DATA CHEM LABORATORIES, INC.

METHAMPHETAMINE AND ILLICIT DRUGS, PRECURSORS, AND ADULTERANTS ON WIPES BY SOLID PHASE EXTRACTION

NIOSH 9109, ISSUE 1

BACKUP DATA REPORT, ABRIDGED VERSION

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I. INTRODUCTION

In December 2002 DataChem Laboratories (DCL) received a request from NIOSH to develop a method for determining methamphetamine on surfaces using gauze wipes. This method was to be used by NIOSH in a collaborative research project with the National Jewish Medical and Research Center (NJMRC) in a study of the contamination within clandestine drug laboratories and the hazards they present to first responders and occupants. [1] Three methods for analysis of drugs on wipes were subsequently developed. The first method uses a liquid-liquid extraction cleanup procedure and derivatization for analysis by GC-MS. The second method uses solid-phase extraction cleanup with a different kind of derivatization for analysis by GC-MS. The third method uses LC-MS without derivatization and is still in the process of development.

This abridged Backup Data Report presents the evaluation results for the second method, the solid-phase extraction (SPE) cleanup procedure, NIOSH 9109, "Methamphetamine and Illicit Drugs, Precursors, and Adulterants on Wipes by Solid Phase Extraction" [2]. It is an abridged version of the Backup Data Report for NIOSH 9109 [3].

The first method for methamphetamine, precursors, and related illicit drugs was previously developed under the name NIOSH 9106 [4]. It uses liquid-liquid extraction to clean up the acid desorbate from cotton and synthetic gauze wipes. That method, though effective, takes at least two days to prepare large sets of samples (more than 20 samples). It is more labor intensive than the second method that is reported in this Backup Data Report in that it involves

many repeated capping and uncapping operations of test tubes, several tumbling operations, several tedious aspiration operations, multiple nitrogen blow-down operations, and so on.

The second method was inspired by an article in a research journal describing a solid phase extraction cleanup technique for sympathomimectic amines that looked promisingly faster, and used a set of derivatization agents that did not require preheating or removal. The article was authored by Dr. David Crockett. [5] The procedure was adapted to the analysis of wipe samples for methamphetamine for inclusion in the NIOSH Manual of Analytical Methods as NIOSH 9109.

The greatest advantage of NIOSH 9109 is that the Method is less time consuming and labor intensive than NIOSH 9106. First, the twisting on and off of many caps repeatedly is greatly reduced. Second, time consuming tumbling operations are reduced from three operations down to one. Third, evaporation to dryness steps are cut from two to one. Fourth, there is no heating of the derivatives. All of this adds up to a great savings in time and labor.

Both NIOSH 9106 and NIOSH 9109 are identical up through the desorption of the wipe sample media with dilute sulfuric acid desorbate. Thereafter the methods differ in the techniques for sample cleanup and derivatization.

A third method is designated as NIOSH 9111 and uses HPLC-MS as the analytical instrumentation. NIOSH 9111 uses the same wipe sample media and dilute sulfuric acid desorption procedure as NIOSH 9106 and 9109. It differs in that the desorbate solution is analyzed directly by LC-MS without any further sample treatment. It requires an LC-MS with an atmospheric pressure ionization interface.

A comparison of the operations in the three procedures developed for methamphetamine is given in Table 1 below.

TABLE 1. COMPARISON OF THE NIOSH 9106, 9109, AND 9111 PROCEDURES

Method:	NIOSH 9106	NIOSH 9109	NIOSH 9111 (Proposed)
Procedure:	Liquid-liquid Extraction	Solid Phase Extraction	HPLC-MS
Derivatization Reagent(s):	Chlorodifluoroacetic or Pentafluoropropionic anhydride	Mixed silylation-acylation reagent: MSTFA [1] + MBHFBA [2]	None
Desorption Step:	1. Uncap 50-mL sample tube; 2. Add internal standard; 3. Add desorption solution (0.2 N sulfuric acid) 4. Cap 50-mL sample tube; 5. Tumble 50-mL sample tubes; 6. Uncap 50-mL sample tube;	1. Uncap 50-mL sample tube; 2. Add internal standard; 3. Add desorption solution; 4. Add 2 drops mixed indicator; 5. Cap 50-mL sample tube; 6. Tumble 50-mL sample tubes; 7. Uncap 50-mL sample tube;	1. Uncap 50-mL sample tube; 2. Add internal standard; 3. Add desorption solution (0.2 N sulfuric acid) 4. Cap 50-mL sample tube; 5. Tumble 50-mL sample tubes; 6. Uncap 50-mL sample tube;
Cleanup and Extraction Steps:	7. Transfer 10 mL sample to 25-mL cleanup tube; 8. Cap 50-mL sample tube; 9. Add 10 mL hexane to cleanup tube; 10. Cap 25-mL cleanup tube; 11. Tumble sample with hexane; 12. Uncap 25-mL cleanup tube; 13. Aspirate hexane layer; 14. Add 2 drops mixed indicator, 15. 0.5 mL sodium hydroxide, 16. and 10 mL methylene chloride to cleanup tube; 17. Cap 25-mL cleanup tube; 18. Tumble 25-mL cleanup tube; 19. Uncap 25-mL cleanup tube; 20. Aspirate aqueous base layer; 21. Transfer sample to drying columns; 22. Collect eluate in 14-mL collection-derivatization tubes; 23. Rinse columns with 2 mL CH_2Cl_2, combine eluates; 24. Add 100 µL 0.3 N methanolic HCl; 25. Add 5-6 µL crystal violet solution; 26. Evaporate methylene chloride to dryness under nitrogen;	8. Condition SPE columns; 9. Transfer 5 mL sample to SPE columns; 10. Cap 50-mL sample tube; 11. Rinse SPE columns with 2 mL 0.3 N hydrochloric acid; 12. Rinse SPE columns with 2 mL methanol; 13. Pull air through SPE columns to dry; 14. Add 2 mL elution solvent (80:20:2 methylene chloride:IPA:NH_4OH); 15. Collect eluate in 10-mL collection-derivatization tubes; 16. Add 100 µL 0.3 N methanolic HCl; 17. Add 5-6 µL crystal violet solution; 18. Evaporate SPE eluates to dryness under nitrogen;	7. Transfer 2 mL to HPLC autosampler vial.
Derivatization Step:	27. Add 100 µL of chlorodifluoroacetic or pentafluoropropionic anhydride derivatization reagent; 28. Cap 14-mL derivatization tube; 29. Heat derivatization reagent mix; 30. Uncap 14-mL derivatization tube; 31. Evaporate derivatization reagent to dryness; 32. Add 1 mL of reconstitution solvent; 33. Transfer sample to GC vials; 34. Cap 2-mL GC vial and analyze.	19. Add 100 µL of acetonitrile; 20. Add 25 µL of MSTFA; 21. Cap 10-mL derivatization tube; 22. Uncap 10-mL derivatization tube; 23. Add 25 µL of MBHFBA; 24. Cap 10-mL derivatization tube; 25. Vortex gently; 26. Uncap 10-mL derivatization tube; 27. Transfer sample to 300 µL GC vials; 28. Cap 2-mL GC vial and analyze.	8. Cap HPLC autosampler vial and analyze.

(1) MSTFA = N-Methyl-N-trimethylsilyl-trifluoroacetamide
(2) MBHFBA = N-Methyl-N,N-bisheptafluorobutyramide

There are some advantages and disadvantages to each procedure. The liquid-liquid extraction procedure (NIOSH 9106) gives much cleaner chromatograms and makes it much easier to detect non-target drugs for clients who require a drug screen. The solid-phase-extraction procedure is faster and easier to perform than NIOSH 9106 and the mixed derivatization reagent is more effective for compounds containing phenolic groups and multiple hydroxy groups (e.g. morphine, epinephrine, etc.) making NIOSH 9109 potentially applicable to a wider array of drugs, and their metabolites. The third method, NIOSH 9111, is the fastest of all the procedures to perform but is limited to the analysis of methamphetamine, although it attains the same level of sensitivity as the other methods.

II. SCOPE AND OBJECTIVES

A. Introduction

This solid phase extraction (SPE) technique for methamphetamine was developed in accordance with the principles set forth in the NIOSH publication "Guidelines for Air Sampling and Analytical Method Development and Evaluation" [6] and was evaluated as to whether it would meet the accuracy criterion requirement given therein, which is that with a 95% confidence a result will be within ±25% of the true value. Since the method was for surface wipe sampling and not air sampling, the procedures set forth in the guidelines had to be modified. No simulated vapor and aerosol sampling recovery study was performed. The precision and accuracies for NIOSH 9110 were therefore calculated from a desportion efficiency study and do not include sampling error.

However, a limited surface recovery study is reported. Several surfaces and wipe methods were tested. Recovery rates vary greatly by surface material wiped, especially between porous rough surfaces compared to smooth non-porous surfaces and by wipe procedure. The sampling recovery data were not used to compute measurement bias, overall precision and overall accuracy for the method for three reasons. First, surface recoveries vary greatly by surface material and only 6 surfaces were tested. Second, test surfaces were liquid spiked just prior to sampling and the sampling surface recovery test did not replicate recoveries of drug vapors and dusts deposited on surfaces for an extended period of time. Third, surface recovery is dependent upon the wsip procedure used and a comprehensive test of wipe prcedures used or specified by various legal jurisdictions was not undertaken.

Much of the method development and evaluation, including the desorption procedure and the long-term storage stability study, was accomplished in the development of the first method, NIOSH 9106, and is reported in the Backup Data Report for that method. [7]. It was not necessary to repeat these studies for the second method since they pertain to the media itself and not to the particular cleanup or derivatization procedures used.

The studies uniquely necessary for NIOSH 9109 were as follows:

1. Adaption of Solid Phase Extraction (SPE) cleanup and derivatization procedures to wipe sample desorbates.
2. Estimation of limit of detection (LODs) and quantitation (LOQs) for NIOSH 9110.
3. Calculation overall precision and accuracy for NIOSH 9110.
4. Determination of drug recoveries from various spiked surfaces.

B. Wipe Media

The same wipe media and desorbate solutions evaluated for NIOSH 9106 were evaluated for NIOSH 9110 since there was enough desorbate solution left for this second method. The media tested were cotton gauze, MIRASORB™, NU GAUZE™, TOPPER™, and AlphaWipe™. The three synthetic or engineered gauzes (MIRASORB™, NU GAUZE™, TOPPER™), all products of Johnson & Johnson, were discontinued recently (after the evaluations had been completed). Although equivalent products from other manufacturers still exist, only the results for cotton gauze are reported in this abbreviated report.

C. Target Analytes

The same analytes were tested as in NIOSH 9106, because they had already been spiked on the wipe media for NIOSH 9106 and sufficient desorbate solution remained to provide aliquots for evaluation by the second method. These analytes included methamphetamine, (and its common precursors, ephedrine and pseudoephedrine), amphetamine (and its precursor, phenylpropanol-amine), caffeine and phentermine (adulterants), MDMA, MDEA (an MDMA designer alternate), phencyclidine, and cocaine. Cocaine was also included with the mixture of analytes evaluated for NIOSH 9106 but it was not a viable analyte because it appears to hydrolyze significantly to methyl ecgonine at some stage in the NIOSH 9106 procedure. It is, however, reported as a viable analyte in NIOSH 9109. The use of a deuterated analog of cocaine as an internal standard might have made the determination of cocaine possible in NIOSH 9106. PCP was included because it is a drug of clandestine manufacture that is seeing a resurgence. [8]

Other drugs that were included in the spiking solution for both methods included several opiates: morphine, codeine, and hydrocodone but recoveries were variable. All three opiates were detectable with better peak shapes than in NIOSH 9106. This is probably due to the better stability of trimethylsilyl ethers of the phenolic groups and the crowded alcoholic groups.

However, results were still not good enough for reporting. It is highly probable that if deuterated analogs of the opiates were used for internal standards, this method could be applicable to them as well.

Caffeine had poor chromatographic peak shape by the second (SPE) method and is therefore not reported.

D. Internal Standards

The same internal standards that were used in NIOSH 9106 are used in this method. These included the more highly deuterated compounds, amphetamine-D_{11} and methamphetamine-D_{14} and the sterically hindered N-propylamphetamine for the sterically hindered MDEA. N-Propylamphetamine was found to be essential in both methods for determining MDEA, a similarly hindered amine. A deuterated analog of MDEA would probably have been just as acceptable. Two non-deuterated internal standards were also tested, one a primary amine (4-phenyl-butylamine) and the other an N-methyl secondary amine (N-methyl phenethylamine). 4-Phenyl-butylamine was only good for the ephedrine type compounds and results are not presented. N-Methyl phenethylamine was approximately as good as methamphetamine-D_{14} and results are presented only for the LOD study but not the precision and accuracy study in order to keep this backup data report as concise as possible.

III. METHOD DEVELOPMENT

A. Introduction

The steps in the development of NIOSH 9109 are discussed in the unabridged Backup Data Report for NIOSH 9109. [3] This abridged version will only give a synopsis of the steps that are unique to the solid phase extraction (SPE) and derivatization procedures. The details of the complete procedure are given in the method, NIOSH 9109. [2]

B. Synopsis of the Solid Phase Extraction and Derivatization Steps

Unique to NIOSH 9109 is the use of SPE columns. The target analytes and co-extracted contaminants are separated using SPE columns. The SPE column that was used in Dr. Crocket's method was Clean Screen™ [5]. In order to not be limited to just one product, it was decided that several other brands should be tested to see whether success was limited to this brand, and to see if this critical piece of equipment could be substituted. This was to avoid the possibility that a corporate decision to discontinue this product (as happened with the Johnson & Johnson synthetic gauze media) could sabotage the method. Accordingly three other brands were selected in addition to Clean Screen™. The four columns tested were as follows:

a. Waters Oasis™ MCX 3cc (60mg), from Waters Corp, Milford, Massachusetts.

b. Clean Screen™ #CSDAU303, 300mg/3mL from United Chemical Technologies, Inc. Bristol, PA.

c. Speedisk™ H2O-Philic SC-DVB, from J.T.Baker, Phillipsburg, NJ.

d. BOND ELUT-CERTIFY™, 200mg/3mL from Varian Inc, Harbor City, CA.

These products included at least two types of mixed-phase cation exchange SPE columns. One type was based on a silica support (Clean Screen™ and BOND ELUT-CERTIFY™). The other type was based upon an organic polymer (Waters Oasis™ MCX and Speedisk™ H2O-Philic SC-DVB). The bed of the Speedisk™ was very thin, essentially a disc. The silica based columns had a higher resistance to flow, requiring higher vacuums to initiate flow. While "one column volume" (3 mL) was the usual volume for loading, rinsing, and elution for the silica based columns, the organic based supports could get by with smaller rinse and elution volumes: 2 mL for Waters Oasis™ MCX and 1 mL for the Speedisk™. The Speedisk™ also had very

little resistance to flow, and at one point during elution it flowed under gravity alone. Only the Waters Oasis™ MCX column was used for the full evaluation steps (precision and accuracy studies). This was partly because Waters Corporation is a major player in the analytical chemistry industry and probably a reliable supplier of this SPE column for a long time. The decision was also made to use the Waters Oasis™ MCX column because Waters' product literature (at the time at least) was very detailed and descriptive and gave much helpful advice; it helped develop confidence in the product. The easy re-wetting ability of an organic matrix was another deciding factor.

All brands are described as mixed phase columns, having some hydrophilic adsorption capacity as well as cation exchange ability. The hydrophilic nature of the columns gives them the ability to adsorb organic cations better with higher capacity. Only the results with the Waters Oasis columns are given in this report.

A synopsis of the steps involved with the SPE columns is given below.

1. SPE Column Loading Step: Methamphetamine and related amines are extracted from the aqueous acid using the cation exchange SPE columns. Five milliliters of the aqueous acid desorbate was transferred to the SPE columns. Even though the loading capacity of the columns was listed as 3 mL, 5 mL was easily accommodated by all columns. The maximum amount of sample that could be applied to the columns was not investigated.

In all cases care was maintained to keep flow rates reasonably slow (around 1 mL or less per minute) by adjusting the vacuum in the vacuum manifold box.

Enough desorbate remains in the 50-mL polypropylene centrifuge tubes to allow a second extraction if one is needed, such as for duplicate samples, lost samples, or samples that needed to

be diluted and re-extracted. The target analytes in the acidic desorption solution were found to be stable for at least a week under refrigeration, with the possible exception of cocaine.

2. Rinse (Cleanup) Step: As cations, amphetamines and related amines are adsorbed from acidic aqueous solution by the cation-exchange SPE columns. Because the SPE columns also had some hydrophobic character, they have the capacity to adsorb many other non-cationic and neutral organic compounds from aqueous solution. As such the SPE columns are referred to as "mixed-phase" SPE columns. The non-cationic compounds are washed off the column with one column volume of 0.3 N aqueous hydrochloric acid and then one column volume of methanol. The methanol also removes the last traces of water from the column. The methanol is added in portions in order to make sure the water is fully purged.

It was found that the SPE columns were effective at eliminating the non-ionic detergents that were found in certain synthetic gauze wipes (i.e. J&J TOPPER™), making TOPPER™ an acceptable medium for wiping in NIOSH 9109 (a moot point since it has been discontinued). In contrast, the detergents could not be removed in the cleanup procedure of NIOSH 9106 and affected the derivatization so badly that TOPPER™ was entirely unacceptable as a medium for NIOSH 9106. Another brand still available, Kendall's Curity™ Sponges, is apparently identical in construction to TOPPER™ and has the same problems when used in the liquid-liquid extraction cleanup procedure of NIOSH 9106.

3. On-Column Drying Step: After rinsing the SPE columns with aqueous hydrochloric acid and methanol, air is pulled through the columns for 15 minutes to dry them. Some types of SPE columns should not be completely air dried because they are difficult to re-wet again. Whether the two brands of silica based columns were among those was not known because of a lack of product information. However, the columns with silica based supports had high

resistance to air flow and did not dry completely in any case. Claims were made in product literature that the organic based columns did not need preconditioning or rewetting after drying and may be thoroughly air dried prior to addition of the elution solvent because re-wetting by organic solvent was facilitated by the organic nature of the support.

This on-column air drying replaces the necessity of having to dry the extracts by passing them through a drying column packed with drying salts.

4. Elution Step: Following the SPE loading, cleanup, and air drying steps, collection tubes (9 to 10-mL 13 mm × 100 mm glass test tubes) were positioned inside the vacuum manifold under each column and the analytes were eluted with 3 mL of a mixture of methylene chloride, isopropanol, and ammonium hydroxide in an 80:20:2 volumetric ratio. This mixture, or nearly identical mixtures, was quite universal in the literature for mixed-phase cationic SPE extraction columns. Some column manufactures or journal articles listed the formula either as 78:20:2 or as 2 mL of ammonium hydroxide added per 100 mL of 20% isopropanol in methylene chloride. These are approximately the same ratios. This solution de-protonates the amine and allows them to be desorbed as the free base into the eluent, methylene chloride and isopropanol.

5. Acid Keeper: After elution, 100µL of 0.3 N hydrochloric acid in methanol was added to the SPE column eluate in the collection tubes as a keeper in order to convert the amines to the salt form upon evaporation of the solvent. This is not enough acid to neutralize all of the ammonium hydroxide, but it appears that there is enough chloride ion to convert the target analytes to their non-volatile chloride salts as the excess ammonium hydroxide is evaporated. The target analytes are apparently protonated by the ammonium ion as it converts to ammonia in the evaporation process. The excess chloride ion remains as ammonium chloride. This residue of ammonium chloride does not hinder the derivatization reagent, and in fact actually helps

moderate the MSTFA, which in the absence of the ammonium chloride causes serious over-silylation of the primary amines, an annoying and significant side reaction otherwise. [9]

6. Crystal Violet Visualization Reagent: As with NIOSH 9106, 5-6 µL of crystal violet in isopropanol (about 2-3 mg/mL) was added to the SPE column eluate to aid in visualization of the dried residue. The crystal violet is not critical to the success of the method, but it is a very convenient tool for visualizing the dried residue. It is not affected by nor does it interfere with either the derivatization or chromatography of the analytes. Unlike in NIOSH 9106, the crystal violet does not go through a series of color changes but remains blue to blue-violet throughout the drying process whether in solution or as a dried residue. A color change does develop if water gets into the in the reconstituted samples after derivatization reagent is added, such as if the caps on the GC vials are not tight, or the vials are not re-capped after analysis. The color changes from deep blue or blue-violet to a pale blue or turquoise. If water gets into the samples, the derivatives are apparently broken down or do not form properly upon injection into the GC. This is a convenient indicator of when the samples have expired. As long as the deep blue to purple color remained, the samples could be successfully reanalyzed. The vials must be promptly recapped after analysis.

7. Nitrogen Evaporation: The SPE column eluates were evaporated to dryness under a stream of nitrogen while the tubes were held in a water bath. The temperature of the water bath was kept between 30 and 40 °Celsius. The vigor at which nitrogen was blown into the tubes using 16 gauge needles was such that the surface of the solvent was rippled but no splashing occurred. No losses of analyte have been observed for a few minutes past the point of dryness as long as the hydrochloric acid keeper solution had been added prior to evaporation.

8. Adding Derivatization Reagents and Acetonitrile Diluent: The dried residue was dissolved with the addition of 100 µL acetonitrile (with or without a secondary internal standard). This was followed by the addition of 25 µL of MSTFA followed by 25 µL of MBHFBA. The tubes were kept capped between additions of solvent and reagents to prevent adsorption of atmospheric moisture. No more than 5-6 tubes were opened at a time; usually just one was opened at a time. The relative humidity of the laboratory in which these studies were made usually varied between 20-40% at 24 °C.

9. Secondary Internal Standard: An optional secondary internal standard, 4,4'-dibromooctafluoro-biphenyl (DBOFB), was included in the acetonitrile reconstitution solvent. It is totally unaffected by the derivatizing agent. It can be used to monitor the proper functioning of the autosampler, and can be used to check on proper tuning of the mass spectrometer throughout the analytical set. Degradation of the tuning can be signaled by a gradual shift in the relative abundance of m/z 456 to m/z 296 or a shift in the mass axes of either ion.

C. Derivatization Reagent

The mixed silylation-acylation reagents MSTFA and MBHFBA had several advantages and disadvantages. The principle advantage was that perfluorinated acid anhydride derivatization reagents did not work well with the dried residues from the SPE columns, presumably because of the unavoidable presence of the ammonium chloride residues. The second advantage was that derivatization begins to take place at room temperature and is finished with the on-column injection. No separate heating in an oven, drying, and reconstitution were required or recommended. The third advantage was that more stable derivatives of phenolic groups were afforded, making it possible to analyze a wider variety of compounds.

The major disadvantage of the reagent was the noisy background of the chromatograms due to many breakdown compounds of the reagents. The background noise did not interfere with the quantification of the target analytes, but only made it difficult to observe the potential presence of non-target analytes. Another disadvantage of the reagent was the production of multiple derivatives of the several types of analytes. One of the alternate derivatives was due to oversilylation of the primary amines. [9] Oversilylation appeared to be suppressed by the presence of residual ammonium chloride and the oversilylation artifacts did not seriously diminish the peak area of the major derivative product. A second type of artifact was the formation of trifluoroacetyl derivatives of secondary amines, an unintended side reaction of MSTFA. The relative abundance of these was quite low and did not interfere with the abundance of or the ability to quantify the primary heptafluorobutyryl derivatives.

D. Using Internal Standards

A fortuitous decision had already been made to use internal standards. By adding them to the samples prior to desorption, the small differential residual volumes of wetting solvent (isopropanol or methanol) could be compensated for. A discussion of the process of selecting the internal standards is given in the Backup Data Report for NIOSH 9106. [9]

Only four of the internal standards studied for NIOSH 9106 were used for the evaluation of sample stability and precision and accuracy of NIOSH 9109. These were amphetamine-D_{11}, methamphetamine-D_{14}, N-propylamphetamine, and N-methylphenethylamine. Only results for the first three are reported in this abridged report.

Several observations were made about internal standards in the precision and accuracy study for this method.

1. Location of Deuterium Labeling: The more highly substituted the side chain is, the better the mass separation between the quantification ions for the target analyte and the internal standard. If only the ring is substituted, the quantification ions for both the analyte and internal standard are the same and independent quantification of either can be impossible, unless another, usually a less abundant and rather non-ubiquitous ion (not subject to co-eluting interference), is used. Ring-labeled only internal standards are not recommended. Deuterium labeling must be included in the side chain containing the nitrogen being derivatized.

2. Level of Deuterium Labeling: The more highly substituted the entire molecule is, the earlier it elutes with respect to the parent compound, which makes integration of the internal standard and parent compound easier in the presence of each other, especially where there is a potential common ion between the two.

3. Purity of Deuterium Labeling: The contamination of the deuterated analog with parent compound must not exceed 1% in order to achieve a detection limit of 0.05 µg/sample.

4. Steric Hindrance: Hindered amines (e.g., MDEA and N-propylamphetamine) derivatized much more completely with the NIOSH 9109 procedure than in NIOSH 9106. Yet there was still some steric hindrance affect. Thus an internal standard that is a hindered amine (e.g., N-propylamphetamine or a labeled MDEA) was still needed for MDEA to pass the NIOSH precision and accuracy criteria.

IV. GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC CONDITIONS

The gas chromatographic and mass spectrometer operating conditions are given in NIOSH 9109 and are summarized in Table 2.

TABLE 2. RECOMMENDED GC-MS CONDITIONS (SCAN MODE)

Column Parameters:	
Stationary phase	DB-5ms, 0.5 µm film thickness
Dimension	30 meters long × 0.32 mm i.d fused silica capillary
Oven Temperatures:	
Initial temperature	90 °C
Initial temperature hold time	2 minutes
Temperature ramp	10 °C/minute
Final temperature	310 °C
Final temperature hold time	11 minutes
Transfer line temperature	285 °C
Injection Port Conditions:	
Carrier Gas	Helium
Head Pressure	About 5-10 psi in constant pressure mode or 2-3 psi at 90 °C in constant flow mode. (1)
Injection mode	Splitless for 0.8 to 1 minute
Injection Volume	2 µL
Temperature	255 °C
Tuning Criteria:	Using perfluorotributylamine (1) m/z 69, 100% m/z 119, 40-50% m/z 502, 2-4%
Scan Delay:	4 Minutes
Scan Range:	29-470 AMU (other ranges are acceptable, e.g. 45-500 AMU)
Scan Rate:	About 2 scans per second
Quantification	Quantify on extracted ion chromatogram (EIC) rather than total ion chromatogram (TIC) using primary ions (m/z) recommended in Table 3. (2)

(1) With the above tuning criteria, the relative abundance of m/z 456 of the secondary internal standard, 4,4'-dibromooctafluorobiphenyl, were in the range of 80-120% of m/z 296.

(2) 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. EIC have better signal to noise ratios and less interference than TIC.

The limits of detection and precision and accuracy were determined for this backup data report using the scan mode. SIM mode conditions can be used as well. SIM mode conditions are given in NIOSH 9109. Briefly, in the SIM mode not more than 10 ions (m/z) were monitored at any given time. Dwell times for up to five ions (m/z) did not exceed 100 milliseconds. Dwell times for 5 to 10 ions (m/z) did not exceed 50 milliseconds. Ions (m/z) for quantitation in

extracted ion current profiles (scan mode) or for data acquisition (SIM mode) are given in Table 3.

TABLE 3. QUANTITATION IONS FOR SCAN MODE (ACQUISITION IONS FOR SIM MODE)

Heptafluorobutyryl-trimethylsilyl- and Heptafluorobutyryl- Derivatives [1]	Quantitation (Acquisition) Ions [2]		
Target Analytes and Internal Standards:	Retention Time [3] (minutes)	Primary Ion (m/z) [4] (Quantification Ion)	Secondary Ion and Approx. Relative Abundance [5] (Relative to the Primary Ion)
Amphetamine-D_{11} (I$)	8.46	**244**	128 70%
Amphetamine	8.54	**240**	118 70%
Phentermine	8.72	**254**	132 12%
N-Methyl phenethylamine (I$)	8.54	**240**	104 100%
Methamphetamine-D_{14} (I$)	9.86	**261**	213 30%
Methamphetamine	9.94	**254**	210 35%
Phenylpropanolamine	10.49	**179**	240 18%
N-Propylamphetamine (I$)	11.05	**282**	240 85%
Ephedrine	11.40	**179**	254 17%
Pseudoephedrine	11.68	**179**	254 15%
Dibromooctafluorobiphenyl [6]	12.82	**296**	456 100%
MDMA	13.81	**254**	162 80%
MDEA	14.19	**268**	162 60%
Phencyclidine	15.62	**200**	242 35%
Cocaine	18.65	**182**	82 110%

(1) Derivatives from the mixed reagent: MSTFA + MBHFBA.
(2) Ions used in scan mode (quantification) and SIM mode (acquisition and quantification).
(3) Example retention times are dependant upon GC column and instrument conditions.
(4) The suggested primary ions are not necessarily the base peaks in the mass spectra of the analytes.
(5) Secondary ions 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.
(6) Dibromooctafluorobiphenyl is an optional secondary internal standard useful for monitoring autosampler performance and instrument tuning.

V. LIMIT OF DETECTION

A. Introduction and Objective

The concentration levels for the limits of detection (LOD) and quantitation (LOQ) for the Long-term Storage Stability Study and the Precision and Accuracy were already determined in NIOSH 9106. Although previously determined, the values were determined again for NIOSH

9109 from the same liquid calibration standards that were used for the precision and accuracy evaluations in both NIOSH 9106 and NIOSH 9109.

There are no national health-based or feasibility-based surface contamination standards, criteria or guidelines for clandestine drug laboratory decontamination. However, several states have feasibility-based surface contamination limits. The most common limit is 0.1 µg of methamphetamine for a sample of 100 square centimeters of surface area wiped. Some jurisdictions require 1 square foot (929 cm^2) to be wiped. In either case, the most common required sensitivity is 0.1 µg per sample for methamphetamine. In addition, state surface contamination standards for other drugs (ephedrine, pseudoepedrine, and Ecstasy (MDMA)) are also 0.1 µg per 100 square centimeters of surface area wiped or 0.1 µg per sample.[10]

TABLE 4. STATE MAXIMUM SURFACE CONTAMINATION LIMITS

There are no national health-based or feasibility-based surface contamination standards, criteria or guidelines for clandestine drug laboratory decontamination. However, several states have feasibility-based surface contamination limits.

State Surface Contamination Limit[10]*		Methamphetamine	Ephedrine	Pseudoepedrine	Ecstasy (MDMA)
0.5µ/100 cm^2		Colorado			
1.0µ/ft^2	(Equivalent to 0.11 µ/100 cm^2)	Minnesota			
0.1µ/100 cm^2		Alaska Arizona Arkansas California Idaho Montana North Carolina Tennessee Utah Washington	Arizona Utah	Arizona Utah	Arizona Utah
0.5 µ/ft^2	(Equivalent to 0.05 µ/100 cm^2)	Oregon			

* State surface contamination limits are provided as an aid to those seeking additional information. NIOSH has not established health-based or feasibility-based airborne Recommended Exposure Limits (RELs) or surface contamination guidelines for clandestine drug laboratories and therefore inclusion of state surface contamination limits does not constitute endorsement by NIOSH. The National Alliance for Model State Drug Laws (NAMSDL) (http://www.natlalliance.org/) periodically summarizes state feasibility-based decontamination limits and proposed state legislative requirements and guidelines. However, state requirements and guidelines are subject to change and therefore the most recent state guidance should be obtained from directly from the state.

The LOD and LOQ were determined by a modification of NIOSH SOP 018 [11] as described by Burkart [12]. The calibration curve was set up using duplicate spiked and extracted liquid standards for each concentration level and not duplicate injections for the same standards.

The method uses liquid standards rather than media standards. For media other than cotton gauze (or other acceptable media as mentioned in the unabridged Backup Data Report for NIOSH 9109) media standards are recommended.

B. Reagents and Supplies

Although the spiking solutions and procedures were previously described in the Backup Data Report for NIOSH 9106, they are repeated here for convenience.

a. Mixed analyte spiking solution (See Table 5.);

TABLE 5. MIXED ANALYTE SPIKING SOLUTION (1)

	Analyte	Source	Lot Number	Calculated Concentration as Free Base in µg/mL
1	D-Amphetamine HCl	Alltech	413	50.00322
2	L-Ephedrine HCl	Alltech	1505	50.29991
3	MDEA HCl	Alltech	3506	47.63766
4	MDMA HCl	Alltech	6852	45.28192
5	D-Methamphetamine HCl	Alltech	389	50.03214
6	Phencyclidine HCl	Alltech	1293-33	50.07406
7	Phentermine HCl	Sigma	105F-0129	50.34771
8	(±)-Phenylpropanolamine HCl	Sigma	91F-0298	50.40394
9	Pseudoephedrine HCl	Sigma	32K-1358	50.28431
10	Cocaine	Alltech	1800	50.17747

(1) The mixture was made up in methanol, HPLC grade, B&J lot CB331.

b. Internal standard spiking solution (See Table 6.);

TABLE 6. INTERNAL STANDARD SPIKING SOLUTION (1)

	Analyte	Source	Lot Number	Calculated Concentration as Free Base in µg/mL
1	(±)-Amphetamine-D_{11}, HCl	Cerilliant	35129-58A	50.00
2	N-Propyl amphetamine	Alltech	1604	83.099
3	N-Methylphenethylamine	Aldrich	002309 HI	200.784
4	(±)-Methamphetamine-D_{14},HCl	Cerilliant	30902-25G	100.00

(1) The mixture was made up in methanol. About 2 µL of powdered crystal violet was added to about 10 mL of the spiking solution to act as a visual reminder of which samples were spiked.

C. Spiking Schedule and Derivatization Procedure

Liquid standards were prepared in duplicate as follows. Three milliliters of isopropanol were added to empty 50-mL polypropylene centrifuge tubes. The isopropanol was spiked with analyte spiking solution according to the following schedule.

TABLE 7. SPIKING SCHEDULE FOR CALIBRATION STANDARDS USED IN THE LOD/LOQ AND PRECISION AND ACCURACY STUDIES

		Amount Applied per Concentration Level in Microliters						
Media	IPA mL	µL of analyte spiking solution applied			µL of 1/10 dilution of analyte spiking solution applied			
		300× LOQ Level	100× LOQ Level	30× LOQ Level	10× LOQ Level	3× LOQ Level	1× LOQ Level	0.5× LOQ Level
None (liquid standards only)	3	600	200	60	200	60	20	10

After the addition of the analyte spiking solution, 50 µL of internal standard spiking solution was added to each tube. After spiking, 40 mL of desorption solution (0.2 N aqueous sulfuric acid) was added to each tube. The resulting sample concentrations after spiking are given in the following table.

TABLE 8. CONCENTRATION OF ANALYTES AT EACH CONCENTRATION LEVEL

	Analyte	Calculated Concentration in µg/sample [1]						
		300× LOQ Level	100× LOQ Level	30× LOQ Level	10× LOQ Level	3× LOQ Level	1× LOQ Level	0.5× LOQ Level
1	D-Amphetamine	30.00193	10.00064	3.00019	1.00006	0.30002	0.10001	0.0500
2	L-Ephedrine	30.17995	10.05998	3.01799	1.00600	0.30180	0.10060	0.05030
3	MDEA	28.58259	9.52753	2.85826	0.95275	0.28583	0.09528	0.04764
4	MDMA	27.16915	9.05638	2.71692	0.90564	0.27169	0.09056	0.04528
5	D-Methamphetamine	30.01928	10.00643	3.00193	1.00064	0.30019	0.10006	0.05003
6	Phencyclidine	30.04444	10.01481	3.00444	1.00148	0.30044	0.10015	0.05008
7	Phentermine	30.20862	10.06954	3.02086	1.00695	0.30209	0.10070	0.05035
8	Phenylpropanolamine	30.24236	10.08079	3.02424	1.00808	0.30242	0.10081	0.05040
9	Pseudoephedrine	30.17059	10.05686	3.01706	1.00569	0.30171	0.10057	0.05028
10	Cocaine	30.25642	10.08547	3.02564	1.00855	0.302564	0.10086	0.05043

(1) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors.

The tubes were capped securely and tumbled for 2-3 hours (along with the cotton and synthetic media samples for the precision and accuracy evaluation study). After tumbling 5 mL of the desorbates were extracted using the SPE procedure and derivatized according to the method as described in an earlier section. The samples were analyzed by GC-MS in the scan mode (see NIOSH 9109 for details of procedure) with separate concentration levels analyzed on separate days due to the size of the precision and accuracy study.

D. Results

The LOD and LOQ for each analyte, normalized against each applicable internal standard are summarized in the table below. The 300× LOQ standards were not used in the calculations.

TABLE 9. LIMITS OF DETECTION USING DUPLICATE LIQUID STANDARDS, EACH CONCENTRATION LEVEL ANALYZED ON SEPARATE DAYS [1]

	Analyte	LOD in µg/sample [2]					
		Internal Standard [3]					
		D_{11}-Amp	D_{14}-Meth	D_{14}-Meth [4]	N-MPEA	N-PAmph	N-PAmp [4]
1	D-Amphetamine	**0.1100**	**0.1440**	**0.1157**	**0.1383**	---	---
2	Cocaine	0.6092	0.3503	0.7269	0.3581	---	---
3	L-Ephedrine	0.1835	**0.0854 ***	**0.0738 ***	**0.0962**	---	---
4	MDEA	---	---	---	---	**0.1009**	**0.1311**
5	MDMA	**0.1117**	**0.1012**	**0.1125**	**0.1065**	---	---
6	D-Methamphetamine	0.1943	**0.1195**	**0.0950 ***	**0.1468**	---	---
7	Phencyclidine	0.6265	0.3926	0.3258	0.3972	---	---
8	Phentermine	0.1925	**0.1026**	**0.0975 ***	**0.1462**	---	---
9	Phenylpropanolamine	**0.1090**	**0.1343**	0.1750	**0.1247**	---	---
10	Pseudoephedrine	0.1630	**0.1311**	**0.1262**	**0.1135**	---	---

Bold values are LODs that round to 0.1 µg/sample (100 cm^2).

* Lowest standard was about 0.1 µg/sample.

(1) LOD calculated using the procedure of Burkart [12].

(2) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors.

(3) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

(4) From calibration curve (for quantifying AlphaWipe™).

TABLE 10. LIMITS OF QUANTITATION USING DUPLICATE LIQUID STANDARDS, EACH CONCENTRATION LEVEL ANALYZED ON SEPARATE DAYS [1]

	Analyte	LOQ in µg/sample [2]					
		Internal Standard [3]					
		D_{11}-Amp	D_{14}-Meth	D_{14}-Meth [4]	N-MPEA	N-PAmp	N-PAmp [4]
1	D-Amphetamine	0.3663	0.4819	0.3869	0.4626	---	---
2	Cocaine	1.8356	1.1196	2.2530	1.1429	---	---
3	L-Ephedrine	0.6107	0.2854	0.2463	0.3211	---	---
4	MDEA	---	---	---	---	0.3353	0.4356
5	MDMA	0.3679	0.3356	0.3734	0.3526	---	---
6	D-Methamphetamine	0.6417	0.3980	0.3164	0.4884	---	---
7	Phencyclidine	2.0005	1.2954	1.0768	1.3090	---	---
8	Phentermine	0.6374	0.3420	0.3248	0.4870	---	---
9	Phenylpropanolamine	0.3625	0.4487	0.5846	0.4163	---	---
10	Pseudoephedrine	0.5443	0.4397	0.4232	0.3799	---	---

(1) LOQ calculated using the procedure of Burkart [12].

(2) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors.

(3) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

(4) From calibration curve (for quantifying AlphaWipe™).

E. Observations and Discussion

The LOD and LOQ values presented in Tables 9 and 10 above are conservatively high. There are several reasons for this. One reason is because the 0.05 µg/sample level unintentionally was not analyzed. In general when lower calibration standards are included, lower LODs are achievable.

A second reason is that these liquid standards were not analyzed on the same day. These were the liquid standards used in the precision and accuracy study and there were so many samples that each different concentration level ended up being analyzed on a separate day. It took almost two days for each separate concentration level to be analyzed (there were six replicates for each of the six media plus media blanks and the calibration standards for each concentration level). The lowest two concentration levels were reanalyzed four and six weeks later due to a need to clean the mass spectrometer source and only the values from the reanalysis were used. It is impressive, however, that standards analyzed over a period of several days and weeks still fit well to a quadratic function with an r-squared of greater than 0.995 (in all but 6 cases). The r-squared values are presented in Table 11.

TABLE 11. R-SQUARED FOR QUADRATIC CURVES USING DUPLICATE LIQUID STANDARDS, EACH LEVEL ANALYZED ON SEPARATE DAYS

	Analyte	r-Squared (1)					
		Internal Standard (2)					
		D_{11}-Amp	D_{14}-Meth	D_{14}-Meth (3)	N-MPEA	N-PAmp	N-PAmp (3)
1	D-Amphetamine	0.9989	0.9987	0.9956	0.9981	---	---
2	Cocaine	**0.9908** (4)	**0.9906** (4)	0.9979 (4)	0.9961 (4)	---	---
3	L-Ephedrine	0.9980	0.9989	0.9976	0.9993	---	---
4	MDEA	---	---	---	---	0.9981	0.9986
5	MDMA	0.9956	0.9966	0.9987	0.9992	---	---
6	D-Methamphetamine	0.9974	0.9988	0.9997	0.9989	---	---
7	Phencyclidine	0.9963 (4)	0.9961 (4)	0.9986 (4)	0.9983 (4)	---	---
8	Phentermine	0.9961	0.9970	0.9983	0.9991	---	---
9	Phenylpropanolamine	**0.9941**	**0.9937**	0.9963	0.9978	---	---
10	Pseudoephedrine	0.9954	**0.9940**	**0.9948**	0.9963	---	---

Bold numbers are r-squared values less than 0.9950.

(1) For a 5 point quadratic standard curve from 0.1 through 10 µg/sample.

(2) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

(3) From a separate calibration curve (for quantifying AlphaWipe™).

(4) For a 4 point standard curve from 0.3 through 10 µg/sample.

The r-squared values are much better when all standards are analyzed on the same day. This is demonstrated, for example, for a typical set of field samples analyzed in the scan mode where all the r-squared values were 0.9996 through 0.9999. The LODs and LOQs for this typical analysis are tabulated below along with r-squared values. The range of this calibration curve was from about 0.05 to 60 µg/sample. Only five analytes were analyzed in this sample set. Only two internal standards were used. All of the LODs for the equivalent analytes were approximately equal to or lower than those in Table 9.

TABLE 12. LIMITS OF DETECTION, QUANTITATION, AND R-SQUARED VALUES FOR A TYPICAL ANALYSIS, ALL LEVELS ANALYZED ON THE SAME DAY [1]

	Analyte	Int. Std: D_{11}-Amphetamine			Int. Std: D_{14}-Methamphetamine		
		LOD [2] µg/sample	LOQ [2] µg/sample	r-Squared	LOD [2] µg/sample	LOQ [2] µg/sample	r-Squared
1	D-Amphetamine	0.0960	0.3198	0.9999	**0.0365** [3]	0.1217	0.9998
2	L-Ephedrine	0.1624	0.5409	0.9999	0.0979	0.3264	0.9999
3	D-Methamphetamine	**0.0680**	0.2265	0.9999	**0.0278** [3]	0.0927	0.9996
4	Phenylpropanolamine	**0.0502**	0.1675	0.9999	**0.0210** [3]	0.0699	0.9998
5	Pseudoephedrine	0.1976	0.6577	0.9999	0.1295	0.4312	0.9999

Bold values are those where the LOD is much better (lower) than for the multiple day analyses (Compare with LODs in Table 9).
(1) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors. .
(2) LOD and LOQ calculated using the procedure of Burkart [12]
(3) Lowest standard was about 0.05 µg/sample, so values should be raised to 0.05 µg/sample.

The above data show that the LODs are equivalent to or better when the calibration standards are analyzed on a single day. Thus, the LODs determined from calibration standards analyzed on sequential days are conservative estimates. This data should be sufficient to verify that for methamphetamine, at least, an LOD of 0.1 µg/sample is easily obtainable and that lower levels can be obtained if lower calibration standards are analyzed.

Lower LODs are also usually achievable using a SIM mode operation of the mass spectrometer.

F. Method Detection Limit

In spite of the problems associated with the use of method detection limits (MDLs) [13], Washington State has required laboratories applying for certification to perform a method detection limit (MDL) study for methamphetamine in the manner that EPA uses for environmental samples [14]. In an MDL study only one concentration level is selected at about three times the expected limit for detectability [15]. The MDL is calculated by multiplying the standard deviation of seven replicates times the Students t value at the 99% confidence interval for the number of replicates analyzed.

In order to show that the method can satisfy such a requirement, even though MDLs are not required by NIOSH methods, MDLs were calculated. According to 40 CFR Ch.1 Part 136, Appendix B, a minimum of seven replicates is to be used for MDL calculations. [15] Media standards were not prepared. However, in the precision and accuracy study there were several sets of six replicate spiked samples that could serve as media standards. Therefore MDLs were calculated from the set of six replicate samples prepared at the 1× LOQ level for the precision and accuracy study. The 1× LOQ level is by definition about three times the LOD. Hence the 1× LOQ level should qualify. For cocaine and phencyclidine the 3× LOQ level results were used instead (the 1× LOQ levels were undetectable). The results are tabulated below.

TABLE 13. MDLS CALCULATED FROM THE PRECISION AND ACCURACY STUDY SAMPLE RESULTS (1)

	Analyte	MDL in µg/sample (2)				
		Internal Standard (2)				
		D_{11}-Amp	D_{14}-Meth	N-MPEA	D_{14}-Meth (3)	N-PAmp
1	D-Amphetamine	0.0246	0.0213	0.0391	0.0242	---
2	Cocaine	0.1600	0.1327	0.1127	0.1239	---
3	L-Ephedrine	0.0179	0.0170	0.0189	0.0164	---
4	MDEA	---	---	---	---	0.0592
5	MDMA	0.0167	0.0175	0.0296	0.0352	---
6	D-Methamphetamine	0.0168	0.0179	0.0164	0.0222	---
7	Phencyclidine	0.0988	0.0996	0.1035	0.4748	---
8	Phentermine	0.0255	0.0325	0.0407	0.0284	---
9	Phenylpropanolamine	0.0283	0.0257	0.0331	0.0250	---
10	Pseudoephedrine	0.0196	0.0200	0.0191	0.0232	---

(1) MDL calculated using the standard deviation of the 1× LOQ level times the Student's t-value for 6 replicates (at the 99% confidence interval). Cocaine and phencyclidine MDL calculated using the standard deviation of the 3× LOQ level.

(2) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

(2) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors.

The resulting MDLs are lower (as would be expected) than the LODs calculated by Burkart's procedure because the precisions in the 1× LOQ level samples were relatively small.

The MDL for methamphetamine is at least 20% of the required action level for Washington State (0.1 μg/sample) and therefore meets their MDL requirement.

The problems of using a single concentration level for determining decision or detection levels is discussed by Dr. Gibbons. [13] The greatest problem is that of nonconstant variance, that is, the MDL calculates at lower and lower concentration levels each time the set of test replicates is made up at lower concentration levels. Another problem is that the MDL does not reflect the levels that are detectable or that will be reported using a calibration curve, which considers variance over several concentration levels (as do the Burkart's method and the NIOSH SOP 018.). Nevertheless, the MDLs are calculated for convenience for those that require such an expression of sensitivity.

Table 14 gives the LODs from Table 9 rounded to the nearest whole number. It also gives the MDLs from Table 13 in rounded numbers. The values meet the MDL required of Washington State for methamphetamine (an MDL of 1/5 the action level of 0.1 μg/100 cm^2).

TABLE 14. LIMIT OF DETECTION AND MINIMUM DETECTABLE LEVELS [1]

Compound	Int. std.[2]	Estimated LOD [3] µg/sample liquid stds [4]	Estimated LOD [3] µg/sample liquid stds [5]	MDL[6] µg/sample cotton gauze media stds
1 Amphetamine	D_{11}-Amp	0.1	0.1	0.02
	D_{14}-Meth	0.1	0.05 (0.04)	0.02
	NMPEA	0.1		0.04
2 Cocaine	D_{11}-Amp	0.6		0.2 [8]
	D_{14}-Meth	0.4		0.1 [8]
	NMPEA	0.4		0.1 [8]
3 (L)-Ephedrine	D_{11}-Amp	0.2	0.2	0.02
	D_{14}-Meth	0.1	0.1	0.02
	NMPEA	0.1		0.02
4 MDEA	N-PAmp	0.1		0.06
5 MDMA	D_{11}-Amp	0.1		0.02
	D_{14}-Meth	0.1		0.02
	N-MPEA	0.1		0.03
6 Methamphetamine	D_{11}-Amp	0.2	0.07	0.02
	D_{14}-Meth	0.1	0.05 (0.03)	0.02
	N-MPEA	0.1		0.02
7 Phencyclidine	D_{11}-Amp	0.6		0.1 [8]
	D_{14}-Meth	0.4		0.1 [8]
	N-MPEA	0.4		0.1 [8]
8 Phentermine	D_{11}-Amp	0.2		0.03
	D_{14}-Meth	0.1		0.03
	N-MPEA	0.1		0.04
9 (±)-Norephedrine [7]	D_{11}-Amp	0.1	0.05	0.03
	D_{14}-Meth	0.1	0.05 (0.02)	0.03
	N-MPEA	0.1		0.03
10 Pseudoephedrine	D_{11}-Amp	0.2	0.2	0.02
	D_{14}-Meth	0.1	0.1	0.02
	N-MPEA	0.1		0.02

(1) Complete data is given in Appendix 1 of the unabridged Backup Data Report [3].

(2) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

(3) LODs based upon liquid standards. LODs vary according to individual instruments, GC columns and conditions, media interferences, and internal standards used. LODs were calculated using the procedure of Burkart [12]. LODs are calculated as the standard error of the lowest three standards analyzed in replicate divided by the slope of the calibration curve.

(4) LODs determined from liquid standards analyzed on separate days. These LODs are conservative since the lowest calibration standard for these determinations was 0.1 µg/sample. Lower LODs have been achieved in actual practice using lower concentration calibration standards. Data summarized from Table 9.

(5) LODs determined from standards analyzed on a single day. The lowest standard was 0.05 µg/sample. The values in brackets are LODs which calculated below the low standard, 0.05 µg/sample. Data is taken from Table 12.

(6) MDLs are calculated on spiked media. MDLs are provided to satisfy regulatory agencies requiring this expression of sensitivity. Six replicates at the 1× LOQ level (or 3× LOQ with cocaine and phencyclidine) were used. MDLs were

calculated as the standard deviation times the Student's t value (at the 99% confidence interval) for 6 replicates (3.365) [15]. Normally seven replicates are required. Data is taken from Table 13.

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

(8) 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.

VI. LONG-TERM SAMPLE STORGE STABILITY

The criterion for long-term sample storage stability is that the recoveries for samples stored under ambient conditions on day 7 should be within 10% of the recoveries determined for day zero. This is to ensure analyte stability on media during un-refrigerated shipment. To accomplish this, the target analytes are spiked onto media and divided randomly into groups to be analyzed on different days. At least six replicates were stored at room temperature for seven days. The others were stored at refrigerated temperatures for up to thirty days. The original study was reported in the Backup Data Report for NIOSH 9106. Nevertheless, the final results for cotton gauze are reported here for convenience.

TABLE 15. LONG TERM STORAGE STABILITY ON COTTON GAUZE

		Percent Recovery [1]					
Analyte	Internal Standard [3]	Zero Day at Room Temp	7 Days at 4 °C	14 Days at 4 °C	21 Days at 4 °C	30 Days at 4 °C	7 Days at Room Temp
Amphetamine	D_{11}-Amp	89.84	**98.95**	**98.44**	**96.83**	**100.52**	**94.52**
L-Ephedrine	D_{14}-Meth	**110.68**	**90.09**	**105.40**	**97.49**	**94.84**	**90.49**
MDEA	N-PAmp	**94.40**	**102.17**	**104.69**	**104.05**	**98.94**	**102.12**
MDMA	D_{14}-Meth	**99.47**	**100.81**	**103.33**	**105.10**	**98.91**	**103.15**
Methamphetamine	D_{14}-Meth	**96.20**	**99.44**	**98.51**	**96.39**	**97.96**	**93.47**
	D_{11}-Amp	85.29	**98.83**	89.81	**97.64**	**98.74**	**100.61**
	N-MPEA	**90.33**	**95.70**	89.14	**94.77**	**95.98**	**97.65**
Norephedrine [2]	D_{11}-Amp	**117.11**	**101.79**	**103.12**	**99.71**	**94.29**	**92.67**
Phencyclidine	D_{14}-Meth	**96.81**	**99.44**	**112.27**	**105.27**	**102.90**	**97.74**
Phentermine	D_{11}-Amp	88.17	**99.98**	**98.57**	**98.2**	**101.95**	**101.48**
Pseudoephedrine	D_{14}-Meth	**93.07**	**102.78**	**105.57**	**97.15**	**99.64**	**91.12**

Bold values are recoveries greater than 90%.

(1) All samples were stored at 4 °C, ±2 °C except those stored for 7 days at room temperature. These were stored at 24-26 °C

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

(3) Internal standards: D_{11}-Amp = Amphetamine-D_{11}, D_{14}-Meth = Methamphetamine-D_{14}, N-MPEA = N-Methylphenethylamine, N-PAmp = N-Propyl amphetamine.

Storage stability for all analytes on cotton gauze met the storage criteria.

Recoveries are not normalized to the zero day samples and are reported as-is. Such normalization was not needed due to generally high recoveries for the other days.

VII. PRECISION AND ACCURACY

A. Objective

The Precision and Accuracy Study determined whether the method can produce a result that is within ±25% of the true value with 95% confidence, which is the criterion for an acceptable method.

B. Scope and Limitations

In the NIOSH "Guidelines for Air Sampling and Analytical Method Development and Evaluation" [6], the Precision and Accuracy evaluation presumes that both a desorption efficiency and a simulated sampling efficiency study will be performed. However, this method is not an air sampling method and no simulated sampling efficiency study can be clearly performed. Precision and accuracy have to be determined from what is essentially a desorption efficiency study on the wipe media. Therefore, the acceptable desorption efficiency will not be as low as 75% but between 90 to 110% which is the limit for the mean bias after correction for desorption efficiency.

A surface recovery study was made using various surface types. The results of this surface recovery study are reported in this Backup Data Report in a following section. The results of the surface recoveries were not used in the calculation of precision and accuracy.

The following specific criteria were set as objectives (and were met):

a. Overall precision: ≤10%;

b. Accuracy: ≤25%;

c. Mean bias: ≤±10%.

C. Reagents and Supplies

a. Media (See Table 16.).

TABLE 16. MEDIA FOR PRECISION AND ACCURACY STUDY

	Media	Size	Ply	Lot Number
1	Cotton gauze (Caring brand)	3" × 3"	12-ply	1167807

Other media (MIRASORB™, NU GAUZE™, SOF-WICK™, TOPPER™, and AlphaWipe™) were evaluated but only cotton gauze is reported in the abridged report.

b. Mixed analyte spiking solution (See Table 17.).

TABLE 17. MIXED ANALYTE SPIKING SOLUTION (1)

	An	Source	Lot Number	Calculated Concentration as Free Base in µg/mL
1	D-Amphetamine HCl	Alltech	413	50.00322
2	L-Ephedrine HCl	Alltech	1505	50.29991
3	MDEA HCl	Alltech	3506	47.63766
4	MDMA HCl	Alltech	6852	45.28192
5	D-Methamphetamine HCl	Alltech	389	50.03214
6	Phencyclidine HCl	Alltech	1293-33	50.07406
7	Phentermine HCl	Sigma	105F-0129	50.34771
8	(±)-Phenylpropanolamine HCl	Sigma	91F-0298	50.40394
9	Pseudoephedrine HCl	Sigma	32K-1358	50.28431
10	Cocaine	Alltech	1800	50.17747

(1) The mixture was made up in methanol, HPLC grade, B&J lot CB331.

c. Internal standard spiking solution (See Table 18.);

TABLE 18. INTERNAL STANDARD SPIKING SOLUTION (1)

	Analyte	Source	Lot Number	Calculated Concentration as Free Base in µg/mL
1	(±)-Amphetamine-D_{11}, HCl	Cerilliant	35129-58A	50.00
2	N-Propylamphetamine	Alltech	1604	83.099
3	(±)-Methamphetamine-D_{14},HCl	Cerilliant	30902-25G	100.00

(1) The mixture was made up in methanol. About 2 µL of powdered crystal violet was added to about 10mL of the spiking solution to act as a visual reference of which samples were spiked.

Methyl phenethylamine was also evaluated but results are not reported to afford brevity in this abridged report.

d. Solid-Phase Extraction Columns: Waters Oasis™ MCX 3cc (60mg), from Waters Corp, Milford, Massachusetts.

e. Desorption and extraction solvents and other reagents as described in NIOSH 9109.

D. Procedure

Media were added to the polypropylene centrifuge tubes. To each tube containing wipe media a volume of isopropanol (IPA) was added followed by an appropriate volume of analyte spiking solution according to the schedule in Table 19. Six replicates were prepared at each level for each wipe media. The preparation of the liquid standards is described in section V on the evaluation of the limit of detection.

TABLE 19. SPIKING SCHEDULE FOR PRECISION AND ACCURACY STUDY

Wipe Media	Number of wipes per tube	IPA mL	Amount Applied per Concentration Level in Microliters					
			µL of analyte spiking solution applied			µL of 1/10 dilution of analyte spiking solution applied		
			300× LOQ Level	100× LOQ Level	30× LOQ Level	10× LOQ Level	3× LOQ Level	1× LOQ Level
Cotton Gauze	2	3	600	200	60	200	60	20

The final theoretical concentration of analytes at each concentration level is given in table 20.

TABLE 20. CONCENTRATION OF ANALYTES AT EACH LEVEL

	Analyte	Calculated Concentration in µg/sample (1)					
		300× LOQ Level	100× LOQ Level	30× LOQ Level	10× LOQ Level	3× LOQ Level	1× LOQ Level
1	D-Amphetamine	30.00193	10.00064	3.00019	1.00006	0.30002	0.10001
2	L-Ephedrine	30.17995	10.05998	3.01799	1.00600	0.30180	0.10060
3	MDEA	28.58259	9.52753	2.85826	0.95275	0.28583	0.09528
4	MDMA	27.16915	9.05638	2.71692	0.90564	0.27169	0.09056
5	D-Methamphetamine	30.01928	10.00643	3.00193	1.00064	0.30019	0.10006
6	Phencyclidine	30.04444	10.01481	3.00444	1.00148	0.30044	0.10015
7	Phentermine	30.20862	10.06954	3.02086	1.00695	0.30209	0.10070
8	Phenylpropanolamine	30.24236	10.08079	3.02424	1.00808	0.30242	0.10081
9	Pseudoephedrine	30.17059	10.05686	3.01706	1.00569	0.30171	0.10057
10	Cocaine	30.25642	10.08547	3.02564	1.00855	0.30256	0.10086

(1) The number of significant figures was kept large until the final calculations to avoid cumulative rounding off errors.

After spiking the samples, 50 µL of internal standard spiking solution was added to each tube using a Hamilton PB600 series repeating dispenser. The addition of internal standard was

made several microliters at a time in several locations around the wipes. Following addition of internal standard solution, 40 mL of desorption solution (0.2 N aqueous sulfuric acid) was added to each sample. The tubes were capped securely and tumbled for 2 to 3 hours for cotton gauze. The samples were put into the walk-in cooler until the desorbates were extracted.

On successive days the samples were removed from the walk-in cooler and extracted according to the NIOSH 9109 procedure. Briefly, the procedure was as follows:

1. Preconditioned SPE column with 2 mL methanol followed with 2 mL deionized water (Type II ASTM).

2. Transferred 5 mL of each desorbate to 3-mL SPE columns mounted on a vacuum manifold. Discarded eluates.

3. Rinsed SPE columns with 2 mL 0.3 Normal aqueous hydrochloric acid. Discarded eluate.

4. Rinsed with 2 mL methanol. Discarded eluate.

5. Dried columns by pulling air through columns for 15 minutes at high vacuum.

6. Arranged 10-mL collection tubes in aspirator and added 100 µL of 0.3 N hydrochloric acid in methanol and 5-6 µL of crystal violet indicator solution to each collection tube.

7. Eluted each SPE column with 2 mL of freshly prepared 80:20:2 v/v mixture of methylene chloride:isopropanol:ammonium hydroxide. Collected eluates in the collection tubes.

8. Evaporated the solutions to dryness under a stream of nitrogen in a water bath between 30-40 °C. The crystal violet remains a blue to blue-violet color as the samples go to dryness. At dryness the crystal violet helps to reveal whether the residue is dry or not.

9. The residues were reconstituted with 100 µL of acetonitrile and mixed gently by tapping.

10. To the acetonitrile was added 25 µL of MSTFA followed by 25 µL MBHFBA. The tubes were capped after addition of reagent and mixed by vortexing.

11. The solutions were transferred to 300 to 500-µL mini-GC vials and analyzed by GC-MS in the scan mode using the conditions specified earlier in the section on GC-MS conditions .

E. Analysis and Results

The samples were analyzed by GC-MS using the GC-MS conditions described in an earlier section. The full data, micrograms per sample recovered at each level for each replicate along with the calculated bias, precision, and accuracy are given in Appendix 1.

Accuracy was calculated using a formula given by Dr. Eugene Kennedy of NIOSH [16] rather than using the nomogram in the NIOSH Guidelines for Method Development and Evaluation manual [6]. The formula is as follows:

If the absolute value of the bias is less than $\hat{S}_{rT}/1.645$, the accuracy is

1.96 times the square root of the sum of bias squared and $\hat{S}_{rT}$ squared;

$1.96 \times \sqrt{((\text{bias})^2 + (\hat{S}_{rT})^2)}$.

If the absolute value of the bias is equal to or greater than $\hat{S}_{rT}/1.645$, the accuracy is

the absolute value of the bias plus the value $\hat{S}_{rT}$ times 1.645;

$|\text{bias}| + (\hat{S}_{rT} \times 1.645)$.

Where $\hat{S}_{rT}$ = overall (pooled) precision.

A criterion for the overall bias is that the bias must be less than ±10% (±0.10). This was met with at least one set of combination of internal standard and medium for every analyte. Cotton was the overall universal medium. D_{11}-Amphetamine was generally better for the primary

amines, but not exclusively so, and D_{14}-methamphetamine a better internal standard for the N-methyl amines and phencyclidine, but not exclusively so.

The internal standard, N-propylamphetamine, was absolutely necessary for the similarly hindered MDEA to pass.

Bartlett's test was used to determine homogeneity of precision. The F' test (Dr. Eugene Kennedy, PhD, [17]) was used to determine homogeneity of bias. Only those concentration levels that passed both the Bartlett's and the F' tests were used for calculating overall precision ($\hat{S}_{rT}$) and average bias. Accuracy was then calculated from these. In calculating the homogeneities of the precisions and biases from the various concentration levels an effort was made to omit as few concentration levels as possible. Where possible, an effort was made to conserve the lowest concentration level in order to keep the applicable range as low as possible. Higher concentration levels having "inlier" CVs were omitted when necessary in order to obtain more a conservative overall precision. This gives a more conservative estimate of the pooled CV as well. The concentration levels that had to be omitted and other details are noted in part B of Tables 22 through 26.

A summary of the precision and accuracy data for analytes on cotton gauze for three internal standards is given in Table 21.

TABLE 21. SUMMARY OF PRECISION AND ACCURACY ON COTTON GAUZE [1]

Compound	Internal Standard[2]	Range [3] µg/sample	Overall Accuracy	Overall Precision $\hat{S}_{rT}$	Bias Average	Bias 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
Cocaine	D_{11}-Amp	1.0-30	15.8	0.0469	+0.0810	+0.0416 to +0.1375
	D_{14}-Met	3.0-30	13.3	0.0422	+0.0631	+0.0003 to +0.1294
(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
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
(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
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
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
(±)-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
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

(1) 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" × 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:
D_{11}-Amp = Amphetamine-D_{11}
D_{14}-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 (1× LOQ to 300× LOQ).

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

Tables 22 through 26 give the recovery data used for calculation the precision and accuracy summarized in Table 21. Tables 22 and 23 pertain to recoveries of nine analytes determined with the internal standard amphetamine-D_{11}. Tables 24 and 25 pertain to recoveries

of nine analytes determined with the internal standard methamphetamine-D_{14}. Table 26 pertains to recoveries of MDEA determined with the internal standard N-propyl amphetamine.

Each table is organized into two parts. Part A gives recoveries for each of the six replicates for each of the six concentration levels. For each concentration level the average recovery, group precision (CVi), group bias, and average percent recoveries are given.

In part B the calculated accuracy, overall precision, mean bias, and range of bias is given. The results of the test for homogeneity of group bias (the Bartlett's test) is given along with the calculated Chi^2 is given and a yes or no notation as to whether the Chi^2 passed at the 0.95 or 0.975 significance level. The results of the F' test for homogeneity of group bias is given along with the calculated F' and a yes or no notation as to whether the F' test passed at an alpha = 0.05 or 0.025 value.

There are up to four optional ways of calculating precision and accuracy. In Option #1 the overall precision and accuracy were calculated for all six concentration levels (no concentration levels omitted) except with cocaine and phencyclidine where the precision and accuracy were calculated for five concentration levels (4 degrees of freedom) because the 1× LOQ level was omitted due to non-detectability. If both the Bartlett's and F' tests for homogeneity passed, and the accuracy was less than 25%, then the overall precision and accuracy values used and the final method precision and accuracy values and were final and entered into Table 21.

If the overall precision and accuracy criteria could not be met when no concentration levels were omitted, then the lowest concentration level was omitted and the results presented in Option #2. For cocaine and phencyclidine, both the 1× LOQ and 3× LOQ levels were omitted and presented as Option #2 (except in Table 24b. the 1× LOQ and 300× LOQ levels for cocaine

were omitted and presented as Option #2). In all cases this solution was rejected because there were other combinations of five concentration levels (four concentration levels in the case of cocaine and phencyclidine) that either…

1) gave a lower Chi^2,
2) conserved the lowest concentration level so that the applicable range could be kept as low as possible without a great increase in the overall precision and accuracy, or
3) gave a more conservative overall precision by omitting a higher concentration level having an inlier CV which skewed the overall precision to a probably unrealistic value.

These alternate combinations are presented as Option #3.

In the case of cocaine, phencyclidine, and MDEA an Option #4 is presented which has a higher Chi^2 than Option #3 but which passes the precision and accuracy criteria better for the same degrees of freedom.

Comments for each individual option selected are given in the footnotes for Tables 22 through 26 following Table 25.

TABLE 22A. MICROGRAMS RECOVERED (INT. STD. = D_{11}-AMPHETAMINE)

PART A	Micrograms per Sample Recovered from Cotton Gauze				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{11}-Amphetamine				
Test Level Replicate	Amphetamine	Cocaine	Ephedrine	MDMA	Methamphetamine
Amount Applied =	30.00193	30.25642	30.17995	27.16915	30.01928
300× LOQ 1	28.006	29.616	29.325	25.825	29.334
300× LOQ 2	30.228	31.915	32.584	27.642	31.619
300× LOQ 3	29.464	32.525	32.090	28.052	30.210
300× LOQ 4	28.644	31.068	28.925	26.250	28.619
300× LOQ 5	28.631	31.358	31.080	29.554	30.050
300× LOQ 6	28.087	32.614	31.077	27.806	31.316
Average µg/sample =	28.843	31.516	30.847	27.521	30.191
CVi =	0.02967	0.03538	0.04738	0.04876	0.03786
Group Bias =	-0.03862	0.04163	0.02209	0.01297	0.00573
Average % Recovery =	**96.14**	**104.16**	**102.21**	**101.30**	**100.57**
Amount Applied =	10.00064	10.08547	10.05998	9.05638	10.00643
100× LOQ 1	9.778	10.379	10.298	9.126	10.220
100× LOQ 2	9.777	10.627	9.497	9.148	9.742
100× LOQ 3	10.116	10.609	9.899	9.193	10.130
100× LOQ 4	10.361	10.596	10.235	8.955	9.720
100× LOQ 5	10.576	11.323	10.901	9.647	10.270
100× LOQ 6	10.284	10.849	10.618	9.725	10.825
Average µg/sample =	10.148	10.731	10.241	9.299	10.151
CVi =	0.03187	0.03041	0.04886	0.03348	0.04004
Group Bias =	0.01478	0.06397	0.01802	0.02676	0.01447
Average % Recovery =	**101.48**	**106.40**	**101.80**	**102.68**	**101.45**
Amount Applied =	3.00019	3.02564	3.01799	2.71692	3.00193
30× LOQ 1	2.9280	3.5714	2.8635	2.8008	3.0572
30× LOQ 2	2.8525	3.0334	2.7929	2.4246	2.8756
30× LOQ 3	2.8806	2.4866	2.8754	2.4279	3.0388
30× LOQ 4	3.0174	3.3168	3.1201	2.7977	3.1631
30× LOQ 5	2.8534	3.7335	3.1354	2.9401	3.0766
30× LOQ 6	3.1004	3.8486	3.0792	3.0807	3.1313
Average µg/sample =	2.9387	3.3317	2.9778	2.7453	3.0571
CVi =	0.03421	0.15242	0.05051	0.09772	0.03284
Group Bias =	-0.02049	0.10116	-0.01333	0.01045	0.01838
Average % Recovery =	**97.95**	**110.12**	**98.67**	**101.04**	**101.84**
Amount Applied =	1.00006	1.00855	1.00600	0.90564	1.00064
10× LOQ 1	0.9807	1.0204	0.9033	0.8895	0.9729
10× LOQ 2	0.9999	1.2287	0.9389	0.9739	0.9964
10× LOQ 3	0.9926	1.1601	0.9318	0.8965	0.9244
10× LOQ 4	0.9784	1.1444	0.9532	0.9755	0.9619
10× LOQ 5	0.9414	1.2179	0.9240	0.9675	0.9433
10× LOQ 6	0.9547	1.1118	1.0177	0.9369	1.0312
Average µg/sample =	0.9746	1.1472	0.9448	0.9400	0.9717
CVi =	0.02301	0.06655	0.04165	0.04153	0.03930
Group Bias =	-0.02545	0.13749	-0.06082	0.03791	-0.02894
Average % Recovery =	**97.46**	**113.75**	**93.92**	**103.79**	**97.11**
Amount Applied =	0.30002	0.30256	0.30180	0.27169	0.30019
3× LOQ 1	0.2980	0.3966	0.3145	0.3094	0.2980
3× LOQ 2	0.2599	0.3275	0.3209	0.2784	0.3161
3× LOQ 3	0.2723	0.3428	0.2880	0.2810	0.3005
3× LOQ 4	0.3215	0.3310	0.3042	0.2958	0.3107
3× LOQ 5	0.2917	0.4507	0.3348	0.3023	0.3312
3× LOQ 6	0.2625	0.3735	0.2959	0.3103	0.3141
Average µg/sample =	0.2843	0.3704	0.3097	0.2962	0.3118
CVi =	0.08384	0.12836	0.05536	0.04674	0.03848
Group Bias =	-0.05234	0.22404	0.02623	0.09021	0.03855
Average % Recovery =	**94.77**	**122.40**	**102.62**	**109.02**	**103.86**
Amount Applied =	0.10001	0.10086	0.10060	0.09056	0.10006
1× LOQ 1	0.1122	ND	0.0997	0.1036	0.1072
1× LOQ 2	0.1069	ND	0.0899	0.1043	0.1065
1× LOQ 3	0.1022	ND	0.1003	0.1054	0.1032
1× LOQ 4	0.1036	ND	0.0989	0.0949	0.1112
1× LOQ 5	0.0914	ND	0.0949	0.1050	0.1100
1× LOQ 6	0.1094	ND	0.1056	0.0952	0.1177
Average µg/sample =	0.1043		0.0982	0.1014	0.1093
CVi =	0.07001		0.05420	0.04889	0.04558
Group Bias =	0.04277		-0.02369	0.11965	0.09230
Average % Recovery =	**104.28**		**97.63**	**111.97**	**109.23**

ND = Not detected.

TABLE 22B. PRECISION AND ACCURACY (INT. STD. = D_{11}-AMPHETAMINE)

PART B	Parameters for Calculating Precision and Accuracy, and Results				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{11}-Amphetamine				
	Amphetamine	Cocaine	Ephedrine	MDMA	Methamphetamine
OPTION #1			See notes 1 and 4.	See notes 1 and 5.	
Test(Concentration) Levels Omitted	NONE	1× LOQ	NONE	NONE	NONE
Degrees of freedom =	5	4	5	5	5
Accuracy =	**10.3015**	**27.1978**	**9.8284**	**14.3068**	**8.9489**
Overall Precision ($\hat{S}_{rT}$) =	0.05087	0.09624	0.04987	0.05678	0.03920
Chi^2 =	13.264	16.928	0.491	7.654	0.531
pass @ 0.95?	no	no	**YES**	**YES**	YES
pass @ 0.975?	no	no	**YES**	**YES**	YES
Mean bias =	-0.01323	+0.11366	-0.00525	+0.04966	+0.02342
from	-0.05234	+0.04163	-0.06082	+0.01045	-0.02894
to	+0.04277	+0.22404	+0.02623	+0.11965	+0.09230
F' =	1.87899	2.19199	1.74197	2.43592	3.12304
pass @ 0.05?	YES	YES	**YES**	**YES**	no
pass @ 0.025?	YES	YES	**YES**	**YES**	no
OPTION #2					
Test(Concentration) Levels Omitted	1× LOQ	1× LOQ 3× LOQ			1× LOQ
Degrees of freedom =	4	3			4
Accuracy =	**10.2246**	**22.8140**			**7.6438**
Overall Precision ($\hat{S}_{rT}$) =	0.04610	0.08637			0.03779
Chi^2 =	11.496	15.332			0.223
pass @ 0.95?	no	no			YES
pass @ 0.975?	no	no			YES
Mean bias =	-0.02442	+0.08606			+0.00964
from	-0.05234	+0.04163			-0.02894
to	+0.01478	+0.13749			+0.03855
F' =	0.99134	0.92182			1.09910
pass @ 0.05?	YES	YES			YES
pass @ 0.025?	YES	YES			YES
OPTION #3	See notes 1 and 2.				See notes 1 and 6.
Test(Concentration) Levels Omitted	3× LOQ	100× LOQ 300× LOQ 1× LOQ			300× LOQ
Degrees of freedom =	4	2			4
Accuracy =	**8.1486**	**35.3762**			**9.1861**
Overall Precision ($\hat{S}_{rT}$) =	0.04122	0.12130			0.03946
Chi^2 =	7.885	2.895			0.513
pass @ 0.95?	**YES**	YES			**YES**
pass @ 0.975?	**YES**	YES			**YES**
Mean bias =	-0.00540	+0.15423			+0.02695
from	-0.03862	+0.10116			-0.02894
to	+0.04277	+0.22404			+0.09230
F' =	1.83920	1.02706			3.29175
pass @ 0.05?	**YES**	YES			no
pass @ 0.025?	**YES**	YES			**YES**
OPTION #4		See notes 1 and 3.			
Test(Concentration) Levels Omitted		3× LOQ 30× LOQ 1× LOQ			
Degrees of freedom =		2			
Accuracy =		**15.8220**			
Overall Precision ($\hat{S}_{rT}$) =		0.04692			
Chi^2 =		3.368			
pass @ 0.95?		**YES**			
pass @ 0.975?		**YES**			
Mean bias =		+0.08103			
from		+0.04163			
to		+0.13749			
F' =		2.33612			
pass @ 0.05?		**YES**			
pass @ 0.025?		**YES**			

TABLE 23A. MICROGRAMS RECOVERED (INT. STD. = D_{11}-AMPHETAMINE)

Part A	Micrograms per Sample Recovered from Cotton Gauze				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{11}-Amphetamine				
Test Level Replicate	Phencyclidine	Phentermine	Phenylpropanolamine	Pseudoephedrine	
Amount Applied =	30.04444	30.20862	30.24236	30.17059	
300× LOQ 1	26.898	29.819	30.902	27.723	
300× LOQ 2	31.428	31.437	32.563	29.452	
300× LOQ 3	31.231	31.988	33.749	31.395	
300× LOQ 4	30.273	30.448	30.897	28.639	
300× LOQ 5	29.387	30.120	30.116	28.714	
300× LOQ 6	32.116	31.219	31.414	30.456	
Average µg/sample =	30.222	30.839	31.607	29.397	
CVi =	0.06245	0.02726	0.04189	0.04554	
Group Bias =	0.00591	0.02085	0.04511	-0.02566	
Average % Recovery =	**100.59**	**102.09**	**104.51**	**97.43**	
Amount Applied =	10.01481	10.06954	10.08079	10.05686	
100× LOQ 1	10.290	10.221	11.094	9.624	
100× LOQ 2	10.164	9.817	10.793	9.433	
100× LOQ 3	10.169	10.176	10.295	8.946	
100× LOQ 4	10.247	9.714	11.134	9.187	
100× LOQ 5	11.002	10.942	11.724	10.448	
100× LOQ 6	11.445	11.294	11.566	9.506	
Average µg/sample =	10.553	10.361	11.101	9.524	
CVi =	0.05120	0.06070	0.04680	0.05395	
Group Bias =	0.05370	0.02893	0.10121	-0.05297	
Average % Recovery =	**105.37**	**102.89**	**110.12**	**94.70**	
Amount Applied =	3.00444	3.02086	3.02424	3.01706	
30× LOQ 1	3.3529	3.0462	3.1267	3.1835	
30× LOQ 2	3.0412	2.9930	2.8864	2.9725	
30× LOQ 3	3.1982	2.9878	3.0786	2.9024	
30× LOQ 4	3.2493	3.1990	3.3626	3.1564	
30× LOQ 5	3.2378	3.0015	3.0242	3.2056	
30× LOQ 6	3.5026	3.1692	2.9887	3.2362	
Average µg/sample =	3.2637	3.0661	3.0779	3.1094	
CVi =	0.04741	0.03071	0.05258	0.04424	
Group Bias =	0.08628	0.01498	0.01773	0.03062	
Average % Recovery =	**108.63**	**101.50**	**101.77**	**103.06**	
Amount Applied =	1.00148	1.00695	1.00808	1.00569	
10× LOQ 1	1.0933	1.0420	1.0123	0.8750	
10× LOQ 2	1.0869	1.0450	1.0530	0.8896	
10× LOQ 3	1.0607	0.9932	1.0770	0.8716	
10× LOQ 4	1.0908	1.0573	1.1243	0.9823	
10× LOQ 5	1.0950	0.9670	1.0355	0.9335	
10× LOQ 6	1.0939	0.9830	1.0284	1.0094	
Average µg/sample =	1.0868	1.0146	1.0551	0.9269	
CVi =	0.01205	0.03746	0.03839	0.06302	
Group Bias =	0.08516	0.00758	0.04663	-0.07834	
Average % Recovery =	**108.52**	**100.76**	**104.66**	**92.17**	
Amount Applied =	0.30044	0.30209	0.30242	0.30171	
3× LOQ 1	0.3377	0.3043	0.3312	0.2808	
3× LOQ 2	0.3654	0.3024	0.3281	0.2967	
3× LOQ 3	0.3364	0.2942	0.3061	0.2788	
3× LOQ 4	0.3500	0.3056	0.3141	0.2828	
3× LOQ 5	0.3521	0.2994	0.3444	0.3113	
3× LOQ 6	0.2813	0.2945	0.3013	0.3137	
Average µg/sample =	0.3372	0.3001	0.3209	0.2940	
CVi =	0.08705	0.01631	0.05139	0.05325	
Group Bias =	0.12217	-0.00669	0.06098	-0.02549	
Average % Recovery =	**112.22**	**99.33**	**106.10**	**97.45**	
Amount Applied =	0.10015	0.10070	0.10081	0.10057	
1× LOQ 1	ND	0.1008	0.1068	0.1019	
1× LOQ 2	ND	0.1170	0.0903	0.1036	
1× LOQ 3	ND	0.1097	0.1009	0.0955	
1× LOQ 4	ND	0.1188	0.0927	0.1102	
1× LOQ 5	ND	0.1116	0.1002	0.1106	
1× LOQ 6	ND	0.1014	0.0837	0.1082	
Average µg/sample =		0.1099	0.0958	0.1050	
CVi =		0.06902	0.08769	0.05561	
Group Bias =		0.09124	-0.05001	0.04406	
Average % Recovery =		**109.12**	**95.00**	**104.41**	

ND = Not detected.

TABLE 23B. PRECISION AND ACCURACY (INT. STD. = D_{11}-AMPHETAMINE)

Part B	Parameters for Calculating Precision and Accuracy, and Results				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{11}-Amphetamine				
	Phencyclidine	Phentermine	Phenylpropanolamine	Pseudoephedrine	
OPTION #1		See notes 1 and 8.			
Test(Concentration) Levels Omitted	1× LOQ	NONE	NONE	NONE	
Degrees of freedom =	4	5	5	5	
Accuracy =	**16.5119**	**10.0916**	**12.8322**	**10.9646**	
Overall Precision ($\hat{S}_{rT}$) =	0.05743	0.04435	0.05555	0.05298	
Chi^2 =	13.060	12.201	4.806	0.832	
pass @ 0.95?	no	no	YES	YES	
pass @ 0.975?	no	**YES**	YES	YES	
Mean bias =	+0.07064	+0.02615	+0.03694	-0.01796	
from	+0.00591	-0.00669	-0.05001	-0.07834	
to	+0.12217	+0.09124	+0.10121	+0.04406	
F' =	1.98995	1.90453	3.29512	3.21159	
pass @ 0.05?	YES	**YES**	no	no	
pass @ 0.025?	YES	**YES**	no	no	
OPTION #2					
Test(Concentration) Levels Omitted	1× LOQ 3× LOQ		1× LOQ	1× LOQ	
Degrees of freedom =	3		4	4	
Accuracy =	**13.5419**		**13.0873**	**11.8768**	
Overall Precision ($\hat{S}_{rT}$) =	0.04721		0.04653	0.05244	
Chi^2 =	9.416		0.666	0.796	
pass @ 0.95?	no		YES	YES	
pass @ 0.975?	no		YES	YES	
Mean bias =	+0.05776		+0.05433	-0.03037	
from	+0.00591		+0.01773	-0.07834	
to	+0.08628		+0.10121	+0.03062	
F' =	1.73533		1.30567	2.23220	
pass @ 0.05?	YES		YES	YES	
pass @ 0.025?	YES		YES	YES	
OPTION #3	See notes 1 and 7.		See notes 1 and 9.	See notes 1 and 10.	
Test(Concentration) Levels Omitted	1× LOQ 10× LOQ		100× LOQ	10× LOQ	
Degrees of freedom =	3		4	4	
Accuracy =	**17.2176**		**12.1539**	**10.0104**	
Overall Precision ($\hat{S}_{rT}$) =	0.06393		0.05714	0.05073	
Chi^2 =	2.217		4.475	0.413	
pass @ 0.95?	**YES**		**YES**	**YES**	
pass @ 0.975?	**YES**		**YES**	**YES**	
Mean bias =	+0.06702		+0.02409	-0.00589	
from	+0.00591		-0.05001	-0.05297	
to	+0.12217		+0.06098	+0.04406	
F' =	2.01692		2.29006	2.31456	
pass @ 0.05?	**YES**		**YES**	**YES**	
pass @ 0.025?	**YES**		**YES**	**YES**	

TABLE 24A. MICROGRAMS RECOVERED (INT. STD. = D_{14}-METHAMPHETAMINE)

Part A	Micrograms per Sample Recovered from Cotton Gauze				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{14}-methamphetamine				
Test Level Replicate	Amphetamine	Cocaine	Ephedrine	MDMA	Methamphetamine
Amount Applied =	30.00193	30.25642	30.17995	27.16915	30.01928
300× LOQ 1	27.356	29.027	28.486	25.185	28.569
300× LOQ 2	27.781	29.801	29.771	25.548	29.078
300× LOQ 3	27.387	30.645	29.653	26.189	28.080
300× LOQ 4	28.691	31.067	28.818	26.183	28.548
300× LOQ 5	27.462	30.291	29.638	26.056	28.768
300× LOQ 6	26.146	30.761	28.759	25.987	29.140
Average µg/sample =	27.471	30.265	29.187	25.858	28.697
CVi =	0.02984	0.02464	0.01922	0.01566	0.01364
Group Bias =	-0.08437	0.00029	-0.03289	-0.04825	-0.04404
Average % Recovery =	**91.56**	**100.03**	**96.71**	**95.17**	**95.60**
Amount Applied =	10.00064	10.08547	10.05998	9.05638	10.00643
100× LOQ 1	9.825	10.464	10.431	9.189	10.322
100× LOQ 2	10.308	11.061	9.930	9.541	10.174
100× LOQ 3	10.657	10.988	10.353	9.540	10.569
100× LOQ 4	10.531	10.703	10.358	9.001	9.750
100× LOQ 5	10.436	11.263	10.808	9.540	10.096
100× LOQ 6	9.441	10.310	9.812	9.168	10.143
Average µg/sample =	10.200	10.798	10.282	9.330	10.175
CVi =	0.04604	0.03416	0.03520	0.02570	0.02652
Group Bias =	0.01988	0.07066	0.02207	0.03019	0.01689
Average % Recovery =	**101.99**	**107.07**	**102.21**	**103.02**	**101.69**
Amount Applied =	3.00019	3.02564	3.01799	2.71692	3.00193
30× LOQ 1	2.8906	3.5674	2.8216	2.7798	3.0245
30× LOQ 2	2.9555	3.1311	2.8842	2.4988	2.9736
30× LOQ 3	2.8192	2.4146 Grubbs outlier at 5%	2.8121	2.3752	2.9827
30× LOQ 4	2.9173	3.2356	3.0205	2.7214	3.0691
30× LOQ 5	2.6735	3.5822	2.9517	2.7940	2.8996
30× LOQ 6	2.7935	3.5698	2.7788	2.8247	2.8355
Average µg/sample =	2.8416	3.2501	2.8782	2.6657	2.9642
CVi =	0.03595	0.13935	0.03227	0.06920	0.02855
Group Bias =	-0.05286	0.07419	-0.04634	-0.01887	-0.01258
Average % Recovery =	**94.71**	**107.42**	**95.37**	**98.11**	**98.74**
Amount Applied =	1.00006	1.00855	1.00600	0.90564	1.00064
10× LOQ 1	0.9968	1.0279	0.9148	0.8981	0.9842
10× LOQ 2	0.9741	1.1883	0.9146	0.9460	0.9669
10× LOQ 3	1.0638	1.2348	0.9915	0.9516	0.9843
10× LOQ 4	1.0233	1.1883	0.9921	1.0136	1.0006
10× LOQ 5	1.0215	1.3137	0.9951	1.0412	1.0178
10× LOQ 6	0.9071	1.0462	0.9702	0.8886	0.9775
Average µg/sample =	0.9978	1.1665	0.9631	0.9565	0.9886
CVi =	0.05371	0.09466	0.03997	0.06375	0.01826
Group Bias =	-0.00230	0.15665	-0.04269	0.05618	-0.01209
Average % Recovery =	**99.77**	**115.66**	**95.73**	**105.62**	**98.79**
Amount Applied =	0.30002	0.30256	0.30180	0.27169	0.30019
3× LOQ 1	0.2975	0.4015	0.3142	0.3078	0.2966
3× LOQ 2	0.2438	0.3082	0.3057	0.2618	0.2963
3× LOQ 3	0.2646	0.3376	0.2818	0.2728	0.2914
3× LOQ 4	0.3047	0.3147	0.2915	0.2803	0.2934
3× LOQ 5	0.2584	0.3935	0.3047	0.2695	0.2932
3× LOQ 6	0.2404	0.3404	0.2769	0.2857	0.2875
Average µg/sample =	0.2682	0.3493	0.2958	0.2797	0.2931
CVi =	0.10097	0.11293	0.04986	0.05762	0.01150
Group Bias =	-0.10595	0.15452	-0.01988	0.02929	-0.02374
Average % Recovery =	**89.41**	**115.45**	**98.01**	**102.93**	**97.63**
Amount Applied =	0.10001	0.10086	0.10060	0.09056	0.10006
1× LOQ 1	0.1028	ND	0.0959	0.0971	0.0984
1× LOQ 2	0.1048	ND	0.0889	0.1035	0.1048
1× LOQ 3	0.1009	ND	0.0997	0.1053	0.1024
1× LOQ 4	0.1027	ND	0.0984	0.0953	0.1108
1× LOQ 5	0.0880	ND	0.0934	0.1029	0.1067
1× LOQ 6	0.1044	ND	0.1033	0.0924	0.1128
Average µg/sample =	0.1006		0.0966	0.0994	0.1060
CVi =	0.06290		0.05233	0.05226	0.05027
Group Bias =	0.00594		-0.03976	0.09775	0.05915
Average % Recovery =	**100.59**		**96.02**	**109.78**	**105.92**

ND = Not detected.

TABLE 24B. PRECISION AND ACCURACY (INT. STD. = D_{14}-METHAMPHETAMINE)

Part B	Parameters for Calculating Precision and Accuracy, and Results				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{14}-Methamphetamine				
	Amphetamine	Cocaine	Ephedrine	MDMA	Methamphetamine
OPTION #1			See notes 1 and 12.		
Test (Concentration) Levels Omitted	NONE	1× LOQ	NONE	NONE	NONE
Degrees of freedom =	5	4	5	5	5
Accuracy =	**13.4711**	**24.3647**	**9.1937**	**11.1378**	**5.5101**
Overall Precision ($\hat{S}_{rT}$) =	0.05964	0.09263	0.03973	0.05133	0.02798
Chi^2 =	9.453	16.162	5.265	11.841	14.263
pass @ 0.95?	YES	no	**YES**	no	no
pass @ 0.975?	YES	no	**YES**	YES	no
Mean bias =	-0.03661	+0.09126	-0.02658	+0.02438	-0.00273
from	-0.10595	+0.00029	-0.04634	-0.04825	-0.04404
to	+0.01988	+0.15665	+0.02207	+0.09775	+0.05915
F' =	3.46294	2.06511	1.31289	3.78423	3.37230
pass @ 0.05?	no	YES	**YES**	no	no
pass @ 0.025?	no	YES	**YES**	no	no
OPTION #2					
Test(Concentration) Levels Omitted	1× LOQ	1× LOQ 300× LOQ		1× LOQ	1× LOQ
Degrees of freedom =	4	3		4	4
Accuracy =	**14.2111**	**28.3166**		**10.2026**	**4.9381**
Overall Precision ($\hat{S}_{rT}$) =	0.05896	0.10283		0.05114	0.02083
Chi^2 =	9.337	7.410		11.734	5.659
pass @ 0.95?	YES	YES		no	YES
pass @ 0.975?	YES	YES		no	YES
Mean bias =	-0.04512	+0.11400		+0.00971	-0.01511
from	-0.10595	+0.07066		-0.04825	-0.04404
to	+0.01988	+0.15665		+0.05618	+0.01689
F' =	3.47653	0.88300		2.33220	1.27049
pass @ 0.05?	no	YES		YES	YES
pass @ 0.025?	no	YES		YES	YES
OPTION #3	See notes 1 and 11.			See notes 1 and 14.	See notes 1 and 15.
Test(Concentration) Levels Omitted	3× LOQ	100× LOQ 300× 1× LOQ		300× LOQ	3× LOQ
Degrees of freedom =	4	2		4	4
Accuracy =	**10.2704**	**32.1070**		**13.0684**	**5.9292**
Overall Precision ($\hat{S}_{rT}$) =	0.04721	0.11709		0.05579	0.03022
Chi^2 =	3.246	0.687		4.385	9.326
pass @ 0.95?	**YES**	YES		**YES**	**YES**
pass @ 0.975?	**YES**	YES		**YES**	**YES**
Mean bias =	-0.02274	+0.12845		+0.03891	+0.00147
from	-0.08437	+0.07419		-0.01887	-0.04404
to	+0.01988	+0.15665		+0.09775	+0.05915
F' =	2.85955	0.63486		2.09432	3.17225
pass @ 0.05?	no	YES		**YES**	no
pass @ 0.025?	**YES**	YES		**YES**	**YES**
OPTION #4		See notes 1 and 12.			
Test(Concentration) Levels Omitted		#3 in 30× LOQ omitted. 1× LOQ 3× LOQ 10× LOQ			
Degrees of freedom =		2			
Accuracy =		**13.2568**			
Overall Precision ($\hat{S}_{rT}$) =		0.04223			
Chi^2 =		3.8769			
pass @ 0.95?		no			
pass @ 0.975?		YES			
Mean bias =		+0.06311			
from		+0.00029			
to		+0.12942			
F' =		4.03345			
pass @ 0.05?		no			
pass @ 0.025?		YES			

TABLE 25A. MICROGRAMS RECOVERED (INT. STD. = D_{14}-METHAMPHETAMINE)

Part A	Micrograms per Sample Recovered from Cotton Gauze				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{14}-methamphetamine				
Test Level Replicate	Phencyclidine	Phentermine	Phenylpropanolamine	Pseudoephedrine	
Amount Applied =	30.04444	30.20862	30.24236	30.17059	
300× LOQ 1	26.307	29.098	30.166	26.993	
300× LOQ 2	29.137	28.942	29.965	27.117	
300× LOQ 3	29.238	29.767	31.397	29.195	
300× LOQ 4	30.251	30.439	30.913	28.530	
300× LOQ 5	28.278	28.884	28.885	27.492	
300× LOQ 6	30.099	29.087	29.260	28.358	
Average µg/sample =	28.885	29.369	30.098	27.948	
CVi =	0.05027	0.02085	0.03169	0.03149	
Group Bias =	-0.03860	-0.02778	-0.00478	-0.07368	
Average % Recovery =	**96.14**	**97.22**	**99.52**	**92.63**	
Amount Applied =	10.01481	10.06954	10.08079	10.05686	
100× LOQ 1	10.400	10.321	11.381	9.633	
100× LOQ 2	10.642	10.271	11.522	9.908	
100× LOQ 3	10.585	10.634	10.818	9.214	
100× LOQ 4	10.352	9.736	11.433	9.111	
100× LOQ 5	10.937	10.851	11.783	10.266	
100× LOQ 6	10.867	10.623	10.888	8.528	
Average µg/sample =	10.630	10.406	11.304	9.443	
CVi =	0.02237	0.03776	0.03332	0.06579	
Group Bias =	0.06147	0.03340	0.12137	-0.06099	
Average % Recovery =	**106.15**	**103.34**	**112.14**	**93.90**	
Amount Applied =	3.00444	3.02086	3.02424	3.01706	
30× LOQ 1	3.3276	3.0110	3.0960	3.1472	
30× LOQ 2	3.1401	3.0996	2.9868	3.0776	
30× LOQ 3	3.1433	2.9280	3.0228	2.8349	
30× LOQ 4	3.1552	3.1030	3.2707	3.0505	
30× LOQ 5	3.0624	2.8227	2.8457	3.0121	
30× LOQ 6	3.2013	2.8683	2.6972	2.9150	
Average µg/sample =	3.1717	2.9721	2.9865	3.0062	
CVi =	0.02792	0.03979	0.06656	0.03782	
Group Bias =	0.05565	-0.01614	-0.01247	-0.00359	
Average % Recovery =	**105.57**	**98.39**	**98.75**	**99.64**	
Amount Applied =	1.00148	1.00695	1.00808	1.00569	
10× LOQ 1	1.1056	1.0558	1.0271	0.8867	
10× LOQ 2	1.0580	1.0162	1.0270	0.8668	
10× LOQ 3	1.1242	1.0582	1.1498	0.9274	
10× LOQ 4	1.1317	1.1017	1.1741	1.0239	
10× LOQ 5	1.1718	1.0430	1.1185	1.0067	
10× LOQ 6	1.0419	0.9326	0.9800	0.9629	
Average µg/sample =	1.1055	1.0346	1.0794	0.9457	
CVi =	0.04382	0.05522	0.07273	0.06716	
Group Bias =	0.10390	0.02744	0.07077	-0.05961	
Average % Recovery =	**110.39**	**102.74**	**107.08**	**94.04**	
Amount Applied =	0.30044	0.30209	0.30242	0.30171	
3× LOQ 1	0.3420	0.3034	0.3310	0.2808	
3× LOQ 2	0.3531	0.2850	0.3118	0.2835	
3× LOQ 3	0.3344	0.2863	0.2993	0.2734	
3× LOQ 4	0.3407	0.2901	0.3004	0.2717	
3× LOQ 5	0.3265	0.2674	0.3119	0.2844	
3× LOQ 6	0.2701	0.2716	0.2808	0.2942	
Average µg/sample =	0.3278	0.2840	0.3059	0.2813	
CVi =	0.09032	0.04589	0.05480	0.02912	
Group Bias =	0.09105	-0.05998	0.01138	-0.06752	
Average % Recovery =	**109.11**	**94.00**	**101.14**	**93.25**	
Amount Applied =	0.10015	0.10070	0.10081	0.10057	
1× LOQ 1	ND	0.0942	0.1018	0.0984	
1× LOQ 2	ND	0.1157	0.0894	0.1029	
1× LOQ 3	ND	0.1092	0.1003	0.0951	
1× LOQ 4	ND	0.1187	0.0924	0.1099	
1× LOQ 5	ND	0.1091	0.0984	0.1091	
1× LOQ 6	ND	0.0980	0.0818	0.1062	
Average µg/sample =		0.1075	0.0940	0.1036	
CVi =		0.08975	0.08135	0.05735	
Group Bias =		0.06741	-0.06737	0.03014	
Average % Recovery =		**106.74**	**93.26**	**103.01**	

ND = Not detected.

TABLE 25B. PRECISION AND ACCURACY (INT. STD. = D_{14}-METHAMPHETAMINE)

Part B	Parameters for Calculating Precision and Accuracy, and Results				
Scan Mode	UNITS = µg/sample (sample is desorbed in 40 mL 0.2 N sulfuric acid) INTERNAL STANDARD = D_{14}-Methamphetamine				
	Phencyclidine	Phentermine	Phenylpropanolamine	Pseudoephedrine	
OPTION #1		See notes 1 and 17.		See notes 1 and 19.	
Test(Concentration) Levels Omitted	1× LOQ	NONE	NONE	NONE	
Degrees of freedom =	4	5	5	5	
Accuracy =	**14.1379**	**10.3570**	**12.3472**	**12.2547**	
Overall Precision ($\hat{S}_{rT}$) =	0.05270	0.05269	0.05980	0.05066	
Chi^2 =	11.306	10.580	6.704	6.294	
pass @ 0.95?	no	**YES**	YES	**YES**	
pass @ 0.975?	no	**YES**	YES	**YES**	
Mean bias =	+0.05469	+0.00406	+0.01982	-0.03921	
from	-0.03860	-0.05998	-0.06737	-0.07368	
to	+0.10390	+0.06741	+0.12137	+0.03014	
F' =	3.71929	2.94850	5.22977	2.76797	
pass @ 0.05?	no	no	no	no	
pass @ 0.025?	no	**YES**	no	**YES**	
OPTION #2					
Test(Concentration) Levels Omitted	1× LOQ 3× LOQ		1× LOQ		
Degrees of freedom =	3		4		
Accuracy =	**10.7849**		**12.6866**		
Overall Precision ($\hat{S}_{rT}$) =	0.03784		0.05447		
Chi^2 =	3.754		5.134		
pass @ 0.95?	YES		YES		
pass @ 0.975?	YES		YES		
Mean bias =	+0.04560		+0.03726		
from	-0.03860		-0.01247		
to	+0.10390		+0.12137		
F' =	5.38432		3.89743		
pass @ 0.05?	no		no		
pass @ 0.025?	no		no		
OPTION #3			See notes 1 and 18.		
Test(Concentration) Levels Omitted	3× LOQ 300× LOQ 1× LOQ		100× LOQ		
Degrees of freedom =	2		4		
Accuracy =	**12.7397**		**12.5028**		
Overall Precision ($\hat{S}_{rT}$) =	0.03266		0.06379		
Chi^2 =	2.216		4.146		
pass @ 0.95?	YES		**YES**		
pass @ 0.975?	YES		**YES**		
Mean bias =	+0.07367		-0.00049		
from	+0.05565		-0.06737		
to	+0.10390		+0.07077		
F' =	0.83112		2.49802		
pass @ 0.05?	YES		**YES**		
pass @ 0.025?	YES		**YES**		
OPTION #4	See notes 1 and 16.				
Test(Concentration) Levels Omitted	30× LOQ 100× LOQ 1× LOQ				
Degrees of freedom =	2				
Accuracy =	**15.8743**				
Overall Precision ($\hat{S}rT$) =	0.06482				
Chi^2 =	2.884				
pass @ 0.95?	**YES**				
pass @ 0.975?	**YES**				
Mean bias =	+0.05212				
from	-0.03860				
to	+0.10390				
F' =	4.36268				
pass @ 0.05?	no				
pass @ 0.025?	**YES**				

TABLE 26A. MICROGRAMS RECOVERED FOR MDEA

Part A Wipe Media =	Micrograms per Sample Recovered from Cotton Gauze		
	Cotton Gauze	Cotton Gauze	Cotton Gauze
Internal Standard = Test Level Replicate	D_{11}-Amp See note 20.	D_{14}-Met See note 20.	**nPAmp** See note 21.
Amount Applied =	28.58259	28.58259	28.58259
300× LOQ 1	23.161	38.988	26.074
300× LOQ 2	22.369	34.583	25.923
300× LOQ 3	19.921	29.056	26.849
300× LOQ 4	20.101	31.841	25.714
300× LOQ 5	19.532	29.090	26.106
300× LOQ 6	20.471	30.381	27.844
Average µg/sample =	20.926	32.323	26.418
CVi =	0.07062	0.11955	0.03017
Group Bias =	-0.26788	0.13086	-0.07572
Average % Recovery =	**73.21**	**113.09**	**92.43**
Amount Applied =	9.52753	9.52753	9.52753
100× LOQ 1	11.251	11.500	9.686
100× LOQ 2	9.336	9.691	9.573
100× LOQ 3	10.123	10.532	9.960
100× LOQ 4	9.487	9.541	9.686
100× LOQ 5	10.259	10.161	9.989
100× LOQ 6	10.776	10.245	9.883
Average µg/sample =	10.205	10.278	9.796
CVi =	0.07203	0.06825	0.01743
Group Bias =	0.07115	0.07880	0.02819
Average % Recovery =	**107.12**	**107.88**	**102.82**
Amount Applied =	2.85826	2.85826	2.85826
30× LOQ 1	2.3143	2.2703	2.8107
30× LOQ 2	3.5890	2.3072	2.5451
30× LOQ 3	2.2240	2.1620	2.4340
30× LOQ 4	2.7193	2.6361	2.7095
30× LOQ 5	2.8295	2.6788	2.9295
30× LOQ 6	3.2116	2.9496	2.9066
Average µg/sample =	2.8146	2.5007	2.7226
CVi =	0.18568	0.12087	0.07335
Group Bias =	-0.01527	-0.12511	-0.04747
Average % Recovery =	**98.47**	**87.49**	**95.25**
Amount Applied =	0.95275	0.95275	0.95275
10× LOQ 1	1.2074	1.2234	0.8644
10× LOQ 2	1.1778	1.1452	0.8959
10× LOQ 3	1.0730	1.1404	0.9217
10× LOQ 4	1.1559	1.2024	0.9658
10× LOQ 5	1.1667	1.2578	1.0148
10× LOQ 6	1.0379	0.9826	0.9574
Average µg/sample =	1.1365	1.1586	0.9367
CVi =	0.05807	0.08407	0.05748
Group Bias =	0.19281	0.21609	-0.01688
Average % Recovery =	**119.28**	**121.61**	**98.31**
Amount Applied =	0.28583	0.28583	0.28583
3× LOQ 1	0.3725	0.3693	0.3426
3× LOQ 2	0.3491	0.3257	0.2775
3× LOQ 3	0.3978	0.3846	0.3275
3× LOQ 4	0.3958	0.3727	0.3244
3× LOQ 5	0.3852	0.3397	0.2972
3× LOQ 6	0.3499	0.3190	0.2948
Average µg/sample =	0.3750	0.3518	0.3107
CVi =	0.05797	0.07755	0.07917
Group Bias =	0.31216	0.23094	0.08691
Average % Recovery =	**131.22**	**123.09**	**108.69**
Amount Applied =	0.09528	0.09528	0.09528
1× LOQ 1	0.1103	0.1009	0.1113
1× LOQ 2	0.1391	0.1366	0.1410
1× LOQ 3	0.0989	0.0980	0.1103
1× LOQ 4	0.0862	0.0861	0.0971
1× LOQ 5	0.1085	0.1051	0.1143
1× LOQ 6	0.0803	0.0768	0.0900
Average µg/sample =	0.1039	0.1006	0.1107
CVi =	0.20176	0.20374	0.15884
Group Bias =	0.09035	0.05571	0.16155
Average % Recovery =	**109.03**	**105.57**	**116.15**

ND = Not detected.

TABLE 26B. PRECISION AND ACCURACY FOR MDEA

Part B. Parameters for Calculating Precision and Accuracy, and Results			
Wipe Media =	**Cotton Gauze**	**Cotton Gauze**	**Cotton Gauze**
Internal Standard =	D_{11}-Amp	D_{14}-Met	**nPAmp**
OPTION #1			
Test(Concentration) Levels Omitted	NONE	NONE	NONE
Degrees of freedom =	5	5	5
Accuracy =	**27.3208**	**29.7277**	**16.8804**
Overall Precision ($\hat{S}_{rT}$) =	0.12389	0.12121	0.08306
Chi^2 =	16.646	8.510	23.742
pass @ 0.95?	no	YES	no
pass @ 0.975?	no	YES	no
Mean bias =	+0.06389	+0.09788	+0.02276
from	-0.26788	-0.12511	-0.07572
to	+0.31216	+0.23094	+0.16155
F' =	12.78240	5.55395	4.78340
pass @ 0.05?	no	no	no
pass @ 0.025?	no	no	no
OPTION #2			
Test(Concentration) Levels Omitted	1× LOQ	1× LOQ	1× LOQ
Degrees of freedom =	4	4	4
Accuracy =	**22.9500**	**26.5201**	**11.1876**
Overall Precision ($\hat{S}_{rT}$) =	0.10138	0.09659	0.05686
Chi^2 =	11.586	2.555	11.640
pass @ 0.95?	no	YES	no
pass @ 0.975?	no	YES	no
Mean bias =	+0.05859	+0.10632	-0.00500
from	-0.26788	-0.12511	-0.07572
to	+0.31216	+0.23094	+0.08691
F' =	23.52257	9.69422	4.76674
pass @ 0.05?	no	no	no
pass @ 0.025?	no	no	no
OPTION #3		See note 23.	
Test(Concentration) Levels Omitted	1× LOQ 30× LOQ	30× LOQ	100× LOQ 300× LOQ
Degrees of freedom =	3	4	3
Accuracy =	**18.4009**	**34.1987**	**21.6168**
Overall Precision ($\hat{S}_{rT}$) =	0.06502	0.12128	0.10023
Chi^2 =	0.400	8.435	6.058
pass @ 0.95?	YES	**YES**	**YES**
pass @ 0.975?	YES	**YES**	**YES**
Mean bias =	+0.07706	+0.14248	+0.04602
from	-0.26788	+0.05571	-0.04747
to	+0.31216	+0.23094	+0.16155
F' =	51.40567	1.89279	3.72528
pass @ 0.05?	no	**YES**	no
pass @ 0.025?	no	**YES**	**YES**
OPTION #4	See note 22.		See notes 1 and 24.
Test(Concentration) Levels Omitted	1× OQ 3× LOQ 300× LOQ		1× LOQ 300× LOQ
Degrees of freedom =	2		3
Accuracy =	**27.9926**		**12.3569**
Overall Precision ($\hat{S}_{rT}$) =	0.11978		0.06176
Chi^2 =	7.2932		8.626
pass @ 0.95?	no		no
pass @ 0.975?	**YES**		**YES**
Mean bias =	+0.08290		+0.01268
from	-0.01527		-0.04747
to	+0.19281		+0.08691
F' =	3.54823		3.17602
pass @ 0.05?	**YES**		no
pass @ 0.025?	**YES**		**YES**

Notes:

(1) Values selected for Table 21.

(2) Amphetamine (using amphetamine D_{11} internal standard): The 3× LOQ had an un-poolable negative bias of -0.05234.

(3) Cocaine (using amphetamine D_{11} internal standard): The 1× LOQ level was omitted for all options because it was undetectable. In Option #2, the Omitting the 100× and 300× LOQ levels for cocaine gives homogenous data with the lowest Chi^2 for 2 degrees of freedom. But the accuracy is >30%. The 100× and 300× LOQ levels have the best recoveries and need to be conserved. The #3 replicate in the 30× LOQ level had an obviously low recovery, but it was not a Grubbs outlier at the 1% or 5% levels (% risk of false rejection). Nevertheless, if replicate #3 was omitted, an acceptable accuracy was obtained (OPTION #4). Instead, the 30× LOQ and the 3× LOQ levels were both omitted (OPTION #3) giving acceptable accuracy and precisions. The lower end of the applicable range was raised to 0.3 µg per sample.
GENERAL COMMENTS ON COCAINE: Recoveries are generally high at the low concentration levels. This was not the case when single-point calibration of the liquid standards was used indicating that the quadratic curve does not fit the data when the internal standard was amphetamine-D_{11} or methamphetamine-D_{14}. It is probable that if a deuterated analog of cocaine (e.g., cocaine-D_3) was used, a better curve fit would result with better recoveries and precisions at the lower concentration levels, giving a better overall precision and accuracy.

(4) Ephedrine (using amphetamine D_{11} internal standard): All levels have poolable group CVs and biases.

(5) MDMA (using amphetamine D_{11} internal standard): All levels have poolable group CVs and biases.

(6) Methamphetamine (using amphetamine D_{11} internal standard): Omitting the 1× LOQ level, both tests for homogeneity pass. However, the recovery and precision at the 1× LOQ level are reasonable (109% with a precision of 4.6%). By omitting the 300× LOQ level instead, both tests for homogeneity also pass and the 1× LOQ level is conserved for the sake of extending the applicable range down to the 1× LOQ level. The accuracy is only slightly larger (9.1861 up from 7.6438), but this is still well below the 25% limit and reflects the accuracy at the action level which is set by several states for the allowable residual level for methamphetamine.

(7) Phencyclidine (using amphetamine D_{11} internal standard): The 1× LOQ level was un-measurable. The 10× LOQ level had an inlier CV that made it non-homogenous with the other group CVs, therefore the 10× LOQ level was omitted.

(8) Phentermine (using amphetamine D_{11} internal standard): All levels have poolable group CVs and biases. The 3× LOQ level had an inlier CV which was non-homogenous.

(9) Phenylpropanolamine (using amphetamine D_{11} internal standard): Both tests for homogeneity pass when the 1× LOQ level is omitted. The Chi^2 is larger if the 100× LOQ level, which has a large bias (+10.1%), is omitted, but it allows the 1× LOQ level to be conserved with little change in either the overall CV or the accuracy, allowing the applicable range to extend to the 1× LOQ level.

(10) Pseudoephedrine (using amphetamine D_{11} internal standard): Both tests for homogeneity pass when the 1× LOQ level is omitted. But the Chi^2 is lower if the 10× LOQ level is omitted resulting in little change in either the overall CV or the accuracy and the 1× LOQ

level is also conserved allowing the applicable range to extend down to the 1× LOQ level.

(11) Amphetamine (using methamphetamine D_{14} internal standard): The 3× LOQ level had a large un-poolable negative bias of -0.10595. The CV at the 3× LOQ level was large (0.10097) but poolable.

(12) Cocaine (using methamphetamine D_{14} internal standard): The 1× LOQ level was omitted for all options because it was undetectable. In OPTION #2, omitting the 300× LOQ levels gives homogenous data with the lowest Chi^2 for 3 degrees of freedom. But the accuracy is >25% (28.3%). In OPTION #3, omitting the 100× and 300× LOQ levels gives homogenous data with the lowest Chi^2 for 2 degrees of freedom. But the accuracy is again >25% (32.1%).
The 300× LOQ level has a near inlier CV which makes it non-homogenous with all other group CVs. Unfortunately, if the tests for homogeneity are to be met, any combination of levels that excludes the 300× LOQ level results in accuracies in excess of 25%. One other option (OPTION #4) was to remove the #3 replicate in the 30× LOQ level which was obviously low. It was not a Grubbs outlier at the 1% level (% risk of false rejection) but was an outlier at the 5% level, and if it was omitted, acceptable overall precision and accuracy are obtained. See note (3) above for GENERAL COMMENTS ON COCAINE.

(13) Ephedrine (using methamphetamine D_{14} internal standard): All levels have poolable group CVs and biases.

(14) MDMA (using methamphetamine D_{14} internal standard): The 300× LOQ level had a non-poolable inlier CV. The 300× LOQ level also had a bias that was non-homogenous, although by itself it was not large (-4.8%).

(15) Methamphetamine (using methamphetamine D_{14} internal standard): Omitting the 1× LOQ level, both tests for homogeneity pass. However, there are inlier CVs at 3 levels: the 3×, 10×, and 300× LOQ levels. The smallest inlier is at the 3× LOQ level. By omitting the 3× LOQ level, a larger Chi^2 results, but the overall CV rises from 0.02083 to a more conservative 0.03022. The accuracy is a little higher (5.9292, up from 4.9381), but is well below the limit of 25%, and reflects the accuracy at the important action level set by various states for the allowable residual level for methamphetamine.

(16) Phencyclidine (using methamphetamine D_{14} internal standard): The 1× LOQ level was un-measurable. Both tests for homogeneity pass when either the 3× and 300× LOQ or the 30× and 10× LOQ levels are omitted. The 3× LOQ level has a relatively high group CV (0.09032) and the 300× LOQ level has a relatively low (but reasonable) group bias (-0.03860). The 30× and 100× LOQ levels have relatively small group CVs (0.02792 and 0.02237 respectively). The Chi^2 is lower when the 3× and 300× LOQ levels are omitted, but the 3× LOQ level is conserved (giving a lower applicable range) when the 30× and 100× LOQ levels are omitted. By omitting the 100× and 30× LOQ levels the overall CV increases to a more conservative value (0.06482 from 0.03266) and the accuracy increases only slightly (15.8743 from 12.7397). This is much lower that the 25% limit, and reflects the accuracy that should be expected at the lower limit of the analytical range.

(17) Phentermine (using methamphetamine D_{14} internal standard): All levels have poolable group CVs and biases. The 300× LOQ level had a near inlier CV.

(18) Phenylpropanolamine (using methamphetamine D_{14} internal standard): The 100× LOQ level has a large, non-homogenous bias.

(19) Pseudoephedrine (using methamphetamine D_{14} internal standard): All levels have poolable group CVs and biases.

(20) MDEA: Results for MDEA when amphetamine-D_{11} and methamphetamine-D_{14} are used as internal standards are shown for comparison.

(21) MDEA: Results for MDEA when N-propyl amphetamine, a similarly hindered secondary amine, is used as the internal standard are the only results that meet the precision and accuracy criteria.

(22) MDEA (using amphetamine D_{11} internal standard): Only one combination could be found that passed both tests for homogeneity, but it gave an accuracy >25%. D_{11}-Amphetamine is not a good internal standard for MDEA on cotton gauze.

(23) MDEA (using methamphetamine D_{14} internal standard): Several combinations could be found that passed both tests for homogeneity, but all gave an accuracy >25%.The level with the lowest Chi^2 and fewest levels omitted is presented. D_{14}-Methamphetamine is not a good internal standard for MDEA on cotton gauze.

(24) MDEA (using N-propyl amphetamine internal standard): Only two combinations of four concentration levels gave poolable data (OPTIONS #3 and 4). The one with the lowest Chi^2 is presented as OPTION #3. The 100× LOQ level has an inlier CV. The 300× LOQ level has a relatively large negative bias. Although the Chi^2 is lower and the 1× LOQ level is conserved, the accuracy is relatively large (21.6%) and the overall precision is 0.10023 (10.0%). OPTION #4 gives the other combination which omits the 300× LOQ level for its large negative bias, and the 1× LOQ level which has a large positive bias and large CV. The Chi^2 is larger, and the applicable range only goes down to 0.3ug/sample (which is not unrealistic for this analyte), but the accuracy and the overall precision are better. N-Propylamphetamine is a good internal standard for MDEA on cotton gauze.

OVERALL OBSERVATIONS AND CONCLUSIONS:

1. Amphetamine-D_{11} and methamphetamine-D_{14} are recommended internal standards. N-Propylamphetamine is essential for MDEA determination.

2. Cotton gauze was an acceptable media. There was a preponderance of inlier CVs (CVs < 2%) that created difficulties in obtaining poolable group CVs.

3. At the 1× LOQ level the CVs were generally larger than at higher concentration levels. This also made it a challenge to get poolable data. It is at the 1× LOQ level that the action levels have been set for various states, so there was an effort to conserve this level to the slight detriment of the overall precision and accuracies in order to better reflect precision and accuracies at that level. Methamphetamine fared better than any of the analytes.

4. The method is not optimum for cocaine, but can be used over a higher concentration range. The problem may be due to the length of time the samples sat prior to analyses, since cocaine is subject to hydrolysis. Using a deuterated analog of cocaine for the internal standard (e.g., cocaine-D_3) is recommended.

5. Although the precision and accuracy were acceptable for a range down to the 3× LOQ level, using a deuterated analog of phencyclidine for the internal standard (e.g., phencyclidine-D_5) might help make precision and accuracy even better.

6. There is some degree of steric affect around the derivatized nitrogen. In general, primary amines are better with an internal standard that is a primary amine. N-Methyl secondary amines are better with an internal standard that is the same. N-ethyl secondary amines work with an N-propyl secondary amine, and presumably with other N-ethyl secondary amines.

F. Conclusion

The precision and accuracy criterion were met for methamphetamine and many additional analytes that may be associated with clandestine manufacture, as shown in Table 23. Accuracies are much less than 25% and overall precisions and mean biases are less than 10%.

With some analytes, in order to meet the precision and accuracy criterion, the lower limit of the applicable range had to be raised.

VIII. RECOVERY FROM VARIOUS SURFACES USING DIFFERENT WIPE SOLVENTS AND WIPING TECHNIQUES

A. Introduction and Objective

Doing a wipe recovery study was not part of the original scope for this method development. Several questions kept coming up in e-mails and meetings with NIOSH and officials from the departments of health of various states as to whether there been an actual wipe recovery study performed, whether water could be used as a wipe solvent, and why isopropanol was chosen over methanol. Because of these questions and challenges, it was decided that it was necessary to conduct a controlled surface recovery study at DataChem Laboratories.

A simulated sampling study using a Teflon™ surface is described by OSHA on their web site (no publication has been made of this material) [17]. However, data from such a study would

be only applicable to non-porous and non-wetting surfaces (i.e. Teflon™ surfaces), which would hardly be the case under real sampling situations. In addition, recoveries in such a study would be highly dependent upon individual technique. This was obvious in qualitative studies using crystal violet dye applied to a Teflon™ surface in this laboratory.

Besides testing realistic surface types, different solvents should be tested. Accordingly, distilled water, vinegar (100% Heinz 5% distilled white vinegar), isopropanol, and methanol were selected. Vinegar was tested because it is acidic and it was supposed that a weak acidic solution might be a useful but relatively harmless solvent, compatible with the method.

Two different wipe techniques were tested: Wiping in concentric squares, as described by OSHA [17] and in the Colorado Guidance document [18], and the side-to-side wiping and blotting techniques as described in the Washington State Guidance document [14].

Finally the affect of a second or serial wipe on the previously wiped area for improving was tested to see if recoveries were improved.

B. Procedure

Various surface materials that would be typical in most homes were assembled or located. These were as follows:

1. A section of wall in one of the rooms at DataChem Labs. The wall was gypsum board painted with a latex base paint and was at least several years old.

2. An enamel surface consisting of the lid from an upright clothes washing machine which was removed from the washer and brought into the laboratory.

3. The door from a used Hotpoint refrigerator was removed from its hinges and brought into the laboratory.

4. A small piece of Formica™ countertop was purchased at a local hardware store.

5. A particle board book shelf covered with a veneer of vinyl (with a simulated pattern of maple) was purchased from a local hardware store.

6. A 3 foot × 4 foot piece of varnished hardwood paneling was purchased from a local hardware store. The nature of the varnish was unknown but is assumed not to be a polyurethane varnish but rather a rapid drying lacquer which is easier for a factory to deal with.

All materials were rinsed thoroughly three times with methanol in the area in which the spiking and wiping were to be conducted. Four by four inch squares were drawn on the surfaces with graphite pencil, to give approximately a 100 cm^2 area. Sixty microliters of the same analyte spiking solution used for the precision and accuracy study was spread around within the squares. Crystal violet was added to the spiking solution in order to indicate where the solution was being applied. The solution was kept ½ inch from the edges of each square. It was spread around using the tip of the syringe needle so that most of the surface within ½ inch of the edges was covered. Only about four to six squares were spiked at a time in order to eliminate any variation due to evaporation of the analytes, if any at all. The methanol was allowed to evaporate for at least a minute or two before sampling began.

Sampling was conducted using 3" × 3" 12-ply non-sterile Accolade ™ brand cotton gauze. It was U.S.P type VII, lot number 60305009 (reference number 908293). It was made in China for Banta Health Care Ltd. Neehah, WI 54956 and Rialto CA, 02376. The cotton was very bright white, and appears to have been the bleached variety. (The precision and accuracy study was performed on the unbleached variety.) The change in types of cotton was necessitated because an order for the Caring brand previously used had not arrived yet.

Wiping was conducted as described in NIOSH 9109, folding the gauze in half twice, wetting with a few milliliters of solvent, squeezing out the excess, and then wiping the spiked

areas with either a concentric squares technique or the side-to-side technique, moving from top to bottom in a "Z" pattern. This was followed by reversing the last fold (inverting) so that a fresh surface was exposed, and then wiping the area again in either the concentric squares technique or from top-to-bottom in an "N" pattern, moving from left to right. The gauze was put into a 50-mL polypropylene (PP) centrifuge tube and capped. A second pre-wetted gauze wipe was taken of the same area using the same technique. This gauze was put into a separate 50-mL PP centrifuge tube.

Each sample consisted of approximately 3 µg each of methamphetamine and other drugs.

Liquid and media standards and blanks were prepared by spiking over a range of from 0.025 µg through 6 µg of analytes. The 50-mL PP centrifuge tubes containing the samples, blanks, and standards were capped and stored overnight.

The samples were spiked the next day with 60 µg of internal spiking solution and 30 mL of 0.2 N aqueous sulfuric acid was added. The tubes were capped and tumbled for 2 hours. Because of a lack of sufficient SPE columns on hand in the laboratory, subsequent cleanup, derivatization, and analysis were conducted using the liquid-liquid extraction procedure, NIOSH 9106. Derivatization was conducted using chlorodifluoroacetic anhydride for the latex painted wall samples. But when it was observed that the reagent appeared to be contaminated or degraded, pentafluoropropionic anhydride was used for the other surface samples. When pentafluoropropionic anhydride was used, the derivatization oven temperature was raised from 70 to 90 °C. Analysis was by GC-MS in the SIM mode. The resulting data should be applicable to both NIOSH 9106 and NIOSH 9109 since surface sampling recovery is a function of the media, surface material, and wetting solvent and should be independent of the analytical procedure itself.

C. Results

The recoveries from the various surfaces are summarized in Table 29 and are given in more detail in the following tables and histograms.

With a single exception (phenylpropanolamine), methanol is superior to isopropanol and isopropanol is superior to water or vinegar. Water or vinegar is not recommended.

A second or serial wipe was successful at removing on average about 6% more analyte when water or methanol was used. However, the benefit of a second wipe was greater with isopropanol, averaging 11%. With a second wipe, the recoveries with isopropanol approached those where methanol was used with a single wipe. The 50-mL PP centrifuge tubes easily accommodate a pair of cotton gauze wipes if the size of the gauzes is either 3" × 3" 12-ply or 4" × 4" 8-ply.

Recoveries from the wall using methanol were over 80% regardless of the analyte. With a second wipe using methanol, the recoveries were greater than 90%. What is even more remarkable with methanol is that the precision of recovery for the first wipe was 2.9 to 5.3%, excluding MDEA and cocaine. The precision of recovery using isopropanol was higher, but still single digit, excluding MDEA and cocaine. These precisions are for 6 replicates. It suggests that wipe sampling may not be such a black art, using the right solvent and wiping technique. However, these results are for surfaces spiked just prior to sampling. For walls that have been exposed to drug vapors and dusts for an extended period of time there may be significant penetration of the analytes into the surface material, meaning that a surface wipe might not reveal the true loading of the surface material. Methamphetamine that has deeply penetrated the surface might migrate over time back to the surface after wiping.

The good recoveries with methanol may be due somewhat to the fact that the methanol lifts off some of the surface layer of the paint (on painted surfaces) and also a thin film of dirt. The wall was definitely cleaner (lighter in color) where the methanol samples were taken. The isopropanol hardly made a difference in the color of the patina of the paint on the wall. Results for 5% vinegar are not presented since they are not as good as for isopropanol.

The situation was not too much different with the other sample types. It was interesting that the recoveries were so high for the varnished hardwood surface. The surface was very much textured because it was an authentic wood surface, but it shows that the varnish was effective as sealing the surface. The type of varnish used is not known.

TABLE 27. RECOVERY FROM VARIOUS SURFACES WITH VARIOUS SOLVENTS; ONE WIPE COMPARED TO THE SUM OF TWO WIPES [1]

A. Recovery From Wall (Latex Painted) [2]

	Gauze Wetting Solvent =	Water [3]			Isopropanol [4]			Methanol [5]		
		First Wipe		Plus Second Wipe [6]	First Wipe		Plus Second Wipe [6]	First Wipe		Plus Second Wipe [6]
	TEST COMPOUND [7]	Percent	%RSD	Percent	Percent	%RSD	Percent	Percent	%RSD	Percent
1	Amphetamine	51	14	56	67	6.0	78	**90**	4.0	**96**
2	Cocaine	36	22	36	69	22	**80**	**89**	9.1	**94**
3	Ephedrine	48	23	52	76	7.4	**85**	**91**	4.4	**96**
4	MDMA	40	20	44	61	9.0	70	**88**	5.3	**94**
5	MDEA	45	22	50	69	12	**80**	**90**	11	**97**
6	Methamphetamine	46	16	50	64	7.4	75	**87**	3.5	**94**
7	Phencyclidine	27	26	30	64	9.6	73	**86**	5.2	**91**
8	Phentermine	53	9.2	58	78	6.6	**91**	**95**	2.9	**101**
9	Phenylpropanolamine	58	21	62	**80**	9.3	**95**	**85**	5.0	**94**
10	Pseudoephedrine	49	20	53	73	7.0	**85**	**95**	3.3	**101**

Bold values are recoveries greater than 80%.

B. Recovery of Methamphetamine From Various Surfaces

	Gauze Wetting Solvent =		Isopropanol			Methanol		
			First Wipe		Plus Second Wipe [6]	First Wipe		Plus Second Wipe [6]
	SURFACE MATERIAL [8]	Replicates	Percent	%RSD	Percent	Percent	%RSD	Percent
1	Enamel (lid of washing machine)	4 [9]	58	5.7	68	**81**	2.4	**87**
2	Vinyl veneer on particle board	4 [10]	60	5.2	68	**81**	4.8	**89**
3	Latex painted wall	6 [9]	64	7.4	75	**87**	3.5	**94**
4	Refrigerator door	2 [10]	65	2.9	76	**91**	4.0	**92**
5	Varnished hardwood panel	2 [11]	72	5.4	76	**82**	3.7	**86**
6	Formica™ countertop	4 [10]	75	4.9	**82**	**87**	3.8	**91**

Bold values are recoveries greater than 80%.

(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) Isopropanol was 100%. The average percentage increase in recovery with a second wipe was 11%, about twice that for methanol. Thus there is more benefit from a second wipe when isopropanol is used than when methanol is used.

(5) Methanol was 100%. The average percentage increase in recovery with a second wipe was 6%.

(6) 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. The percent recovery shown in the column represents the sum of the amounts recovered in the first and second wipes. In practice, if a second (serial) wipe is taken, it is to be included with the first wipe as a single sample.

(7) Each pre-measured area was spiked with 3 µg of each analyte in methanol and the methanol allowed to dry for a few minutes prior to wipe sampling.
(8) 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 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.
(9) Samples were taken using the side-to-side and then top-to-bottom wiping technique.
(10) Half of the samples were sampled using the side-to-side wiping technique and half were sampled using the concentric squares wiping technique. There was no significant difference in recoveries. Percent recoveries and %RSDs are for both techniques combined.
(11) Samples were taken using top-to-bottom wiping only (with a back and forth scrubbing motion with the grain of the wood).

TABLE 28. RECOVERY OF METHAMPHETAMINE FROM LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	First Wipe RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	45.60	15.93	4.24	49.84
5% Vinegar	55.10	15.08	6.07	61.17
Isopropanol	64.15	7.40	10.84	74.99
Methanol	87.41	3.46	6.13	93.54

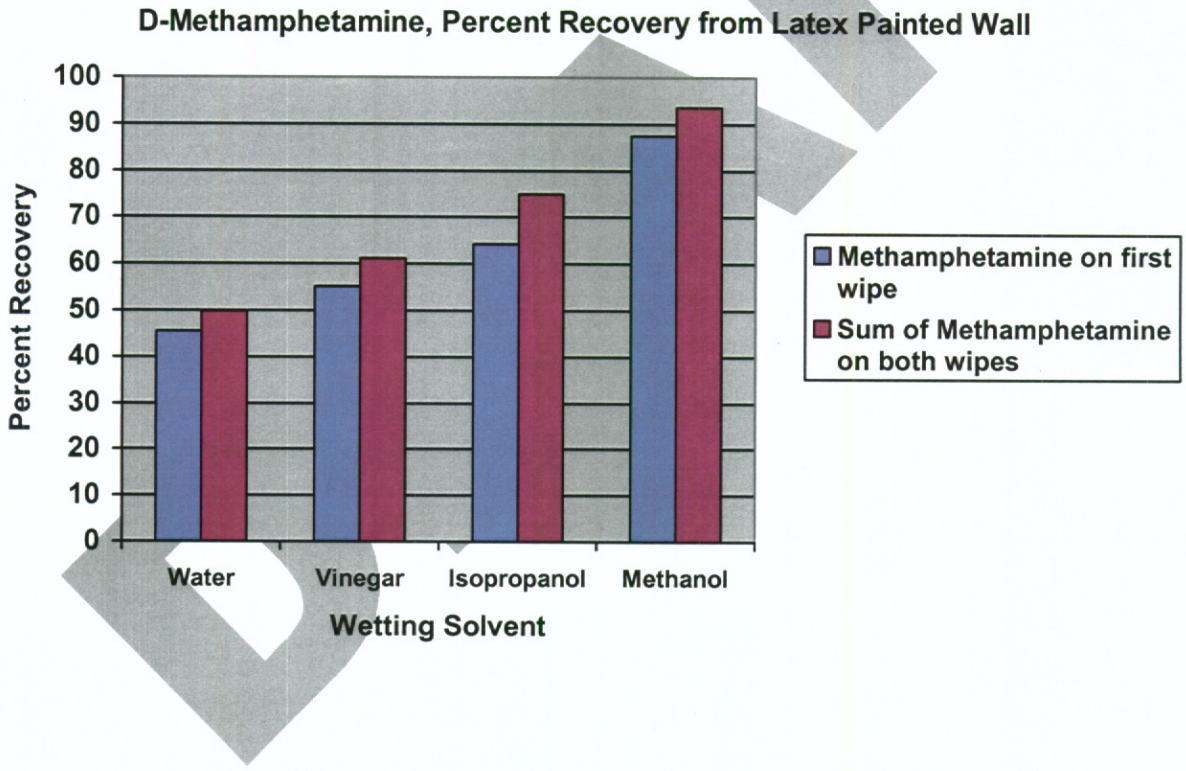


TABLE 29. RECOVERY OF AMPHETAMINE FROM LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	51.08	13.66	4.58	55.66
5% Vinegar	60.56	13.40	6.40	66.96
Isopropanol	66.59	6.05	11.55	78.14
Methanol	89.75	4.03	6.26	96.02

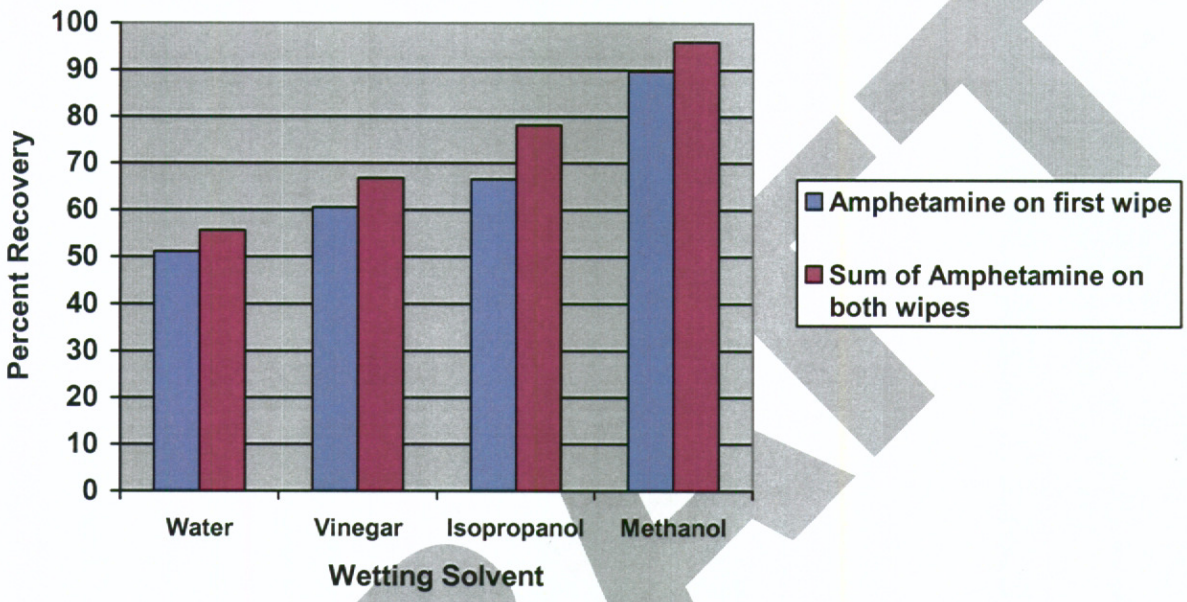


TABLE 30. RECOVERY OF PHENYLPROPANOLAMINE FROM LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	58.07	21.23	3.86	61.93
5% Vinegar	67.11	8.44	7.02	74.13
Isopropanol	79.60	9.27	15.61	95.21
Methanol	85.23	5.05	7.71	93.94

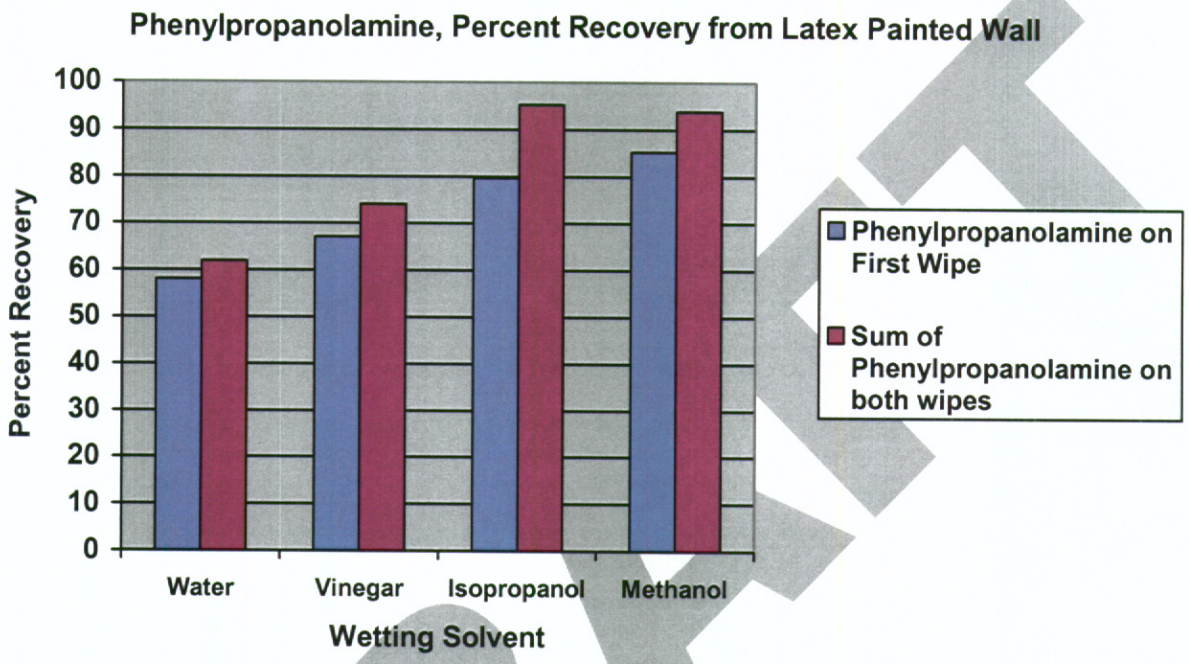


TABLE 31. RECOVERY OF EPHEDRINE FROM LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	48.48	23.11	4.05	52.53
5% Vinegar	52.41	10.78	5.84	58.25
Isopropanol	75.50	7.35	9.87	85.37
Methanol	91.47	4.43	4.58	96.05

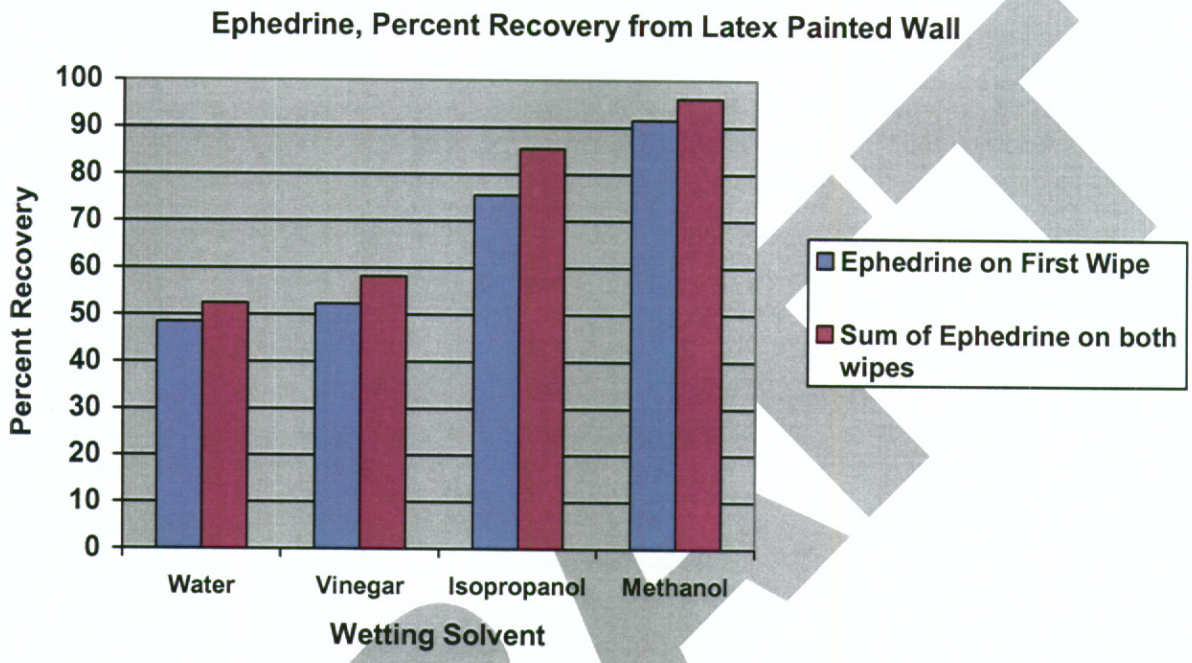


TABLE 32. RECOVERY OF PSEUDOEPHEDRINE FROM LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	49.38	20.34	3.92	53.30
5% Vinegar	55.66	12.55	6.04	61.70
Isopropanol	73.37	7.00	11.84	85.21
Methanol	94.99	3.33	5.89	100.88

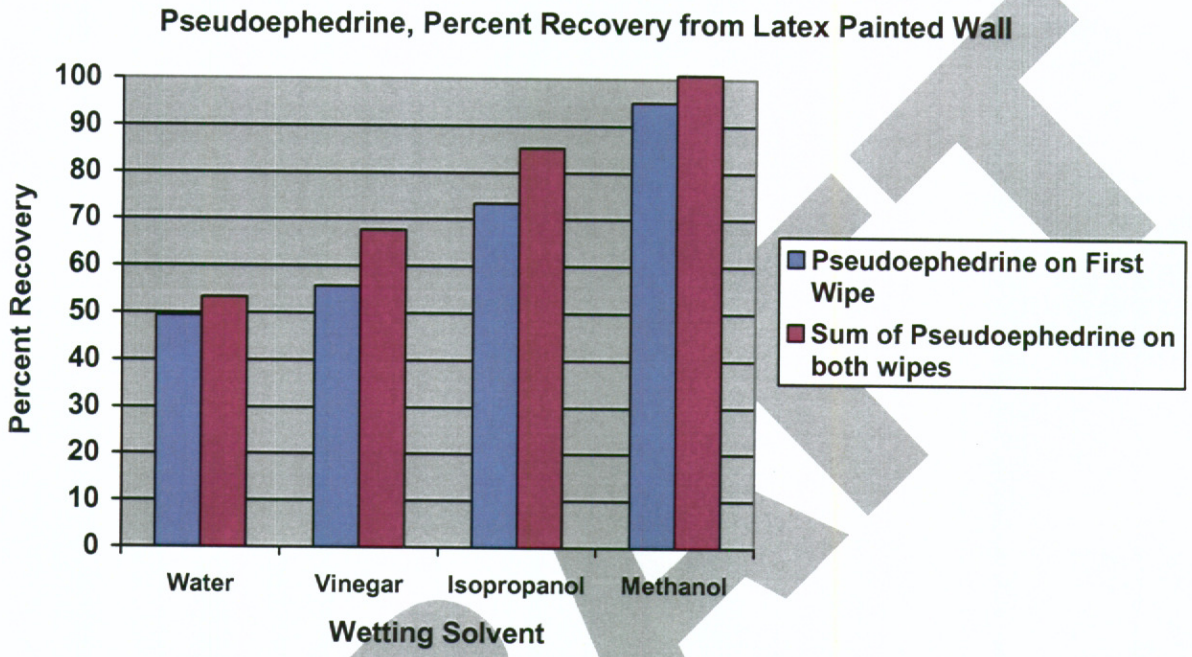


TABLE 33. RECOVERY OF MDMA FROM SPIKED LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	39.93	19.93	3.74	43.67
5% Vinegar	45.97	16.26	5.35	51.32
Isopropanol	61.15	9.02	9.10	70.25
Methanol	87.82	5.34	5.73	93.55

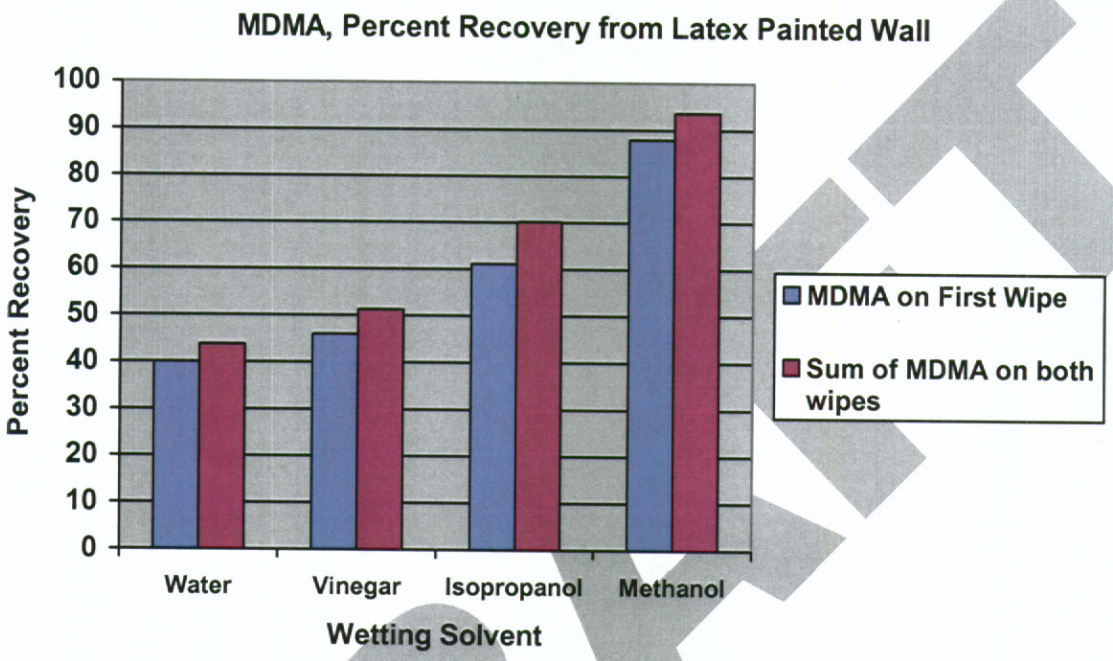


TABLE 34. RECOVERY OF MDEA FROM SPIKED LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	44.74	22.07	5.12	49.96
5% Vinegar	50.40	21.92	7.35	57.75
Isopropanol	68.65	11.74	11.69	80.34
Methanol	89.91	11.17	7.03	96.94

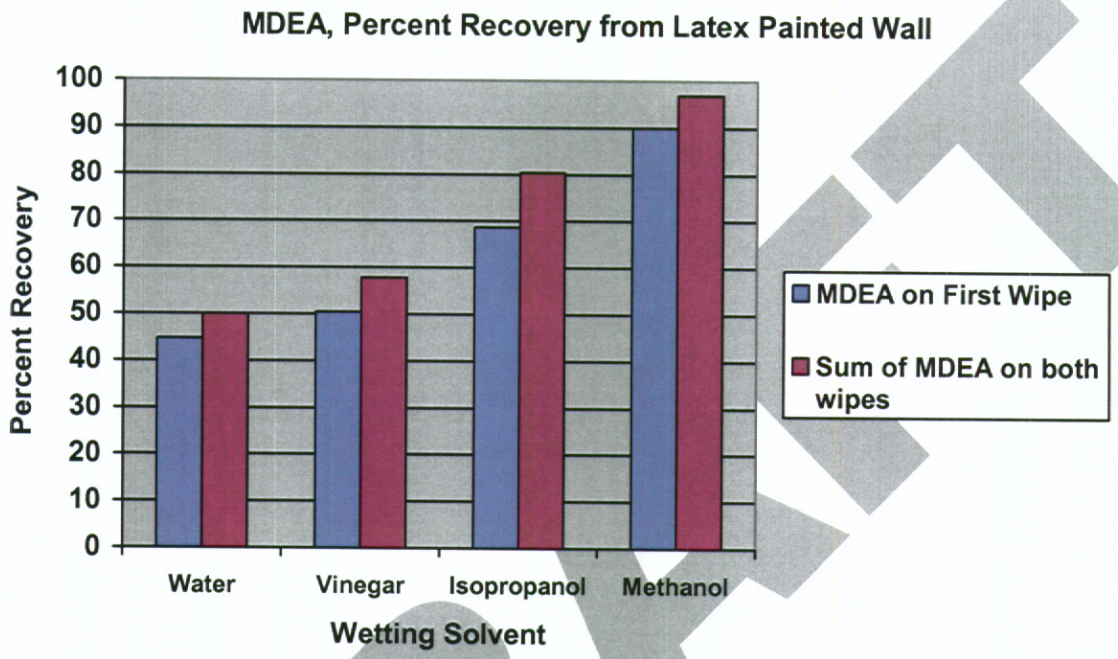


TABLE 35. RECOVERY OF PHENCYCLIDINE FROM SPIKED LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	26.66	26.26	3.33	29.99
5% Vinegar	34.46	19.75	5.14	39.60
Isopropanol	64.31	9.58	8.77	73.08
Methanol	86.22	5.20	5.02	91.24

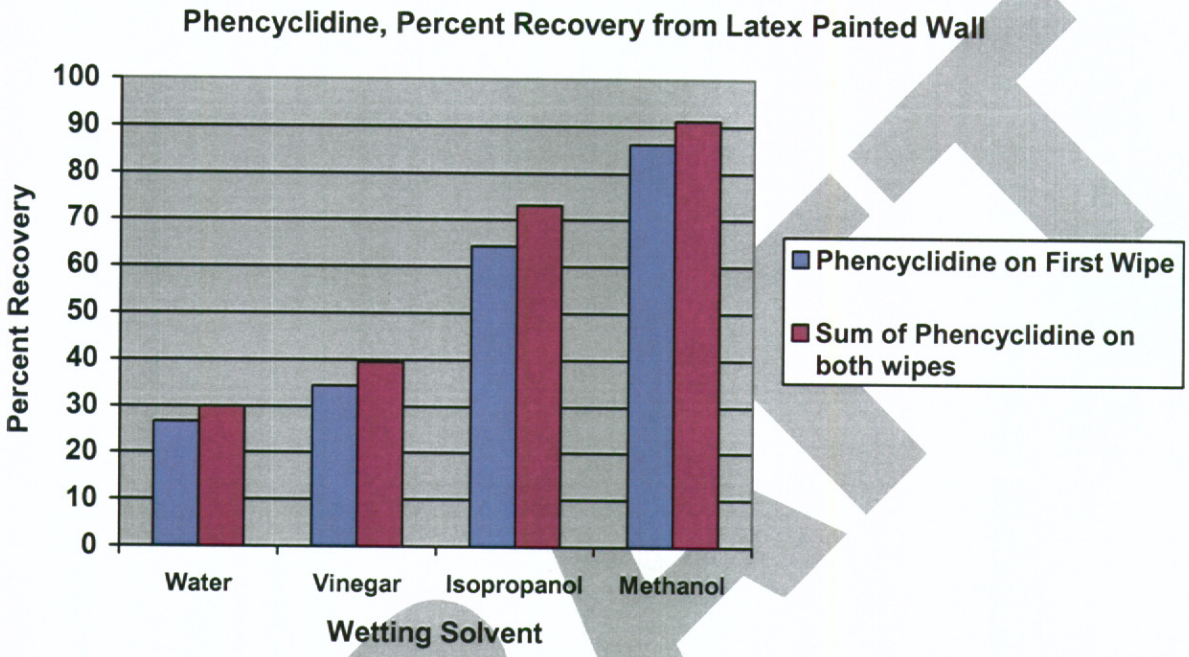


TABLE 36. RECOVERY OF PHENTERMINE FROM SPIKED LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	52.99	9.19	5.45	58.44
5% Vinegar	66.85	12.80	7.67	74.52
Isopropanol	77.59	6.58	13.02	90.61
Methanol	94.72	2.93	6.07	100.79

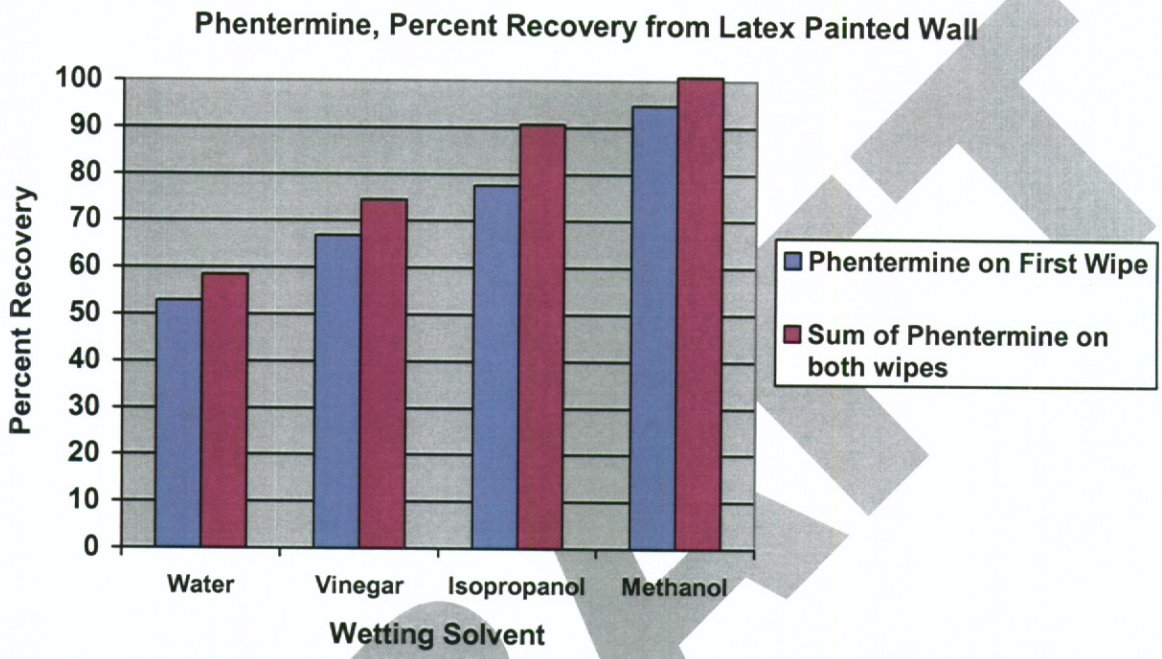


TABLE 37. RECOVERY OF COCAINE FROM SPIKED LATEX PAINTED WALL

Solvent	Percent Recovery First Wipe Percent	RSD	Second Wipe Percent	Sum of Both Wipes Percent
Water	36.34	21.68	NA	36.34
5% Vinegar	49.89	22.73	4.26	54.15
Isopropanol	69.41	22.25	10.67	80.08
Methanol	89.14	9.07	4.62	93.76

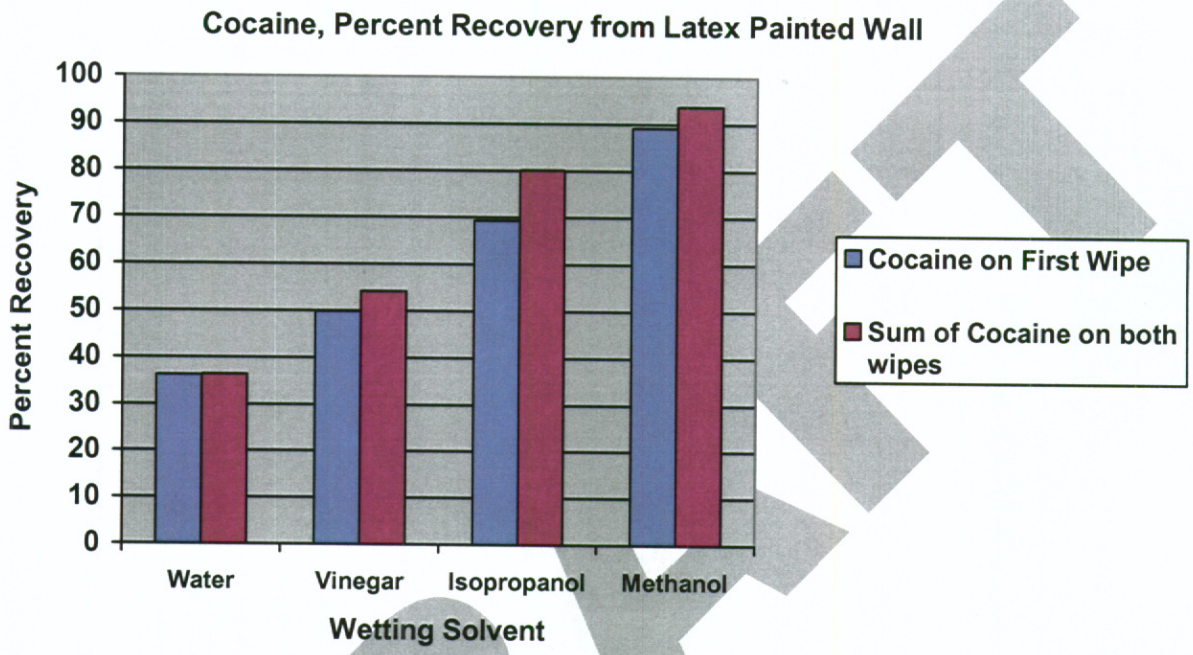


TABLE 38. RECOVERY OF METHAMPHETAMINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	64.81	10.80	75.61
	Methanol	90.55	4.38	91.93
Varnished hardwood (new)	Isopropanol	71.62	4.88	76.49
	Methanol	82.00	4.31	86.31
Formica countertop (new)	Isopropanol	75.41	6.50	81.90
	Methanol	86.66	4.69	91.35
Vinyl veneer particle board (new)	Isopropanol	60.06	7.85	67.91
	Methanol	80.54	8.67	89.20
Enamel (Washing machine)	Isopropanol	58.34	9.32	67.66
	Methanol	80.58	6.72	87.30
Latex painted wall	Isopropanol	64.15	10.84	74.99
	Methanol	87.41	6.13	93.55

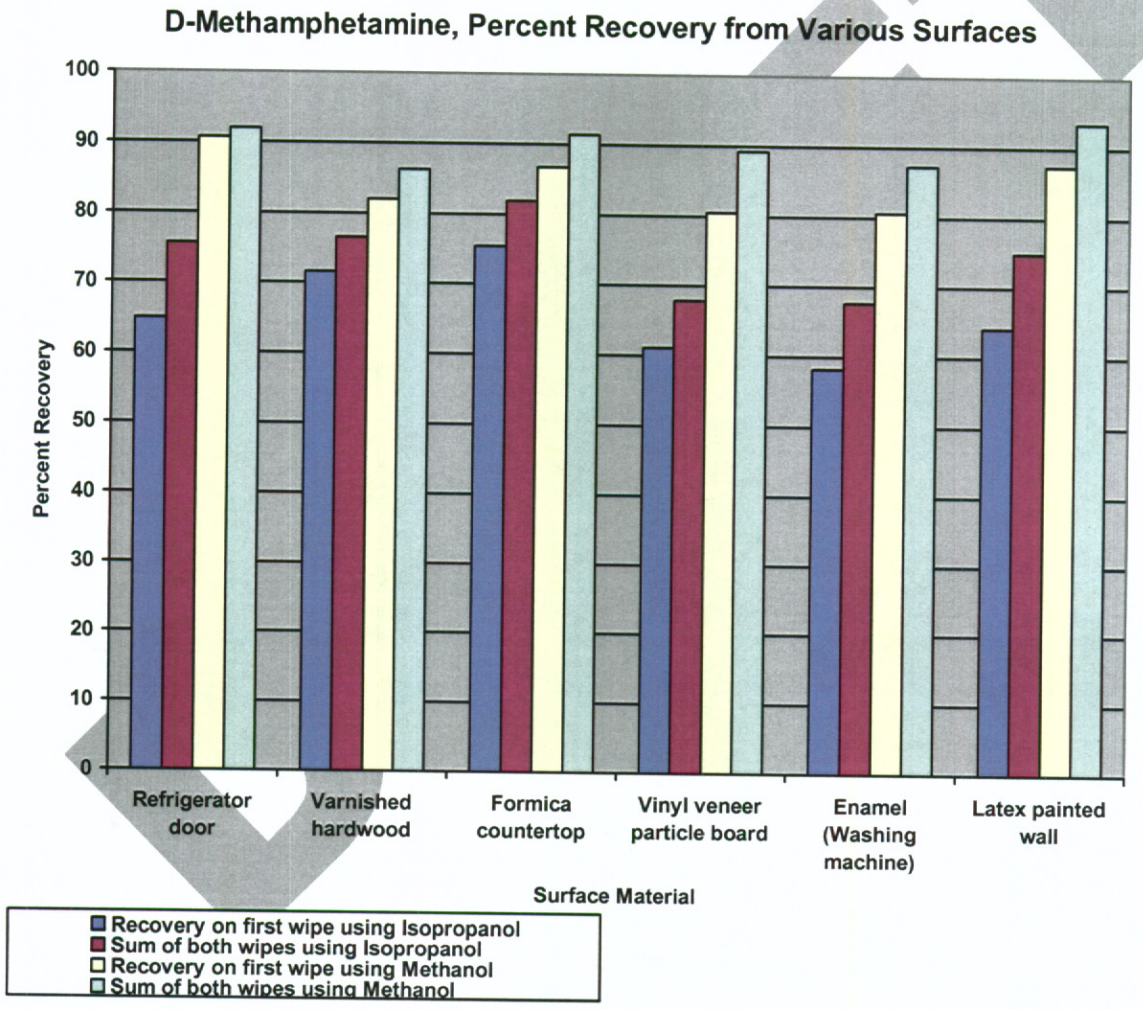


TABLE 39. RECOVERY OF AMPHETAMINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	67.88	11.70	79.57
	Methanol	92.14	3.93	96.07
Varnished hardwood (new)	Isopropanol	73.03	4.88	77.91
	Methanol	82.85	4.04	86.89
Formica countertop (new)	Isopropanol	78.14	6.88	85.02
	Methanol	87.74	4.07	91.82
Vinyl veneer particle board (new)	Isopropanol	60.06	8.70	68.76
	Methanol	83.43	7.97	91.40
Enamel (Washing machine)	Isopropanol	58.61	10.16	68.77
	Methanol	81.08	6.58	87.66
Latex painted wall	Isopropanol	66.59	11.55	78.14
	Methanol	89.76	6.26	95.02

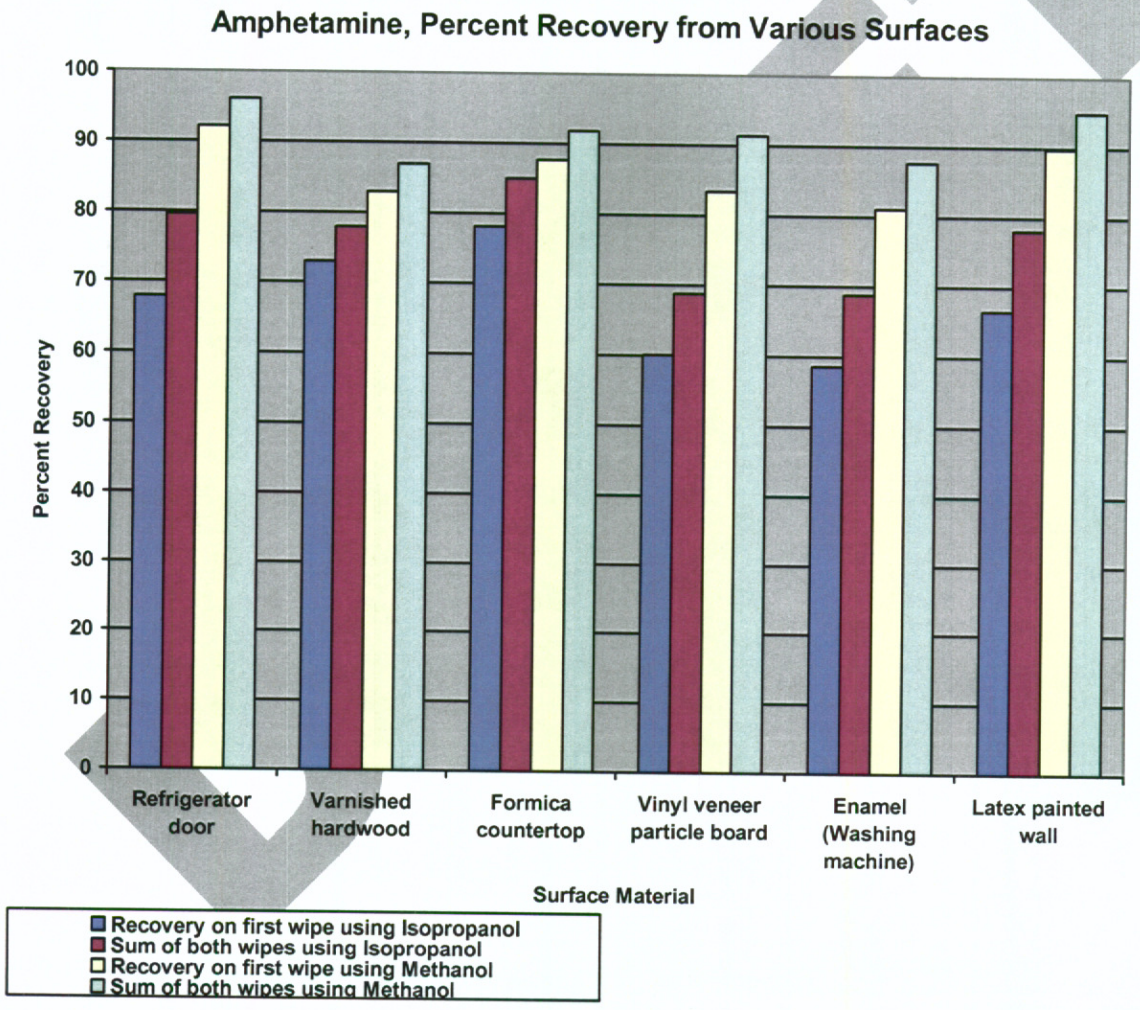


TABLE 40. RECOVERY OF MDMA FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	57.87	10.01	67.88
	Methanol	94.64	5.85	100.48
Varnished hardwood (new)	Isopropanol	68.89	4.26	73.16
	Methanol	86.11	4.16	90.26
Formica countertop (new)	Isopropanol	74.13	6.32	80.45
	Methanol	89.60	5.56	95.16
Vinyl veneer particle board (new)	Isopropanol	50.30	6.24	56.55
	Methanol	77.80	10.28	88.08
Enamel (Washing machine)	Isopropanol	57.04	8.47	65.51
	Methanol	80.76	7.95	88.72
Latex painted wall	Isopropanol	61.15	9.10	70.25
	Methanol	87.82	5.73	93.54

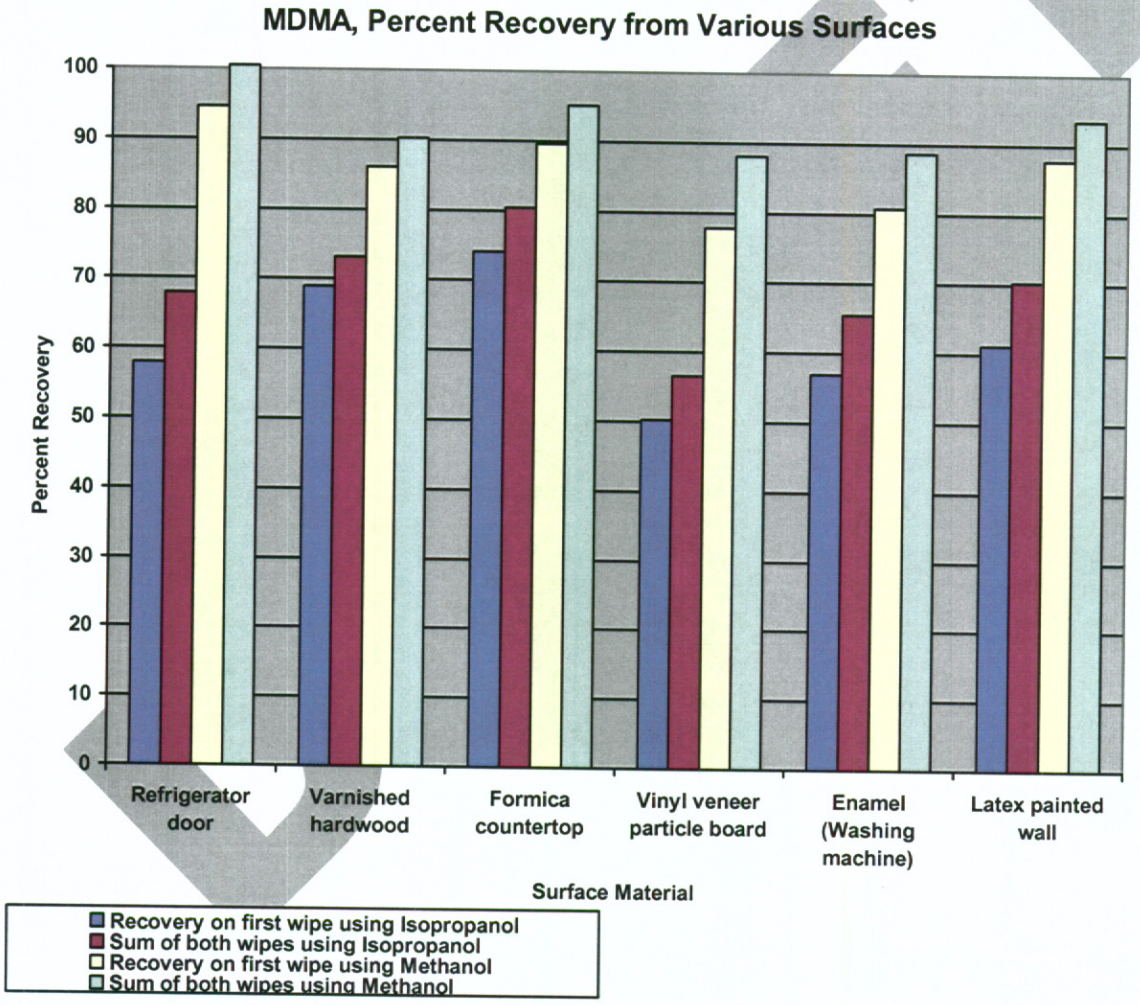


TABLE 41. RECOVERY OF MDEA FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	63.77	10.44	74.21
	Methanol	96.59	4.81	101.39
Varnished hardwood (new)	Isopropanol	72.54	4.35	76.88
	Methanol	86.47	3.99	90.46
Formica countertop (new)	Isopropanol	78.61	7.06	85.67
	Methanol	93.98	4.78	98.76
Vinyl veneer particle board (new)	Isopropanol	56.06	7.40	63.46
	Methanol	83.92	8.90	92.82
Enamel (Washing machine)	Isopropanol	65.73	10.03	75.76
	Methanol	88.72	6.43	95.16
Latex painted wall	Isopropanol	68.65	11.69	80.34
	Methanol	89.91	7.03	96.94

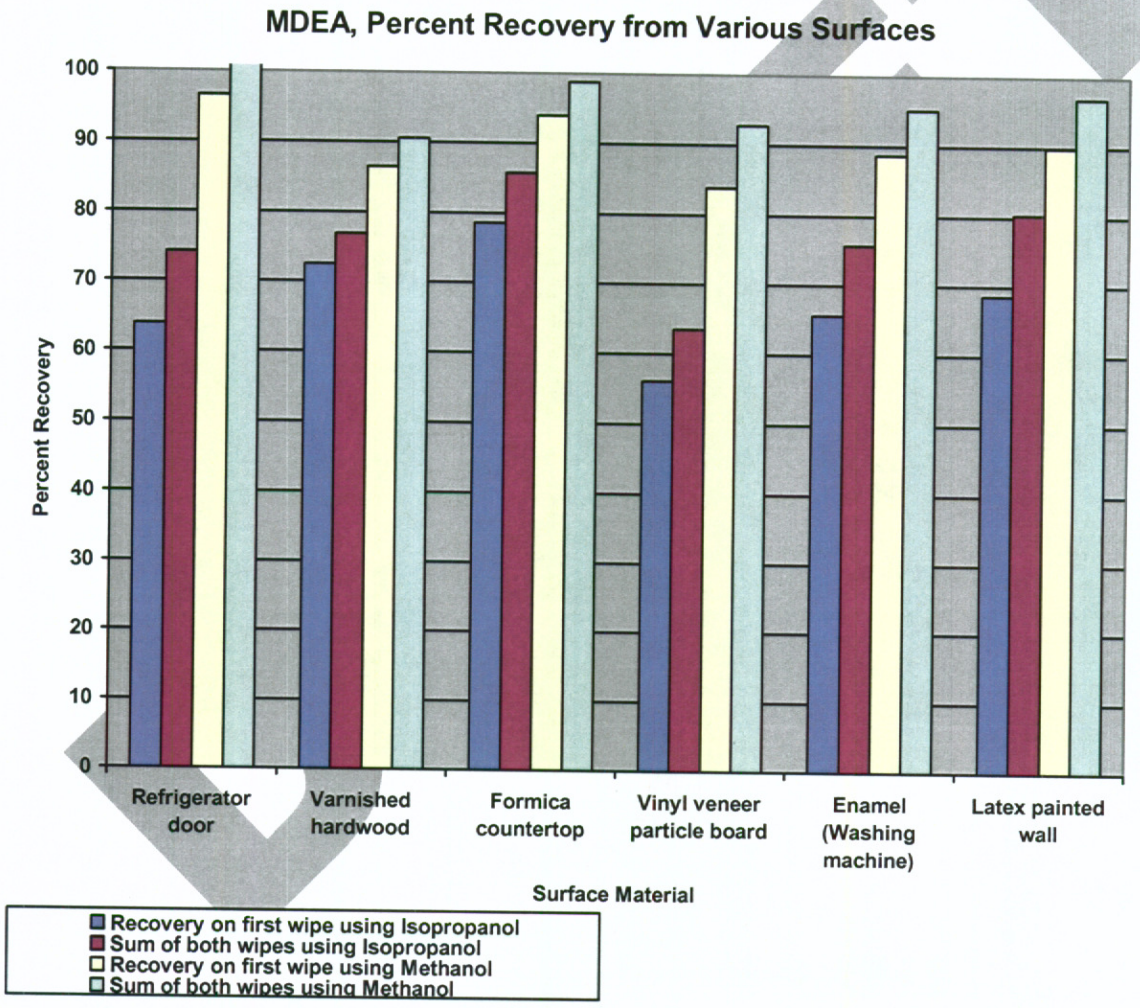


TABLE 42. RECOVERY OF EPHEDRINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	78.39	11.74	90.13
	Methanol	103.66	4.36	108.01
Varnished hardwood (new)	Isopropanol	84.70	5.53	90.23
	Methanol	93.28	4.43	97.71
Formica countertop (new)	Isopropanol	85.58	7.22	92.80
	Methanol	96.78	4.14	100.92
Vinyl veneer particle board (new)	Isopropanol	74.71	8.05	82.77
	Methanol	94.05	8.11	102.16
Enamel (Washing machine)	Isopropanol	68.37	9.83	78.20
	Methanol	92.46	6.35	98.80
Latex painted wall	Isopropanol	75.50	9.87	85.37
	Methanol	91.47	4.58	96.05

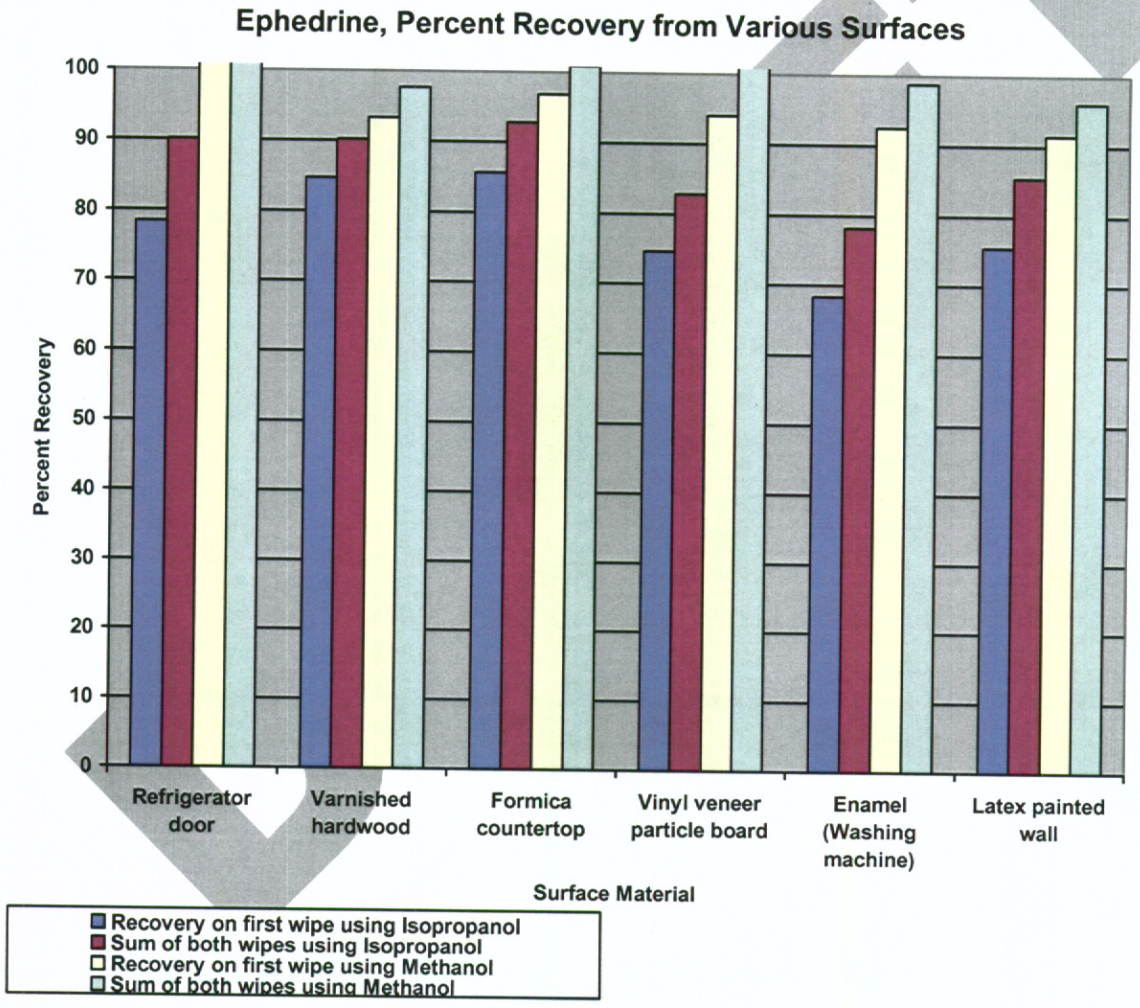


TABLE 43. RECOVERY OF PSEUDOEPHEDRINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	79.81	11.66	91.47
	Methanol	101.60	4.14	105.75
Varnished hardwood (new)	Isopropanol	81.76	5.31	87.07
	Methanol	88.32	4.07	92.38
Formica countertop (new)	Isopropanol	82.04	6.88	88.92
	Methanol	94.53	4.19	98.72
Vinyl veneer particle board (new)	Isopropanol	73.31	8.33	81.65
	Methanol	94.80	7.89	102.69
Enamel (Washing machine)	Isopropanol	70.36	9.88	80.25
	Methanol	88.94	6.05	94.99
Latex painted wall	Isopropanol	73.37	11.84	85.20
	Methanol	94.99	5.89	100.88

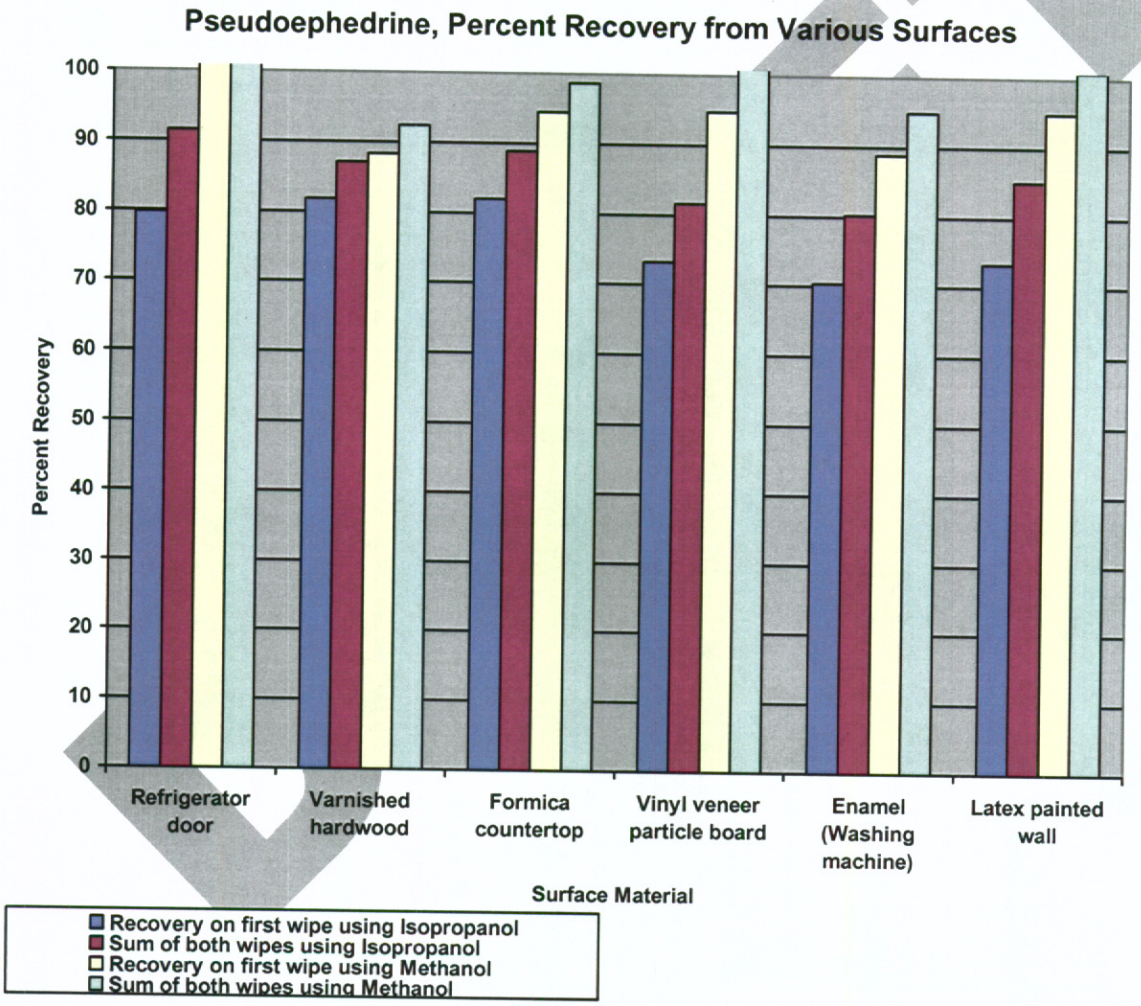


TABLE 44. RECOVERY OF PHENYLPROPANOLAMINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	60.27	14.77	75.04
	Methanol	91.29	5.44	96.73
Varnished hardwood (new)	Isopropanol	68.55	6.42	74.97
	Methanol	81.72	4.02	85.74
Formica countertop (new)	Isopropanol	74.30	8.13	82.43
	Methanol	88.83	4.61	93.44
Vinyl veneer particle board (new)	Isopropanol	52.98	10.16	63.15
	Methanol	79.32	9.16	88.48
Enamel (Washing machine)	Isopropanol	62.12	13.42	75.55
	Methanol	83.86	8.03	91.89
Latex painted wall	Isopropanol	79.60	15.61	95.21
	Methanol	85.23	7.71	92.94

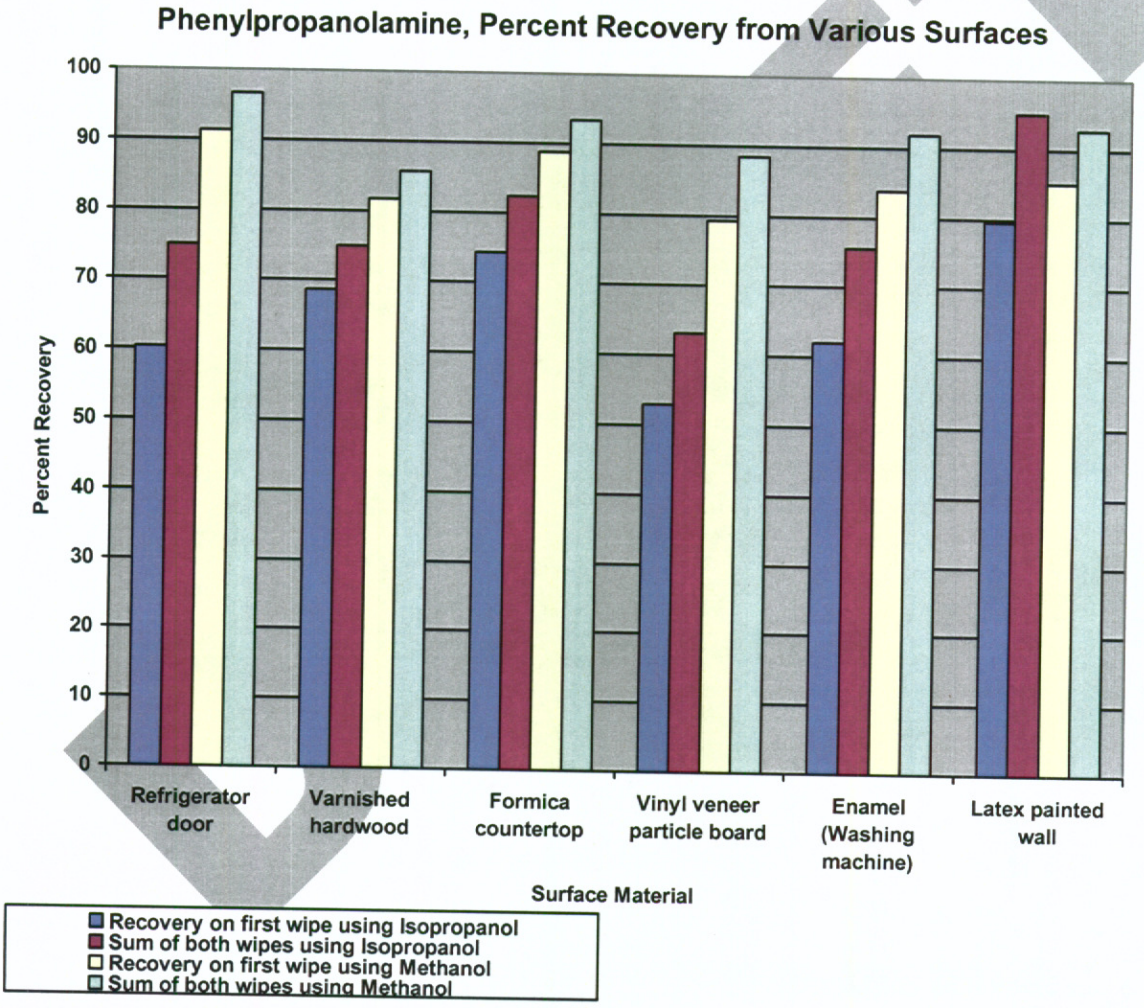


TABLE 45. RECOVERY OF PHENCYCLIDINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	72.02	11.87	83.89
	Methanol	93.69	4.41	98.1
Varnished hardwood (new)	Isopropanol	74.42	4.99	79.41
	Methanol	85.45	4.26	89.71
Formica countertop (new)	Isopropanol	79.84	8.32	88.16
	Methanol	93.29	4.51	97.80
Vinyl veneer particle board (new)	Isopropanol	63.05	9.11	72.16
	Methanol	88.07	7.58	93.65
Enamel (Washing machine)	Isopropanol	73.09	9.44	82.53
	Methanol	84.69	6.63	91.32
Latex painted wall	Isopropanol	64.31	8.77	73.08
	Methanol	86.22	5.02	91.25

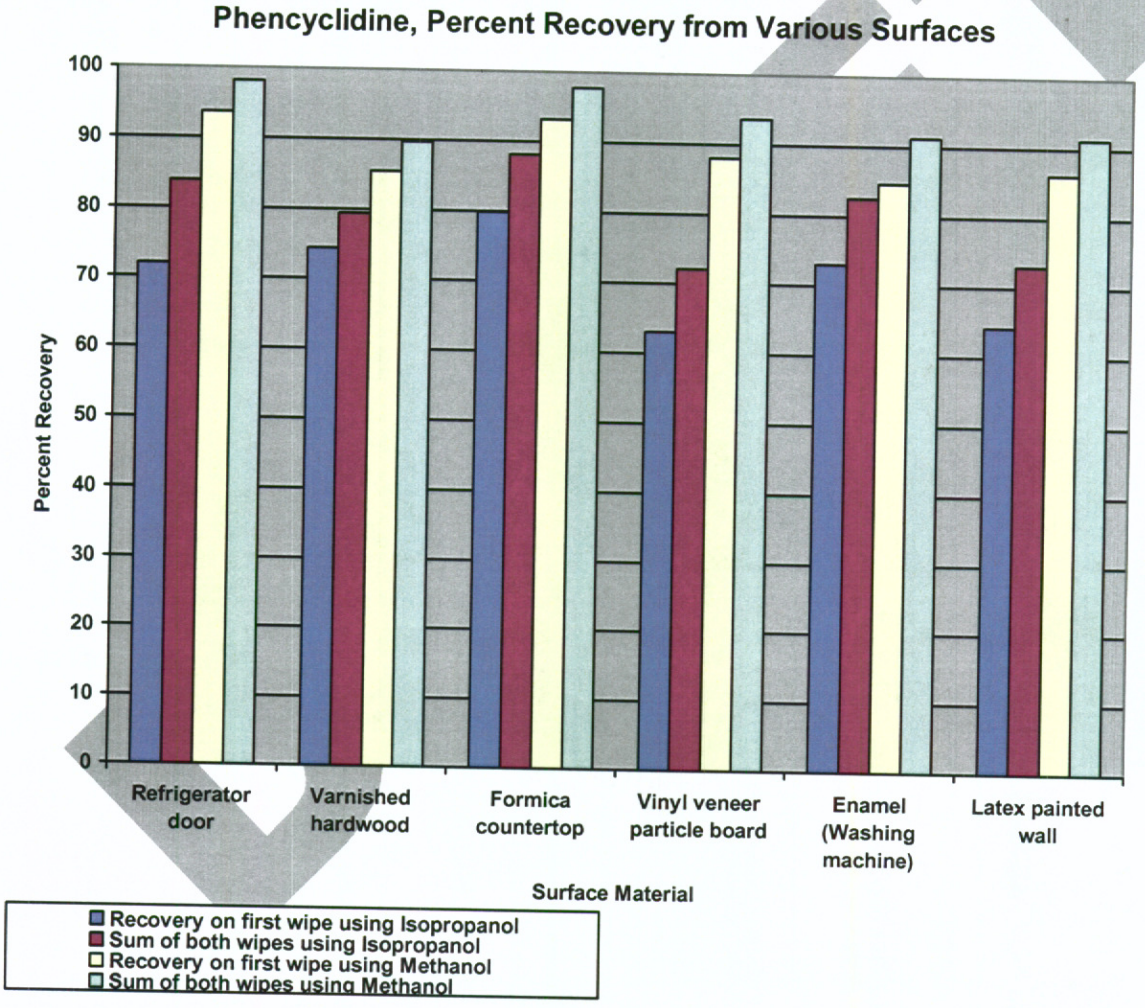
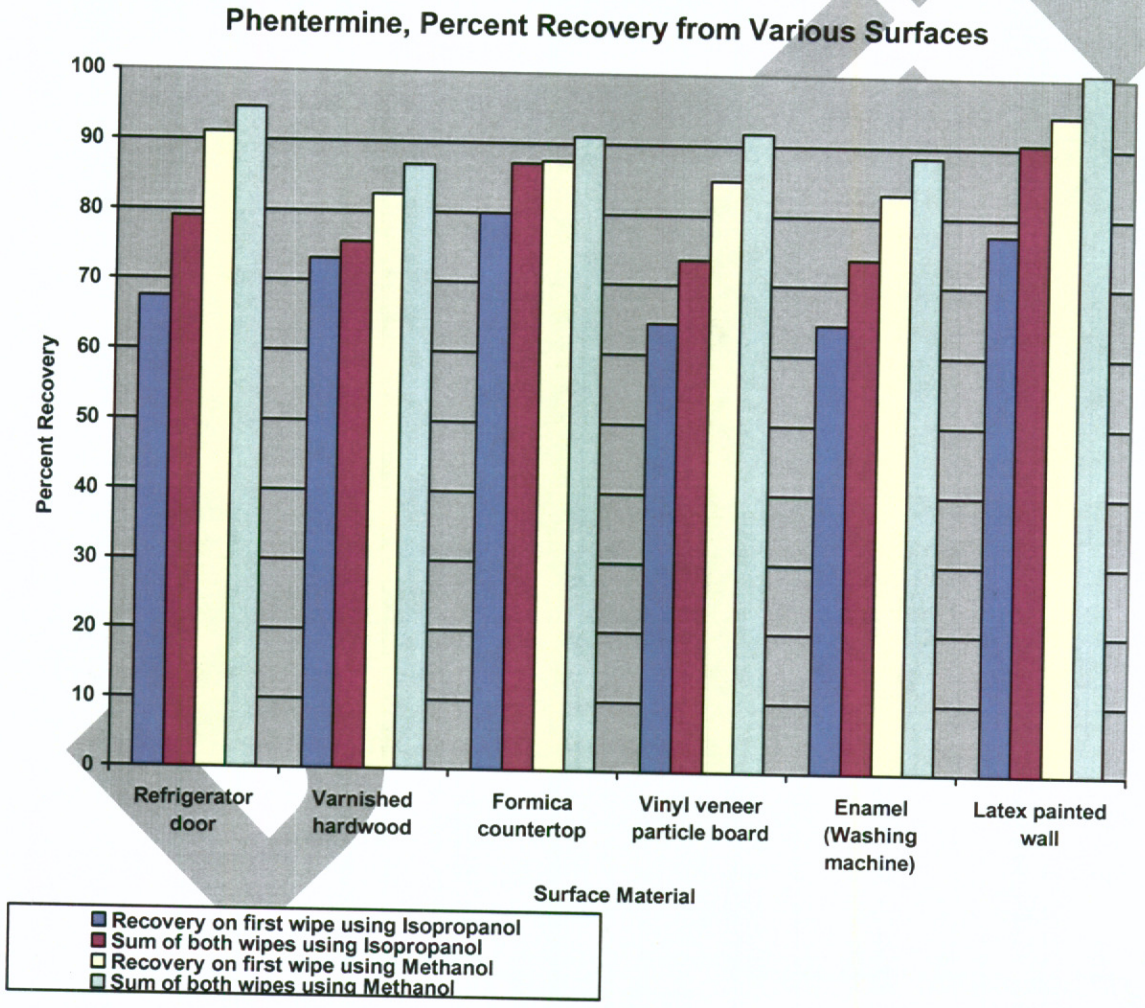


TABLE 46. RECOVERY OF PHENTERMINE FROM VARIOUS SURFACES

Surface	Gauze Wetting Solvent	Percent Recovery		
		First Wipe Percent	Second Wipe Percent	Sum of Both Wipes Percent
Refrigerator door	Isopropanol	67.57	11.43	79.00
	Methanol	91.07	3.60	94.67
Varnished hardwood (new)	Isopropanol	73.19	2.43	75.62
	Methanol	82.48	4.24	86.71
Formica countertop (new)	Isopropanol	80.00	7.08	87.08
	Methanol	87.45	3.52	90.97
Vinyl veneer particle board (new)	Isopropanol	64.47	9.19	73.66
	Methanol	84.94	6.78	91.72
Enamel (Washing machine)	Isopropanol	64.50	9.41	73.91
	Methanol	83.29	5.32	88.60
Latex painted wall	Isopropanol	77.59	13.02	90.61
	Methanol	94.72	6.07	100.79



IX. FINAL CONCLUSIONS:

With the proper pairing of internal standards to target analytes, the method passed the precision and accuracy and storage stability criteria for NIOSH analytical methods.

No synthetic gauze was better than cotton gauze, and due to its universal availability and excellent overall performance, it is the preferable wipe material.

GC-MS in the scan mode is able to attain the required limit of detection for methamphetamine (0.1 µg/sample). Additional sensitivity is possible in the SIM mode. The low calibration standard should be at least 0.05 µg/sample.

SPE columns are an effective way to clean up the sample desorbates, save time in the process, and reduce level of effort. SPE columns remove non-ionic surfactants better than the liquid-liquid extraction cleanup procedure of NIOSH 9106.

The mixed silylation-acylation derivatization reagents (MSTFA + MBHFBA) are effective for the SPE cleanup column eluates. The mixed reagent has problems such as oversilylation, but these problems are not insurmountable and can be neglected for routine analyses using the procedure as outlined. The mixed reagent may be especially suitable for phenolic and hydroxyl containing analytes.

Methanol is a better solvent for wetting the cotton gauze for wipe sampling than either water or isopropanol. Isopropanol is acceptable as a wetting solvent but better recoveries result with a second, serial wipe. The 50-mL PP centrifuge tubes can be used a sample containers and are large enough for a second gauze sample of the right size (3" × 3" 12-ply or 4" × 4" 8-ply).

Using the proper internal standards it is likely that application of this method can be extended to the analysis of a variety of amines and amphetamine like substances in a variety of media.

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