 mL	60 µL	300 µL		30 mL	60
CS10	0	3 mL	60 µL	1000 µL		30 mL	200
Quality Control Samples[11]							
QB (media blank)	1	3 mL	60 µL	0.0 µL		30 mL	0.0
QC (matrix spike)	1	3 mL	60 µL	3-300 µL	or 20-60 µL	30 mL	0.2-60
QD (matrix spike duplicate)	1	3 mL	60 µL	3-300 µL	or 20-60 µL	30 mL	0.2-60

(1) Gauze wipes may be added to the calibration standards but are not necessary if cotton gauze is used. Blank gauze wipes must always be added to the quality control samples, QB, QC, and QD.

(2) a. If a sample consists of 2 gauze wipes, the volume of desorption solution must be increased to 40 mL to accommodate the second wipe. The shipping container should be a 50-mL polypropylene centrifuge tube or equivalent to accommodate the extra volume of desorption solution for 2 wipes. It is not critical to know the exact volume of desorption solution and wetting alcohol used per sample. It only needs to be enough to cover the samples and to permit free percolation through the samples. See step 7.
b. If a set of samples consists predominantly of 2 gauze wipes, the QB, QC, and QD should also consist of 2 wipes and treated as per the samples. The volume of isopropanol (or methanol) added to the QC samples should be increased to 4 mL for 2 gauze wipes to simulate samples containing 2 gauze wipes.

(3) If methanol was used for wipe sampling, it should also be used in the calibration standards, blanks, and QCs instead of isopropanol.

(4) Concentration of internal standards in the internal standard spiking solution is approximately 200 µg/mL as the free base. It is critical to know the exact volume of internal standard spiking solution that is added to the calibration standards, samples, blanks, and quality control samples. The volume spiked into the samples may vary with sample size but the volume spiked into each of the calibration standards must not vary. See step 7b.

(5) For quality control samples, spike onto wipe media within the shipping container. For liquid calibration standards (in lieu of media calibration standards), spike into the isopropanol (or methanol).

(6) Concentration of analytes in the target analyte spiking solution is approximately 200 µg/mL as the free base.

(7) Concentration of analytes in the diluted spiking solution for this table is approximately 10.0 µg/mL as the free base and can be prepared by diluting 100 µL of the target analyte spiking solution to 2 mL in methanol.

(8) Desorption solution is 0.1 M sulfuric acid in deionized water.

(9) This is µg per total sample irrespective of the total desorption solution volume or the area wiped.

(10) Select 6 calibration standards from the list to cover the analytical range plus the blank.

(11) Prepare one set of quality control samples for every 20 samples or less.

Table 8a. Precision and accuracy in scan mode for cotton gauze[1]

Compound	Internal Standard[2]	Range[3] µg/sample	Accuracy	Overall Precision $\hat{S}_{rT}$	Bias	
					Average	Range
(D)-Amphetamine	D_{11}-Amp	0.1-30	8.1	0.0412	-0.0054	-0.0386 to +0.0428
	D_{14}-Met	0.1-30	10.3	0.0472	-0.0227	-0.0844 to +0.0199
	NMPhen	0.1-30	13.2	0.0662	-0.0120	-0.0931 to +0.0290
Cocaine	D_{11}-Amp	1.0-30	15.8	0.0469	+0.0810	+0.0416 to +0.1375
	D_{14}-Met	3-30	13.3	0.0422	+0.0631	+0.0003 to +0.1294
	NMPhen	0.3-30	20.2	0.0729	+0.0823	-0.0092 to +0.1359
(L)-Ephedrine	D_{11}-Amp	0.1-30	9.8	0.0499	-0.0052	-0.0608 to +0.0262
	D_{14}-Met	0.1-30	9.2	0.0397	-0.0266	-0.0463 to +0.0221
	NMPhen	0.1-30	11.2	0.0493	-0.0284	-0.0775 to +0.0302
MDEA	N-PAmp	0.3-29	12.4	0.0618	+0.0127	-0.0475 to +0.0869
MDMA	D_{11}-Amp	0.1-27	14.3	0.0568	+0.0497	+0.0104 to +0.1197
	D_{14}-Met	0.1-27	13.1	0.0558	+0.0389	-0.0189 to +0.0978
	NMPhen	0.3-27	11.9	0.0605	+0.0007	-0.0570 to +0.0360
(D)-Methamphetamine	D_{11}-Amp	0.1-10	9.2	0.0395	+0.0270	-0.0289 to +0.0923
	D_{14}-Met	0.1-30	5.9	0.0302	+0.0015	-0.0440 to +0.0592
	NMPhen	0.3-30	6.9	0.0334	+0.0113	-0.0534 to +0.0448
Phencyclidine	D_{11}-Amp	0.3-30	17.2	0.0639	+0.0670	+0.0059 to +0.1222
	D_{14}-Met	0.3-30	15.9	0.0648	+0.0521	-0.0386 to +0.1039
	NMPhen	0.3-30	16.0	0.0638	+0.0547	-0.0474 to +0.0886
Phentermine	D_{11}-Amp	0.1-30	10.1	0.0444	+0.0261	-0.0067 to +0.0912
	D_{14}-Met	0.1-30	10.4	0.0527	+0.0041	-0.0600 to +0.0674
	NMPhen	1.0-30	8.2	0.0400	+0.0121	-0.0378 to +0.0407
(±)-Norephedrine[4]	D_{11}-Amp	0.1-30	12.2	0.0571	+0.0241	+0.0500 to +0.0610
	D_{14}-Met	0.1-30	12.5	0.0638	-0.0005	-0.0674 to +0.0708
	NMPhen	0.1-30	13.3	0.0675	+0.0036	-0.0533 to +0.0476
Pseudoephedrine	D_{11}-Amp	0.1-30	10.0	0.0507	-0.0059	-0.0530 to +0.0441
	D_{14}-Met	0.1-30	12.3	0.0507	-0.0392	-0.0737 to +0.0301
	NMPhen	1.0-30	15.6	0.0716	-0.0350	-0.0813 to +0.0617

(1) Backup Data Report [2]. Values are for the heptafluorobutyryl and mixed heptafluorobutyryl-trimethylsilyl derivatives and analysis by GC-MS in scan mode. Each sample consisted of a pair of 3" x 3" 12-ply cotton gauze pads. There were 6 replicate samples per concentration level and six concentration levels evaluated from approximately 0.1 to 30 µg/sample.

(2) Internal Standards

Deuterated:
D_{11}-Amp = Amphetamine-D_{11}
D_{14}-Met = Methamphetamine-D_{14}

Non-deuterated:
NMPhen = N-Methyl phenethylamine
N-PAmp = N-Propyl amphetamine

(3) Range used for calculation of precision, accuracy, and bias. The entire range studied for all analytes was approximately 0.1 to 30 µg/sample (1xLOQ to 300xLOQ).

(4) (±)-Norephedrine = (±)-phenylpropanolamine.

Table 8b. Precision and accuracy in scan mode for AlphaWipe®[1]

Compound	Internal Standard[2]	Range[3] µg/ sample	Accuracy	Overall Precision $\hat{S}_{rT}$	Bias	
					Average	Range
(D)-Amphetamine	D14-Met	0.1-30	17.2	0.0611	-0.0712	-0.1066 to -0.0468
Cocaine	D14-Met	0.3-30	17.7	0.0901	-0.0014	-0.0246 to +0.0252
(L)-Ephedrine	D14-Met	0.1-30	10.7	0.0432	-0.0362	-0.0638 to -0.0039
MDEA	N-PAmp	0.3-29	9.6	0.0425	-0.0240	-0.0453 to +0.0416
MDMA	D14-Met	0.3-27	11.4	0.0498	-0.0297	-0.0612 to +0.0095
(D)-Methamphetamine	D14-Met	0.1-30	8.7	0.0430	-0.0114	-0.0483 to +0.0625
Phencyclidine	D14-Met	0.3-30	13.0	0.0391	+0.0658	+0.0216 to +0.1418
Phentermine	D14-Met	0.3-30	10.4	0.0295	-0.0560	-0.0917 to -0.0266
(±)-Norephedrine[4]	D14-Met	0.1-30	12.6	0.0577	+0.0282	-0.0220 to +0.0937
Pseudoephedrine	D14-Met	0.1-30	13.5	0.0592	-0.0352	-0.1001 to -0.0020

(1) Backup Data Report [1]. Values are for the heptafluorobutyryl and mixed heptafluorobutyryl-trimethylsilyl and analysis by GC-MS in scan mode (see p 9109-1 for GC and MS conditions). Each sample consisted of a pair of 3" x 3" 12-ply cotton gauze pads. There were 6 replicate samples per concentration level and six concentration levels evaluated from approximately 0.1 to 30 µg/sample.

(2) Internal Standards: D14-Met = Methamphetamine-D_{14}, N-PAmp = N-Propyl amphetamine.

(3) Range used for calculation of precision, accuracy, and bias. The entire range studied for all analytes was approximately 0.1 to 30 µg/sample (1xLOQ to 300xLOQ).

(4) (±)-Norephedrine = (±)-phenylpropanolamine.

Table 9a. Recommended internal standards[1] and best application

COMPOUND NAME	CAS	MW as free base	Quant. Ion	Secondary Ion	COMMENTS
(±)-Amphetamine-D_{11}	not available	146.12	244	128	Preferred analog for amphetamine
(±)-Amphetamine-D_8	145225-00-9	143.15	243	126	Alternate for amphetamine-D_{11}
(±)-Amphetamine-D_6	not available	141.16	244	123	Alternate for amphetamine-D_{11}
(±)-Methamphetamine-D_{14}	not available	163.12	261	213	Preferred methamphetamine analog
(±)-Methamphetamine-D_{11}	152477-88-8	160.15	260	213	Alternate for methamphetamine-D_{14}
(±)-Methamphetamine-D_9	not available	158.16	261	213	Alternate for methamphetamine-D_{14}
N-Methylphenethylamine	589-08-2	135.23	240	104	Alternate for methamphetamine-D_{14}
Phencyclidine-D_5	60124-86-9	248.35	205	96	Use only for phencyclidine
MDEA-D_6[2]	160227-44-1	213.22	268	162	Use only for MDEA
N-Propylamphetamine[2]	not available	177.29	282	240	Alternate for MDEA-D_6

(1) Care must be exercised in the selection of internal standards for each analyte because of differences in derivatization efficiencies due to structural differences.

a. Deuterated analogs of each target analyte may be acceptable as internal standards if they are isotopically pure enough and their ions do not interfere with the quantification ions (usually base peaks) of the target analyte, especially at the limit of detection for the target analyte. Conversely it is also important that ions in the target analyte, especially at high concentrations, do not interfere with the quantification ion (usually base peaks) of any deuterated analog used as the internal standard.

b. The more highly deuterated an analog, the more it will chromatographically separate from the target analyte, reducing interference from common ions.

c. Phentermine and mephentermine have been used as internal standards. Such use is not advised in this method because of their reported occasional use as adulterants in certain illicit drugs such as MDMA.

(2) N-Propylamphetamine and MDEA-D_6 are only applicable to MDEA and other hindered amines (e.g., fenfluramine and MBDB) due to similar steric hindrance at the nitrogen (N-ethyl or N-propyl substitution) which affects derivatization efficiency.

Table 9b. Recommended best application of internal standards[1]

	Recommended Deuterated Internal Standards				Recommended Alternate Non-deuterated Internal Standards[3]	
Target Analyte	Amphetamine-D_{11}[2]	Methamphetamine-D_{14}[2]	MDEA-D_6[1]	Phencyclidine-D_5	N-Methylphenethylamine	N-Propylamphetamine[1]
Amphetamine	X	X			X	
Cocaine	X	X			X	
Ephedrine	X	X			X	
MDEA			X			X
MDMA	X	X			X	
Methamphetamine	X	X			X	
Phencyclidine	X	X		X	X	
Phentermine	X	X			X	
(±)-Norephedrine[4]	X	X			X	
Pseudoephedrine	X	X			X	

(1) N-Propylamphetamine and MDEA-D_6 are only applicable to MDEA and other hindered amines (e.g., fenfluramine and MBDB) due to similar steric hindrance at the nitrogen (N-ethyl or N-propyl substitution) which affects derivatization efficiency.

(2) The alternate deuterated compounds listed in part A above may be used. Avoid ring-labeled amphetamine-D_5 (CAS 65538-33-2) since the primary (quantification) ion is the same as for amphetamine and GC peaks overlap significantly. Also avoid methamphetamine-D_5 (CAS 60124-88-1) since GC peaks significantly overlap.

(3) The listed non-deuterated compounds are acceptable as internal standards for the listed target analytes for the applicable ranges and limits of detection listed in Tables 8a and 8b respectively. Non-deuterated internal standards might not be permissible. Consult regulations of agency having legal jurisdiction.

(4) (±)-Norephedrine is the same as (±)-phenylpropanolamine.

Table 10a. Recovery from wall (latex painted) with various solvents; one wipe compared with the sum of two wipes[1,2]

	Water[3]			Isopropanol			Methanol		
	First Wipe		Plus Second Wipe[4]	First Wipe		Plus Second Wipe[4]	First Wipe		Plus Second Wipe[4]
Test Compounds[5]	Percent	%RSD	Percent	Percent	%RSD	Percent	Percent	%RSD	Percent
Amphetamine	51	14	56	67	6.0	78	90	4.0	96
Cocaine	36	22	36	69	22	80	89	9.1	94
Ephedrine	48	23	52	76	7.4	85	91	4.4	96
MDMA	40	20	44	61	9.0	70	88	5.3	94
MDEA	45	22	50	69	12	80	90	11	97
Methamphetamine	46	16	50	64	7.4	75	87	3.5	94
Phencyclidine	27	26	30	64	9.6	73	86	5.2	91
Phentermine	53	9.2	58	78	6.6	91	95	2.9	101
Phenylpropanolamine	58	21	62	80	9.3	95	85	5.0	94
Pseudoephedrine	49	20	53	73	7.0	85	95	3.3	101

(1) Backup Data Report for NIOSH 9109 [1]. Area of each sample was 100 cm^2.

(2) Wall was an existing standard gypsum board wall painted with a latex based paint. Painted surface was at least one year old. There were six replicates for each solvent tested.

(3) Water was deionized water (ASTM type II). Note low recovery and high %RSD.

(4) For the serial wipe study, each 100-cm^2 area was wiped again with a fresh pre-wetted gauze wipe and the amount recovered was determined separately. In practice, a second (serial) wipe is included with the first gauze wipe; both gauze wipes constitute a single sample. The percent recoveries shown in the column represent the sum of the amounts recovered in both the first and second wipes.

(5) Each pre-measured area was spiked with 3 µg of each analyte in methanol and the methanol allowed to dry for several minutes prior to wipe sampling.

Table 10b. Recovery of methamphetamine from various surfaces with various solvents; one wipe compared with the sum of two wipes[1]

		Isopropanol			Methanol		
		First Wipe		Plus Second Wipe[2]	First Wipe		Plus Second Wipe[2]
Surface Material[3]	Replicates	Percent	%RSD	Percent	Percent	%RSD	Percent
Enamel (lid of washing machine)	4[4]	58	5.7	68	81	2.4	87
Vinyl veneer on particle board	4[5]	60	5.2	68	81	4.8	89
Latex painted wall	6[4]	64	7.4	75	87	3.5	94
Refrigerator door	2[5]	65	2.9	76	91	4.0	92
Varnished hardwood panel	2[6]	72	5.4	76	82	3.7	86
Formica® countertop	4[5]	75	4.9	82	87	3.8	91

(1) Backup Data Report for NIOSH 9109 [2]. Area of each sample was 100 cm^2.

(2) For the serial wipe study, each 100-cm^2 area was wiped again with a fresh pre-wetted gauze wipe and the amount recovered was determined separately. In practice, a second (serial) wipe is included with the first gauze wipe; both gauze wipes constitute a single sample. The percent recoveries shown in the column represent the sum of the amounts recovered in both the first and second wipes.

(3) The refrigerator door and the washing machine lid were from used appliances. The vinyl-veneered particle board (a book shelf), the Formica® countertop, and the varnished hardwood paneling were all purchased new. All surfaces of used and new materials were pre-cleaned with multiple rinses of methanol prior to spiking. Each pre-measured 100-cm^2 square was spiked with 3 µg methamphetamine.

(4) Samples were taken using the side-to-side and then top-to-bottom wiping technique.

(5) Half of the samples were wiped using the side-to-side wiping technique and half were wiped using the concentric squares wiping technique. There were no significant differences in recoveries. Percent recoveries and %RSDs are for both techniques combined.

(6) Samples were taken each time using only top-to-bottom wiping with the grain of the wood in an "N" pattern.

TABLE 11. Gas chromatographic retention times for heptafluorobutyryl and trimethylsilyl derivatives of selected drugs of abuse, precursors, and potential adulterants[1]

GC Peak No.	Compound	Derivative Form[2]	Notes[3]	Retention Time Minutes[4]	Relative Retention Time (5)	Relative Retention Time (6)	Ions (Significant m/z)[7] 1′	2′[7]	3′[7]
1	Acetaminophen[8]	N,N′- bis-TMS-	Pri.deriv.	12.30	0.9594	1.2374	206	280 [90]	295 [70]
2	Acetaminophen[8]	N-HFB-N′-TMS-	Minor peak	10.37	0.8089	1.0433	330	404 [80]	419 [30]
3	Aminorex	N,N′- bis-HFB-	Major peak	14.12	1.1014	1.4205	385	342 [30]	169 [40]
4	Aminorex	N-HFB-N′-TMS-	Major peak	16.59	1.2941	1.6690	261	146 [48]	128 [45]
5	Amphetamine	N-HFB-	Pri.deriv.	8.54	0.6661	0.8592	240	118 [70]	169 [20]
6	Amphetamine	N-HFB-N-TMS-	OS artifact	9.21	0.7184	0.9266	312	91 [50]	313 [10]
7	Amphetamine-D_5, ring labeled (I$)[9]	N-HFB-	Pri.deriv.	8.47	0.6607	0.8521	240	123 [85]	96 [55]
8	Amphetamine-D_5,ring labeled (I$)[9]	N-HFB-N-TMS-	OS artifact	9.17	0.7153	0.9225	312	96 [45]	73 [95]
9	Amphetamine-D_6 (I$)[9]	N-HFB-	Pri.deriv.	8.45	0.6591	0.8501	244	123 [70]	93 [45]
10	Amphetamine-D_6 (I$)[9]	N-HFB-N-TMS-	OS artifact	9.14	0.7129	0.9195	316	93 [40]	73 [75]
11	Amphetamine-D_8 (I$)[9]	N-HFB-	Pri.deriv.	8.46	0.6599	0.8511	243	126 [75]	96 [40]
12	Amphetamine-D_8 (I$)[9]	N-HFB-N-TMS-	OS artifact	9.16	0.7145	0.9215	315	96 [25]	73 [55]
13	Amphetamine-D_{11} (I$)[9]	N-HFB-	Pri.deriv.	8.46	0.6599	0.8511	244	128 [70]	98 [45]
14	Amphetamine-D_{11} (I$)[9]	N-HFB-N-TMS-	OS artifact	9.14	0.7129	0.9195	316	98 [60]	73 [70]
15	Atropine[8]	O-TMS-	Pri.deriv.	18.86	1.4711	1.8974	124	361 [9]	82 [17]
16	BDB	N-HFB-	Pri.deriv.	13.35	1.0413	1.3431	135	176 [50]	254 [12]
17	BDB	N-HFB-N-TMS-	OS artifact	13.65	1.0647	1.3732	326	135 [60]	73 [90]
18	Benzoyl ecgonine	O-TMS-		19.18	1.4961	1.9296	82	240 [45]	361 [25]
19	Benzyl piperazine[10] ("Legal XTC")	N-HFB-	Pri.deriv.	13.73	1.0710	1.3813	91	372 [30]	281 [30]
20	4-Bromo-2,5-DMPEA[11] (Nexus)	N-HFB-	Pri.deriv.	15.79	1.2317	1.5885	242	244 [98]	229 [75]
21	4-Bromo-2,5-DMPEA[11] (Nexus)	N-HFB-N-TMS-	OS artifact	16.22	1.2652	1.6318	229	231 [98]	298 [85]
22	Bupropion (Wellbutrin®, Zyban®)	parent		12.15	0.9477	1.2223	44	100 [45]	111 [20]
23	Caffeine[8]	parent		14.89	1.1615	1.4980	194	109 [45]	67 [45]
24	S-(-)-Cathinone (from Khat plant)	N-HFB-	Pri.deriv.	10.21	0.7964	1.0272	105	77 [45]	240 [15]
25	S-(-)-Cathinone (from Khat plant)	N-HFB-N-TMS-	OS artifact	10.89	0.8495	1.0956	105	312 [68]	77 [55]
26	Chlorpheniramine[8]	parent		16.74	1.3058	1.6841	203	205 [32]	167 [22]
27	Cocaine	parent		18.65	1.4548	1.8763	82	182 [90]	303 [20]
28	Codeine	O-HFB-	Minor peak	19.59	1.5281	1.9708	282	283 [20]	
29	Codeine	O-TMS-	Pri.deriv.	20.72	1.6162	2.0845	371	343 [25]	234 [55]
30	Dextromethorphan[8]	parent		18.10	1.4119	1.8209	271	270 [62]	214 [40]
31	Diazepam (Valium® etc.)	parent		20.80	1.6225	2.0926	256	283 [90]	284 [75]
32	Dibromooctafluorobiphenyl (I$)[9]	parent		12.82	1.0000	1.2897	296	456 [100]	454 [50]
33	N,N-Dimethyltryptamine (DMT)	N-HFB-	Pri.deriv.	13.00	1.0140	1.3078	58	129 [15]	42 [15]
34	N,N-Dimethyltryptamine (DMT)	N-TMS-	Minor peak	15.02	1.1716	1.5111	58	73 [12]	202 [10]
35	Ecgonine, methyl ester	O-TMS-		11.72	0.9142	1.1791	82	96 [75]	83 [75]
36	Ephedrine	N-HFB-O-TMS-	Pri.deriv.	11.40	0.8892	1.1469	179	254 [17]	327 [10]
37	1S,2R(+)-Ephedrine-D_3 (I$)[9]	N-HFB-O-TMS-	Pri.deriv.	11.36	0.8861	1.1429	179	257 [20]	330 [10]
38	N-Ethyl amphetamine	N-HFB-	Pri.deriv.	10.33	0.8058	1.0392	268	240 [35]	118 [15]
39	Fenfluramine[8]	N-HFB-	Pri.deriv.	10.12	0.7894	1.0181	268	240 [35]	159 [22]
40	Fenfluramine-D_{10} (I$)[9]	N-HFB-	Pri.deriv.	10.01	0.7808	1.0070	277	245 [35]	160 [15]

Table 11 continued

TABLE 11 (continued). Gas chromatographic retention times for heptafluorobutyryl and trimethylsilyl derivatives of selected drugs of abuse, precursors, and potential adulterants[1]

GC Peak No.	Compound	Derivative Form[2]	Notes[3]	Retention Time Minutes[4]	Relative Retention Time (5)	Relative Retention Time (6)	Ions (Significant *m/z*)[7] 1′	2′[7]	3′[7]
41	Fentanyl (Sublimaze® etc.)	parent		22.97	1.7917	2.3109	245	146 [60]	189 [33]
42	Flunitrazepam (Rohypnol®, roofies)[10]	parent		22.20	1.7317	2.2334	312	285 [95]	286 [90]
43	Hydrocodone (Lortab® etc.)	HFB-	Minor peak	19.47	1.5187	1.9588	495	438 [50]	298 [40]
44	Hydrocodone (Lortab® etc.)	TMS-	Minor peak	20.82	1.6240	2.0946	371	356 [50]	234 [55]
45	Hydrocodone (Lortab® etc.)	parent	Pri.deriv.	20.93	1.6326	2.1056	299	242 [50]	243 [35]
46	Hydromorphone (Dilaudid®)	O-HFB-O′-TMS-	Minor peak	19.85	1.5484	1.9970	308	267 [92]	358 [75]
47	Hydromorphone (Dilaudid®)	O,O′-bis-TMS-	Minor peak	20.98	1.6365	2.1107	414	429 [100]	234 [75]
48	Hydromorphone (Dilaudid®)	O-TMS-	Pri.deriv.	21.21	1.6544	2.1338	357	300 [55]	342 [28]
49	Ketamine ("special K")[8][10]	parent	Major peak	15.24	1.1888	1.5332	180	182 [32]	209 [22]
50	Lidocaine[8]	N-TMS-	Major peak	13.69	1.0679	1.3773	86	220 [75]	73 [45]
51	Lidocaine[8]	parent	Major peak	15.28	1.1919	1.5372	86	58 [10]	91 [5]
52	LSD (MW-519, scanned only to 470)	HFB-	Pri.deriv.	24.61	1.9197	2.4759	417	221 [95]	418 [45]
53	MBDB	N-TMS-	Minor peak	14.30	1.1154	1.4386	144	73 [50]	135 [15]
54	MBDB	N-HFB-	Pri.deriv.	14.44	1.1264	1.4527	268	176 [75]	210 [50]
55	MDA	N-HFB-	Pri.deriv.	12.54	0.9782	1.2616	135	162 [55]	240 [12]
56	MDA	N-HFB-N-TMS-	OS artifact	12.88	1.0047	1.2958	312	73 [58]	135 [48]
57	MDEA[10]	N-HFB-	Pri.deriv.	14.19	1.1069	1.4276	268	162 [60]	240 [50]
58	MDEA-D6 (I$)[9]	N-HFB-	Pri.deriv.	14.13	1.1022	1.4215	274	165 [46]	244 [35]
59	MDMA[10]	N-HFB-	Pri.deriv.	13.81	1.0772	1.3893	254	162 [80]	135 [45]
60	Meperidine (Demerol® etc.)	parent		13.97	1.0897	1.4054	247	246 [55]	218 [50]
61	Mephentermine	N-HFB-	Pri.deriv.	10.38	0.8097	1.0443	268	210 [95]	
62	Mescaline	N-HFB-	Pri.deriv.	14.68	1.1451	1.4769	181	194 [45]	179 [30]
63	Mescaline	N-HFB-N-TMS-	OS artifact	15.26	1.1903	1.5352	181	73 [35]	
64	Methamphetamine	N-HFB-	Pri.deriv.	9.94	0.7754	1.0000	254	210 [35]	118 [22]
65	Methamphetamine-D5 (I$)[9]	N-HFB-	Pri.deriv.	9.86	0.7691	0.9920	258	213 [30]	92 [20]
66	Methamphetamine-D9 (I$)[9]	N-HFB-	Pri.deriv.	9.84	0.7676	0.9899	261	213 [30]	123 [18]
67	Methamphetamine-D11 (I$)[9]	N-HFB-	Pri.deriv.	9.84	0.7676	0.9899	260	213 [25]	126 [20]
68	Methamphetamine-D14 (I$)[9]	N-HFB-	Pri.deriv.	9.86	0.7691	0.9920	261	213 [30]	128 [20]
69	Methaqualone	parent		18.31	1.4282	1.8421	235	250 [30]	233 [28]
70	S-(-)-Methcathinone ("Cat")	N-HFB-	Pri.deriv.	10.55	0.8229	1.0614	254	210 [35]	105 [100]
71	4-Methoxyamphetamine	N-HFB-	Pri.deriv.	11.40	0.8892	1.1469	121	148 [40]	240 [10]
72	4-Methoxyamphetamine	N-HFB-N-TMS-	OS artifact	11.87	0.9259	1.1942	312	121 [100]	73 [100]
73	cis-(±)-4-Methylaminorex ("U4Euh")	N,N′-bis-HFB-	Minor peak	13.78	1.0749	1.3863	399	169 [70]	160 [75]
74	cis-(±)-4-Methylaminorex ("U4Euh")	N-HFB-N′-TMS-	Pri.deriv.	16.78	1.3089	1.6881	275	160 [60]	117 [30]
75	(-)-N-Methylephedrine[12]	O-TMS-	Pri.deriv.	9.66	0.7535	0.9718	72	73 [13]	163 [5]
76	(+)-N-Methylephedrine[12]	O-TMS-	Pri.deriv.	9.71	0.7574	0.9769	72	73 [13]	163 [5]
77	N-Methylphenethylamine (I$)[9]	N-HFB-	Pri.deriv.	9.54	0.7441	0.9598	240	104 [100]	169 [40]
78	Methylphenidate (Ritalin®)	N-HFB-	Pri.deriv.	15.38	1.1997	1.5473	280	281 [10]	

Table 11 continued

TABLE 11 (continued). Gas chromatographic retention times for heptafluorobutyryl and trimethylsilyl derivatives of selected drugs of abuse, precursors, and potential adulterants[1]

GC Peak No.	Compound	Derivative Form[2]	Notes[3]	Retention Time Minutes[4]	Relative Retention Time (5)	Relative Retention Time (6)	Ions (Significant m/z)[7] 1′	2′[7]	3′[7]
79	N-Methyl pseudoephedrine[12]	O-TMS-	Pri.deriv.	9.66	0.7535	0.9718	72	73 [13]	163 [5]
80	Morphine	O-HFB-O′-TMS-	Minor peak	19.97	1.5577	2.0091	340	324 [28]	341 [25]
81	Morphine	O,O′-bis-TMS-	Pri.deriv.	21.08	1.6443	2.1207	429	414 [50]	401 [35]
82	Nicotine	parent		8.86	0.6911	0.8913	84	133 [35]	162 [18]
83	Norpseudoephedrine (Cathine)	N-HFB-O-TMS-	Pri.deriv.	10.39	0.8105	1.0453	179	180 [18]	240 [18]
84	Norpseudoephedrine (Cathine)	N-HFB-N,O-bis-TMS-	OS artifact	11.26	0.8783	1.1328	179	180 [18]	312 [10]
85	Oxycodone (OxyContin®)	TMS-	Pri.deriv.	21.66	1.6895	2.1791	387	388 [30]	372 [30]
86	Phencyclidine (PCP)	parent	Major peak	15.62	1.2184	1.5714	200	242 [35]	243 [25]
87	Phencyclidine (PCP)	N-HFB-dehydro-	Artifact	19.85	1.5484	1.9970	91	159 [60]	280 [10]
88	Phencyclidine-D5 (I$)[9]	parent	Major peak	15.59	1.2161	1.5684	205	96 [42]	246 [25]
89	Phencyclidine-D5 (I$)[9]	N-HFB-dehydro-	Artifact	19.83	1.5468	1.9950	96	164 [65]	280 [10]
90	Phenethylamine[8]	N-HFB-	Pri.deriv.	8.58	0.6693	0.8632	104	91 [60]	169 [15]
91	Phenethylamine[8]	N-HFB-N-TMS-	Pri.deriv.	9.51	0.7418	0.9567	298	105 [40]	220 [10]
92	Phentermine[8]	N-HFB-	Pri.deriv.	8.72	0.6802	0.8773	254	132 [12]	214 [8]
93	4-Phenyl-1-butylamine (I$)[9]	N-HFB-	Pri.deriv.	11.47	0.8947	1.1539	91	104 [25]	176 [22]
94	Phenylephrine[8]	N-HFB-O,O′-bis-TMS-	Pri.deriv.	13.94	1.0874	1.4024	267	268 [25]	240 [12]
95	Phenylpropanolamine	N-HFB-O-TMS-	Pri.deriv.	10.49	0.8183	1.0553	179	180 [18]	240 [18]
96	Phenylpropanolamine	N-HFB-N,O-bis-TMS-	OS artifact	11.01	0.8588	1.1076	179	180 [18]	312 [10]
97	N-Propyl amphetamine (I$)[9]	N-HFB-	Pri.deriv.	11.05	0.8619	1.1117	282	240 [85]	118 [20]
98	Pseudoephedrine	N-HFB-O-TMS-	Pri.deriv.	11.68	0.9111	1.1751	179	254 [15]	73 [75]
99	Theophylline [8]	parent	Major peak	15.50	1.2090	1.5594	237	252 [57]	223 [14]
100	Trifluoromethylphenyl piperazine [10]	N-HFB-	Pri.deriv.	13.76	1.0733	1.3843	200	229 [70]	172 [73]

(1) Actual retention times may vary depending on individual GC column and GC conditions. Gas chromatographic and mass spectrometer conditions used as on p. 9109-1.

(2) Derivative form. HFB = heptafluorobutyryl derivative. TMS = trimethylsilyl derivative. N- = attachment to nitrogen atom. O- = attachment to oxygen atom. Not all forms are presented. Trifluoroacetyl derivatives are not presented. Underivatized compounds are identified as a "parent" compound. Parent compounds that have poor chromatographic peak shapes under the conditions used are not presented. Spectra for the derivatives are given in the Backup Data Report (Appendix-II). [2]

(3) Major and minor peaks are identified where two or more forms are possible. In some cases two major peaks may exist. Pri.deriv. = Primary derivative, a major peak. The major peak or the primary derivative should be used for quantitation. OS artifact = Oversilylation artifact [18]. Oversilylation artifacts occur where a primary amine is substituted with both a heptafluorobutyryl and a trimethylsilyl group. Under the specified conditions of extraction and derivatization these remain as minor components and are of little concern.

(4) Retention times are not the same as in Table 6 or Figures 1 and 2 in this method since these data were obtained on a different instrument. Relative retention times should be approximately the same.

(5) Retention time relative to 4,4′-dibromooctafluorobiphenyl.

(6) Retention time relative to the heptafluorobutyryl derivative of methamphetamine.

(7) Significant ions that can be used for quantification and qualitative identification are given. The base peaks are not necessarily included, especially if they are low mass (<100 AMU). Numbers in brackets indicate the approximate relative abundance of the secondary (2′) and tertiary (3′) ions relative to the primary (1′) ion and not necessarily to the base peak of each mass spectrum. Relative abundance varies with different tuning criteria and cleanliness of the mass spectrometer source. The 1′ or 2′ ions are recommended for quantification. All ions are selected as much as possible above *m/z* 100 to avoid interference from low mass co-eluting interferences. The 2′ and 3′ ions are selected as much as possible for nearness to the primary ion to minimize false negatives from skewing of spectra as the mass spectrometer source becomes contaminated with use. Ubiquitous ions (e.g., *m/z* 73, 91, and 169) are avoided as much as possible.

(8) Intentional or unintentional adulterants. For example, phentermine may be added to MDMA and caffeine added to methamphetamine intentionally. Chlorpheniramine is an unintentional adulterant when pseudoephedrine containing chlorpheniramine is used as a methamphetamine precursor.

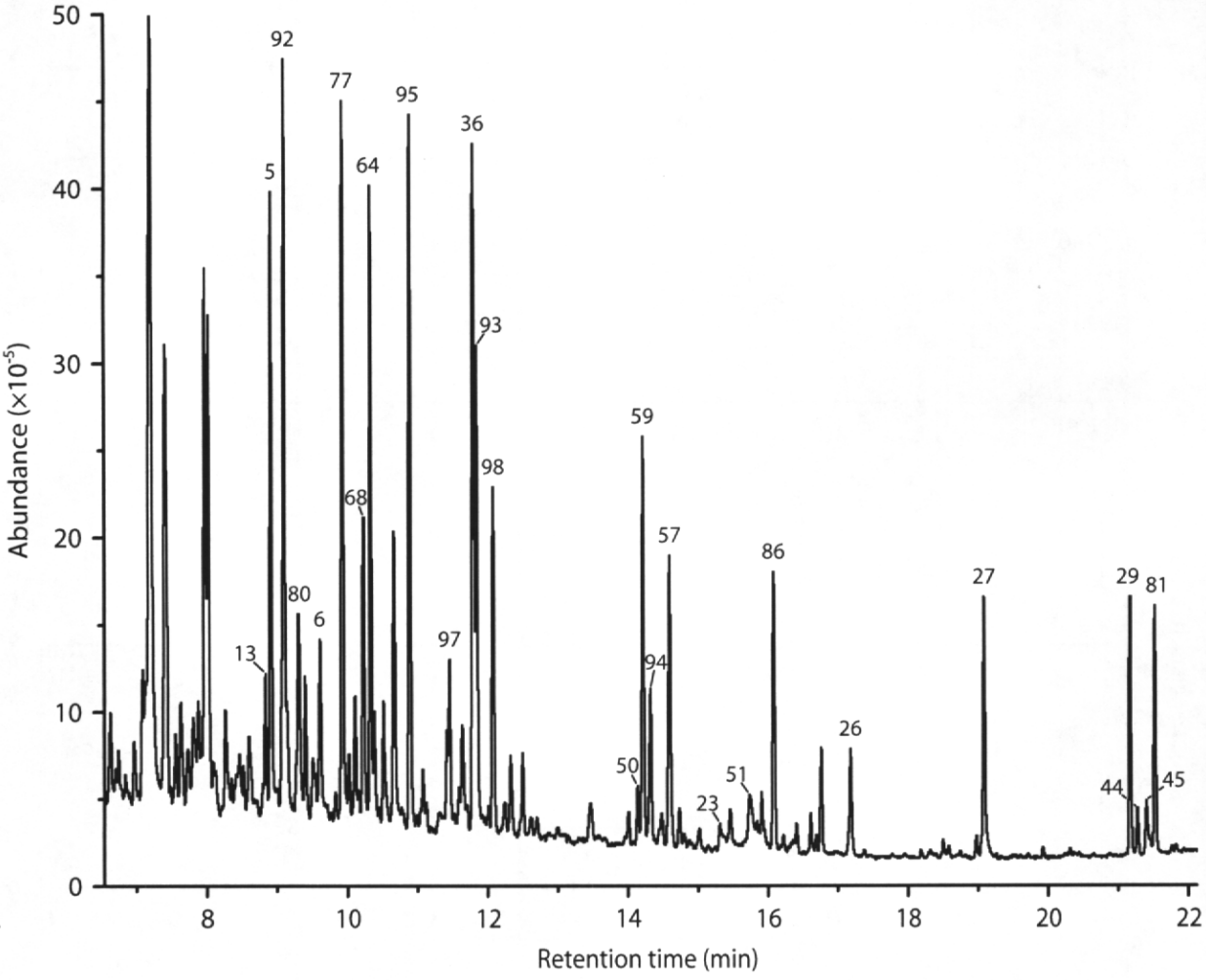
(9) (I$) = Internal standard. The best results are obtained using internal standards that are deuterated analogs of the target analyte, or those that are chemically and structurally similar to the target analytes.

(10) Typical "club drugs" (piperazine analogs as ecstasy substitutes, ketamine and flunitrazepan as predatory drugs).

(11) 4-Bromo-2,5-DMPEA = 4-Bromo-2,5-dimethoxyphenethylamine (Nexus).

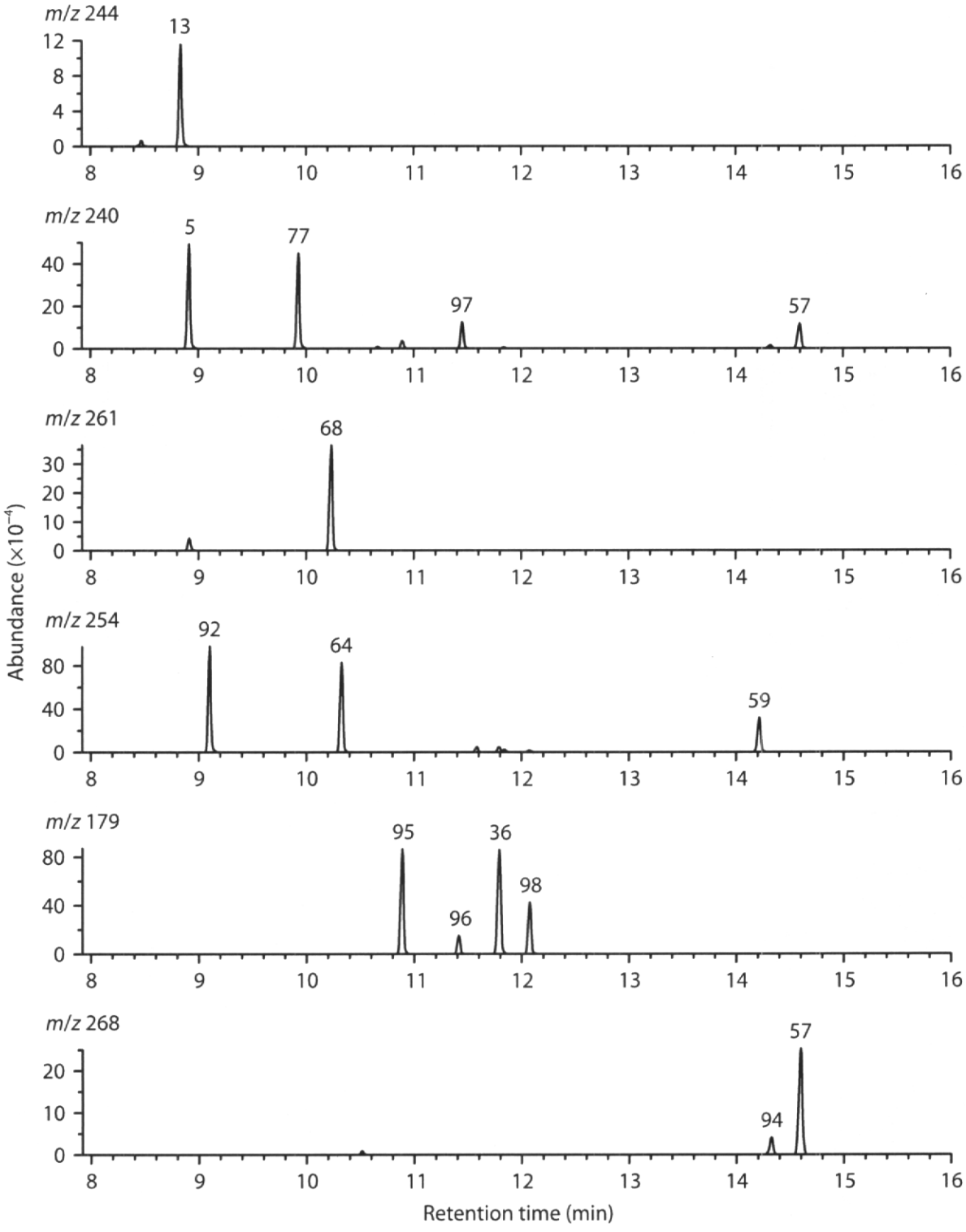
(12) Presence of (+)-norephedrine, N-methylpseudoephedrine and/or N-methylephedrine in pseudoephedrine or ephedrine indicates extracts of Ephedra spp. as source of methamphetamine precursor. Presence of amphetamine and N,N-dimethylamphetamine in methamphetamine final product also suggests the same source. [19, 20, 21]

Figure 1. Typical chromatogram of mixed heptafluorobutyryl and trimethylsilyl derivatives by GC-MS in scan mode (time in minutes)



GC Peak Identification: See Table 11 for identification of numbered GC peaks. (But note that retention times in Table 11 do not correspond to those in Figure 1 because a different DB-5 column and instrument was used.)

Figure 2. Typical extracted ion chromatograms (EIC) of mixed heptafluorobutyryl and trimethylsilyl derivatives by GC-MS in scan mode (time in minutes)



GC Peak Identification: See Table 11 for identification of numbered GC peaks. (But note that retention times in Table 11 do not correspond to those in Figure 1 because a different DB-5 column and instrument was used.)

APPENDIX:

A. REAGENTS and SOLUTIONS:

1. 4,4'-Dibromooctafluorobiphenyl is optional. It is useful for monitoring instrument tuning and autosampler performance.
2. Primary amines form Schiff bases and enamines with ketones and aldehydes. These may in turn form derivatives with the acylating reagents. The use of acetone must strictly be avoided prior to the analytes being derivatized. Glassware and equipment rinsed with acetone must be thoroughly dried. Toluene should be avoided for making up standard solutions because it usually contains benzaldehyde, an oxidation product of toluene. Condensation products have been observed between primary amines and benzaldehyde. The only solvents recommended for the preparation of stock solutions and dilutions thereof are methanol (preferably) and isopropanol.

B. EQUIPMENT:

1. Wipe media: Besides cotton gauze, 4"X4" (10 cm x 10 cm) 4-ply MIRASORB® (Johnson and Johnson), and 4"X4" (10 cm x 10 cm) AlphaWipe® (TX1004, Texwipe Corp) were acceptable wipe media and can be used in the absence of cotton gauze. MIRASORB®, a non-woven cotton/polyester blend, is discontinued but counterparts exist that claim to be of identical construction and fiber composition. AlphaWipe® is a hydrophilic, highly adsorbent, tightly knitted continuous filament polyester wipe. Precision and accuracy data for MIRASORB® are given in the Backup Data Report [2].
2. Shipping containers: The 50-mL polypropylene centrifuge tubes with caps are preferred for one or two gauze wipes and are not as breakable as the 40-mL VOA vials. The 40-mL VOA vials are acceptable for single gauze wipes. Larger containers (glass with a PTFE lined cap) should be used for combining more than two gauze wipes into a single sample. The size of the container for two or more wipes should be approximately 25 mL per gauze wipe (e.g., a minimum size of 100-mL for up to four gauze wipe samples). There needs to be enough extra headspace in the shipping container to allow the desorption solution to cover the gauze wipes and to percolate freely through the wipe sample(s) during mixing.
3. Each regulatory agency having legal jurisdiction over the contaminated site may require different but specific off-site preparation and on-site sampling procedures. It is important to consult local regulatory agencies or departments of health having legal jurisdiction over contaminated sites to determine specific sampling, quality control, analyses, and reporting requirements.

C. SAMPLING:

1. Follow specific requirements of surface area to be wiped (usually 100 cm^2 or 1000 cm^2) and action threshold (or maximum allowable residual level) set by the state or specified by the client. Uptake rates depend upon the wipe sampling method used, so the specific wipe technique used must be specified, and any deviations from the required wipe sampling requirements noted.
   Note: To ensure that samples have not been tampered with, the use of custody seals and a chain-of-custody form is strongly recommended.
2. Prepare a rigid template from disposable cardstock or a sheet of PTFE having either a 10 cm × 10 cm or 32 cm × 32 cm square-cut hole. The template must be able to retain its shape during wiping to ensure that the areas wiped were either 100 cm^2 or 1000 cm^2. Secure the template(s) to the area(s) to be wiped (e.g., with tape along outside edge of template). If a single-use disposable template is not used, clean the template between samples to avoid cross-contamination, and provide the laboratory with a blank wipe of the cleaned template between samples to determine that no cross-contamination has occurred.
3. A template might not always be applicable, as in curved or odd-shaped areas such as around burners on stove tops or a fan blade. In such cases sample an area as close to either 100 cm^2 or 1000 cm^2 as feasible and provide the measurement to the regulatory agency and to the analytical laboratory for proper reporting. Tape can be used to delineate the sampling area.
4. It is recommended to provide extra wipe media from the same lot for required media blanks, field-equipment blanks, samples, and quality-control samples.

5. Gauze in sterile packaging is recommended to minimize the chance for cross-contamination, which can more easily occur with open bulk packaged cotton gauze.
6. To prevent contamination in the field, another alternative is to pre-wet and insert the gauze wipes into the sample containers off-site. This avoids any possibility of the bottle of methanol or isopropanol becoming contaminated on-site with methamphetamine (or other analytes). If the wipes were prepared off-site, then remove pre-wetted gauze wipe from sample container, opening only one sample container at a time. In either case, squeeze out and discard any excess solvent from the gauze wipe. Use fresh latex or nitrile gloves for each separate sample and blank. Do not use vinyl gloves due to the potential for leaching of phthalate plasticizers and contamination of the samples.
7. Wipe techniques
   a. Concentric Squares Wiping Technique (particularly suitable for smooth and non-porous surfaces and described by OSHA [22]): Fold the pre-wetted gauze in half and then fold in half again. Using firm pressure wipe the area within the template. Start at one of the inside corners of the template and wipe in concentric squares, progressing toward the center. End with a scooping motion. Without allowing the gauze to touch any other surface, reverse the last fold so that the exposed side of the gauze is facing inward and using a fresh surface of the gauze, wipe the same area in the same manner as before. Roll or fold the gauze again and insert into the shipping container.
   b. Side-to-side Wiping (or Blotting) Technique (particularly suitable for rough, porous, and/or soiled surfaces): Fold the pre-wetted gauze in half and then fold in half again. Using firm pressure wipe or blot the area within the template with at least five overlapping side-to-side horizontal passes (see NOTE) beginning at the top and progressing to the bottom in a "Z" pattern. End with a scooping motion. If blotting, blot at least five times on each horizontal pass (see NOTE). Without allowing the gauze to touch any other surface, reverse the last fold so that the exposed side of the gauze is facing inward. Using a fresh surface of the gauze, wipe or blot the area again with at least five overlapping top-to-bottom vertical passes beginning at the left side and progressing to the right in an "N" pattern. If blotting, blot at least five times on each vertical pass. Roll or fold the gauze again and insert into the shipping container. Blotting is suggested in areas so soiled or rough that the threads of the gauze media are continually snagged.
      NOTE: On areas larger than 100 cm^2, more than five passes and blots will be needed.
   c. Repeat or Serial Wiping: If isopropanol is used for wiping, a serial or repeat wipe sample of the same area with a fresh gauze wipe will improve sampling efficiency. (See recoveries for second wipe in Tables 10a and 10b.) For serial wiping, repeat the wiping procedure described above (APPENDIX 7a or 7b) with a fresh gauze wipe. Place the second gauze wipe into the same shipping container as the first gauze. The 50-mL polypropylene centrifuge tubes are large enough to contain up to two gauze wipes.
      NOTE: If the area to be wiped remains substantially wet from the first gauze, the second gauze wipe might be used in the dry state to soak up the residual solvent from the first gauze wipe.
8. Composite sampling: Composite samples are allowed by some regulatory agencies. Their use for quantitative purposes may be subject to the permission and guidance of regulatory agencies. Refer to guidelines of regulatory agency for directions on composite sampling. A basic default guideline for composite sampling is as follows: Do not mix inconsistent samples, that is, areas wiped must be equal in area, sampled areas must have the same high or low probability of contamination, and sampled areas must relate to a specific target appliance or site and not to several appliances or incongruous sites combined.
   NOTE: Composite samples cannot meet specific action-threshold requirements for discrete sampling locations. Nor do composite samples consisting of four wipes, for example, improve the sensitivity by decreasing the LOD four fold; instead it raises the LOD by a factor related to the extra volume of desorption solution that is required to desorb a larger number of wipes. The following example illustrates these two points. Assume that the action level was 0.1 µg/100 cm^2. If the analysis gave an LOD of 0.06 µg/sample for a single wipe or discrete sample covering an area of 100 cm^2, then the LOD for the analysis could be expressed as 0.06

µg/100 cm^2, which is low enough to be able to determine whether any discrete sample is at or exceeds the action level. Now if a composite of four wipes was taken, each with an area of 100 cm^2 for a total area wiped of 400 cm^2, the LOD for that composite sample is not 0.06 µg/400 cm^2 nor is it 0.015 µg/100 cm^2; it is actually several times larger than 0.06 µg/400 cm^2. First of all it increases relative to the ratio of the volume of desorption solution used to desorb the sample compared to that used for the calibration standards. Secondly it has nothing to do with the AREA that was wiped, because the LOD for the calibration curve is determined in terms of µg per sample, independent of the area. To explain the first point, assume approximately 90 mL was used (for ease in calculation) to desorb the four wipes and 30 mL (the normal amount for a single wipe) was used to desorb each calibration standard. The calculation of the LOD for the four composited samples would be µg/sample x (desorption volume for 4 wipes)/(desorption volume for the calibration standards), or 0.06 µg/sample x (90 mL/30 mL), or 0.18 µg/sample for the composited sample. Since the area wiped for the composite sample was 400 cm^2, the LOD for that sample could be expressed as 0.18 µg/400 cm^2. Regarding the second point, this value, 0.18 µg/400 cm^2, cannot be construed or mathematically reduced to 0.045 µg/100 cm^2 because it cannot be known whether three of the four wipes were blank and the fourth wipe just under the value of 0.18 µg. Hence, the effective LOD per individual wipe has to be regarded not only as 0.18 µg/400 cm^2 but also as 0.18 µg/100 cm^2 because any value determined for entire 400 cm^2 might have come from just one of those 100 cm^2 areas. Thus, for composite samples, the LOD must be expressed in terms of the entire area wiped and not extrapolated to some portion thereof. In this example, an LOD of 0.18 µg/100 cm^2 is above the action threshold of 0.1 µg/100 cm^2, meaning that this composite sample cannot satisfy the requirement that residual levels be below 0.1 µg/100 cm^2. It remains for the regulatory agency and not the laboratory to determine how to apply results for composite samples to the established action levels. The same consideration that is given above for the LOD applies to results that are greater than the LOD. To avoid confusion in reporting concentrations for composite samples, it is recommended that the sample concentration (in µg/sample, whatever the sample size) and the total area wiped (in cm^2) be reported separately. For example, a result of 0.4 µg/sample for a sample consisting of four separate wipes of 100 cm^2 each (for a total area wiped of 400 cm^2), is to be reported as 0.4 µg/400 cm^2 and not averaged to 0.1 µg/100 cm^2. This manner of reporting may be required by some regulatory agencies.

9. For quality assurance purposes, regulatory agencies may require duplicate samples to be taken in the field. If such is the case, an area contiguous with and adjacent to the first area, if possible, should be wiped as described under SAMPLING. Do not re-wipe the previously wiped area. This sample is a blind sample and should not be identifiable by the analytical laboratory as a duplicate of any other sample. These are distinct from the laboratory duplicates of a single sample described in step 14 of the method. Field duplicates are useful for evaluating the consistency of sampling technique, assuming uniformity of contamination on adjacent sampling sites. Laboratory duplicates are useful for evaluating consistency of sample preparation and instrumental analysis.

D. DESORPTION FROM MEDIA:

1. An internal standard spiking solution volume of 60 µL was selected for ease in scaling from 60 µL per 30 mL to 80 µL per 40 mL of desorption solution. In either case the rate of 2 µL internal standard spiking solution per mL desorption solution was used. However, any convenient volume of internal standard spiking solution (e.g., 50 µL) that can be delivered reproducibly is acceptable. Whatever volume is chosen, there must be no variation in the volume of the internal standard spiking solution used in preparing each of the calibration standards. If spiking strategy A is used (see step D3 of APPENDIX), it is critical to know the exact volume of internal standard spiking solution that is applied to each sample (V_1), the media blanks (V_5), and the calibration standards (V_2), since these volumes are used for internal standard spiking solution volume corrections in step 19.

2. It is not necessary to know the exact volume of desorption solution added to each sample or the volume of residual wetting alcohol because differences in the volumes are normalized through the use of internal standards added prior to desorption.
3. Alternate strategy for spiking internal standards (spiking strategy B below): By using the exact same volume of internal standard spiking solution in all samples, blanks, QC samples, and calibration standards, regardless of the volume of desorption solution added or residual wetting alcohol, the volume corrections in step 19 (V_1/V_2 and V_5/V_2) drop out of the equation. However, the internal standard GC peak areas must still be measurable in samples where larger volumes of desorption solution are used (such as for composite samples). Because of the increased dilution of the internal standard in larger samples, this approach should be limited to desorption solution volumes of about 120 mL or less.

NOTE: There are two separate strategies for handling larger samples requiring larger volumes of desorption solvent. These are outlined below as strategies A and B.

Number of Wipes	Size of Shipping Container (mL)	Volume of Internal Standard Spiking Solution (µL)		Volume of Desorption Solution (mL) (Strategies A and B)
		Strategy A	Strategy B	
1	40 to 50	60	60	30
2	50	80	60	40
4 (e.g., composite)	100 to 120	160	60	80
		Apply volume correction factors at step 19.	Do not apply volume correction factors at step 19.	

With either strategy, if two gauze wipes were included in the samples, then use 40 mL of desorption solution. If four gauze wipes were included in the samples, then use 80 mL of desorption solution.

a. In strategy A, the volume of internal standard spiking solution is kept at a constant ratio of 2 µL per mL of desorption solution added. This enables larger samples to be desorbed without diminishing the area of the GC peak for the internal standard. However, a volume correction factor (V_1/V_2) is needed in the final calculations in step 19. Therefore, the exact volume of internal standard added to each of the samples relative to that added to the calibration standards must be known.

b. In strategy B, the volume of internal standard spiking solution is kept constant for all samples and calibration standards, but need not be exactly 60 µL. This enables the final calculations to be made in step 19 without a volume correction factor. However, the area of the GC peak for the internal standard will vary with sample desorption volume and the internal standard must be concentrated enough to be measurable where larger volumes of desorption solution are used.

E. SOLID PHASE EXTRACTION PROCEDURE:

Two columns (Clean Screen® and BOND ELUT-CERTIFY®) are based upon a silica support. The other two (Oasis® and Speedisk®) are based upon an organic polymer support. The precision and accuracy data in Tables 8a and 8b apply to the Waters Oasis® MCX 3cc/60 mg column.

F. DERIVATIZATION:

There are unique advantages and disadvantages in using the mixed MSTFA + MBHFBA reagent. The disadvantages with some possible remedies are listed as follows.

1. A few percent of trifluoroacetyl derivatives of secondary amines are formed (presumably from MSTFA) in competition to the intended heptafluorobutyryl derivatives.

a. Remedy #1: This artifact is eliminated by replacing MSTFA with MSHFBA (N-methyl-N-trimethylsilyl heptafluorobutyramide, Alltech Associates, Deerfield, IL). However, precision and accuracy were not evaluated for NIOSH 9109 using MSHFBA instead of MSTFA.
b. Remedy #2: If ephedrine compounds or compounds containing free hydroxyl groups are not to be analyzed, MSTFA might be omitted and MBHFBA used alone.

2. Use of the mixed reagent often results in over-silylation, the production of unintended silylation artifacts [18], particularly of amides. The primary over-silylation artifact with primary amines is the N-trimethylsilyl derivative of the N-acyl derivative. The GC peak area for this artifact can be significant; under certain circumstances it is nearly equal to that of the intended N-acyl derivative.
   a. Remedy #1: The presence of ammonium chloride from the SPE eluates seems to prevent or greatly reduce over-silylation of amides. These artifacts can be ignored when using the SPE columns with the 80:20:2 methylene chloride:isopropanol:ammonium hydroxide eluent.
   b. Remedy #2: If ephedrine compounds or compounds containing free hydroxyl groups are not to be analyzed, silylating reagents (MSTFA or its alternate, MSHFBA) might be omitted and MBHFBA used alone.
3. The mass spectrometer may need more frequent cleaning to maintain sensitivity. This is offset by the shorter sample preparation time, especially for large numbers of samples.
4. When the fused silica capillary columns become exposed to the mixed silanization-acylation reagents, the column may become unsuitable for other types of samples.
5. The chromatograms are cluttered with silylation by-products making it difficult to detect low levels of unknown (non-target) compounds if a drug screen for unknown compounds is an objective. For this objective, the liquid-liquid extraction procedure of NIOSH 9106 [4] provides cleaner chromatograms with less interference from reagent by-products.
6. The advantages of the mixed MSTFA+ MBHFBA reagent, when used with SPE, are as follows:
   a. Faster preparation time (no heating in an oven, no cool-down time, no evaporation or neutralization of the reagents, and no reconstitution with solvent thereafter).
   b. No heat or acid induced isomerization or dehydroxylation of the ephedrine or other hydroxyl containing compounds (e.g., ephedrine, norephedrine, pseudoephedrine, phenylephrine, etc.).
   c. The method can be extended to easily hydrolyzed phenolic and polyhydroxy compounds of aryl-alkyl-amines (e.g., Albuterol, epinephrine and metabolites [10], metabolites of MDMA, and phenylephrine) because of the thermal stability of the trimethylsilyl ether groups on phenols and trimethylsilyl ester groups.
   d. Hindered amines such as MDEA are derivatized more completely but still require an internal standard with structural similarity.

G. MEASUREMENT:

Recoveries for the laboratory control matrix spike samples (QC and QD) must meet the guidelines of the specific regulatory agency involved (80-120% is a reasonable target in the absence of specific guidance).

NOTE 1: The QC samples (QC and QD) in this method may be referred to in some guidance documents as matrix spike and matrix spike duplicate samples (MS/MSD) but serve the same purpose. Analyze and report field-equipment blanks as samples. Do not subtract their values from any other sample.

Recoveries of CCV standards must meet guidelines of regulatory agency (80-120% is a reasonable target in the absence of specific guidance). The CCV standards may be referred to in some guidance documents as 'QC samples' but such QCs are equivalent to liquid standards (not matrix spiked samples) and serve the same purpose of the CCVs in this method.

NOTE 2: With the GC/MS it is possible to achieve the lower limit of 0.05 µg or less per sample for methamphetamine in either the scan mode or SIM mode. The scan mode is essential where the identification of unknowns is an analytical objective. If lower limits of detection are desired or difficult to obtain in the scan mode, or for routine target compound only analyses, the instrument may be operated in the SIM mode.

H. MAKING DILUTIONS:

If the samples exceed the upper calibration range for the analysis, one of the following procedures may be used to estimate the high level concentrations.

1. Dilution procedure A (dilution of the derivatization mixture within a GC vial): Transfer an aliquot of the derivatization sample mixture from the GC vial to a clean low-volume GC vial and add acetonitrile, MSTFA, and MBHFBA. For example, for a 10:1 dilution transfer 20 µL of sample to a clean vial and add 120 µL of acetonitrile and 30 µL each of MSTFA and MBHFBA, for a total volume of 200 µL. For a 4:1 dilution, transfer 50 µL of sample to a clean vial and add 100 µL of acetonitrile and 25 µL each of MSTFA and MBHFBA, for a total volume of 200 µL. Cap the GC vial, mix by inversion a few times, and analyze diluted sample. Do not include the dilution factor in step 19 since the internal standard will be diluted along with the target analyte.

   NOTE: For dilutions greater than 10, the internal standard may become too diluted to quantify. In such a case, use the following procedure B.

2. Dilution procedure B (dilution of the original sample desorbate): In this procedure, an aliquot of the original sample desorbate is diluted with a simulated blank solution and then transferred to a SPE column in step 8d. For example, for a 10:1 dilution, dilute 0.5 mL of sample desorbate solution from step 7f in a clean test tube containing 4.5 mL of a simulated blank solution, mix, and then transfer the entire contents to a pre-conditioned SPE column. For a 50:1 dilution, dilute 0.1 mL of sample desorbate solution from step 7f in a clean test tube containing 4.9 mL of a simulated blank solution, mix, and then transfer the entire contents to a pre-conditioned SPE column. Proceed thereafter to step 8d as normal. The simulated sample blank should be prepared identically to the sample needing dilution, using the same volumes of internal standard spiking solution and desorption solution that were used with the sample in the original desorption. For example, if the original sample was desorbed with 40 mL desorption solution with 80 µL of added internal standard spiking solution, then prepare the simulated blank in the same way. The volume of wetting alcohol is estimated (e.g., about 3 mL per 3"x3" 12-ply cotton gauze wipe). Include a dilution factor (V_3/V_4) in the calculations in step 19 (e.g., V_3/V_4 = 5 mL divided by the volume in mL of original desorbate diluted to 5 mL with solution from the simulated blank). The dilution factor in the above examples are 5 mL/0.5 mL or 10 for a 10:1 dilution and 5 mL/0.1 mL or 50 for a 50:1 dilution. Correct for differences in internal standard spiking solution volumes in step 19 (if applicable) using for V_1 the volume of internal standard spiking solution which was added to the original undiluted sample.

   Caution: This dilution procedure gives quantitative results only if the residual volume of methanol (or isopropanol) used for wetting the sample wipes was exactly the same as the volume used in preparing the calibration standards (normally about 3 mL, see Table 7). Deviations of a few milliliters in residual wetting alcohol will not affect the results for undiluted samples but will amount to an error of a few percent in the final results of samples that are diluted.

   The potential error due to differences in residual wetting solvent can be estimated for specific volumes of desorption solution and wetting alcohol. Assume the sample wipes and calibration standards are both desorbed in 30 mL of desorption solution and 3 mL of alcohol is added to the calibration standards. The potential error in volume (and final results) in the samples is approximately ±3.03% (inversely proportional) per mL difference in the residual alcohol in the samples (i.e. ±1 mL difference in 33 mL). For 40 mL of desorption solution and 4 mL of alcohol added to the calibration standards, the error is ±2.27% for every mL difference (i.e. ±1 mL difference in 44 mL). However, since the volume of residual wetting alcohol is not known and cannot be determined once the sample wipe has been desorbed, the actual error cannot be determined.

   However, the maximum possible error can be calculated. Since the maximum amount of alcohol that a 3"x3" 12-ply (or 4"x4" 8-ply) cotton gauze can hold is about 6 mL when saturated (dripping wet), there can only be a deviation of plus or minus 3 mL from the 3 mL alcohol added to the calibration standards. Therefore, the maximum error in a result

due to differences in the volume of residual alcohol in a cotton gauze sample compared to the standards can only be three times the error for a 1 mL difference in volume. Since the error for ±1 mL is ±3.03%, the maximum error for ±3 mL is three times larger, or ±9.1%. In practice, the error will be less than this because it is unlikely that the gauze samples will be completely dry or completely saturated after squeezing out the excess alcohol and wiping a surface. The practical amount of alcohol that remains in the 3"x3" 12-ply (or 4"x4" 8-ply) cotton gauze wipes when the excess is squeezed out is between 1 and 2 mL. This translates into an error that is between +3% and +6% in the final results for diluted samples. Undiluted samples will not be affected. This error is within the overall accuracy for the method for methamphetamine.

3. Dilution procedure C (dilution of desorbates from dried samples): Dilution errors for over-range samples may be corrected by knowing the exact amount of residual alcohol in the samples. The volume (or weight) of residual solvent in each gauze wipe might be determined by the difference between a wet weight and dry weight. Better yet, the error might be eliminated for diluted samples by adding, after the samples are dried (without taking any weight), the same known volume of wetting alcohol that is added to the calibration standards (i.e. 3 mL). Thereafter, if any samples need dilution, there will be no dilution errors due to differences in residual alcohol, because all samples and standards will have the same volume of alcohol and total volume of desorption solution. However, air drying of the samples is not recommended because of the possible loss of methamphetamine due to its volatility when it is not in the salt form, which form cannot be assured in field samples. Also, manipulating the samples for weighing and drying might introduce contamination. Drying is not recommended as a procedure for analytes having a vapor pressure high enough to be lost in the process, or that tend to form azeotropes with alcohols, especially when the critical action levels for remedial cleanup are at the lower end of the method calibration range. Drying is not an option if the samples have already been desorbed.