METHOD 8318

N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8318 is used to determine the concentration of N-methylcarbamates in soil, water and waste matrices. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Aldicarb (Temik)	116-06-3
Aldicarb Sulfone	1646-88-4
Carbaryl (Sevin)	63-25-2
Carbofuran (Furadan)	1563-66-2
Dioxacarb	6988-21-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb (Mesurol)	2032-65-7
Methomyl (Lannate)	16752-77-5
Promecarb	2631-37-0
Propoxur (Baygon)	114-26-1

[a] Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) of Method 8318 for determining the target analytes in organic-free reagent water and in soil are listed in Table 1.

1.3 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 aqueous samples with methylene chloride, and from soils, oily solid waste and oils with acetonitrile. The extract solvent is exchanged to methanol/ethylene glycol, and then the extract is cleaned up on a C-18 cartridge, filtered, and eluted on a C-18 analytical column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantitated fluorometrically.

2.2 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 organic-free 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.

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

3.0 INTERFERENCES

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

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

3.3 Impurities in solvents and reagents are additional sources of interferences. Before processing any samples, the analyst must demonstrate daily, through the analysis of solvent blanks, that the entire analytical system is interference free.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 An HPLC system capable of injecting 20 µL aliquots and performing multilinear gradients at a constant flow. The system must also be equipped with a data system to measure the peak areas.

4.1.2 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5 µm).

4.1.3 Post Column Reactor with two solvent delivery systems (Kratos PCRS 520 with two Kratos Spectroflow 400 Solvent Delivery Systems, or equivalent).

4.1.4 Fluorescence detector (Kratos Spectroflow 980, or equivalent).

4.2 Other apparatus

4.2.1 Centrifuge.

4.2.2 Analytical balance - $\pm$ 0.0001 g.

4.2.3 Top loading balance - $\pm$ 0.01 g.

4.2.4 Platform shaker.

4.2.5 Heating block, or equivalent apparatus, that can accommodate 10 mL graduated vials (Sec. 4.3.11).

4.3 Materials

4.3.1 HPLC injection syringe - 50 µL.

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

4.3.3 Volumetric pipettes, Class A, glass, assorted sizes.

4.3.4 Reverse phase cartridges, (C-18 Sep-Pak^{R} [Waters Associates], or equivalent).

4.3.5 Glass syringes - 5 mL.

4.3.6 Volumetric flasks, Class A - Sizes as appropriate.

4.3.7 Erlenmeyer flasks with teflon-lined screw caps, 250 mL.

4.3.8 Assorted glass funnels.

4.3.9 Separatory funnels, with ground glass stoppers and teflon stopcocks - 250 mL.

4.3.10 Graduated cylinders - 100 mL.

4.3.11 Graduated glass vials - 10 mL, 20 mL.

4.3.12 Centrifuge tubes - 250 mL.

4.3.13 Vials - 25 mL, glass with Teflon lined screw caps or crimp tops.

4.3.14 Positive displacement micro-pipettor, 3 to 25 µL displacement, (Gilson Microman [Rainin #M-25] with tips, [Rainin #CP-25], or equivalent).

4.3.15 Nylon filter unit, 25 mm diameter, 0.45 µm pore size, disposable (Alltech Associates, #2047, or equivalent).

5.0 REAGENTS

5.1 HPLC grade chemicals shall be used in all tests. It is intended that all reagents shall 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 lowering the accuracy of the determination.

5.2 General

5.2.1 Acetonitrile, CH_3CN - HPLC grade - minimum UV cutoff at 203 nm (EM Omnisolv #AX0142-1, or equivalent).

5.2.2 Methanol, CH_3OH - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #MX0488-1, or equivalent).

5.2.3 Methylene chloride, CH_2Cl_2 - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #DX0831-1, or equivalent).

5.2.4 Hexane, C_6H_{14} - pesticide grade - (EM Omnisolv #HX0298-1, or equivalent).

5.2.5 Ethylene glycol, $HOCH_2CH_2OH$ - Reagent grade - (EM Science, or equivalent).

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

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

5.2.8 Phosphoric acid, H_3PO_4 - reagent grade.

5.2.9 pH 10 borate buffer (J.T. Baker #5609-1, or equivalent).

5.2.10 o-Phthalaldehyde, $o\text{-}C_6H_4(CHO)_2$ - reagent grade (Fisher #O-4241, or equivalent).

5.2.11 2-Mercaptoethanol, $HSCH_2CH_2OH$ - reagent grade (Fisher #O-3446, or equivalent).

5.2.12 N-methylcarbamate neat standards (equivalence to EPA standards must be demonstrated for purchased solutions).

5.2.13 Chloroacetic acid, $ClCH_2COOH$, 0.1 N.

5.3 Reaction solution

5.3.1 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.

5.4 Standard solutions

5.4.1 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 with Teflon lined screw caps or crimp tops. Replace every six months.

5.4.2 Intermediate standard solution: prepare a mixed 50.0 mg/L solution 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 with Teflon lined screw caps or crimp tops. Replace every three months.

5.4.3 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 with Teflon lined screw caps or crimp tops. Replace every two months, or sooner if necessary.

5.4.4 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. 5.4.1. 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 with a Teflon lined screw cap or crimp top. Replace every three months.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Store samples at 4°C and out of direct sunlight, from the time of collection through analysis. N-methylcarbamates are sensitive to alkaline hydrolysis and heat.

6.3 All samples must be extracted within seven days of collection, and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Water, domestic wastewater, aqueous industrial wastes, and leachates

7.1.1.1 Measure 100 mL of sample into a 250 mL separatory funnel and extract by shaking vigorously for about 2 minutes with 30 mL of methylene chloride. Repeat the extraction two more times. Combine all three extracts in a 100 mL volumetric flask and dilute to volume with methylene chloride. If cleanup is required, go to Sec. 7.2. If cleanup is not required, proceed directly to Sec. 7.3.1.

7.1.2 Soils, solids, sludges, and heavy aqueous suspensions

7.1.2.1 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for this determination

should be weighed out at the same time as the portion used for analytical determination.

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

7.1.2.1.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.1.2.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL Erlenmeyer flask with a Teflon-lined screw cap. Add 50 mL of acetonitrile and shake for 2 hours 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 two more times with 20 mL of acetonitrile and 1 hour shaking each time. Decant and combine all three extracts. Centrifuge the combined extract at 200 rpm for 10 min. Carefully decant the supernatant into a 100 mL volumetric flask and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Sec. 7.3.2.

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

7.1.3.1 Determination of sample % dry weight - Follow Secs. 7.1.2.1 through 7.1.2.1.1.

7.1.3.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL Erlenmeyer flask with a Teflon-lined screw cap. Add 60 mL of hexane and shake for 1 hour on a platform shaker. Add 50 mL of acetonitrile and shake for an additional 3 hours. Allow the mixture to settle (5-10 min), then decant the solvent layers into a 250 mL separatory funnel. Drain the acetonitrile (bottom layer) through filter paper into a 100 mL volumetric flask. Add 60 mL of hexane and 50 mL of acetonitrile to the sample extraction flask and shake for 1 hour. Allow the mixture to settle, then decant the mixture into the separatory funnel containing the hexane from the first extraction. Shake the separatory funnel for 2 minutes, allow the phases to separate, drain the acetonitrile layer through filter paper into the volumetric flask, and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Sec. 7.3.2.

7.1.4 Non-aqueous liquids such as oils

7.1.4.1 Extraction - 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. Add 25 mL of acetonitrile to the sample funnel, shake for 2 minutes, allow the phases to

Repeat the extraction with another 25 mL portion of acetonitrile, combining the extracts. Dilute to volume with acetonitrile. (Dilution factor = 5). Proceed to Sec. 7.3.2.

7.2 Cleanup - Pipet 20.0 mL of the extract into a 20 mL glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Dissolve the ethylene glycol residue in 2 mL of methanol, pass the extract through a pre-washed C-18 reverse phase cartridge, and collect the eluate in a 5 mL volumetric flask. Elute the cartridge with methanol, and collect the eluate until the final volume of 5.0 mL is obtained. (Dilution factor = 0.25) Using a disposable 0.45 µm filter, filter an aliquot of the clean extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.3 Solvent Exchange

7.3.1 Water, domestic wastewater, aqueous industrial wastes, and leachates:

Pipet 10.0 mL of the extract into a 10 mL graduated glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Dilution factor = 0.1). Using a disposable 0.45 µm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids:

Elute 15 mL of the acetonitrile extract through a C-18 reverse phase cartridge, prewashed with 5 mL of acetonitrile. Discard the first 2 mL of eluate and collect the remainder. Pipet 10.0 mL of the clean extract into a 10 mL graduated glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Additional dilution factor = 0.1; overall dilution factor = 0.5). Using a disposable 0.45 µm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Sec. 7.4.

7.4 Sample Analysis

7.4.1 Analyze the samples using the chromatographic conditions, post-column reaction parameters and instrument parameters given in Secs. 7.4.1.1, 7.4.1.2, 7.4.1.3 and 7.4.1.4. Table 2 provides the retention

times that were obtained under these conditions during method development. A chromatogram of the separation is shown in Figure 1.

7.4.1.1 Chromatographic Conditions (Recommended)

Solvent A: Organic-free 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
Solvent delivery system program:

Time (min)	Function	Value	Duration (min)	File
0.00	FR	1.0		0
0.00	B%	10%		0
0.02	B%	80%	20	0
20.02	B%	100%	5	0
25.02	B%	100%	5	0
30.02	B%	10%	3	0
33.02	B%	10%	7	0
36.02	ALARM		0.01	0

7.4.1.2 Post-column Hydrolysis Parameters (Recommended)

Solution: 0.05 N aqueous sodium hydroxide
Flow Rate: 0.7 mL/min
Temperature 95° C
Residence Time: 35 seconds (1 mL reaction coil)

7.4.1.3 Post-column Derivatization Parameters (Recommended)

Solution: o-phthalaldehyde/2-mercaptoethanol (Sec. 5.3.1)
Flow Rate: 0.7 mL/min
Temperature 40° C
Residence time: 25 seconds (1 mL reaction coil)

7.4.1.4 Fluorometer Parameters (Recommended)

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

7.4.2 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.

7.5 Calibration:

7.5.1 Analyze a solvent blank (20 µL of methanol) to ensure that the system is clean. Analyze the calibration standards (Sec. 5.4.3), starting with the 0.5 mg/L standards and ending with the 5.0 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.5.2 Using the established calibration mean response factors, check the calibration of the instrument at the beginning of each day by analyzing the 2.0 mg/L mixed standard. If the concentration of each analyte falls within the range of 1.70 to 2.30 mg/L (i.e., within $\pm$ 15% of the true value), the instrument is considered to be calibrated and the analysis of samples may proceed. If the observed value of any analyte exceeds its true value by more than $\pm$ 15%, the instrument must be recalibrated (Sec. 7.5.1).

7.5.3 After 10 sample runs, or less, the 2.0 mg/L standards must be analyzed 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 $\pm$ 15%) may require a re-analysis of the samples.

7.6 Calculations

7.6.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean RF} = \overline{RF} = \frac{(\sum_{i}^{5} RF_i)}{5}$$

$$\%\text{RSD of } \overline{RF} = \frac{[(\sum_{i}^{5} RF_i - \overline{RF})^2]^{1/2} / 4}{\overline{RF}} \text{ X } 100\%$$

7.6.2 Calculate the concentration of each N-methylcarbamate as follows:

$$\mu g/g \text{ or } mg/L = (\overline{RF}) \text{ (area of signal) (dilution factor)}$$

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank for each matrix type, that all glassware and reagents are interference free. Each time there is a change of reagents, a method blank must be processed as a safeguard against laboratory contamination.

8.2 A QC check solution must be prepared and analyzed with each sample batch that is processed. Prepare this solution, at a concentration of 2.0 mg/L of each analyte, from the 40.0 mg/L mixed QC standard solution (Sec. 5.4.4). The acceptable response range is 1.7 to 2.3 mg/L for each analyte.

8.3 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.

8.4 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.

9.0 METHOD PERFORMANCE

9.1 Table 1 lists the single operator method detection limit (MDL) for each compound in organic-free reagent water and soil. Seven/ten replicate samples were analyzed, as indicated in the table. See reference 7 for more details.

9.2 Tables 2, 3 and 4 list the single operator average recoveries and standard deviations for organic-free reagent water, wastewater and soil. Ten replicate samples were analyzed at each indicated spike concentration for each matrix type.

9.3 The method detection limit, accuracy and precision obtained will be determined by the sample matrix.

10.0 REFERENCES

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

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

3. Klotter, Kevin, 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. Federal Register, "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", Friday, October 26, 1984, 49, No. 209, 198-199.

7. Okamoto, H.S., D. Wijekoon, C. Esperanza, J. Cheng, S. Park, J. Garcha, S. Gill, 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.

TABLE 1
ELUTION ORDER, RETENTION TIMES[a] AND
SINGLE OPERATOR METHOD DETECTION LIMITS

Compound	Retention Time (min)	Method Detection Limits[b] Organic-free Reagent Water (µg/L)	Soil (µg/kg)
Aldicarb Sulfone	9.59	1.9[c]	44[c]
Methomyl (Lannate)	9.59	1.7	12
3-Hydroxycarbofuran	12.70	2.6	10[c]
Dioxacarb	13.50	2.2	>50[c]
Aldicarb (Temik)	16.05	9.4[c]	12[c]
Propoxur (Baygon)	18.06	2.4	17
Carbofuran (Furadan)	18.28	2.0	22
Carbaryl (Sevin)	19.13	1.7	31
α-Naphthol[d]	20.30	-	-
Methiocarb (Mesurol)	22.56	3.1	32
Promecarb	23.02	2.5	17

[a] See Sec. 7.4 for chromatographic conditions

[b] MDL for organic-free reagent water, sand, soil were determined by analyzing 10 low concentration spike replicate for each matrix type (except where noted). See reference 7 for more details.

[c] MDL determined by analyzing 7 spiked replicates.

[d] Breakdown product of Carbaryl.

TABLE 2
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR ORGANIC-FREE REAGENT WATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	225	75.0	7.28	3.24
Methomyl (Lannate)	244	81.3	8.34	3.42
3-Hydroxycarbofuran	210	70.0	7.85	3.74
Dioxacarb	241	80.3	8.53	3.54
Aldicarb (Temik)	224	74.7	13.5	6.03
Propoxur (Baygon)	232	77.3	10.6	4.57
Carbofuran (Furadan)	239	79.6	9.23	3.86
Carbaryl (Sevin)	242	80.7	8.56	3.54
Methiocarb (Mesurol)	231	77.0	8.09	3.50
Promecarb	227	75.7	9.43	4.1

[a] Spike Concentration = 300 µg/L of each compound, n = 10

TABLE 3
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR WASTEWATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	235	78.3	17.6	7.49
Methomyl (Lannate)	247	82.3	29.9	12.10
3-Hydroxycarbofuran	251	83.7	25.4	10.11
Dioxacarb	[b]	-	-	-
Aldicarb (Temik)	258	86.0	16.4	6.36
Propoxur (Baygon)	263	87.7	16.7	6.47
Carbofuran (Furadan)	262	87.3	15.7	5.99
Carbaryl (Sevin)	262	87.3	17.2	6.56
Methiocarb (Mesurol)	254	84.7	19.9	7.83
Promecarb	263	87.7	15.1	5.74

[a] Spike Concentration = 300 µg/L of each compound, n = 10

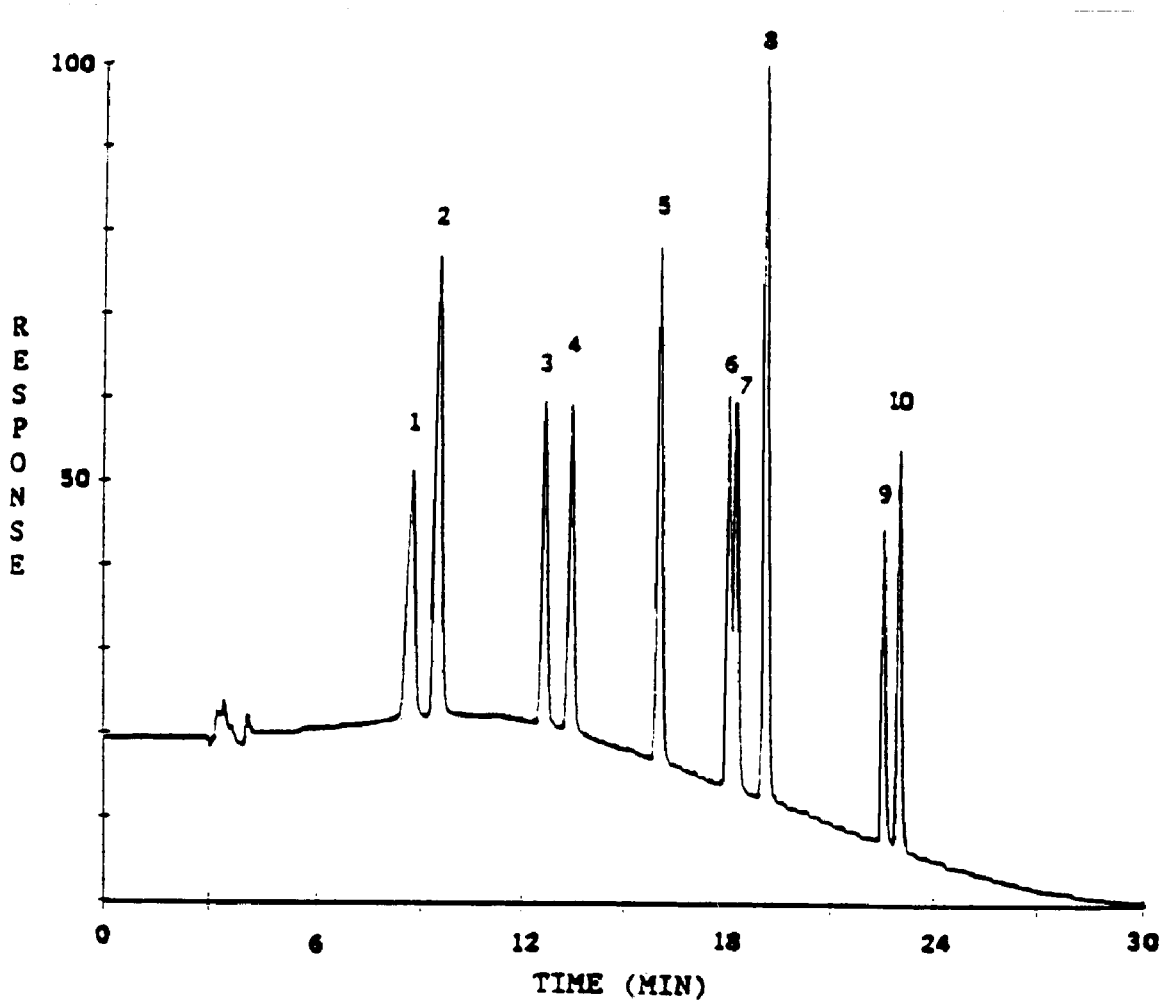
[b] No recovery

TABLE 4
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR SOIL

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	1.57	78.5	0.069	4.39
Methomyl (Lannate)	1.48	74.0	0.086	5.81
3-Hydroxycarbofuran	1.60	80.0	0.071	4.44
Dioxacarb	1.51	75.5	0.073	4.83
Aldicarb (Temik)	1.29	64.5	0.142	11.0
Propoxur (Baygon)	1.33	66.5	0.126	9.47
Carbofuran (Furadan)	1.46	73.0	0.092	6.30
Carbaryl (Sevin)	1.53	76.5	0.076	4.90
Methiocarb (Mesurol)	1.45	72.5	0.071	4.90
Promecarb	1.29	64.7	0.124	9.61

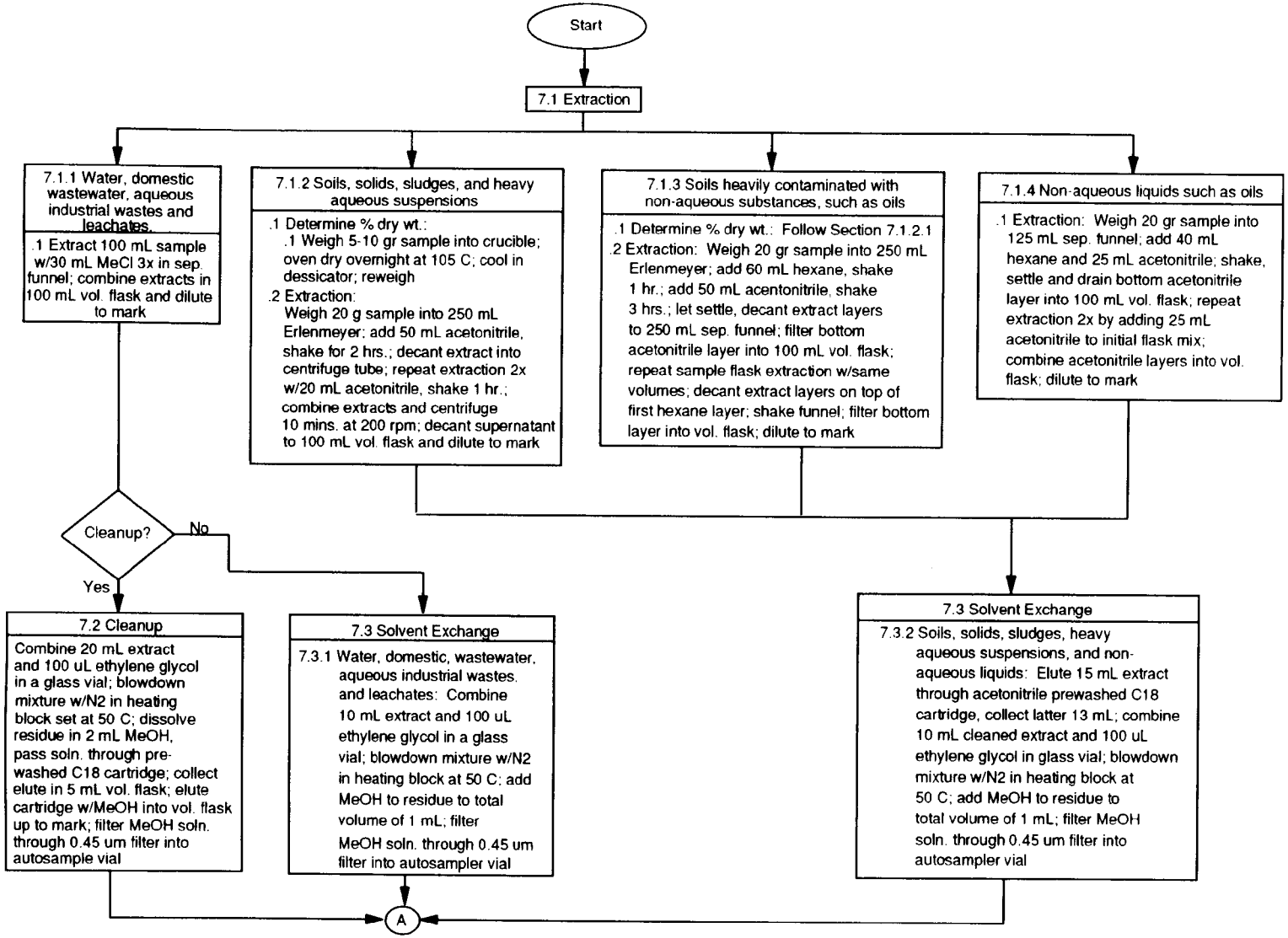
[a] Spike Concentration = 2.00 mg/kg of each compound, n = 10

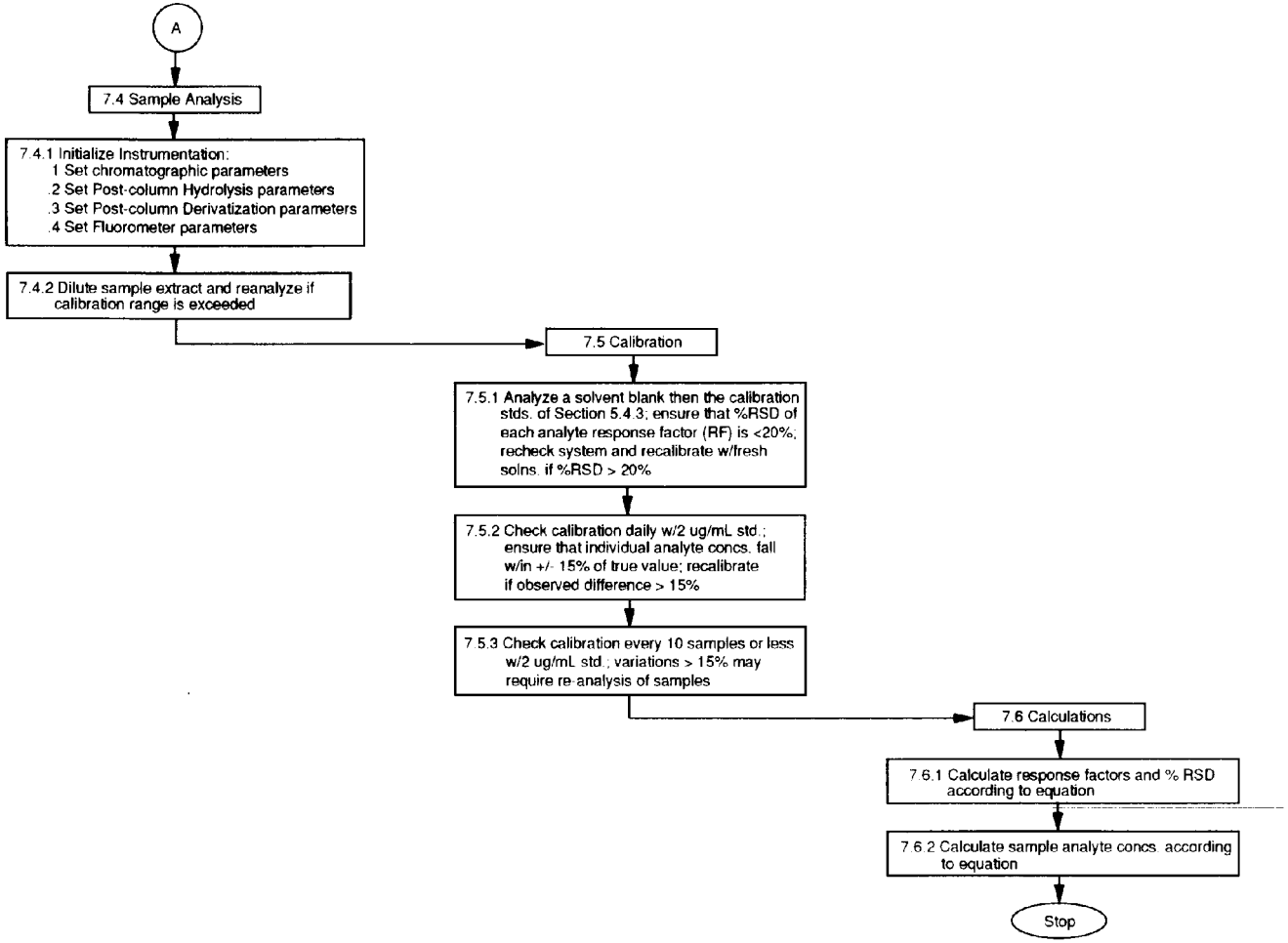
FIGURE 1



1.00 µg/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


Start
7.1 Extraction
7.1.1 Water, domestic wastewater, aqueous industrial wastes and leachates.
.1 Extract 100 mL sample w/30 mL MeCl 3x in sep. funnel; combine extracts in 100 mL vol. flask and dilute to mark
7.1.2 Soils, solids, sludges, and heavy aqueous suspensions
.1 Determine % dry wt.:
.1 Weigh 5-10 gr sample into crucible; oven dry overnight at 105 C; cool in dessicator; reweigh
.2 Extraction:
Weigh 20 g sample into 250 mL Erlenmeyer; add 50 mL acetonitrile, shake for 2 hrs.; decant extract into centrifuge tube; repeat extraction 2x w/20 mL acetonitrile, shake 1 hr.; combine extracts and centrifuge 10 mins. at 200 rpm; decant supernatant to 100 mL vol. flask and dilute to mark
7.1.3 Soils heavily contaminated with non-aqueous substances, such as oils
.1 Determine % dry wt.: Follow Section 7.1.2.1
.2 Extraction: Weigh 20 gr sample into 250 mL Erlenmeyer; add 60 mL hexane, shake 1 hr.; add 50 mL acentonitrile, shake 3 hrs.; let settle, decant extract layers to 250 mL sep. funnel; filter bottom acetonitrile layer into 100 mL vol. flask; repeat sample flask extraction w/same volumes; decant extract layers on top of first hexane layer; shake funnel; filter bottom layer into vol. flask; dilute to mark
7.1.4 Non-aqueous liquids such as oils
.1 Extraction: Weigh 20 gr sample into 125 mL sep. funnel; add 40 mL hexane and 25 mL acetonitrile; shake, settle and drain bottom acetonitrile layer into 100 mL vol. flask; repeat extraction 2x by adding 25 mL acetonitrile to initial flask mix; combine acetonitrile layers into vol. flask; dilute to mark
Cleanup?
No
Yes
7.2 Cleanup
Combine 20 mL extract and 100 uL ethylene glycol in a glass vial; blowdown mixture w/N2 in heating block set at 50 C; dissolve residue in 2 mL MeOH, pass soln. through pre-washed C18 cartridge; collect elute in 5 mL vol. flask; elute cartridge w/MeOH into vol. flask up to mark; filter MeOH soln. through 0.45 um filter into autosample vial
7.3 Solvent Exchange
7.3.1 Water, domestic, wastewater, aqueous industrial wastes. and leachates: Combine 10 mL extract and 100 uL ethylene glycol in a glass vial; blowdown mixture w/N2 in heating block at 50 C; add MeOH to residue to total volume of 1 mL; filter MeOH soln. through 0.45 um filter into autosampler vial
7.3 Solvent Exchange
7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids: Elute 15 mL extract through acetonitrile prewashed C18 cartridge, collect latter 13 mL; combine 10 mL cleaned extract and 100 uL ethylene glycol in glass vial; blowdown mixture w/N2 in heating block at 50 C; add MeOH to residue to total volume of 1 mL; filter MeOH soln. through 0.45 um filter into autosampler vial
A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7.4 Sample Analysis
7.4.1 Initialize Instrumentation:
1 Set chromatographic parameters
.2 Set Post-column Hydrolysis parameters
.3 Set Post-column Derivatization parameters
.4 Set Fluorometer parameters
7.4.2 Dilute sample extract and reanalyze if calibration range is exceeded
7.5 Calibration
7.5.1 Analyze a solvent blank then the calibration stds. of Section 5.4.3; ensure that %RSD of each analyte response factor (RF) is <20%; recheck system and recalibrate w/fresh solns. if %RSD > 20%
7.5.2 Check calibration daily w/2 ug/mL std.; ensure that individual analyte concs. fall w/in +/- 15% of true value; recalibrate if observed difference > 15%
7.5.3 Check calibration every 10 samples or less w/2 ug/mL std.; variations > 15% may require re-analysis of samples
7.6 Calculations
7.6.1 Calculate response factors and % RSD according to equation
7.6.2 Calculate sample analyte concs. according to equation
Stop