

ASSAY OF CHEMICAL AGENTS IN SOLID AND AQUEOUS SAMPLES BY GAS CHROMATOGRAPH/MASS SPECTROMETRY, ELECTRON IMPACT (GC/MS/EI)

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 purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

This method describes the analysis of chemical agents in aqueous and solid samples by gas chromatography/mass spectrometry (GC/MS). The method has been applied to concrete, charcoal, wood, water, brine, ash, coral, sand, and soil. It involves introduction of the sample into gas chromatograph with mass spectrometric detector. Samples can either be directly injected or desorbed from a solid sorbent. 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 Abstract Service Registry Number

1.1 Additionally, this method may be applicable to other chemically similar compounds and chemical agent degradation products.

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.

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).

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 should consult the disclaimer statement at the front of the manual and the information in Chapter 2 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 responses to Federal testing requirements. The information contained in this method is provided by SW-846 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 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the handling of chemical agents. Each analyst must demonstrate the ability to generate acceptable results with this method. This method is intended to be a supplement to – but it is NOT intended to be a substitute for – formal training of an analyst in the basic principles of gas chromatography and mass spectrometry.

2.0 SUMMARY OF THE METHOD

2.1 This method provides the procedures for analysis of the referenced compounds from extracts of solid and aqueous samples. Prior to analysis, appropriate sample preparation techniques must be used as described in Methods 3571 and 3572. The following table summarizes the approach to the listed compounds.

Analyte	Tube/Conversion Pad (if solid sorbent introduction is used)
GB	Chromosorb 106
VX	Chromosorb 106/AgF
HD	Tenax TA

2.2 Sample extracts will be analyzed by GC/MS.

2.3 The sample may be introduced into the instrument by direct extract injection or by deposition on and thermal desorption from a solid sorbent tube (DAAMS). These sorbent

tubes are part of the Army's Depot Area Air Monitoring System (DAAMS). DAAMS is used in this method text to reference the specific configuration of sorbent tube and the gas chromatography used by the Army.

2.4 Prior to analysis, appropriate sample preparation techniques must be used as described in Methods 3571 and 3572.

3.0 DEFINITIONS

Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All 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 guidance on the cleaning of glassware.

4.2 Volatile organics, phosphorous and sulfur-containing compounds can interfere with the method performance and affect the results.

4.3 These chemical agents can decompose in the presence of moisture, light, and elevated temperature.

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 There are specific requirements for operations with chemical agents that must be met. The laboratory should have these included in a Chemical Hygiene Plan prior to conducting operations with agents.

5.3 Personal Protective Equipment (PPE) requirement is safety glasses, lab coat, and protective gloves. The availability of response equipment and support personnel should be as indicated in a specific laboratory chemical hygiene plan.

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

5.5 Risk is primarily associated with compromise of protective gloves.

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 common laboratory glassware (e. g., beakers and flasks).

6.2 Personal Protective Equipment

6.3 Syringes

6.4 For thermal desorption method

6.4.1 Gas chromatograph/mass spectrometer (GC/MS) with inlet modified to accept 3-mm transfer tubes

6.4.2 Injection (transfer) sorbent tubes (3-mm X 2-cm bed size) packed with 60 by 80 mesh Chromosorb-106 or Tenax TA, or equivalent.

6.4.3 DAAMS tubes (6-mm or 8-mm X 3-cm bed size) packed with 60 by 80 mesh Chromosorb-106 or Tenax TA, or equivalent.

6.4.4 DB-624 column, 30-m

6.4.5 DAAMS aluminum heating block or manifold

6.4.6 Dynatherm ACEMS (optional)

6.5 For liquid injection method

6.5.1 GC/MS with splitless injector

6.5.2 DB-1701 30-meter column

6.5.3 Autosampler vials

6.6 The columns listed in this section were the columns used to develop the method performance data. The listing of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use these columns or other capillary columns provided that the laboratories document method performance data

(e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

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 the use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Tetrachlorobenzene, $C_6Cl_4H_2$

7.3 Silver fluoride conversion pads for analysis of VX / DEETP using thermal desorption techniques. The silver fluoride pads are used to convert VX and DEETP into their G-analogs and are commonly referred to as V to G conversion pads. The pads can be purchased from CAMSCO in various mm sizes, 6 mm part # is VG0316-3125, "or equivalent".

7.4 O- Isopropyl methylphosphonofluoridate; Sarin (GB)

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

7.6 Bis(2-chloroethyl)sulfide (HD)

7.7 Diisopropyl fluorophosphate (DFP), $C_6H_{14}F-O_3-P$

7.8 2-Chloroethyl ethyl sulfide (CEES), C_4H_9-Cl-S

7.9 Diethyl ethylthiophosphonate (DEETP)

7.10 Dichloromethane (DCM), CH_2Cl_2 , optima grade

7.11 2-propanol (IPA), $(CH_3)_2CHOH$, optima grade

7.12 Standard Solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.13 Stock standard solutions (1000 mg/L) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.13.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in optima grade 10% / 90% 2-propanol / dichloromethane and dilute to volume in a 100-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the

concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

7.13.2 Transfer the stock standard solutions into bottles fitted with PTFE-lined screw-caps or crimp tops. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.13.3 Stock standard solutions of chemical agent that are usually supplied by an approved Government Agency are typically certified as stable for 6 months. However, it is the analyst's responsibility to ensure proper storage and performance verification of stock standard solutions. Stock standard solutions should be replaced after 6 months if necessary, and should be replaced sooner, if comparison with check standards indicates a problem.

7.14 Calibration standards - A minimum of five different concentrations should be prepared through dilution of the stock standards with 10% / 90% 2-propanol / dichloromethane. The concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration standards may be used, when stored appropriately, for up to 30 days if the analyst can adequately demonstrate the prepared standards are stable for the time period selected. See Method 8000 for additional information on the preparation of calibration standards.

7.15 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.15.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest, as described in Sec. 7.14.

7.15.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

7.15.3 Analyze each calibration standard according to Sec. 11.0.

7.16 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one or two surrogates recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample collection, preservation, and storage for samples containing these agents are described in Methods 3571 and 3572.

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 Quality Assurance Project Plan (QAPP) 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 Refer to Method 8000 for specific determinative method QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Method 8000.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

9.4 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 is trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 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. Each time samples are extracted and cleaned up 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. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis.

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum this should include the analysis of QC samples including a method blank, a matrix spike, a matrix duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike

samples, and replicate samples should be subjected to the same analytical (Sec. 11.0) procedures as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000

9.7 If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.4 for calibration and standardization information.

11.0 PROCEDURE

11.1 Introduction / preparation methods

Sample preparation follows either Method 3571 or 3572. The analytical assay can be performed by thermal desorption or liquid injection.

11.1.1 Thermal Desorption GC/MS Method

This technique employs a solid sorbent for extract or standard concentration followed by thermal desorption into the analytical system. There are a number of commercially available instruments that automate this process. The Dynatherm ACEMS

is one. The following section presents basic information for manually running this technique and is provided for information. Alternate approaches to concentrating extract volumes are available where vendor determined operating instructions should be utilized. Figure 1 presents a line drawing for major steps in the extract concentration thermal desorption analysis process.

11.1.1.1 Adsorption of Agents onto Solid Sorbents.

A volume of extract or standard is added onto a plug of glass wool located immediately in front of a solid sorbent bed. Air is purged through the resin bed resulting in the analytes being adsorbed onto the resin bed. The analytical process is initiated by thermally transferring this concentrated mass.

11.1.1.1.1 GB.

Extracts or standards are added to the glass wool plug and adsorbed onto Chromosorb 106.

11.1.1.1.2 HD.

Extracts or standards are added to the glass wool plug and adsorbed onto Texax TA.

11.1.1.1.3 VX.

Extracts or standards must be added to a silver fluoride (AgF) pad located in front of the glass wool. The AgF pad is used to convert VX to G-analog. During this process, the surrogate DEETP is also converted to its corresponding analog. GB is unaffected by this pad but HD will not transfer through this pad.

11.1.1.2 Assay of Solid Sorbent Tubes

11.1.1.2.1 Spike 50 μ L of the organic layer from the extract, into the glass wool inside the DAAMS tube or onto the AgF conversion pad connected to the short end side of the DAAMS sorbent tube. Continue airflow for 5 minutes after the tube has been spiked.

11.1.1.2.2 The tube is removed from vacuum and connected by Swagelok union to a 3-mm transfer or injection tube. The glass wool end of the DAAMS tube is positioned closest to the transfer tube. The other end is lowered into an aluminum-heating block at 220 °C. The sorbent tube is connected via Swagelok to a Helium purge. Helium flow is set at ~200-250 mL/min and run for 3 minutes.

11.1.1.2.3 To utilize the instrument injector for thermal desorption, the inlet must be configured to accept transfer tubes. For manual desorption, a gas line must be installed that will connect and supply regulated carrier gas through the transfer tube. In this configuration, the inlet provides the heat to transfer material to the head of the column.

11.1.1.2.4 The transfer tube is inserted into a modified injection port and the instrument run is started.

11.1.2 Liquid Injection Method

11.1.2.1 Withdraw 500 μL of extract for each sample or standard and place in an appropriately labeled auto sampler vial.

11.1.2.2 Spike each vial with the same concentration of internal standard. Tetrachlorobenzene at a concentration of 0.10 $\text{ng}/\mu\text{L}$ for all samples and standards is suggested.

11.1.2.3 Cap the auto sampler vial and place, in sequence, on the auto sampler tray.

11.1.2.4 Initialize the sequence in the software according to the samples and standards on the tray. Injection volume must be the same for samples and calibration standards.

11.2 Suggested chromatographic conditions

11.2.1 Thermal Desorption

Use a DB-624 30-meter column and set the injector to 200 $^{\circ}\text{C}$.

Oven Program:

- GB, DFP, VX, DEETP: 90 $^{\circ}\text{C}$ | 1 min | 20 $^{\circ}\text{C}/\text{min}$ | 240 $^{\circ}\text{C}$.
- HD, CEES: 140 $^{\circ}\text{C}$ | 1 min | 25 $^{\circ}\text{C}/\text{min}$ | 240 $^{\circ}\text{C}$ | 3 min.

11.2.2 Liquid Injection Method

Use a DB-1701 30-meter column and set the injector to 220 $^{\circ}\text{C}$.

Oven Program:

- GB, DFP, VX, DEETP: 60 $^{\circ}\text{C}$ | 1 min | 15 $^{\circ}\text{C}/\text{min}$ | 270 $^{\circ}\text{C}$ | 15 min
- HD, CEES: 60 $^{\circ}\text{C}$ | 1 min | 15 $^{\circ}\text{C}/\text{min}$ | 270 $^{\circ}\text{C}$ | 3 min

11.3 Compound Identification

11.3.1 Solid Adsorbent Method

- GB ions: Primary ion 99 m/z , Secondary ion 125 m/z and Tertiary ion 81 m/z .
- DFP ions: Primary ion 101 m/z , Secondary ion 127 m/z .
- Converted VX (g-analog) ions: Primary ion 99 m/z , Secondary ion 81 m/z and Tertiary ion 111 m/z .

- Converted DEETP (g-analog) ions: Primary ion 113 m/z, Secondary ion 84 m/z and Tertiary ion 125 m/z.
- HD ions: Primary ion 109 m/z, Secondary ion 158 m/z. Ions 111 and 160 may be used. Ion 111 will work best because of the higher intensity compared to ion 160.
- CEES ions: Primary ion 124 m/z, Secondary ion 126 m/z.
- Direct VX ions: Primary ion 114 m/z, Secondary ion 127 m/z, Tertiary ion 167 m/z.
- Direct DEETP ions: Primary ion 93 m/z, Secondary ion 122 m/z

11.3.2 Liquid Injection Method

- GB ions: Primary ion 99 m/z, Secondary ion 125 m/z and Tertiary ion 81 m/z.
- DFP ions: Primary ion 101 m/z, Secondary ion 127 m/z.
- VX ions: Primary ion 114 m/z, Secondary ion 127 m/z and Tertiary ion 167 m/z.
- DEETP ions: Primary ion 93 m/z, Secondary ion 122 m/z.
- HD ions: Primary ion 109 m/z, Secondary ion 158 m/z. Ions 111 and 160 may be used. Ion 111 will work best because of the higher intensity compared to on 160.
- CEES ions: Primary ion 124 m/z, Secondary ion 126 m/z.
- Tetrachlorobenzene: Primary ion 216 m/z, Secondary ion 214 m/z.

11.4 Calibration

11.4.1 One of several calibration approaches may be used; however, it must be employed throughout the whole sample set for that particular agent.

11.4.1.1 Linear Regression – A minimum of five points must be run for this type of calibration. The five point calibration curve is deemed valid if the calculated concentration from the regression curve for all target compounds are $\leq 25\%$ across the working range of the method, with the exception of $\leq 35\%$ at the lowest point on the calibration and the R^2 for the regression is ≥ 0.9900 .

11.4.1.2 Response Factors – A minimum of five points must be run for this type of calibration. Sample concentrations are calculated from the mean response factor. The five point calibration is deemed valid if the calculated Percent Relative Standard Deviation (%RSD) of the response factors is less than or equal to 20%.

11.4.1.3 Continuing calibration standards must be run at the beginning and end of each sample sequence to verify initial calibration values. Only 10 samples can be run between continuing calibration standards. The continuing spike level should be approximately the same as that of the second highest spike level for the initial calibration.

11.4.1.4 A continuing calibration standard is deemed valid if the calculated concentration value for each agent is within $\pm 25\%$ difference of the spiked amount and the peak retention agrees within $\pm 5\%$ of the retention time window established by the initial calibration. Note, if a response factor calibration is employed, the continuing calibration standard is deemed valid if the continuing response factor is within $\pm 15\%$ difference of the mean response factor from the calibration curve and the peak retention agrees within $\pm 5\%$ the retention time window established by the initial calibration.

11.4.2 Calibration Standards

11.4.2.1 Solid Adsorbent Method

Calibration Standards:

- GB: 0.5, 1.0, 2.0, 5.0, and 10 ng.
- DFP: 0.5, 1.0, 2.0, 5.0, and 10 ng.
- VX: 1.0, 2.0, 5.0, 10 and 20 ng.
- AgF-derivatized DEETP: 1.0, 2.0, 5.0, 10 and 20 ng.
- HD: 0.1, 0.2, 0.5, 1.0, and 2.0 ng.
- CEES: 0.1, 0.2, 0.5, 1.0, and 2.0 ng.

11.4.2.2 Liquid Injection Method

- GB: 0.005, 0.010, 0.016, 0.020, and 0.030 ng/ μ L.
- DFP: 0.005, 0.010, 0.016, 0.020, and 0.030 ng/ μ L.
- VX: 0.01, 0.02, 0.04, 0.08, and 0.16 ng/ μ L.
- DEETP: 0.01, 0.02, 0.04, 0.08, and 0.16 ng/ μ L.
- HD: 0.005, 0.010, 0.016, 0.020, and 0.030 ng/ μ L.
- CEES: 0.005, 0.010, 0.016, 0.020, and 0.030 ng/ μ L.

11.5 Instrument Tuning.

For Samples run by liquid injection GC/MS, it is recommended that DFTPP be run every twelve hours before the analytical sequence to insure that the mass spectrometer is properly

tuned. DFTPP injection time represents the start of a twelve-hour tune window in which samples and standards can be injected. DFTPP tune passes if it meets the following criteria:

51 m/z	30.0 – 80.0 percent of mass 198 m/z
68 m/z	Less than 2.0 percent of mass 69 m/z
69 m/z	Present
70 m/z	Less than 2.0 percent of mass 69 m/z
127 m/z	25.0 – 75.0 percent of mass 198 m/z
197 m/z	Less than 1.0 percent of mass 198 m/z
198 m/z	Base peak, 100 percent relative abundance
199 m/z	5.0 – 9.0 percent of mass 198 m/z
275 m/z	10.0 – 30.0 percent of mass 198 m/z
365 m/z	Greater than 0.75 percent of mass 198m/z
441 m/z	Present but less than mass 443 m/z
442 m/z	40.0 – 110.0 percent of mass 198 m/z
443 m/z	15.0 – 24.0 percent of mass 442 m/z

11.6 Calculations

11.6.1 Initial Calibration Calculations (Concentration is in terms of on column amounts)

11.6.1.1 Linear Equation

Response = B (Conc) + A, where Conc is the calculated concentration and B and A are coefficients calculated by the processing software. For regression output, B is the X coefficient, and A is the constant, where concentration is the Independent variable and Response is the dependent variable. Note: Response is equal to area if no internal standard is used, otherwise it is Target Area * IS Conc. / IS Area. When solved in terms of Concentration, the equation is:

$$\text{Conc.} = (\text{Response} - A) / B$$

11.6.1.2 Calibration by Response Factors (RF)

$$\text{RF} = (\text{Target Area}) / (\text{Target Conc})$$

Mean RF is the average of all Initial Calibration Standard Response Factors. To calculate the % Relative Standard Deviation (%RSD) find the

sample standard deviation for the Initial Calibration Standard Response Factors and divide by the Mean Response Factor.

11.6.2 Sample Concentration Calculations ($\mu\text{g/L}$ or $\mu\text{g/kg}$)

11.6.2.1 Sample Concentration in Water

$$\mu\text{g/L} = (A * B) / (C * D)$$

Where: A = ng or ng/ μL on column amount of target compound

B = Extract volume in μL

C = Volume spiked onto sorbent in μL : for liquid inj.
enter (1)

D = Amount of sample in mL.

11.6.2.2 Sample Concentration in Soil

$$\mu\text{g/kg} = (A * B) / (C * D * E)$$

Where: A = ng or ng/ μL on column amount of target compound

B = Extract volume in μL

C = Volume spiked onto sorbent in μL : for liquid inj.
enter (1)

D = Amount of sample in grams.

E = % Dry Weight

11.7 Agent Identification Criteria

11.7.1 Blanks must have baseline resolution within the RT window. Responses found in the RT window must not exceed 20% of the lowest calibration standard height. Blank responses not meeting this criterion will require further investigation before analyses can proceed.

11.7.2 All surrogate recoveries must be within the QC limits of 50 - 150%.

11.7.3 All blank spike, matrix spike, and matrix spike duplicates recoveries must be within the QC limits of 50 – 150%.

11.7.4 The internal standard area of the samples must be within the 50 – 150% of the continuing calibration standard (CCS) internal standard area.

11.7.5 The %RPD between matrix spike and matrix spike duplicate must be within the QC limit of 35%.

11.7.6 Identification.

11.7.6.1 All peaks within agent retention time window will be considered as a potential agent hit. The agent retention time window is $\pm 5\%$ of the average agent retention time found from the two continuing calibration standards bracketing the unknown response.

11.7.6.2 Confirmation of Agent peaks

Analysis by GC/MS can be confirmed by the ion traces from the primary, secondary, and tertiary ions. Re-analysis using an alternate column is not required.

The target analyte is considered detected and is submitted for quantitation if both the primary ion and the secondary selected mass are present in the chromatograms, are in approximately the same proportions as in the CCS reference spectrum, and both peaks are within 0.20 minutes of the retention time of the calibration standard reference.

The ratio of the two ions in the sample must match the ratio found in the CCS within $\pm 30\%$. If available, use 3rd and 4th ions for confirmation.

Ion abundance percentages are as follows:

- HD: Ion 109 m/z is at 100%, Ion 111 m/z is 33% of mass 109 m/z, Ion 158 m/z is 10% of Ion 109 m/z and Ion 160 m/z is 30% of Ion 158 m/z.
- GB: Ion 99 m/z is at 100%, Ion 81 m/z is 40% of mass 99 m/z and ion 125 m/z is 30% of mass 99 m/z
- VX: (g-analog): Ion 99 m/z 100%, Ion 81 and 111 m/z at 30% of mass 99 m/z.
- VX: (Direct): Ion 114 m/z 100%, Ion 127 and 167 m/z less than 5% of Ion 114 m/z.
- Note that interferences in any of the ion ratios may distort the identification process. Additionally, 3rd and 4th ion fragments have low responses and may not be readily observed depending on the mass. The analyst must evaluate the sample against reference spectra to reach a conclusion.
- The use of secondary columns on GC/MS will provide another piece of information to aid in confirmation of unknowns.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 See Sec. 11.6 for information regarding data analysis and calculations.

12.2 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

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 goals for users of the methods. Instead, performance goals should be developed on a project-specific basis and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Single operator accuracy and precision studies have been conducted using spiked samples of solid and aqueous media. Tables 1 and 2 provide single-laboratory performance data for the three agents in soil by direct injection and DAAMS thermal desorption.

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 operation. 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 EPA 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* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N. W. Washington, D. C. 20036, <http://www.acs.org>.

15.0 WASTE MANAGEMENT

15.1 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The EPA 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 Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

15.2 Agent-contaminated materials must be thoroughly decontaminated prior to disposal. The laboratory chemical hygiene plan will contain the procedures to be followed.

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, GD, 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

The following tables and figure are referenced by the method.

Table 1

EXAMPLE OF SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION FOR
SOIL – DIRECT INJECTION METHOD

Compound	Mean Rec. (%)	%RSD	Spike Conc. µg/kg	Recovery Range (%)	# Analyses
GB	120	12.3	15	99.6 – 145	7
HD	107	2.9	16	103 – 112	7
VX	91	19	28	61–110	7

Table 2

EXAMPLE OF SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION FOR
SOIL – DAAMS INJECTION METHOD

Compound	Mean Rec. (%)	%RSD	Spike Conc. µg/kg	Recovery Range (%)	# Analyses
GB	85	7.2	1	78 - 95	7
HD	89	5.4	50	84 - 94	7
VX	77	6.9	20	71 – 85	7

Table 3

EXAMPLE OF SINGLE LABORATORY OPERATOR ACCUACY AND PRECIISION FOR
WATER – DIRECT INJECTION

Compound	Mean Rec. (%)	%RSD	Spike Conc. µg/kg	Recovery Range (%)	# Analyses
GB	83	5.7	15	77 - 89	7
HD	111	2.5	16	105 - 114	7
VX	69	10.7	28	55 – 74	7

Table 4

EXAMPLE OF SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION FOR
ASH – DIRECT INJECTION

Compound	Mean Rec. (%)	%RSD	Spike Conc. µg/kg	Recovery Range (%)	# Analyses
GB	123	8.5	15	103 – 135	7
HD	105	6	16	98 - 113	7
VX	114	17	28	95 - 151	7

Figure 1

DAAMS Analytical Sequence

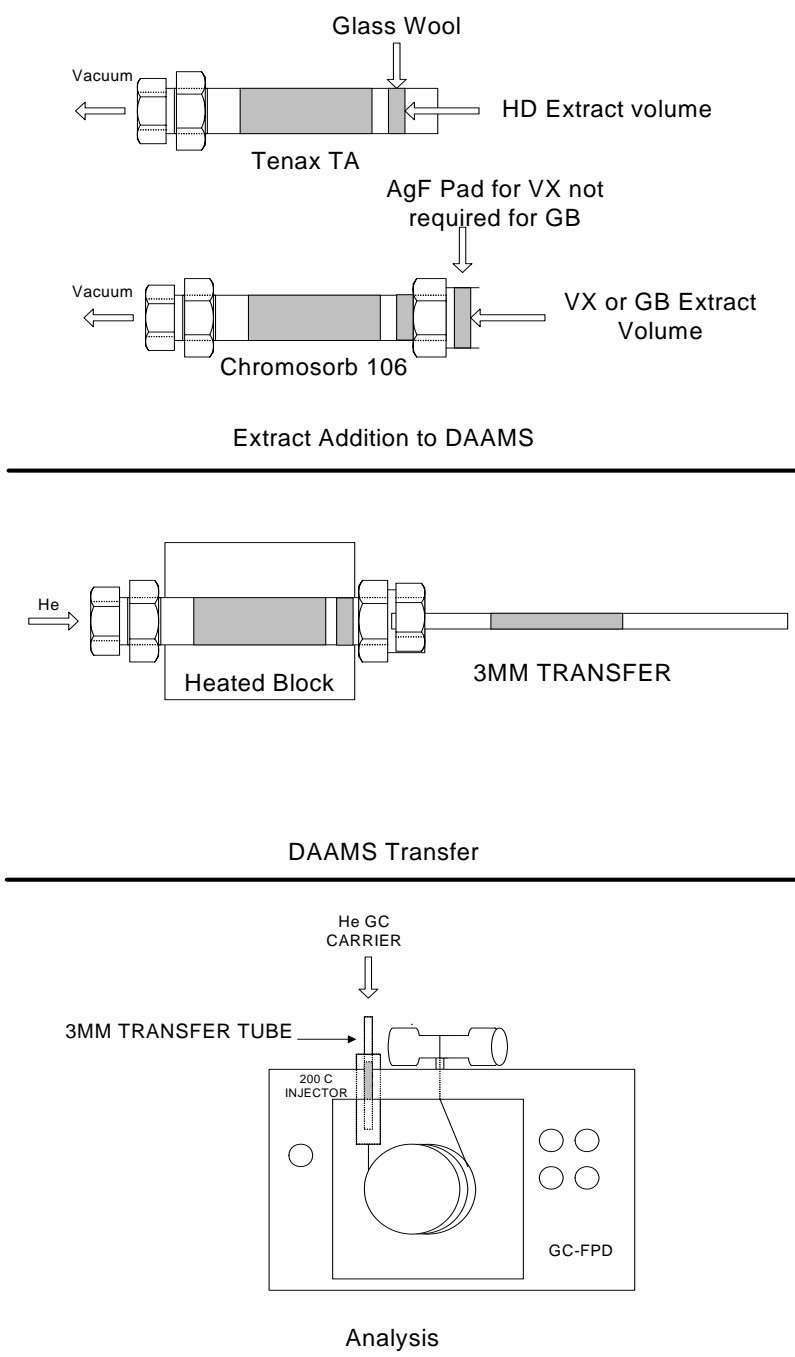


Figure 1. DAAMS Analytical Sequence