Analysis of Methamphetamine on Wipes by GC/MS–SIM Mode or GC/MS/MS Spectrometry

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Analysis of Methamphetamine on Wipes by GC/MS–SIM Mode or GC/MS/MS Spectrometry

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EXECUTIVE SUMMARY

Recent legislations required DTSC to adopt a health-based target remediation standard for methamphetamine residue. The environmental Chemistry Laboratory-Los Angeles Branch (ECL-LA) was assigned the task to develop sampling protocols and analytical methods for the collection and analysis of methamphetamine residue. NIOSH Method 9106, “Methamphetamine and illicit drugs, precursors, and adulterants on wipes by liquid-liquid extraction”, has been modified for the methamphetamine analysis. Four different surfaces commonly found in contaminated buildings (i.e., glass, flat painted drywall, semi-gloss painted drywall and fabric) with methamphetamine residues have been sampled by a wipe method and analyzed by gas chromatography/mass spectrometry (GC/MS) or gas chromatography/mass spectrometry/mass spectrometry (GC/MS/MS).

This method is designed for wipe samples and uses a stable isotope-labeled analogue of methamphetamine as the internal standard to calculate the concentration for appropriate analytes. The samples were prepared for analysis by GC/MS or GC/MS/MS using a liquid-liquid extraction method. After samples were extracted, a derivatizing reagent was added to make the derivative of methamphetamine. The methamphetamine derivative was analyzed by GC/MS or GC/MS/MS.

Results indicated that glass plate and semi-gloss painted drywall plate have excellent percent recovery. Flat painted drywall has acceptable recovery but fabric only has roughly 17% recovery. Based on this study, the estimated limit of quantitation (LOQ) of this method for methamphetamine is 0.05 µg/wipe(100 cm²).
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INTRODUCTION

Methamphetamine (CAS No. 537-46-2), an illegal stimulant, is a water and alcohol soluble compound with a melting point of 170-175°C. Methamphetamine is easily made and can be made anywhere. During methamphetamine production, toxic chemical residues including methamphetamine are released into the surrounding areas and absorbed into building materials. As a result, people living in those buildings are exposed to the hazards of those residues. Recent legislations required DTSC to adopt a health-based target remediation standard for methamphetamine residue.

NIOSH Method 9106 has been modified for methamphetamine analysis in this study. Other methamphetamine precursors (e.g., Phenyl-2-Propanone) and analogs (e.g., Amphetamine) may be analyzed by this method. This method is designed for wipe samples and uses a stable isotope-labeled analogue as internal standard to calculate the concentration for appropriate analytes. The samples are prepared by using a liquid-liquid extraction method. After samples are extracted, a derivatizing reagent is added to make the derivative of methamphetamine. The derivative is derived and reconstituted and analyze by GC/MS or GC/MS/MS.

MATERIALS AND METHODS

Chemicals and Reagents:

1) Solvents (analytical grades): Dichloromethane, Hexane, Isopropanol, Methanol, Toluene, Acetone.

2) Concentrated Sulfuric and Hydrochloric Acids (analytical grades).

3) Sodium Hydroxide, A.C.S grade.

4) Anhydrous granular Sodium Sulfate and anhydrous granular Potassium Carbonate. (AR grade)

5) Bromothymol Blue [CAS 76-59-5], ≥95%, A.C.S.; Phenolphthalein, [CAS 77-09-8], A.C.S.; Crystal Violet [CAS 548-62-9], ≥95%, A.C.S.

6) Amphetamine-d_{11} (surrogate), Cerilliant Catalog # A-019
(±)-Methamphetamine-d_{14} (Internal Standard), Cerilliant Catalog # M-009

7) (±)-Methamphetamine, Cerilliant Catalog # M-093

8) Desorption solution: 0.2 N Sulfuric Acid. Add 22 ml conc. Sulfuric Acid to make 4 liters deionized water.

9) Calibration Standards – a minimum of five different concentrations of calibration standards should be prepared. The lowest standard should be at or below the minimum detection objective of the project. The calibration range should cover the possible sample concentration range. The calibration should not exceed the working range of the GC/MS system. Keep refrigerated (<6°C). Protect solutions from light.

10) Matrix spike standards – If available, a standard will be used for spiking.

11) Mixed Bromothymol Blue and Phenolphthalein pH indicator solution: 1 mg/ml each in 4:1 (v/v) Isopropanol: reagent water.

12) 10 N Sodium Hydroxide Solution – 40 grams of Sodium Hydroxide pellets in 100 ml of reagent water

13) 0.3 N Hydrochloric Acid in Methanol: Dilute 2.5 ml conc. Hydrochloric Acid in about 80 ml Methanol; dilute to 100 ml with Methanol.

14) Crystal Violet indicator: 2-3 mg/mL of Crystal Violet in Isopropanol.

15) Reconstitution solvent: 10% Acetone in Toluene with 0.16 ug/ml of 4,4'-Dibromo-octafluorobiphenyl (instrument monitoring standard).

16) Derivatizing agent: Chlorodifluoroacetic Anhydride, 98% [CAS 2834-23-3].

17) 5 ~ 6 N Sulfuric Acid.

**Equipment:**

1) Gas Chromatographic System: Varian 3800 GC interfaced with L1200 Mass/Mass Selective Detector. The MS should be capable of scanning from 35 to 500 amu every second using the electron impact ionization mode.

2) Column: Varian, VF-5ms (equivalent to CP-sil 8 CB Low-Bleed/MS), 30 m x 0.25 mm ID, 0.25 µm

3) Microsyringes-10, 25, 50,100 and 1000 µL (Hamilton model 700 series).

4) Screw top glass vials (2 and 4 mL capacity) with caps with Teflon liners.

5) Volumetric flasks, Class A-10 mL, 50 mL, 100 mL and 500 ml with ground-glass stoppers.

6) Pipets, Class A, TD-0.5 mL, 1 mL, 5 ml and 10 ml.
7) Empty polypropylene drying columns.

8) 25-ml Glass stopped test tubes with PTFE-faced rubber-lined caps.

9) Nitrogen blow-down apparatus with water bath capable of maintaining 35°C.

10) Rotating mixer capable of 10-30 rpm.

11) Heating oven capable of 70-90°C ± 2°C.

12) Test tube racks resistant to heating at 90°C.

13) Pasteur transfer pipettes.

14) Forceps for handling the gauze wipes.

15) Latex or nitrile gloves. Avoid vinyl gloves.

16) 3” x 3” 12-ply cotton gauzes.

17) 40 ml VOA vials.

18) pH paper.

**Sampling Methods:**

Recommended testing area (100 cm²) is wiped by 3” x 3” 12-ply cotton gauze with Methanol as wetting solvent. A rigid template (10 cm x 10 cm square hole cutout) from cardstock or a Teflon® sheet is prepared to ensure that a constant area wiped. A single-use disposable cardstock is preferred to eliminate cross-contamination. A 3” x 3” 12-ply cotton gauze is wetted with Methanol (about 3-4 ml) on-site and insert into a sample container (40 ml VOA vial). Sampling gauzes maybe prepared in advance and bring to sampling site. This would prevent possible contaminate of the methanol with methamphetamine on-site. Before sampling, squeeze out and discard any excess solvent from the gauze wipe as necessary. Fresh latex or nitrile gloves must be used for each individual sample and blank to avoid Phthalate and cross contamination.

There are two sampling methods recommended by NIOSH 9106 for surface sampling dependent on the type of medias. Two sampling methods were also used in this study. “Concentric squares” wiping technique and “side-to-side” wiping technique are used for non-porous surfaces and porous surfaces, respectively.

**Concentric squares wiping technique (smooth and non-porous surfaces)**

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 above. Roll or fold the gauze and
insert into the shipping container.

Side-to-side wiping technique (rough, porous, or soiled surfaces)

Fold the pre-wetted gauze in half and then fold in half again. Using firm pressure, wipe the area within the template with at least five overlapping side-to-side horizontal passes beginning at the top and progressing to the bottom in a “Z” pattern. End with a scooping motion. Roll and fold the gauze again and insert into the shipping container.

Cap shipping containers securely and keep refrigerated (<6°C). Methamphetamine is stable on the wipe media for at least 7 days at room temperature, refrigeration is recommended as soon as possible. A laboratory media blank (QB) is prepared at the rate of one for every 20 samples. Same lot of cotton gauze and Methanol used for taking sample need to be provided to the analytical Laboratory for preparing these laboratory blanks.

Extraction Procedure:

Sample Preparation

Remove cap from shipping container. The sample wipe should fit loosely in the container. If compacted, loose it with a forceps. Spike exactly 60 µL of 10 µg/ml internal standard (Methamphetamine-d_{14}) and surrogate (Amphetamine-d_{11}) onto each wipe sample. Add 30 ml desorption solution (0.2 N Sulfuric Acid) into shipping container, then use pH paper to measure the pH of solution. If the sample is alkaline enough overcome the acidity of the desorption solution (0.2 N Sulfuric Acid), then the pH must be adjusted to about < 4 with 5 ~ 6 N of Sulfuric Acid drop-wise. Analytes are stable in desorption solution for at least seven days refrigerated (<6°C). Cap container securely and mix contents by inverting the tubes end over end on a rotary mixer at 10-30 rpm for an hour. After mixing, transfer exactly 10 ml of the supernatant via a 10 ml disposable-tip transfer pipette to a 25 ml glass tube.

Sample Clean-up (optional)

If the above extract has an oily appearance, dark in color, or suspected to contain interferences, the clean-up procedure may be used. Add 10 ml of Hexane to each 10 ml aliquot of acid desorbate. Cap container and mix on a rotary mixer at 10-30 rpm for about an hour. Allow to stand for 15-30 minutes for the phase to separate. If an emulsion forms, centrifuge the tubes at 1500-2000 rpm for a few minutes to break emulsion. If emulsion persists, adding about 0.5 ml of Acetonitrile to the surface of the emulsion via transfer pipette and to gentle mix the layers at the interface of the emulsion and then centrifuge again. Aspirate out the organic layer to waste and keep the aqueous layer.

Extraction of analytes into Methylene Chloride

Add 1-2 drops of the mixed pH indicator (Phenolphthalein + Bromothymol Blue) to each sample vial. If samples were sufficiently acidified, the color will turn into yellow. Then, add 0.5 ml of 10 N NaOH to each samples to make PH > 9 – 9.5 and the color will change into purple. If not, add another 0.5 ml of 10 N NaOH and check it again. After that, add 10 ml of Methylene Chloride to each sample. Cap the tube and mix on a rotary
mixer at 10-30 rpm for about an hour and allow standing for 15 – 30 minutes. Aspirate the aqueous (upper) layer to waste and carefully not to move the Methylene Chloride (lower) layer. Prepare Potassium Carbonate-Sodium Sulfate drying column for removing water from the extraction of Methylene Chloride. Add about 1 gram of Anhydrous Potassium Carbonate and 1 gram of Anhydrous Sodium Sulfate on top of the Potassium Carbonate in a suitable polypropylene column having a fritted polyethylene disc or equivalent. Prepare 12-15 ml collection tubes in test tube racks and add 5 µL of Crystal Violet solution and 100 µL of 0.3 N Hydrochloric Acid in Methanol into each collection tube. Position the drying columns over the collection tube. Transfer the Methylene Chloride layer into the drying column, rinse the drying column twice with about 1 ml of Methylene Chloride and combine with sample eluted.

**Derivatization Procedure:**

Evaporate the Methylene Chloride eluents in a “N₂ blow-down” at 35°C over a water bath. The dark color of the Crystal Violet helps make the residue more visible when it is dried. Add 100 µL of Chlorodifluoroacetic Anhydride and recap tube with PTFE-lined autoclavable caps. Heat tubes in an oven at 70-75°C for 20-30 minutes. After heating, allow the tubes to cool to room temperature. Remove caps and evaporate the contents to dryness under a stream of N₂ at room temperature. At the point of dryness the color of the residue turns rapidly to blue or violet. Then, remove the tubes just as soon as the dark-color appears. Reconstitute the dried residue with 1 ml of the reconstitution solvent and mix by vortexing briefly a couple of times. Transfer the reconstitution solution into a GC autosampler vial. Cap vials, label, and analyze by GC/MS or GC/MS/MS. Derivates of methamphetamine are stable at least 7 days at room temperature and 30 days refrigerated (<6°C), refrigeration is recommended as soon as possible.

**Analytical Procedure:**

Derivates of methamphetamine are analyzed by GC/MS or GC/MS/MS, as specified in SOP (Appendix I). Briefly, derivative solutions are placed into 1 ml GC autosampler vial and 2 µl of sample injected into GC/MS or GC/MS/MS system under the condition described below:

**Gas Chromatographic Conditions:**

- Temperature Program:
  - Start at 90°C (1 minute), 8°C/minute → 210°C (2 minutes), 30°C/minute → 280oC (5 minutes). Total run time=25.33 minutes.
  - Front Inlet: Varian 1177 injector
  - Mode-Splitless
  - Injector Temp-270°C
  - Gas-Helium
  - Column: Varian, VF-5ms (equivalent to CP-sil 8 CB Low-Bleed/MS), 30 m x 0.25 mm ID, 0.25 µm
  - Mode-Constant flow
  - Initial Flow -1.0 mL/min.
  - Outlet-MSD or MS/MS
  - Outlet pressure-vacuum
**Mass Spectrometer: (SIM-mode)**
Varian 1200 with GC interface (250°C).
EI: 70 eV
Scan rate: 2/sec
Temperature: 150°C
Target ions: segment 1: 118, 128, 160, 170, and 177 amu
    segment 2: 227, 296 amu

**MS/MS-MRM (Multiple Reaction Mode)mode:**
Varian 1200 with GC interface (250°C)
EI: 70 eV
Temperature: 150°C
MRM mode with 2/sec
Daughter ions: segment 1: 112, 126, and 129 amu.
    segment 2: 246 amu
Collision energy: -15 eV
RESULTS AND DISCUSSION

Four different surfaces commonly found in the building, glass, flat painted drywall, semi-gloss painted drywall and fabric, with methamphetamine residues have been sampled by the wipe method and analyzed by GC/MS or GC/MS/MS. Due to the porosity of the surfaces, two different matrix spike techniques were used in this study. Wet spike technique and dry spike technique were used for non-porous surfaces and porous surfaces, respectively.

**Wet Spike Technique:**

A Methamphetamine spike solution (in Methanol) is transferred onto the testing surface with a syringe. The solution is then dried. The residue on the testing surface is wiped with the 3” x 3” gauze and transferred into 40 ml VOA vial.

**Dry Spike Technique:**

A Methamphetamine spike solution (in Methanol) is transferred onto a 2” x 2” Teflon sheet with a syringe. The Teflon sheet is covered with a beaker to allow the residue to dry. The Teflon sheet is turned up-side-down onto the testing surface. The Methamphetamine residue is transferred by firming rubbing the Teflon sheet against the testing surface. The testing surface is then wiped with the 3” x 3” gauze wetted with Methanol and transferred into 40 ml VOA vial.

Table 1 shows the recovery study for four different surfaces by wet and dry spike techniques. The spike amount of methamphetamine is 0.6 µg/plate.

<table>
<thead>
<tr>
<th>Types of Surfaces</th>
<th>Replicates</th>
<th>Mean Recovery (GC/MS)</th>
<th>%RSD</th>
<th>Mean Recovery (GC/MS/MS)</th>
<th>%RSD</th>
<th>Replicates</th>
<th>Mean Recovery (GC/MS)</th>
<th>%RSD</th>
<th>Mean Recovery (GC/MS/MS)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Plate</td>
<td>5</td>
<td>86%</td>
<td>12</td>
<td>99%</td>
<td>11</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Flat Painted Drywall</td>
<td>5</td>
<td>51%</td>
<td>4.6</td>
<td>55%</td>
<td>4.3</td>
<td>5</td>
<td>74%</td>
<td>11</td>
<td>84%</td>
<td>10</td>
</tr>
<tr>
<td>Semi-Gloss Painted Drywall</td>
<td>5</td>
<td>93%</td>
<td>5.2</td>
<td>90%</td>
<td>5.3</td>
<td>5</td>
<td>92%</td>
<td>10</td>
<td>94%</td>
<td>13</td>
</tr>
<tr>
<td>Fabric</td>
<td>3</td>
<td>16%</td>
<td>17</td>
<td>**</td>
<td>**</td>
<td>3</td>
<td>20%</td>
<td>22</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

*: Because wet spike technique show high percent recovery for non-porous surface, dry spike technique was not necessary to perform.

**: Because the recovery of methamphetamine from fabric is low, there is no enough response to generate stable MS/MS spectrum.

With the wet spike technique, the recovery of glass and semi-gloss painted drywall were > 90% but fabric was only 16% ~ 22%. For flat-painted drywall, recovery was only 51%. If
dry spike technique was used, the recovery of flat painted drywall was higher. According to this result, wet spike technique can result good recovery for glass plate and semi-gloss painted drywall. However, for flat painted drywall (porous surface) dry spike technique is better than wet spike technique. Due to the low recovery, neither technique is suitable for fabric.

**Study of inside materials in drywall and fabric by direct extraction method**

A supplemental extraction method has been developed for highly absorptive materials, such as paper, limestone and fabric. Methamphetamine in MeOH is spiked onto a swatch of the material and place directly into a 40 ml VOA vial. Added 30 ml MeOH into the VOA vial and rotated for one hour. The sample is processed in the same manner as liquid-liquid extraction method and analyze. Table 2 shows the results for the recovery of methamphetamine in several materials. The spike amount of methamphetamine is 0.6 µg/plate.

<table>
<thead>
<tr>
<th>Types of Materials</th>
<th>Wet Spike</th>
<th>Dry Spike</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicates</td>
<td>Mean Recovery (GC/MS)</td>
</tr>
<tr>
<td>Paint on the Drywall</td>
<td>3</td>
<td>94%</td>
</tr>
<tr>
<td>Paper inside the Drywall</td>
<td>3</td>
<td>95%</td>
</tr>
<tr>
<td>Limestone inside the Drywall</td>
<td>3</td>
<td>90%</td>
</tr>
<tr>
<td>Fabric</td>
<td>3</td>
<td>90%</td>
</tr>
</tbody>
</table>

*: Because wet spike technique show high percent recovery for non-porous surface, dry spike technique was not necessary to perform.

From this result, the recoveries of all materials are higher than 90% except dry spike on fabric. Dry spike technique may not be suitable for textured material due to uneven surface and larger space between fibers.

**Recovery study of methamphetamine with various concentrations from glass plate**

Various concentrations of Methamphetamine were spiked onto glass plates to determine the recovery limits of the technique. Table 3 shows the results of the recovery of methamphetamine from glass plate at 0.05 µg/plate, 0.10 µg/plate, and 0.60 µg/plate.
Table 3.

<table>
<thead>
<tr>
<th>Concentration on Glass Plate</th>
<th>GC/MS Methamphetamine</th>
<th>% Recovery</th>
<th>GC/MS/MS Methamphetamine</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 µg/glass #1</td>
<td>0.056</td>
<td>112</td>
<td>0.055</td>
<td>110</td>
</tr>
<tr>
<td>0.05 µg/glass #2</td>
<td>0.047</td>
<td>94</td>
<td>0.047</td>
<td>94</td>
</tr>
<tr>
<td>0.05 µg/glass #3</td>
<td>0.045</td>
<td>90</td>
<td>0.044</td>
<td>88</td>
</tr>
<tr>
<td>0.05 µg/glass #4</td>
<td>0.040</td>
<td>79</td>
<td>0.038</td>
<td>77</td>
</tr>
<tr>
<td>0.05 µg/glass #5</td>
<td>0.049</td>
<td>98</td>
<td>0.049</td>
<td>98</td>
</tr>
<tr>
<td>Average</td>
<td>0.047</td>
<td>95</td>
<td>0.047</td>
<td>93</td>
</tr>
<tr>
<td>RSD%</td>
<td>13</td>
<td>-----</td>
<td>13</td>
<td>-----</td>
</tr>
<tr>
<td>0.10 µg/glass #1</td>
<td>0.077</td>
<td>77</td>
<td>0.090</td>
<td>90</td>
</tr>
<tr>
<td>0.10 µg/glass #2</td>
<td>0.093</td>
<td>93</td>
<td>0.11</td>
<td>108</td>
</tr>
<tr>
<td>0.10 µg/glass #3</td>
<td>0.063</td>
<td>63</td>
<td>0.075</td>
<td>75</td>
</tr>
<tr>
<td>0.10 µg/glass #4</td>
<td>0.096</td>
<td>96</td>
<td>0.11</td>
<td>112</td>
</tr>
<tr>
<td>0.10 µg/glass #5</td>
<td>0.077</td>
<td>77</td>
<td>0.089</td>
<td>89</td>
</tr>
<tr>
<td>Average</td>
<td>0.081</td>
<td>81</td>
<td>0.095</td>
<td>95</td>
</tr>
<tr>
<td>RSD%</td>
<td>16</td>
<td>-----</td>
<td>16</td>
<td>-----</td>
</tr>
<tr>
<td>0.60 µg/glass #1</td>
<td>0.57</td>
<td>95</td>
<td>0.64</td>
<td>107</td>
</tr>
<tr>
<td>0.60 µg/glass #2</td>
<td>0.56</td>
<td>94</td>
<td>0.63</td>
<td>106</td>
</tr>
<tr>
<td>0.60 µg/glass #3</td>
<td>0.44</td>
<td>73</td>
<td>0.50</td>
<td>84</td>
</tr>
<tr>
<td>0.60 µg/glass #4</td>
<td>0.47</td>
<td>78</td>
<td>0.54</td>
<td>90</td>
</tr>
<tr>
<td>0.60 µg/glass #5</td>
<td>0.54</td>
<td>90</td>
<td>0.65</td>
<td>108</td>
</tr>
<tr>
<td>Average</td>
<td>0.52</td>
<td>86</td>
<td>0.59</td>
<td>99</td>
</tr>
<tr>
<td>RSD%</td>
<td>12</td>
<td>-----</td>
<td>11</td>
<td>-----</td>
</tr>
</tbody>
</table>

The result indicated that the recovery of methamphetamine is consistent at the different concentrations. In addition, these results confirmed the calibration range is appropriate for the method. Both GC/MS and GC/MS/MS methods produced comparable results.

**Limit of Quantitation (LOQ) of this method**

The limit of quantitation (LOQ) of this method for methamphetamine is 0.05 µg/wipe. Table 4 shows the results of a 20 replicates, study sample of 0.05 µg/wipe from glass plates.
Table 4.

<table>
<thead>
<tr>
<th>LOQ Study on Glass Plate</th>
<th>GC/MS</th>
<th>GC/MS/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methamphetamine</td>
<td>% Recovery</td>
</tr>
<tr>
<td>0.05 µg/glass #1</td>
<td>0.042</td>
<td>84</td>
</tr>
<tr>
<td>0.05 µg/glass #2</td>
<td>0.044</td>
<td>88</td>
</tr>
<tr>
<td>0.05 µg/glass #3</td>
<td>0.046</td>
<td>92</td>
</tr>
<tr>
<td>0.05 µg/glass #4</td>
<td>0.040</td>
<td>80</td>
</tr>
<tr>
<td>0.05 µg/glass #5</td>
<td>0.035</td>
<td>70</td>
</tr>
<tr>
<td>0.05 µg/glass #6</td>
<td>0.035</td>
<td>70</td>
</tr>
<tr>
<td>0.05 µg/glass #7</td>
<td>0.037</td>
<td>74</td>
</tr>
<tr>
<td>0.05 µg/glass #8</td>
<td>0.044</td>
<td>88</td>
</tr>
<tr>
<td>0.05 µg/glass #9</td>
<td>0.052</td>
<td>104</td>
</tr>
<tr>
<td>0.05 µg/glass #10</td>
<td>0.054</td>
<td>108</td>
</tr>
<tr>
<td>0.05 µg/glass #11</td>
<td>0.043</td>
<td>86</td>
</tr>
<tr>
<td>0.05 µg/glass #12</td>
<td>0.054</td>
<td>108</td>
</tr>
<tr>
<td>0.05 µg/glass #13</td>
<td>0.049</td>
<td>98</td>
</tr>
<tr>
<td>0.05 µg/glass #14</td>
<td>0.053</td>
<td>106</td>
</tr>
<tr>
<td>0.05 µg/glass #15</td>
<td>0.052</td>
<td>104</td>
</tr>
<tr>
<td>0.05 µg/glass #16</td>
<td>0.033</td>
<td>66</td>
</tr>
<tr>
<td>0.05 µg/glass #17</td>
<td>0.053</td>
<td>106</td>
</tr>
<tr>
<td>0.05 µg/glass #18</td>
<td>0.055</td>
<td>110</td>
</tr>
<tr>
<td>0.05 µg/glass #19</td>
<td>0.059</td>
<td>118</td>
</tr>
<tr>
<td>0.05 µg/glass #20</td>
<td>0.058</td>
<td>116</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.047</strong></td>
<td><strong>94</strong></td>
</tr>
<tr>
<td><strong>RSD%</strong></td>
<td><strong>17</strong></td>
<td>-----</td>
</tr>
</tbody>
</table>

These results indicated that, at 0.05 µg/wipe, the sampling and analytical methods are highly reproducible. Based on these results, a Limit of Quantitation (LOQ) can be set at 0.05 µg/wipe.
CONCLUSION

This study was performed to develop sampling and analytical methods for the collection of Methamphetamine residue. The results of this study indicated that glass, flat painted drywall and semi-gloss drywall could be successfully examined by this study but fabric was failed by using wipe sampling method. However, if material needs to be tested are allowed to cut or remove from the site, the extraction method may be a better analytical way to examine methamphetamine residue. Also based on these results, a Limit of Quantitation (LOQ) can be set at 0.05 µg/wipe.

GC/MS/MS was used in this study as a supplemental analytical tool. Due to unpredicted condition in the site, the high selective spectrum of GC/MS/MS may use to reduce the interference from matrix and obtain more reliable results.

REFERENCE

1 NIOSH Method 9106, “Methamphetamine and Illicit Drugs, Precursors, and Adulterants on wipes by liquid-liquid Extraction”, fourth edition.


3 Quality Assurance Laboratory “Standard Operating Procedure for GC/MS Analysis of Ephedrine & Methamphetamine”
SOP 7011-S

Analysis of Methamphetamine on Wipes by GC/MS–SIM Mode or GC/MS/MS spectrometry

1.0 SCOPE AND APPLICATION

1.1 Methamphetamine (CAS No. 537-46-2) is a water and alcohol soluble compound, with a melting point of 170-175°C. NIOSH Method 9106, “methamphetamine and illicit drugs, precursors, and adulterants on wipes by liquid-liquid extraction”, has been modified for methamphetamine analysis. In addition, other methamphetamine precursors (e.g., Phenyl-2-Propanone) and analogs (e.g., Amphetamine) may be analyzed by this method. This method is designed for wipe samples and uses a stable isotope-labeled analogue as internal standard\(^1\) to calculate the concentration for appropriate analytes.

1.2 There are two sampling methods can be used for surface sampling dependent on the type of medias. Concentric squares wiping technique and side-to-side wiping technique are used for non-porous surfaces and porous surfaces, respectively. (See section 7.5.1 and 7.5.2)

1.3 The estimated quantitation limit (EQL) of this method for methamphetamine is 0.05 µg/wipe. EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) or gas chromatography/mass spectrometry/mass spectrometry (GC/MS/MS) using the appropriate sample preparation method. Prior to extraction, samples (wipes) are made acidic by the addition of desorption (0.2 N sulfuric acid) solution before extraction with dichloromethane. After samples are extracted and
dried by “N₂ blow-down”, a derivatizing reagent (chlorodifluoroacetic anhydride) is added into dry residue to make the derivative of methamphetamine. Reconstitute the dried derivative of methamphetamine with 1 ml of the reconstitution solution (10% acetone in toluene), then analyze by GC/MS or GC/MS/MS.

GC/MS is a very powerful method to analyze the structure of organic compounds, but has the difficult in characterizing compounds with a complex mixture. The use of GC/MS/MS tandem technique can provide a better selectivity and signal/noise ratio than that of a GC/MS, especially in high matrix interference. This method allows GC/MS/MS as an optional technique to analyze for methamphetamine.

2.2 The methamphetamine derivative is introduced into the GC/MS or GC/MS/MS. Identification of derivative of methamphetamine is accomplished by comparing its mass spectra by SIM mode or MS/MS with the electron impact (EI) spectra of reference standard. Quantitation is accomplished by comparing the response of a major quantitation ion relative to a deuterated internal standard using a five point calibration curve.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples and spikes must be evaluated for interferences.

3.2 Carryover can sometimes occur when a low concentration sample is analyzed after one of high concentration. Whenever an unusually high sample is encountered, follow such sample with a solvent blank to check for cross-contamination before proceeding with analysis.

4.0 SAFETY

4.1 Methamphetamine is a controlled substance (a stimulant) listed in the U.S. Code of Federal Regulations, Title 21, Part 1308.12 (1995).

4.2 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely defined. Therefore, each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.

5.0 APPARATUS AND SUPPLIES

5.1 Gas Chromatographic System: Varian 3800 GC interfaced with L1200 Mass/Mass Selective Detector. The MS should be capable of scanning from 35 to 500 amu every second using the electron impact ionization mode.

5.2 Column: Varian, VF-5ms (equivalent to CP-sil 8 CB Low-Bleed/MS), 30 m x 0.25 mm ID, 0.25 µm

5.3 Microsyringes-10, 25, 50,100 and 1000 µL (Hamilton model 700 series).

5.4 Screw top glass vials (2 and 4 mL capacity) with caps with Teflon liners.
5.5 Volumetric flasks, Class A-10 mL, 50 mL, 100 mL and 500 ml with ground-glass stoppers.

5.6 Pipets, Class A, TD-0.5 mL, 1 mL, 5 ml and 10 ml.

5.7 Empty polypropylene drying columns.

5.8 25-ml Glass stopped test tubes with PTFE-faced rubber-lined caps.

5.9 Nitrogen blow-down apparatus with water bath capable of maintaining 35°C.

5.10 Rotating mixer capable of 10-30 rpm.

5.11 Heating oven capable of 70-90°C ± 2°C.

5.12 Test tube racks resistant to heating at 90°C.

5.13 Pasteur transfer pipettes.

5.14 Forceps for handling the gauze wipes.

5.15 Latex or nitrile gloves. Avoid vinyl gloves.

5.16 3” x 3” 12-ply cotton gauze

5.17 40 ml VOA vial.

5.18 PH paper.

6.0 REAGENTS AND STANDARDS

6.1 Solvents (analytical grades): Dichloromethane, Hexane, Isopropanol, Methanol, Toluene, Acetone.

6.2 Concentrated sulfuric and hydrochloric acids (analytical grades).

6.3 Sodium hydroxide, A.C.S grade.

6.4 Anhydrous granular sodium sulfate and anhydrous granular potassium carbonate. (AR grade)

6.5 Bromothymol blue [76-59-5], ≥95%, A.C.S.; Phenolphthalein, [77-09-8], A.C.S.; Crystal violet [548-62-9], ≥95%, A.C.S.

6.6 Amphetamine-d11 (surrogate)², Cerilliant Catalog # A-019

6.7 (±)-Methamphetamine-d14 (Internal Standard), Cerilliant Catalog # M-009

6.8 (±)-Methamphetamine, Cerilliant Catalog # M-093
6.9 Desorption solution: 0.2 N sulfuric acid. Add 22 ml conc. Sulfuric acid to make 4 liters deionized water.

6.10 Calibration Standards – a minimum of five different concentrations of calibration standards should be prepared. The lowest standard should be at or below the minimum detection objective of the project. The calibration range should cover the possible sample concentration range. The calibration should not exceed the working range of the GC/MS system. Keep refrigerated (<6°C). Protect solutions from light.

6.11 Matrix spike standards – If available, a standard will be used for spiking.

6.12 Mixed bromothymol blue and phenolphthalein PH indicator solution: 1 mg/ml each in 4:1 (v/v) isopropanol: reagent water.

6.13 10 N Sodium Hydroxide Solution – 40 grams of sodium hydroxide pellets in 100 ml of reagent water

6.14 0.3 N hydrochloric acid in methanol: Dilute 2.5 ml conc. Hydrochloric acid in about 80 ml methanol; dilute to 100 ml with methanol.

6.15 Crystal violet indicator: 2-3 mg/mL of crystal violet in isopropanol.

6.16 Reconstitution solvent: 10% acetone in toluene with 0.16 ug/ml of 4,4'-dibromo-octafluorobiphenyl (instrument monitoring standard)³.

6.17 Derivatizing agent: chlorodifluoroacetic anhydride, 98% [2834-23-3].

7.0 SAMPLING, HANDLING AND STORAGE

7.1 Recommended area (100 cm²) to be wiped by 3” x 3” 12-ply cotton gauze with methanol as wetting solvent.

7.2 Shipping container: 40-ml glass VOA vials.

7.3 Prepare a rigid template (10 cm x 10 cm square hole cut out) from cardstock or a Teflon® sheet. The template must be able to retain its shape during wiping to ensure that the areas wiped. A single-use disposable cardstock is preferred due to the less possibility of cross-contamination.

7.4 Take a 3” x 3” 12-ply cotton gauze and wet it with methanol (about 3-4 ml). Alternatively, Pre-wet and insert the gauze wipes into the sample containers off-site. This avoids any possibility of the bottle of methanol becoming contaminated on-site with methamphetamine. If the wipes were prepared off-site, 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 individual sample and blank. Avoid vinyl gloves due to phthalate contamination.
7.5 Surface Sampling

7.5.1 Concentric squares wiping technique (smooth and non-porous surfaces)
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 above. Roll or fold the gauze and insert into the shipping container.

7.5.2 Side-to-side wiping technique (rough, porous, or soiled surfaces)
Fold the pre-wetted gauze in half and then fold in half again. Using firm pressure, wipe the area within the template with at least five overlapping side-to-side horizontal passes beginning at the top and progressing to the bottom in a “Z” pattern. End with a scooping motion. Roll and fold the gauze again and insert into the shipping container.

7.6 Cap shipping containers securely and keep refrigerated (<6°C). Do not use polyethylene plastic bags. Methamphetamine is stable on the wipe media for at least 7 days at room temperature, refrigeration is recommended as soon as possible.

7.7 Label each individual sample with identification number, date, time, location, and initials of the person who taking the sample.

7.8 Prepare a minimum of one field blank (FB) for every twenty samples (originating from the site), and at least one from individual site being evaluated. Using the same manner as above, remove one gauze from same lot and wet it with methanol, squeeze out excess solvent, wipe an area on the surface of the glove and the edge of the blank template, then insert the wipe into the shipping container.

7.9 A laboratory media blank (QB) is prepared at the rate of one for every 20 samples. Same lot of cotton gauze used for taking sample need to be provided to the analytical Laboratory for preparing these laboratory blanks.

7.10 For wipe samples, depending on the project work plan, duplicate sample may not be available to perform the normal quality control routine such as duplicate and matrix spike and matrix spike duplicate. It is up to the project manager to decide what they would like to be incorporated as quality control measures and collect the proper samples.

8.0 PROCEDURE

8.1 Sample Preparation

8.1.1 Remove cap from shipping container. The sample wipe should fit loosely in
the container. If compacted, loose it with a forceps.

8.1.2 Spike exactly 60 µL of 10 µg/ml internal standard (methamphetamine-d14) and surrogate (amphetamine-d11) onto each wipe sample.

8.1.3 Add 30 ml desorption solution (0.2 N sulfuric acid) into shipping container, then use PH paper to measure the PH of solution. If the sample alkaline enough overcome the acidity of the desorption solution, then the PH must be adjust to about < 4 with diluted (5 to 6 N) sulfuric acid drop-wise. Analytes are stable in the desorption solution for at least seven days refrigerated (<6°C).

8.1.4 Cap container securely and mix contents by inverting the tubes end over end on a rotary mixer at 10-30 rpm for one hour,

8.1.5 After mixing, transfer exactly 10 ml of the supernatant via a 10 ml disposable-tip transfer pipette to a 25 ml glass tube.

8.2 Sample Cleanup

8.2.1 If the above extract has an oily appearance, dark-color, or suspected to contain interferences, the following procedure may be used.

8.2.2 Add 10 ml of hexane to each 10 ml aliquot of acid desorbate.

8.2.3 Cap container and mix on a rotary mixer at 10-30 rpm for about one hour.

8.2.4 Allow to stand for 15-30 minutes for the phase to separate. If an emulsion forms, centrifuge the tubes at 1500-2000 rpm for a few minutes to break emulsion. If emulsion persists, adding about 0.5 ml of acetonitrile to the surface of the emulsion via transfer pipette and to gentle mix the layers at the interface of the emulsion. Centrifuge again.

8.2.5 Aspirate the organic layer to waste. Carefully not to remove any of the aqueous layer.

8.3 Extraction of analytes into methylene chloride

8.3.1 Add 1-2 drops of the mixed PH indicator (phenolphthalein + Bromothymol blue) to each sample vial. If samples were sufficiently acidified, the color will turn into yellow.

8.3.2 Add 0.5 ml of 10 N NaOH to each samples to make PH > 9 – 9.5. If not, add another 0.5 ml of 10 N NaOH and check it again.

8.3.3 Add 10 ml of methylene chloride to each sample.

8.3.4 Cap the tube and mix on a rotary mixer at 10-30 rpm for about one hour and
allow standing for 15 – 30 minutes.

8.3.5 Aspirate the aqueous (upper) layer to waste. Carefully not to move the lower methylene chloride layer.

8.4 Removal of water from the extraction of methylene chloride

8.4.1 Prepare potassium carbonate-sodium sulfate drying column. Add about 1 gram of anhydrous potassium carbonate and 1 gram of anhydrous sodium sulfate on top of the potassium carbonate in a suitable polypropylene column having a fritted polyethylene disc or equivalent.

8.4.2 Prepare some 12-15 ml collection tubes in test tube racks.

8.4.3 Add 5 µL of crystal violet solution and 100 µL of 0.3 N hydrochloric acid in methanol to each collection tube.

8.4.4 Position the drying columns over the collection tube. Transfer the methylene chloride layer into the drying column, rinse the drying column twice with about 1 ml of methylene chloride and combine with sample eluted.

8.5 Derivatization

8.5.1 Evaporate the methylene chloride elutes in a “N₂ blow-down” at 35°C. When the samples are dry, remove and cap the tube immediately to keep moisture out. The dark color of the crystal violet helps make the residue more visible when it is dries.

8.5.2 Add 100 µL of chlorodifluoroacetic anhydride and recap tube with PTFE-lined autoclavable caps.

8.5.3 Heat tubes in an oven at 70-75°C for 20-30 minutes.

8.5.4 After heating, allow the tubes to cool to room temperature. Remove caps and evaporate the contents to dryness under a stream of N₂ at room temperature. At the point of dryness the color of the residue turns rapidly to blue or violet. Then, remove the tubes just as soon as the dark-color appears.

8.5.5 Reconstitute the dried residue with 1 ml of the reconstitution solvent and mix by vortexing briefly a couple of times.

8.5.6 Transfer the reconstitution solution into a GC autosampler vial. Cap vials, label, and analyze by GC/MS or GC/MS/MS. Derivates of methamphetamine are stable at least 7 days at room temperature and 30 days refrigerated (<6°C), refrigeration is recommended as soon as possible.
8.6 Consult the Instrument Manuals for the specifics on the operations of the GC/MS and GC/MS/MS.

8.6.1 Gas Chromatographic Conditions:

**Temperature Program:**

Start at 90°C (1 minute), 8°C/minute → 210°C (2 minutes), 30°C/minute → 280°C (5 minutes). Total run time=25.33 minutes.

**Front Inlet:** Varian 1177 injector
Mode-Splitless
Injector Temp-270°C
Gas-Helium

**Column:** Varian, VF-5ms (equivalent to CP-sil 8 CB Low-Bleed/MS), 30 m x 0.25 mm ID, 0.25 µm
Mode-Constant flow
Initial Flow -1.0 mL/min.
Inlet-Front Inlet
Outlet-MSD or MS/MS
Outlet pressure-vacuum

8.6.2 Mass Spectrometer: (SIM-mode)

Varian 1200 with GC interface (250°C).
EI: 70 eV
Scan rate: 2/sec
Temperature: 150°C
Target ions: segment 1: 118, 128, 160, 170, and 177 amu
segment 2: 227, 296 amu

8.6.3 MS/MS-MRM mode

Varian 1200 with GC interface (250°C)
EI: 70 eV
Temperature: 150°C
MRM mode with 2/sec
Daughter ions: segment 1: 112, 126, and 129 amu.
segment 2: 246 amu
Collision energy: -15 eV

8.7 Before sample analysis, the following procedures must be performed and verified:

8.7.1 The tuning of the GC/MS system must be verified by autotune daily.

8.7.2 A solvent blank must be analyzed to verify that the analytical system is free of contaminants
8.8 Samples should be warmed to ambient temperature before analysis.

8.9 Perform a sample duplicate analysis if duplicate sample is available.

8.10 Perform Laboratory control spike (LCS)/Laboratory control spike duplicate (LSD) analysis for each analytical batch.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Calibration Standards:

Spike exactly 60 µL of 10 µg/ml internal standard (methamphetamine-d14)/surrogate (amphetamine-d11) mixture solution onto each wipe standard.

<table>
<thead>
<tr>
<th>Standard Concentration</th>
<th>Dilution from 10 µg/mL std.</th>
<th>Dilution from 1 µg/mL std.</th>
<th>Volume of MeOH in 40 ml vial</th>
<th>Volume of desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 µg/wipe</td>
<td>---</td>
<td>20 µL onto 3”x3” wipe</td>
<td>3 ml</td>
<td>30 ml</td>
</tr>
<tr>
<td>0.05 µg/wipe</td>
<td>---</td>
<td>50 µL onto 3”x3” wipe</td>
<td>3 ml</td>
<td>30 ml</td>
</tr>
<tr>
<td>0.10 µg/wipe</td>
<td>---</td>
<td>100 µL onto 3”x3” wipe</td>
<td>3 ml</td>
<td>30 ml</td>
</tr>
<tr>
<td>0.20 µg/wipe</td>
<td>20 µL onto 3”x3” wipe</td>
<td>---</td>
<td>3 ml</td>
<td>30 ml</td>
</tr>
<tr>
<td>0.60 µg/wipe</td>
<td>60 µL onto 3”x3” wipe</td>
<td>---</td>
<td>3 ml</td>
<td>30 ml</td>
</tr>
</tbody>
</table>

9.2 At minimum, a 5-point curve is run to determine the linear working range of the system for analysis. The lowest standard should be at or below the minimum detection objective of the project. The calibration range should cover the possible sample concentration range. The calibration should not exceed the working range of the GC/MS system. A relative standard deviation (RSD) is calculated for each target analyte response factor. The average response factors for each analytes must have a relative standard deviation less than 30% RSD to accept the curve for analysis.

9.3 The calibration verification (continuing calibration verification) standard is prepared at a concentration at the midpoint of the calibration range. The calibration curve must be verified at the beginning of daily analytical shift by analyzing the calibration verification standard. For the initial calibration curve to be valid for quantitation, the percent difference between the calibration verification standard response factor and the average response factor from the initial calibration curve must be within ± 25%. If the percent different is greater than ± 25%, corrective action should be taken or the system must be recalibrated.
10.0 QUALITY CONTROL

10.1 The tuning of the GC/MS system must be verified by autotune before any analysis can begin.

10.2 A solvent blank (SB) (reconstitution solution: 10% acetone in toluene) must be analyzed to verify that the analytical system is free of contaminants. There is no necessary to spike IS/Surrogate standard into solvent blank.

10.3 A field blank (FB) must be analyzed at least once per analytical batch within one analytical batch (see Section 7.8). If any contaminants are found above the quantitation limit, appropriate corrective actions should be taken before proceeding with analysis.

10.4 A method blank (QB) must be analyzed at least once per analytical batch within one analytical batch (see Section 7.9). If any contaminants are found above the quantitation limit, appropriate corrective actions should be taken before proceeding with analysis.

10.5 The frequency at which solvent blanks are analyzed should be increased if heavily contaminated samples are encountered. Analyzing solvent blanks between samples is recommended to insure there is no carryover or cross-contamination of samples.

10.6 Laboratory control Spike/ Laboratory control Spike Duplicate (LCS/LCSD)

10.6.1 LCS/LCSD sample analysis should be performed for every batch of samples or every 20 samples, whichever is more frequent for each matrix type.

10.6.2 LCS/LCSD acceptance limits are established by using the statistical evaluation of ± three (3) times the standard deviation of a minimum of 20 data points from sample analyses. Since there are insufficient data to establish the limits at this time, the current acceptance limits are defaulted to standard acceptance of 60-140% for percent recovery and 25% for relative percent difference between duplicate results.

10.6.3 If the LCS/LCSD results exceeded the acceptance limits, then the results will be reported with a disclaimer to the data user.

10.7 0.16 µg/ml of 4, 4'-dibromoocatafluorobiphenyl is added into reconstitute solution for every samples. This compound use for monitoring the performance of instrument and quantitated by external standard method⁴. The acceptance limits is 50 – 200% for percent recovery.
10.8 The internal standard areas are monitored for each shift by comparing the areas of the internal standards in each sample with the average areas of the initial calibration standards. Samples areas are considered acceptable if they fall between 50% - 200% of the average area of the initial calibration standards. Any sample exceeding this criterion must be re-analyzed and, if it fails again, documented and discussed in the report narrative. Surrogate standards acceptance limits are established by using the statistical evaluation of ± three (3) times the standard deviation of a minimum of 20 data points from sample analyses. Since there are insufficient data to establish the limits at this time, the current acceptance limits are defaulted to standard acceptance of 60-140% for percent recovery. Failure of the surrogate standard criteria must be documented in the report narrative.

10.9 Sample Duplicates

For wipe samples, depending on the project work plan, duplicate sample may not be available to perform the normal quality control routine such as duplicate and matrix spike and matrix spike duplicate. It is up to the project manager to decide what they would like to be incorporated as quality control measures.

11.0 METHOD PERFORMANCE

11.1 The Quantitation Limit for wipe sample is dependent on the project work plan.

11.2 This method has been tested only in the Environmental Chemical Laboratory-Los Angeles on a limited number of relatively clean wipe samples. There are insufficient single laboratory accuracy and precision data at this time.

11.3 This method has been applied to clean wipe samples only. The applicability of this method to other matrices has not been determined at this time. Analysts intending to use this method for other matrices should perform the required validation studies before using the method on routine samples.

12.0 DATA ANALYSIS AND CALCULATION

12.1 Qualitative Analysis

12.1.1 An analyte (e.g., listed in Table 1) is identified by comparison of the sample mass spectrum or mass/mass spectrum of a standard of the suspected compound (standard reference spectrum). Standard reference mass spectra are obtained on a GC/MS or GC/MS/MS system. These standard reference spectra can be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify positive identification. 1). Elution of sample component at the same GC relative or absolute retention time as those of the standard component; 2).
Correspondence of the sample component and the standard component mass spectrum or MS/MS.

12.1.2 The sample component relative retention time (RRT) must compare within ± 0.06 RRT units of the RRT of the standard component.

12.1.3 The relative intensities of ions specified must agree within 25% between the standard and sample spectra.

12.1.4 If a compound cannot be verified by all of the criteria in the above but in the technical judgment of the analytical chemist the identification is correct, then the compound may be reported.

12.2 Quantitative Analysis

When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP (extracted ion chromatographic profile) of the primary characteristic ion. Quantification will take place using the internal standard technique. A summary table of internal standard and their corresponding primary, secondary, and daughter ions (MS/MS only) is represented by Table 2.

12.3 Calculate final concentration, $C$, of analyte in µg/wipe.

$$C = c \times \left( \frac{V_1}{V_2} \right) - b$$

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

$$\left( \frac{V_1}{V_2} \right) =$ dilution factor, if applicable

$V_1 =$ 10 ml (Volume of desorbate taken for cleanup step/extracts)

$V_2 =$ volume in ml of desorbate actually taken for cleanup and dilute to 10 ml with blank desorbing solution containing internal standard.

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

12.4 Report concentration, $C'$, in µg per total area wiped (in cm²) as follows:

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

$C =$ µg/sample

$A =$ Total area wiped in cm² per sample

12.5 Calculation for relative response factor (RRF)

$$RRF = \frac{\text{Area of cpd. In Std.}}{\text{Area of I.S.}} \times \frac{\text{conc. of I.S.}}{\text{conc. cpd. In Std.}}$$

12.5 Calculation for percent relative standard deviation (%RSD)

$$%\text{RSD} = \frac{\text{standard deviation of RRFs}}{\text{mean of RRFs}} \times 100$$
12.6 Calculation for percent difference (%D)
\[
\%D = 100 \times \frac{\text{average RRF from initial curve} - \text{RRF cpd. From daily}}{\text{average RRF from initial curve}}
\]

12.7 Calculation for determining concentration of compounds
\[
\text{Conc. of cpd.} = \frac{\text{area of compound in sample}}{\text{area of I.S. in sample}} \times \left(\frac{\text{conc. od I.S.}}{\text{average RRF}}\right) \times \text{dilution factor}
\]

12.7 Calculation for percent recovery (%Rec.)
\[
\%\text{Rec.} = \frac{\text{amount of cpd. Recovered}}{\text{amount of cpd. spiked}} \times 100
\]

12.8 Calculation for relative percent difference (RPD)
\[
\text{RPD} = \frac{\text{Value A} - \text{Value B}}{\text{average of values}} \times 100
\]

13.0 REFERENCES


13.3 Quality Assurance Laboratory “Standard Operating Procedure for GC/MS Analysis of Ephedrine & Methamphetamine”

14.0 ACKNOWLEDGMENTS

This method was developed by the staff of the Organic Analysis Section of the Environmental Chemical Laboratory-Los Angeles, California Department of Toxic Substances Control.

15.0 CONTACTS

For comments and questions, please contact Russ Chin (213) 580-5797 or Kenneth Sinn at (213) 250-3166 at ECL-Los Angeles, 1449 West Temple Street, Room 105, Los Angeles, California 90026.

16.0 MISCELLANEOUS (Tables, Appendices, ETC...)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reporting Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amphetamine-d11 (surrogate)</td>
<td>NA</td>
</tr>
<tr>
<td>Methamphetamine-d14 (Internal Standard)</td>
<td>NA</td>
</tr>
<tr>
<td>4,4’ – dibromooctafluorobiphenyl (Instrument Monitoring Standard)</td>
<td>NA</td>
</tr>
<tr>
<td>Methamphetamine</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 2

Gas Chromatography Retention Times and Mass Ions for Chlorodifluoroacetyl Derivatives of Methamphetamine, Amphetamine-d11, Methamphetamine-d14, and 4, 4’ – dibromoocstafluorobiphenyl

<table>
<thead>
<tr>
<th>Compound Time</th>
<th>Compound</th>
<th>Recommended SIM ions</th>
<th>Multiple Reaction Monitoring Ions (MRM)</th>
<th>Retention (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quantitation Ion</td>
<td>Confirmation Ion</td>
<td></td>
</tr>
<tr>
<td>Amphetamine-d11</td>
<td>160</td>
<td>128</td>
<td>160 -&gt; 112</td>
<td>10.23</td>
</tr>
<tr>
<td>Methamphetamine-d14</td>
<td>177</td>
<td>128</td>
<td>177 -&gt; 129</td>
<td>11.91</td>
</tr>
<tr>
<td>Methamphetamine</td>
<td>170</td>
<td>118</td>
<td>170 -&gt; 126</td>
<td>12.03</td>
</tr>
<tr>
<td>4, 4-dibromoocstafluorobiphenyl</td>
<td>296</td>
<td>227</td>
<td>296 -&gt; 246</td>
<td>13.29</td>
</tr>
</tbody>
</table>
Appendix I

Calibration range, %RSD, and Average Response Factor (SIM- Mode)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linear Range</th>
<th>%RSD</th>
<th>average RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methamphetamine</td>
<td>0.050 – 0.60</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.994</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calibration range, %RSD, and Average Response Factor (MS/MS)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linear Range</th>
<th>%RSD</th>
<th>average RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methamphetamine</td>
<td>0.050 – 0.60</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.861</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Appendix II

**Recovery of Methamphetamine from Glass Plates and Drywall Plates by GC/MS (SIM-Mode)**

<table>
<thead>
<tr>
<th>Surface Material</th>
<th>Replicates</th>
<th>Rinse Solvent</th>
<th>percent</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Plate</td>
<td>7</td>
<td>Methanol</td>
<td>95</td>
<td>12.5</td>
</tr>
<tr>
<td>(0.050 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Plate</td>
<td>7</td>
<td>Methanol</td>
<td>81</td>
<td>16.4</td>
</tr>
<tr>
<td>(0.10 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Plate</td>
<td>7</td>
<td>Methanol</td>
<td>86</td>
<td>16.8</td>
</tr>
<tr>
<td>(0.60 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drywall Plate *(Wet Spike)</td>
<td>7</td>
<td>Methanol</td>
<td>59</td>
<td>12.1</td>
</tr>
<tr>
<td>(0.050 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drywall Plate *(Wet Spike)</td>
<td>7</td>
<td>Methanol</td>
<td>45</td>
<td>10.5</td>
</tr>
<tr>
<td>(0.10 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drywall Plate *(Wet Spike)</td>
<td>7</td>
<td>Methanol</td>
<td>51</td>
<td>4.6</td>
</tr>
<tr>
<td>(0.60 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drywall Plate **(Dry spike)</td>
<td>4</td>
<td>Methanol</td>
<td>74</td>
<td>11.0</td>
</tr>
<tr>
<td>(0.60 µg/wipe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Wet Spike — Spike 0.6 µg methamphetamine directly onto a drywall plate, then wait for it is dried.

**: Dry spike - Spike 0.6µg methamphetamine onto a Teflon sheet and wait for it is dried. After it is dried, face down the Teflon sheet onto a drywall plate and scrub the sheet firmly to transfer methamphetamine to the plate.
Appendix III

The Extraction Recovery of Methamphetamine from Inside Material in Drywall (SIM-Mode)

<table>
<thead>
<tr>
<th>Material</th>
<th>Replicates</th>
<th>Extraction Solvent</th>
<th>percent</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone (0.60 µg/1 g limestone)</td>
<td>3</td>
<td>Desorption solution</td>
<td>90</td>
<td>2.6</td>
</tr>
<tr>
<td>White top paper</td>
<td>3</td>
<td>Desorption solution</td>
<td>94</td>
<td>4.7</td>
</tr>
<tr>
<td>Brown back paper</td>
<td>3</td>
<td>Desorption solution</td>
<td>95</td>
<td>2.9</td>
</tr>
</tbody>
</table>

---

Procedure:

1. Spike 60 µL of 10 ppm of methamphetamine onto three different materials in the drywall.
   a. 1 g of limestone inside the drywall.
   b. 25 cm² of the white front paper of drywall.
   c. 25 cm² of the brown back paper of drywall.

2. Wait for it is dried, then put into 40 ml VOA vial and add 30 ml of desorption solution (0.2 N of sulfuric acid).

3. Follow the procedure in SOP to extract and derivatize samples.

4. Use GC/MS to analyze the recovery of methamphetamine in those different materials.
Appendix IV

The Recovery of Methamphetamine from Fabric by Wet Spike and Dry spike (Wipe Sampling Method)

<table>
<thead>
<tr>
<th>Material</th>
<th>Replicates</th>
<th>Rinse Solvent</th>
<th>percent</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric – Wet Spike</td>
<td>3</td>
<td>Methanol</td>
<td>16.2</td>
<td>16.7</td>
</tr>
<tr>
<td>(0.60 µg/25 cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fabric – Dry spike</td>
<td>3</td>
<td>Methanol</td>
<td>19.6</td>
<td>21.9</td>
</tr>
<tr>
<td>(0.60 µg/25 cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Procedure:

A. Wet Spike:

1. Spike 60 µL of 10 ppm of methamphetamine on the 25 cm² fabric sheet.

2. Wait for it is dried, then wiped fabric sheet by 3” x 3” gauze and put the gauze into a 40 ml VOA vial.

3. Follow the procedure in SOP to extract and derivatize samples.

4. Repeat 3 trials.

5. Use GC/MS to analyze the recovery of methamphetamine.

B. Dry spike:

1. Spike 60 µL of 10 ppm of methamphetamine on the 25 cm² Teflon sheet.

2. Wait for it is dried, then carefully flip Teflon sheet and firmly scratch Teflon sheet on the 25 cm² of fabric sheet to transfer methamphetamine onto the fabric sheet.

3. Use 3” x 3” gauze to wipe the fabric sheet, then put gauze into a 40 ml VOA vial.

4. Follow the procedure in SOP to extract and derivatize samples.

5. Repeat 3 trials.

6. Use GC/MS to analyze the recovery of methamphetamine.
# Appendix V

## The Recovery of Methamphetamine from Fabric by Wet Spike (Extraction Method)

<table>
<thead>
<tr>
<th>Material</th>
<th>Replicates</th>
<th>Extraction Solvent</th>
<th>percent</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric – Wet Spike</td>
<td>3</td>
<td>Desorption solution</td>
<td>90.4</td>
<td>10.7</td>
</tr>
<tr>
<td>(0.60 µg/25 cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Procedure:

1. Spike 60 µL of 10 ppm of methamphetamine on the 25 cm² fabric sheet.
2. Wait for it to be dried, then put it into a 40 ml VOA vial and add 30 ml of desorption solution (0.2 N sulfuric solution).
3. Follow the procedure in SOP to extract and derivatize samples.
4. Repeat 3 trials.
5. Use GC/MS to analyze the recovery of methamphetamine.
GLOSSARY

1. **Internal standard** – The purpose of an internal standard is to provide a reference concentration against which the responses of the target analytes are compared. Mass spectrum allows the use of a stable isotope-labeled analogue as internal standard, in which case the technique is called “Isotope dilution” – mass spectrometry. (see section 12.7)

2. **Surrogate standard** – A surrogate standard is a compound that has properties similar to the target analytes but is not usually exist in an environment sample and should not interfere the identification of the target analytes. A surrogate compound performs a quality control function to measure the method efficiency from the sample matrix.

3. **Instrument monitoring standard** – Dibromooctafluorobiphenyl is a standard useful for monitoring autosampler performance and instrument response.

4. **External standard method** - An external standard method is a direct comparison of the detector response of a pure compound to a sample. To determine the linearity of the method, a standard curve of concentration vs. detector response area is plotted. A straight line is obtained and an unknown concentration of the analyte can be calculated from the plot using response factor or linear regression analysis.