METHOD 3572

EXTRACTION OF CHEMICAL AGENTS FROM WIPE SAMPLES USING MICROEXTRACTION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for the purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method describes the extraction of chemical agents from wipe samples using a microextraction technique. The following compounds have been determined by this method:

Compound Name	CAS No.[a]
GB (*o*-Isopropyl methylphosphonofluoridate)	107-44-8
VX (O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate)	50782-69-9
HD [Bis(2-chloroethyl)sulfide]	505-60-2

[a]Chemical Abstracts Service Registry Number

Additionally, this method may be applicable to other chemically similar compounds and chemical agent degradation products. For a summary of changes in this version, please see Appendix A at the end of this document.

1.2 Other solvent systems may be employed in place of those described here. For any solvent system used, including those mentioned in the method, one needs to demonstrate adequate performance for the analytes of interest.

1.3 There is a risk to the analyst of exposure to chemical agents. The analyst should pay special attention to the safety information in Sec. 5.0.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 This method is restricted to use by, or under supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.6 WARNING: The toxicity of these chemical warfare agents presents the worker with hazards unfamiliar to most experienced laboratory personnel. Special techniques and precautions must be used even for the simplest procedures involving these agents (see Ref. 1 for additional guidance).

2.0 SUMMARY OF METHOD

2.1 This method provides the procedures for sample collection and extraction of the referenced compounds from wipe samples. A separate extract will be required for each agent to be analyzed.

2.2 Materials are surface wiped using a gauze pad (2” x 2” pad). After wiping a surface area, usually 10 cm x 10 cm, the pad is placed into a labeled vial.

2.3 Samples are extracted with 4 mL of 10% 2-propanol (IPA) in dichloromethane by vortex mixing and filtered, if necessary.

2.4 An optional water wash is included for VX that back-extracts the compound from heavy organics that would interfere with the assay. An optional column cleanup procedure utilizes a Carboprep90 column and a silica column to separate GB from heavy organics, if needed. Suitable solvents are used to elute the extract first through the Carboprep90 column, then the silica column.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to the determinative methods to be used for information regarding potential interferences.

4.2 Other phosphorous- and sulfur-containing compounds can interfere with the method performance and affect the result.

4.3 Interferences that can cause the chemical agents to decompose include moisture, light, elevated temperatures, and an improper extraction solvent pH range. The stability of the chemical agents noted in this method is contingent on maintaining the pH ranges as indicated in Sec. 8.2.

4.4 Samples with high organic loading can mask or elute with the agent analyte.

5.0 SAFETY

WARNING: The toxicity of these chemical warfare agents presents the worker with hazards unfamiliar to most experienced laboratory personnel. Special techniques and precautions must be used even for the simplest procedures involving these agents.

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Personal protective equipment (PPE) requirements include safety glasses, lab coat, and protective gloves. The availability of emergency response equipment and support personnel should be as indicated in a laboratory chemical hygiene plan.

5.3 Exposure to chemical agent material is possible from contact. Respiratory exposure can result from spills or improper use of ventilation control.

5.4 Risk is primarily associated with compromise of protective gloves. Compromise is most likely to occur as agent vials are opened.

6.0 EQUIPMENT AND SUPPLIES

6.1 The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all of the common laboratory glassware (e.g., beakers and flasks) that might be used.

6.2 Personal protective equipment

6.3 Vials, 1-, 3-, and 6-dram for sample collection

6.4 Vials, 1-dram for extracts

6.5 Gauze pads, non sterile, 100% cotton, approximately 2" x 2" or 4" x 4" squares available Edwards Medical Supply, or a suitable equivalent. For each sampling event or a specific project application gauze pads from the same manufacturing lot should be used.

6.6 Analytical balance, capable of measuring to the nearest mg

6.7 Pasteur pipettes, 5 ¾," Fisherbrand, or equivalent

6.8 Syringes, 10-µl and 50-µl used for preparing spikes and surrogates

6.9 Volumetric glassware, 2-, 5-, and 10-mL used for preparing spikes and surrogates

6.10 BD syringe filter (10-mL Luer-Lok)

6.11 Whatman nylon syringe filter, 0.45-µm pore size, or equivalent

6.12 Vortex mixer, benchtop, or as noted in Sec. 6.13

6.13 Centrifuge, benchtop

6.14 pH test strips

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Dichloromethane (DCM), CH_2Cl_2, optima grade or equivalent

7.3 2-Propanol (IPA), $(CH_3)_2CHOH$, optima grade or equivalent

7.4 1 N Sodium hydroxide, NaOH

7.5 Sodium chloride, NaCl

7.6 Saturated Glacial Acetic Acid/NaCl solution. Dissolve 7 g of NaCl in 35 mL of glacial acetic acid in a 40-mL vial

7.7 Isopropyl methylphosphonofluoridate; Sarin (GB)

7.8 O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate (VX)

7.9 Bis(2-chloroethyl)sulfide (HD)

7.10 Diisopropyl fluorophosphonate (DFP), C_6-H_{14}-F-O_3-P

7.11 2-Chloroethyl ethyl sulfide (CEES), C_4-H_9-Cl-S

7.12 Diethyl ethylthiophosphonate (DEETP)

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation and storage requirements.

8.1 This method is a microextraction technique in which a particular surface area is wiped with either a 2” x 2” or 4” x 4” gauze pad and extracted with 4.0 mL of 10% IPA in DCM. Because of this, sample collection plans should consider sufficient replicates.

8.2 Holding times

8.2.1 Samples for GB, HD and VX assay must be extracted within 7 days of collection. Extraction times of less than 3 days are preferred. Extracts must be analyzed within 14 days of extraction.

8.2.2 GB undergoes rapid hydrolysis to form hydrogen fluoride, isopropyl methyl phosphonic acid and other compounds. Conditions of pH within a range of 3.5 to 5 will slow this decomposition rate. Stability in organic extracts exceeds 28 days.

8.2.3 HD undergoes hydrolysis to form thiodiglycol and other compounds. Conditions of pH within a range of 3.5 to 5 will slow decomposition rate. Chloride ion can be added to reduce the effects of metal cations. Stability in organic extracts exceeds 28 days.

8.2.4 VX undergoes very rapid hydrolysis under extremely basic conditions, with a half-life of 16 minutes at pH 13 and 1.3 minutes at pH 14. Optimal pH for VX stability (for a half-life of approximately 350 days) was determined to be within a range of 8 to 9. Stability in organic extracts exceeds 28 days. Partitioning is present with non-polar

solvents (hexane).

8.3 Sample collection

The exact number of samples that may be necessary for a particular sampling event, such as possibly collecting samples in duplicate, should be documented in the appropriate project planning documents. It is also important to understand that duplicate wipe samples may not always yield consistent results for precision purposes.

8.3.1 Place 1 mL of IPA onto gauze pad.

8.3.2 Wipe a surface area of 10 cm x 10 cm.

8.3.3 Place the gauze pad into a labeled vial.

8.3.4 Record the vial identification number on the chain of custody and the sample label.

8.3.5 One additional sample from the same general location should be designated as a duplicate for each group of twenty or fewer samples. Two empty vials designated as a blank and LCS, both containing a clean IPA-soaked gauze pad added at the time of sample collection, should be returned with each group of twenty or fewer samples.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Laboratory/Monitoring Quality Assurance Plan (LMQAP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency and lower limit of quantitation (LLOQ)

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000D, Sec. 9.3 for information on how to accomplish a demonstration of proficiency.

The laboratory shall establish the LLOQ as the lowest point of quantitation, which in most cases, is the lowest concentration in the calibration curve. LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. An LLOQ check standard (not part of an initial calibration) is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). The LLOQ check is carried through the same preparation procedures as environmental samples and other QC samples. Recovery of target analytes in the LLOQ check standard should be within established in-house limits, or other such project-specific acceptance limits, to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria ± 20% may be used for the LLOQ acceptance criteria. Additional information on LLOQ can be found in 8000D, Section 9.7.

9.3 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.4 Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs. All instrument operating conditions should be recorded.

9.6 Also see Method 3500 for QC procedures related to extraction and sample preparation procedures and refer to the determinative methods to be used for determinative QC procedures.

9.7 As noted earlier, use of any extraction technique, including solvent extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, in the sample matrix.

9.8 All field and QC samples should be spiked with an appropriate mix of surrogate compounds, if available, in order to track extraction efficiency.

9.9 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on field samples.

10.0 CALIBRATION AND STANDARDIZATION

Calibration is not required for this method.

11.0 PROCEDURE

11.1 Spike the matrix spike, matrix spike duplicate or laboratory control spike (LCS)

with agent. Record spike amounts into controlled notebook.

11.1.1 Suggested GB spike is 40 ng.

11.1.2 Suggested VX spike is 40 ng.

11.1.3 Suggested HD spike for FPD is 120 ng and for GC/MS is 40 ng.

11.2 Spike all samples with appropriate surrogates.

11.2.1 Suggested 40 ng of DFP for GB samples.

11.2.2 Suggested 40 ng of DEETP for VX samples.

11.2.3 Suggested 120 ng of CEES for HD FPD and 40 ng for GC/MS.

11.3 Add 4.0 mL of 10% IPA in dichloromethane to all samples. For VX samples, add 200 µL of 1N sodium hydroxide solution to ensure that the extract is basic, taking care not to overshoot desired pH. More sodium hydroxide may be used if needed. The pH range for VX should be between 8-10.

11.3.1 Check pH with pH paper.

11.3.2 Mix on a vortex mixer for 30 seconds.

11.3.3 Centrifuge the sample for 1 minute at 2000 rpm, if necessary.

11.3.4 If filtration is necessary, filter the solvent extract into another vial.

11.3.5 Store the extract in a refrigerator at <6 °C until analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no determinative data analysis and calculation steps directly associated with this procedure. Follow the directions in the determinative method.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for the purposes of laboratory accreditation.</u>

13.2 Refer to the appropriate determinative method for performance data examples and guidance.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety.
http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the ACS publication listed in Sec. 14.2.

16.0 REFERENCES

1. Applicable documents to support the occupational health program when dealing with chemical agents include AR11-34 (The Army Respiratory Protection Program; AR 40-5 (Preventive Medicine); DA Pam 40-8 (Occupational Health guidelines for the evaluation and Control of Occupational Exposure to Nerve Agents GA, GB, GC, and VX.) and DA Pam 40-173 (Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Mustard Agents H, HD, and HT).

2. Development and Evaluation of an Analytical Method for Determination of GB, VX, and HD in Concrete, SwRI Final Report to PM-ECW, William S. Williamson, Jr. Joseph H. Brewer.

3. Development and Evaluation of an Analytical Method for Determination of GB, VX, and HD in Coral, SwRI Final Report to PM-ECW, William S. Williamson, Jr., Joseph H. Brewer.

4. Development and Evaluation of an Analytical Method for Determination of GB, VX, and HD in Charcoal, SwRI Final Report to PM-ECW, Michael G. MacNaughton, Ph.D., P.E., William S. Williamson, Jr., Joseph H. Brewer.

5. Development and Evaluation of an Analytical Method for Determination of GB, VX, and HD on Surfaces, SwRI Final Report to PM-ECW, Carter Crigler.

6. Laboratory Monitoring and Quality Assurance Plan dated June 2004, Department of Army, Chemical Material Agency.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

There are no tables or figures associated with this method.

Appendix A:

Summary of Revisions to Method 3572 (as compared to previous Revision 0, July, 2007)

1. Improved overall method formatting for consistency with new SW-846 methods style guidance. The format was updated to Microsoft Word.docx.
2. Sections 7.2 and 7.3, added the words “or equivalent” to Optima grade description as that is a trademarked term of Thermo/Fisher Scientific. Optima grade is a high purity gas chromatography grade of solvent.
3. Updated VX stability information has been added to Sec. 8.2.4.
4. LLOQ language added to Section 9.2.
5. Minor editorial and technical revisions were made throughout to improve method clarity. The revision number was changed to one and the footer date to July 2014.