N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

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

1.1 This method is used to determine the concentration of *N*-methylcarbamates in soil, water, and waste matrices. The following RCRA compounds have been determined by this method:

Analyte	CAS No.[a]
Aldicarb (Temik)	116-06-3
Aldicarb sulfone	1646-88-4
Bendiocarb	22781-23-3
Carbaryl (Sevin)	63-25-2
Carbofuran (Furadan)	1563-66-2
m-Cumenyl methylcarbamate	64-00-6
Dioxacarb	6988-21-2
Formetanate hydrochloride	23422-53-9
3-Hydroxycarbofuran	16655-82-6
Methiocarb (Mesurol)	2032-65-7
Methomyl (Lannate)	16752-77-5
Metolcarb	1129-41-5
Mexacarbate	315-18-4
Oxamyl	23135-22-0
Promecarb	2631-37-0
Propoxur (Baygon)	114-26-1
Thiodicarb	59669-26-0

[a]Chemical Abstract Service Registry Number

1.2 This method provides optional matrix-specific extraction procedures that can be applied to aqueous samples, soils, solids, sludges, and oily wastes. In addition, optional extract cleanup procedures are included to remove interferences and improve method sensitivity.

1.3 The sensitivity of this method usually depends on the level of interferences, rather than on the instrumental conditions. Waste samples with a high level of extractable fluorescent compounds are expected to yield significantly higher quantitation limits.

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 required 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 Use of this method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography (HPLC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 *N*-methylcarbamates are extracted from samples using various 3500 series extraction methods, or other methods that are appropriate for the sample matrix. Alternatively, several optional matrix-specific extraction procedures are provided in this method. Those optional procedures include:

2.1.1 Extraction of aqueous samples with methylene chloride in a separatory funnel.

2.1.2 Extraction of soils, solids, sludges, and heavy aqueous suspensions with acetonitrile on a platform shaker.

2.1.3 Extraction of soils that are heavily contaminated with oils or other non-aqueous liquids with hexane, followed by acetonitrile, on a platform shaker.

2.2 Extracts may be subjected to an optional cleanup procedure designed to remove interferences. During cleanup, the solvent is exchanged to methanol for analysis.

2.3 Extracts are analyzed by HPLC, on a C-18 reversed-phase column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantitated fluorometrically.

2.4 Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, fluorescence due to post-column derivatization may be confirmed by substituting the NaOH and *o*-phthalaldehyde solutions with reagent water and reanalyzing the sample. If fluorescence is still detected, then a positive interference is present and care should be taken in the interpretation of the results.

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.

4.2 Fluorescent compounds, primarily alkyl amines and compounds which yield primary alkyl amines upon base hydrolysis, are potential sources of interferences.

4.3 Coeluting compounds that are fluorescence quenchers may result in negative interferences.

4.4 Also refer to Methods 3500 and 8000.

5.0 SAFETY

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 The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

6.0 EQUIPMENT AND SUPPLIES

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).

6.1 High performance liquid chromatograph (HPLC)

An analytical system equipped with a programmable solvent delivery system and all necessary accessories including a high pressure injection valve, analytical column, mobile phase solvent degassing, etc. At a minimum, the solvent delivery system must be capable of handling a binary solvent system, and must be able to accurately deliver flow rates between 0.5 - 3.0 mL/min.

6.1.1 HPLC columns -- An analytical column is necessary and a guard column is highly recommended.

The columns listed in this section were the columns used to develop the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.1.1.1 C-18 reversed-phase column -- 3-5 µm particle size, 100 - 250 mm x 4.6-mm ID.

6.1.1.2 Guard column -- Packing and internal diameter similar to that used in the analytical column.

6.1.2 Post-column reactor equipped with two solvent delivery systems.

6.1.3 Fluorescence detector -- Capable of excitation at 280 nm and emission greater than 389 nm cutoff, at a minimum.

6.1.4 Column heater -- The use of a column heater is recommended to ensure consistent retention times throughout the course of the HPLC analysis. The heater should be capable of maintaining the analytical column at 3 to 5 EC (± 0.1 EC) above the ambient laboratory temperatures.

6.1.5 Autoinjector -- The use of an autoinjector is recommended. The autoinjector should be capable of delivering 1 - 25 µL injections without affecting the chromatography.

6.1.6 HPLC injection syringe -- 50-µL, used if the autoinjector is not used.

6.1.7 Data system -- At a minimum, an integrator compatible with the detector, and capable of measuring peak area and retention time for the eluted peaks. A computer system for instrumental control, data collection and analysis is recommended.

6.2 Analytical balance capable of weighing ± 0.0001 g.

6.3 Top-loading balance capable of weighing ± 0.01 g.

6.4 Volumetric pipettes, Class A -- Glass, assorted sizes.

6.5 Volumetric flasks, Class A -- Glass, assorted sizes.

6.6 Assorted glass funnels.

6.7 Equipment for the optional extraction procedures

The following equipment is used for the optional extraction procedures described in this method.

6.7.1 Centrifuge capable of holding 250-mL tubes.

6.7.2 Platform shaker capable of holding 250-mL Erlenmeyer flasks.

6.7.3 Erlenmeyer flasks fitted with polytetrafluoroethylene (PTFE)-lined screw caps, 250-mL.

6.7.4 Filter paper (Whatman #113 or #114, or equivalent).

6.7.5 Separatory funnels, fitted with ground-glass stoppers and stopcocks -- 250-mL.

6.7.6 Graduated cylinders -- 100-mL.

6.7.7 Centrifuge tubes -- 250-mL.

6.7.8 Vials -- 25-mL, glass fitted with PTFE-lined screw caps or crimp tops.

6.8 Equipment for the optional cleanup techniques

6.8.1 Heating block, or equivalent apparatus, that can accommodate 10-mL graduated vials (see Sec. 6.8.2).

6.8.2 Graduated glass vials -- 10-mL, 20-mL.

6.8.3 Reversed-phase cartridges (Waters Associates C-18 Sep-Pak®, or equivalent).

6.8.4 Nylon filter unit, 25-mm diameter, 0.45-µm pore size, disposable.

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or pesticide-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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Solvents

The choice of solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance

criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

Some of the following solvents may not be needed if the optional extraction and cleanup procedures are not employed.

7.2.1 Acetonitrile, CH_3CN -- HPLC-grade, minimum UV cutoff at 230 nm.

7.2.2 Methanol, CH_3OH -- HPLC-grade, minimum UV cutoff at 230 nm.

7.2.3 Methylene chloride, CH_2Cl_2 -- HPLC-grade, minimum UV cutoff at 230 nm.

7.2.4 Hexane, C_6H_{14} -- Pesticide-grade, or equivalent.

7.2.5 Ethylene glycol, $HOCH_2CH_2OH$ -- Reagent-grade.

7.3 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

7.4 Sodium hydroxide, NaOH -- reagent-grade, 0.05N NaOH solution.

7.5 Phosphoric acid, H_3PO_4 -- reagent-grade.

7.6 Borate buffer, pH 10.

7.7 *o*-Phthalaldehyde, *o*-$C_6H_4(CHO)_2$ -- reagent-grade.

7.8 2-Mercaptoethanol, $HSCH_2CH_2OH$ -- reagent-grade.

7.9 *N*-methylcarbamate neat standards.

7.10 Chloroacetic acid, $ClCH_2COOH$, 0.1 N.

7.11 Reaction solution

Dissolve 0.500 g of *o*-phthalaldehyde in 10 mL of methanol, in a 1-L volumetric flask. To this solution, add 900 mL of organic-free reagent water, followed by 50 mL of the borate buffer (pH 10). After mixing well, add 1 mL of 2-mercaptoethanol, and dilute to the mark with organic-free reagent water. Mix the solution thoroughly. Prepare fresh solutions on a weekly basis, as needed. Protect from light and store under refrigeration.

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.

7.12.1 Stock standard solutions

Prepare individual 1000-mg/L solutions by adding 0.025 g of carbamate to a 25-mL volumetric flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials fitted with PTFE-lined screw caps or crimp tops. Replace every six months, or sooner if necessary.

7.12.2 Intermediate standard solution

Prepare a solution containing all the target compounds at 50.0 mg/L by adding 2.5 mL of each stock solution to a 50-mL volumetric flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials fitted with PTFE-lined screw caps or crimp tops. Replace every three months, or sooner if necessary.

7.12.3 Working standard solutions

Prepare 0.5-, 1.0-, 2.0-, 3.0- and 5.0-mg/L solutions by adding 0.25, 0.5, 1.0, 1.5 and 2.5 mL of the intermediate mixed standard to respective 25-mL volumetric flasks, and diluting each to the mark with methanol. Store solutions, under refrigeration, in glass vials fitted with PTFE-lined screw caps or crimp tops. Replace every two months, or sooner if necessary.

NOTE: Other concentrations may be used as appropriate for the intended application and the operating range of the instrument.

7.12.4 Mixed QC standard solution

Prepare a 40.0-mg/L solution from another set of stock standard solutions, prepared similarly to those described in Sec. 7.12.1. Add 2.0 mL of each stock solution to a 50-mL volumetric flask and dilute to the mark with methanol. Store the solution, under refrigeration, in a glass vial fitted with a PTFE-lined screw cap or crimp top. Replace every three months, or sooner if necessary. Other concentrations may be used, as appropriate for the intended application.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Due to the extreme instability of *N*-methylcarbamates in alkaline media, samples of water, wastewater, and leachates should be preserved immediately after collection by acidifying to pH 4-5 with 0.1 N chloroacetic acid.

8.3 Store samples at #6 EC, and out of direct sunlight, from the time of collection through analysis. *N*-methylcarbamates are sensitive to alkaline hydrolysis and heat.

8.4 All samples need to be extracted within seven days of collection and analyzed within 40 days of extraction.

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. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques that can be applied to this method, which contains its own extraction procedures. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, 3600, or 5000.

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

9.4 Initial demonstration of proficiency

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. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are 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. 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. 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 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 and a laboratory control sample (LCS) in each analytical batch, the addition of surrogates to each field sample and QC sample when surrogates are used, and routine analyses of matrix spike and matrix spike duplicate

aliquots. 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.

9.6.1 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, then laboratories may use one 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 indicates 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 Include a calibration standard after each group of 20 samples in the analysis sequence as a calibration check (it is recommended that a calibration standard be included after every 10 samples to minimize the number of repeat injections). Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The response factors for the calibration should be within ± 20% of the initial calibration. When this calibration verification standard falls out of this acceptance window, the laboratory should stop analyses and take corrective action.

9.6.4 Also see Method 8000 for the details in 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 Surrogate recoveries

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.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.7 for information on calibration and standardization.

11.0 PROCEDURE

Samples may be prepared and extracted using various 3500 series extraction methods or other methods that are appropriate for the sample matrix. Alternatively, optional matrix-specific extraction procedures are provided in this method. These optional procedures use smaller volumes or weights of samples than are nominally employed in the 3500 series methods (e.g., a 100-mL water sample versus a 1-L water sample). The analyst should choose among the possible extraction procedures based on the nature of the samples and the sensitivity required for the intended application. This method also includes optional cleanup and solvent exchange procedures.

Whatever extraction procedure is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

11.1 Extraction of water, wastewater, aqueous industrial wastes, and leachates

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510), a continuous liquid-liquid extractor (Method 3520), solid phase extraction (Method 3535) or other appropriate technique. If one of these techniques is employed, then proceed to Sec. 11.5 once the extraction is complete.

Alternatively, if appropriate for the sensitivity of the intended application, use the approach described below.

11.1.1 Measure 100 mL of sample into a 250-mL separatory funnel.

11.1.2 Add 30 mL of methylene chloride to the separatory funnel, cap, and shake vigorously for about 2 minutes. Allow the phases to separate and drain the organic layer into a clean 100-mL volumetric flask. Repeat the extraction two more times with fresh portions of solvent.

11.1.3 Combine all three extracts in a 100-mL volumetric flask and dilute to 100 mL with methylene chloride. Proceed to Sec. 11.5.

11.2 Extraction of soils, solids, sludges, and heavy aqueous suspensions

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, solid samples are extracted with acetonitrile using one of the Soxhlet extraction methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550), or other appropriate technique or solvents. If one of these techniques is employed, then proceed to Sec. 11.5 once the extraction is complete.

Alternatively, if appropriate for the sensitivity of the intended application, use the approach described below.

11.2.1 Weigh out 20 ± 0.1 g of sample into a 250-mL Erlenmeyer flask fitted with a PTFE-screw cap.

11.2.2 Determination of percent dry weight -- When sample results are to be calculated based on a dry-weight basis, a separate portion of sample should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh an additional 5- to 10-g aliquot of the sample into a tared crucible. Dry this aliquot overnight at 105 EC. Allow it to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

NOTE: This dry weight determination also applies to the use of other extraction techniques for solids (e.g., a 3500 series method), when results are to be calculated on a dry weight basis.

This oven-dried aliquot is not used for the extraction and should be appropriately disposed once the dry weight is determined.

11.2.3 Add 50 mL of acetonitrile to the portion of the sample in the Erlenmeyer flask. Seal the flask and shake for 2 hr on a platform shaker. Allow the mixture to settle (5-10 min), then decant the extract into a 250-mL centrifuge tube. Repeat the extraction twice more, but using 20 mL of acetonitrile and shaking for 1 hr each time.

11.2.4 Combine all three extracts in the centrifuge tube. Centrifuge the combined extract at 200 rpm for 10 min. Carefully decant the supernatant into a 100-mL volumetric flask and dilute to 100 mL with acetonitrile. Proceed to Sec. 11.5.

11.3 Soils heavily contaminated with non-aqueous substances, such as oils

The extraction of soils heavily contaminated with oils and other non-aqueous substances is not generally addressed in the various 3500 series extraction methods for solid samples. Therefore, the procedure outlined below may be more appropriate for such samples. However the choice of extraction procedure is left to the professional judgment of the analyst.

11.3.1 Weigh out 20 ± 0.1 g of sample into a 250-mL Erlenmeyer flask fitted with a PTFE-screw cap.

11.3.2 If dry weight results are needed, determine the dry weight as described in Sec. 11.2.2.

11.3.3 Add 60 mL of hexane to the portion of the sample in the Erlenmeyer flask. Seal the flask and shake for 1 hr on a platform shaker. Without removing the hexane, add 50 mL of acetonitrile and shake for an additional 3 hr. Allow the mixture to settle (5-10 min), then decant the solvent layers into a 250-mL separatory funnel, leaving the sample in the Erlenmeyer flask. Drain the acetonitrile (bottom layer) through filter paper into a 100-mL volumetric flask.

11.3.4 Add 60 mL of hexane and 50 mL of acetonitrile to the original Erlenmeyer flask and shake for an additional 1 hr. Allow the mixture to settle, then decant the solvent mixture into the separatory funnel containing the hexane from the first extraction. Shake the separatory funnel for 2 minutes, allow the phases to separate, and drain the acetonitrile layer through filter paper into the volumetric flask.

11.3.5 Dilute to 100 mL with acetonitrile. Proceed to Sec. 11.5.

11.4 Non-aqueous liquids such as oils

The extraction of oils and other non-aqueous liquids is not generally addressed in the various 3500 series extraction methods. Therefore, the procedure outlined below may be more appropriate for such samples. However the choice of extraction procedure is left to the professional judgment of the analyst.

11.4.1 Weigh out 20 ± 0.1 g of sample into a 125-mL separatory funnel. Add 40 mL of hexane and 25 mL of acetonitrile and vigorously shake the sample mixture for 2 minutes. Allow the phases to separate, then drain the acetonitrile (bottom layer) into a 100-mL volumetric flask.

11.4.2 Add another 25 mL of acetonitrile to the separatory funnel and shake for 2 minutes. Allow the phases to separate and drain the acetonitrile layer into the volumetric flask.

11.4.3 Repeat the extraction with a third 25-mL portion of acetonitrile, combining the extracts in the volumetric flask.

11.4.4 Dilute to 100 mL with acetonitrile. Proceed to Sec. 11.5.

11.5 Cleanup and solvent exchange

This section provides optional cleanup procedures for the extracts from all matrices. While extracts of some very clean water samples may not need cleanup, the use of the cleanup procedures is strongly recommended for water samples and may be essential for the other matrices. These cleanup procedures assume that each sample extract begins with a volume of 100 mL. The volumes described in the cleanup procedures are recommendations, and the analyst is free to employ other volumes, provided that the analyst demonstrates acceptable performance for the intended application. Regardless of the specific volumes that are employed, the analyst should record the volumes at each step, so that the overall dilution factor for the analysis can be determined and the concentration of each target compound can be calculated.

All sample extracts will need solvent exchange prior to analysis. The optional cleanup techniques include a solvent exchange step. However, if the cleanup steps are omitted, proceed to Sec.11.5.3 for solvent exchange.

11.5.1 Cleanup of water sample extracts in methylene chloride

Prior to cleanup, the solvent must be exchanged from methylene chloride to a solvent compatible with the C-18 cleanup cartridge (e.g., methanol). After cleanup, the extract is filtered.

11.5.1.1 Pipet 20.0 mL of the 100-mL extract into a 20-mL glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50 EC,

and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Retain the remaining 80 mL of methylene chloride extract in the volumetric flask in the event that it is needed for dilutions or reanalysis.

11.5.1.2 Dissolve the ethylene glycol residue in 2 mL of methanol.

11.5.1.3 Pass the 2 mL of methanol through a C-18 reversed-phase cartridge, pre-washed with methanol. Collect the eluate in a 5-mL volumetric flask. Elute the cartridge with about 3 mL of methanol, and collect the eluate until a final volume of 5.0 mL is obtained.

11.5.1.4 Using a disposable 0.45-µm filter, filter the cleaned extract directly into a labeled autosampler vial or other suitable container. The extract is now ready for analysis. Proceed to Sec. 11.6. The 5.0-mL volume of methanol represents one-fifth (20/100) of the original sample extract.

11.5.2 Cleanup of acetonitrile extracts of soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids

Acetonitrile is compatible with the C-18 cartridges used for cleanup. Therefore, the solvent exchange step occurs after the cleanup, unlike the methylene chloride extracts of aqueous samples described above.

11.5.2.1 Pass 15 mL of the 100-mL acetonitrile extract through a C-18 reversed-phase cartridge, prewashed with 5 mL of acetonitrile. Discard the first 2 mL of eluate and collect the remainder in a clean flask. Retain the remaining 85 mL of acetonitrile extract in the volumetric flask in the event that it is needed for dilutions or reanalysis.

11.5.2.2 Pipet 10.0 mL of the cleaned extract into a 10-mL graduated glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50EC, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains.

11.5.2.3 Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL.

11.5.2.4 Using a disposable 0.45-µm filter, filter this extract directly into a labeled autosampler vial or other suitable container. The extract is now ready for analysis. Proceed to Sec. 11.6. The 1.0-mL volume of methanol represents one-tenth (10/100) of the original sample extract.

11.5.3 Solvent exchange for extracts that do not undergo cleanup

The final extract solvent must be compatible with the HPLC column. Therefore, if the cleanup steps in Sec. 11.5.2 have been omitted, the analyst must exchange the solvent to methanol or another solvent compatible with the HPLC system. The solvent exchange may be accomplished using the ethylene glycol keeper approach described above, or by other appropriate means, including those described in the 3500 series methods.

11.6 HPLC conditions

Establish HPLC operating conditions appropriate for the target analytes. Optimize the instrumental conditions for resolution of the target analytes and sensitivity. Suggested operating conditions are given below. Other operating conditions may be employed, provided that the analyst can demonstrate performance that is appropriate for the intended application. Table 1 provides the example retention times that were obtained under these conditions during method development. These retention times are for illustrative purposes only. Each laboratory must determine retention times for its specific application of the method. An example chromatogram is shown in Figure 1.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

11.6.1 Recommended solvents and flow rate

Solvent A:	Reagent water, acidified with 0.4 mL of phosphoric acid per liter of water
Solvent B:	Methanol/acetonitrile (1:1, v/v)
Flow rate:	1.0 mL/min
Injection volume:	20 µL

11.6.2 Recommended gradient elution program

Time (min)	Solvent A (%)	Solvent B (%)
0.00	90%	10%
0.02	20%	80%
20.02	0%	100%
25.02	0%	100%
30.02	90%	10%
33.02	90%	10%

11.6.3 Recommended post-column hydrolysis parameters

Solution:	0.05 N aqueous sodium hydroxide
Flow rate:	0.7 mL/min
Temperature:	95 EC
Residence time:	35 sec (1-mL reaction coil)

11.6.4 Recommended post-column derivatization parameters

Solution:	*o*-phthalaldehyde/2-mercaptoethanol
Flow rate:	0.7 mL/min
Temperature:	40 EC
Residence time:	25 sec (1-mL reaction coil)

11.6.5 Recommended fluorometer parameters

Cell:	10 µL
Excitation wavelength:	340 nm
Emission wavelength:	418 nm cutoff filter
Sensitivity wavelength:	0.5 µA
PMT voltage:	-800 V
Time constant:	2 sec

11.7 Calibration

11.7.1 Analyze a solvent blank (20 µL of methanol) to ensure that the system is clean. Analyze the calibration standards (see Sec. 7.12.3), starting with the lowest standard and ending with the highest standard, to avoid memory effects.

11.7.2 Calculate the calibration factor (CF) for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

11.7.3 Calculate the mean calibration factor for each analyte as:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

11.7.4 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

11.7.5 Calibration linearity

If the RSD for each analyte is # 20%, then the response of the instrument is considered linear and the mean calibration factor may be used to quantitate sample results. If the RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

11.7.6 Retention time windows

Method 8000 provides instructions on establishing retention time windows and identification criteria. If column temperature control is not employed, special care should be taken to ensure that temperature shifts do not cause peak misidentification.

11.8 Sample analysis

Analyze the sample extracts using the same HPLC operating conditions that were established in Sec. 11.6.

11.8.1 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hr analytical shift), or calibration standards interspersed within the samples. After 10 sample runs, or less, the mid-range standards should be checked to ensure that the retention times and response factors are still within acceptable limits. Significant variations (i.e., observed concentrations exceeding the true concentrations by more than ± 20%) may necessitate a reanalysis of the samples. See. Sec. 9.6.3.

11.8.2 If the peak areas of the sample signals exceed the calibration range of the system, dilute the extract as necessary and reanalyze the diluted extract.

11.8.3 The calibration factor for each analyte should not exceed a ± 20 percent difference from the mean calibration factor calculated for the initial calibration.

The percent difference is calculated as:

$$\% \text{ Difference } = \frac{CF - \overline{CF}_v}{\overline{CF}} \times 100$$

11.8.4 If the calibration does not meet the ± 20% limit (on the basis of each compound), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ± 20%, then a new initial calibration must be prepared.

11.8.5 When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent misquantitations and possible false negative results, and reinjection of the sample extracts may be necessary. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample

and the standard response is more than 20% below the initial calibration response, then reinjection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

11.8.6 Using the retention time windows established during calibration, identify the peaks in the sample chromatogram.

11.9 Analyte confirmation

Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, the analyst can verify that positive or negative interferences are not present by doing the following check procedures.

11.9.1 Negative interference due to quenching may be examined by spiking the extract with the appropriate standard, at an appropriate concentration, and examining the observed response against the expected response.

11.9.2 Confirm any detected analytes by substituting the NaOH and OPA reagents in the post column reaction system with deionized water, and reanalyze the suspected extract. Continued fluorescence response will indicate that a positive interference is present since the fluorescence response is not due to the post column derivatization. Exercise caution in the interpretation of the chromatogram.

11.10 Calculation of sample results

The calculation of the concentration of each analyte identified in the sample generally follows the procedures outlined in Method 8000 for external standard calibration. However, because the optional matrix-specific extraction and cleanup procedures described in this method involve various dilutions, the equations for the calculations are provided below in detail.

If the optional extraction and cleanup procedures are not employed, then the analyst should consult Method 8000 and adjust the calculations accordingly.

11.10.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_e)(V_t)(D)}{(\overline{CF})(V_s)(V_c)(V_i)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_e = Total volume of the original extract (mL). For aqueous samples extracted using the procedure in Sec. 11.1, this value will be 100 mL.

V_c = Volume of the extract processed through the cleanup steps (mL). For aqueous samples processed through the optional cleanup steps, this value will be 20 mL.

V_t = Total volume of the concentrated methanol extract (µL). For aqueous samples processed through the optional cleanup steps, this volume will be 5000 µL.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless. This dilution factor is in addition to the inherent dilution that occurs during the optional cleanup steps, e.g., it is *not* used to account for V_e/V_c.

CF = Mean calibration factor from the initial calibration (area/ng).

V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards should be the same, unless the analyst can demonstrate acceptable performance using different volumes or conditions.

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units given here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

11.10.2 Non-aqueous samples

$$\text{Concentration (µg/kg)} = \frac{(A_x)(V_e)(V_t)(D)}{(\overline{CF})(W_s)(V_c)(V_i)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_e = Total volume of the original extract (mL). For most non-aqueous samples extracted using the procedure in Sec. 11.2, this value will be 100 mL.

V_c = Volume of the extract *recovered* from the cleanup steps (mL). For most non-aqueous samples processed through the optional cleanup steps, this value will be 10 mL, even though 15 mL of the original extract are passed through the C-18 cartridge.

V_t = Total volume of the concentrated methanol extract (µL). For most non-aqueous samples processed through the optional cleanup steps, this volume will be 1000 µL.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless. This dilution factor is in addition to the inherent dilution that occurs during the optional cleanup steps, e.g., it is *not* used to account for V_e/V_c.

CF = Mean calibration factor from the initial calibration (area/ng).

V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards should be the same, unless the analyst can demonstrate acceptable performance using different volumes or conditions.

W_s = Weight of the non-aqueous sample extracted in g. If units of kilograms are used for this term, multiply the results by 1000.

Using the units given here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

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

12.0 DATA ANALYSIS AND CALCULATIONS

See Secs. 11.10 and 11.11 and Method 8000 for information regarding data analysis and calculations.

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. 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 Table 1 lists example retention times for 10 target compounds in water and soil, developed using the optional sample extraction and cleanup procedures described in Sec. 11.0. The retention times listed in Table 1 are provided for illustrative purposes only. Each laboratory must determine retention times and retention time widows for their specific application of the method.

13.3 Tables 2, 3, and 4 list the single-operator average recoveries and standard deviations for organic-free reagent water, wastewater, and soil prepared using the optional sample extraction and cleanup procedures described in Sec. 11.0. Ten replicate samples were analyzed for each matrix type. The data are taken from References 1 and 6, and are for guidance purposes only.

13.4 Tables 5 and 6 provide single-operator accuracy (as recovery) and precision (as RSD) data for 14 carbamates spiked into bulk quantities of a POTW effluent and a soil. The spiking levels were based on the Universal Treatment Standard (UTS) values for wastewater and non-wastewater. The spiking levels were approximately 80% of the UTS level for the matrix, rounded to two significant figures. Four replicate samples of each matrix were extracted and analyzed. The wastewater samples were prepared by extracting a 1-L sample using continuous liquid-liquid extraction (Method 3520). The soil samples were prepared by extracting a 30-g sample using Soxhlet extraction (Method 3540). Four of the compounds eluted together in a single peak (bendiocarb, thiodicarb, carbofuran, and propoxur) and one pair of compounds

eluted together in another peak (oxamyl and formentanate hydrochloride). The data are summarized in detail in Reference 7, and are provided here for guidance purposes only.

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 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* 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

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 Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. California Department of Health Services, Hazardous Materials Laboratory, "*N*-Methylcarbamates by HPLC," Revision No. 1.0, September 14, 1989.

2. R. T. Krause, *Journal of Chromatographic Science*, 1978, vol. 16, pg 281.

3. Kevin Klotter and Robert Cunico, "HPLC Post Column Detection of Carbamate Pesticides," Varian Instrument Group, Walnut Creek, CA 94598.

4. USEPA, "Method 531. Measurement of *N*-Methylcarbomyloximes and *N*-Methylcarbamates in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization," EPA 600/4-85-054, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

5. USEPA, "Method 632. The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater," EPA 600/4-21-014, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

6. H. S. Okamoto, D. Wijekoon, C. Esperanza, J. Cheng, S. Park, J. Garcha, S. Gill, and K. Perera, "Analysis for *N*-Methylcarbamate Pesticides by HPLC in Environmental Samples,"

Proceedings of the Fifth Annual USEPA Symposium on Waste Testing and Quality Assurance, July 24-28, 1989, Vol. II, 57-71.

7. Science Applications International Corporation, "Carbamates Method Evaluation Report," report for EPA Contract 68-W6-0068, August 25, 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figure referenced by this method.

TABLE 1

EXAMPLE ELUTION ORDER AND RETENTION TIMES

Compound	Retention Time (min)
Aldicarb sulfone	9.59
Methomyl	9.59
3-Hydroxycarbofuran	12.70
Dioxacarb	13.50
Aldicarb	16.05
Propoxur	18.06
Carbofuran	18.28
Carbaryl	19.13
α-Naphthol[a]	20.30
Methiocarb	22.56
Promecarb	23.02

See Sec. 11.6 for chromatographic conditions. Retention times are provided for guidance purposes only. Each laboratory must determine retention times and retention time widows for their specific application of the method.

[a] Breakdown product of Carbaryl.

TABLE 2

EXAMPLE SINGLE-OPERATOR RECOVERY AND PRECISION DATA
FOR SPIKED REAGENT WATER

Compound	Concentration (µg/L)	% Recovery	% RSD
Aldicarb sulfone	225	75	3.2
Methomyl	244	81	3.4
3-Hydroxycarbofuran	210	70	3.7
Dioxacarb	241	80	3.5
Aldicarb	224	75	6.0
Propoxur	232	77	4.6
Carbofuran	239	80	3.9
Carbaryl	242	81	3.5
Methiocarb	231	77	3.5
Promecarb	227	76	4.1

Spiking concentration = 300 µg/L of each compound

n = 10

The data are taken from References 1 and 6.

These data are provided for guidance purposes only.

TABLE 3

EXAMPLE SINGLE-OPERATOR RECOVERY AND PRECISION DATA
FOR SPIKED WASTEWATER

Compound	Concentration (µg/L)	% Recovery	% RSD
Aldicarb sulfone	235	78	7.5
Methomyl	247	82	12.1
3-Hydroxycarbofuran	251	84	10.1
Dioxacarb	NR	-	-
Aldicarb	258	86	6.4
Propoxur	263	88	6.5
Carbofuran	262	87	6.0
Carbaryl	262	87	6.6
Methiocarb	254	85	7.8
Promecarb	263	88	5.7

Spiking concentration = 300 µg/L of each compound

n = 10

NR = No recovery

The data are taken from References 1 and 6.
These data are provided for guidance purposes only.

TABLE 4

EXAMPLE SINGLE-OPERATOR RECOVERY AND PRECISION DATA FOR SPIKED SOIL

Compound	Concentration (mg/kg)	% Recovery	% RSD
Aldicarb sulfone	1.57	79	4.4
Methomyl	1.48	74	5.8
3-Hydroxycarbofuran	1.60	80	4.4
Dioxacarb	1.51	76	4.8
Aldicarb	1.29	65	11.0
Propoxur	1.33	67	9.5
Carbofuran	1.46	73	6.3
Carbaryl	1.53	77	4.9
Methiocarb	1.45	73	4.9
Promecarb	1.29	65	9.6

Spiking concentration = 2.00 mg/kg of each compound

n = 10

The data are taken from References 1 and 6.
These data are provided for guidance purposes only.

TABLE 5

EXAMPLE SINGLE-LABORATORY RECOVERY AND PRECISION DATA
FOR ANALYSIS OF CARBAMATES EXTRACTED FROM WASTEWATER
BY CONTINUOUS LIQUID-LIQUID EXTRACTION (METHOD 3520)

Compound	Spiking Level (µg/L)	Mean % Recovery	% RSD
Aldicarb sulfone	45	42	6.3
Bendiocarb	45	88*	8.6
Carbaryl	5	84	7.2
Carbofuran	5	88*	8.6
m-Cumenyl-methylcarbamate	45	79	7.8
Formetanate hydrochloride	45	43**	6.7
Methiocarb	45	83	9
Methomyl	22	66	3.2
Metolcarb	45	86	6.4
Mexacarbate	45	70	13.3
Oxamyl	45	43**	6.7
Promecarb	45	82	9
Propoxur	45	88*	8.6
Thiodicarb	15	88*	8.6

The asterisks indicate compounds that coelute on the HPLC column. Those marked with one asterisk (*) represent one group of compounds that elute together, those with two asterisks (**) are a second group. The reported recoveries and RSD values are based on the total concentration of all of the compounds that coeluted.

Mean recoveries and RSDs are calculated from the extraction and analysis of four replicate samples. 1-L samples were extracted.

The data are taken from Reference 7.
These data are provided for guidance purposes only.

TABLE 6

EXAMPLE SINGLE-LABORATORY RECOVERY AND PRECISION DATA
FOR ANALYSIS OF CARBAMATES EXTRACTED FROM SOIL
BY SOXHLET EXTRACTION (METHOD 3540)

Compound	Spiking Level (µg/kg)	% Mean Recovery	% RSD
Aldicarb sulfone	2200	78	5.6
Bendiocarb	1100	83*	5.8
Carbaryl	110	107	5.1
Carbofuran	110	83*	5.8
m-Cumenyl-methylcarbamate	1100	77	4.9
Formetanate hydrochloride	1100	73**	6.2
Methiocarb	1100	80	6.3
Metolcarb	1100	84	6.8
Methomyl	110	0	0
Mexacarbate	1100	71	14.8
Oxamyl	2200	73**	6.2
Promecarb	1100	82	5.6
Propoxur	1100	83*	5.8
Thiodicarb	1100	83*	5.8

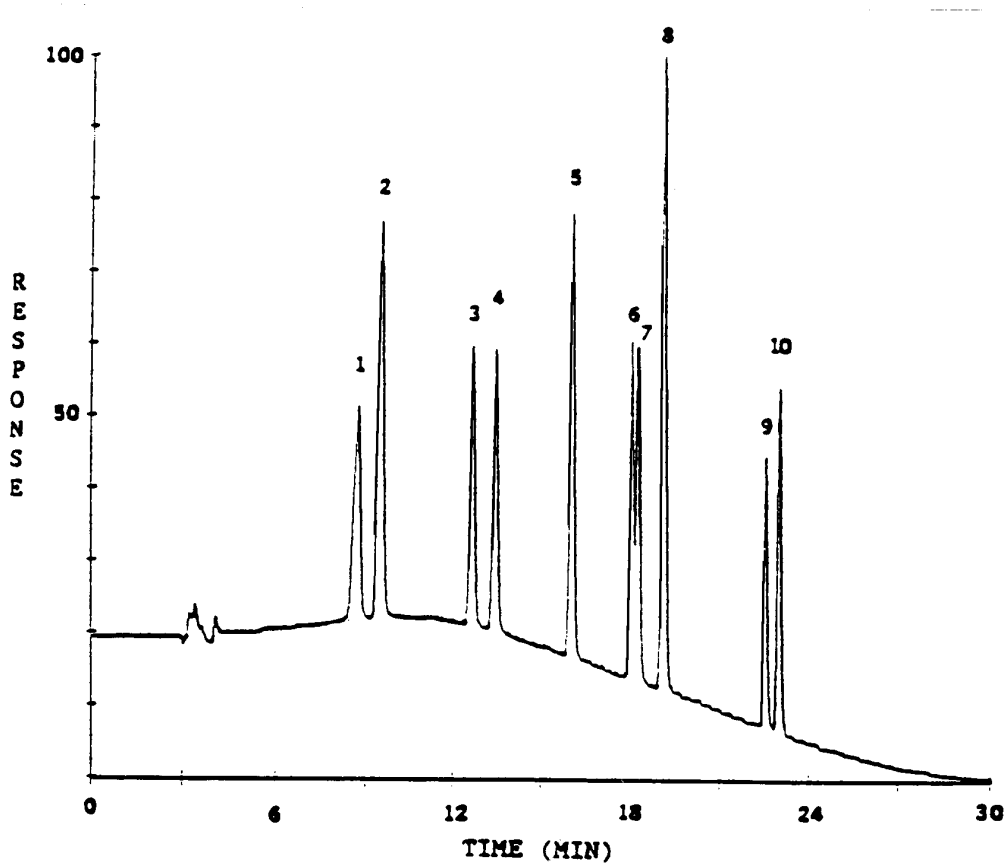
The asterisks indicate compounds that coelute on the HPLC column. Those marked with one asterisk (*) represent one group of compounds that elute together, those with two asterisks (**) are a second group. The reported recoveries and RSD values are based on the total concentration of all of the compounds that coeluted.

Mean recoveries and RSDs are calculated from the extraction and analysis of four replicate samples. 30-g samples were extracted.

The data are taken from Reference 7.
These data are provided for guidance purposes only.

FIGURE 1

EXAMPLE SEPARATION OF 10 OF THE TARGET COMPOUNDS



1.00 mg/mL each of:

1. Aldicarb sulfone
2. Methomyl
3. 3-Hydroxycarbofuran
4. Dioxacarb
5. Aldicarb
6. Propoxur
7. Carbofuran
8. Carbaryl
9. Methiocarb
10. Promecarb

This chromatogram was produced using the instrument operating conditions described in Sec. 7 and is for illustrative purposes only.