

Method 645
***The Determination of Certain
Amine Pesticides and Lethane in
Municipal and Industrial
Wastewater***

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The Determination of Certain Amine Pesticides and Lethane in Municipal and Industrial Wastewater

1. SCOPE AND APPLICATION

- 1.1 This method covers the determination of certain amine pesticides and lethane in municipal and industrial wastewater. The following parameters may be determined by this method.

| <i>Parameter</i> | <i>CAS No.</i> |
|------------------|----------------|
| Alachlor | 15972-60-8 |
| Butachlor | 23184-66-9 |
| Diphenamid | 957-51-7 |
| Fluridone | 59756-60-4 |
| Lethane | 112-56-1 |
| Norflurazon | 27314-13-2 |

- 1.2 The estimated detection limit (EDL) for each parameter is listed in Tables 1 and 2. The EDL was calculated from the minimum detectable response of the nitrogen/phosphorous detector equal to 5 times the gas chromatographic (GC) background noise assuming a 10-mL final extract volume of a 1-L reagent water sample and a GC injection of 5 μ L. The EDL for a specific wastewater may be different depending on the nature of interferences in the sample matrix.
- 1.3 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds listed above, compound identifications should be supported by at least one additional qualitative technique. Section 13 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative confirmation of compound identifications.
- 1.4 This method is restricted to use by or under the supervision of analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2. SUMMARY OF METHOD

- 2.1 The amine pesticides and lethane are removed from the sample matrix by extraction with methylene chloride. The extract is dried, exchanged into hexane, and analyzed by gas chromatography. Column chromatography is used as necessary to eliminate interferences which may be encountered. Measurement of the pesticides is accomplished with a nitrogen/phosphorous specific detector.
- 2.2 Confirmatory analysis by gas chromatography/mass spectrometry is recommended (Section 13) when a new or undefined sample type is being analyzed if the concentration is adequate for such determination.

3. INTERFERENCES

3.1 Solvent, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 9.1

3.1.1 The use of high-purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.1.2 Glassware must be scrupulously cleaned.¹ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. It should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with acetone and pesticide-quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store the glassware inverted or capped with aluminum foil.

3.2 Interferences co-extracted from the samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled. While general cleanup procedures are provided as part of this method, unique samples may require additional cleanup approaches to achieve the detection limits listed in Tables 1 and 2.

4. SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified²⁻⁴ for the information of the analyst.

5. APPARATUS AND EQUIPMENT

5.1 Sample containers: Narrow-mouth glass bottles, 1-L or 1-quart volume, equipped with polytetrafluoroethylene (PTFE)-lined screw-caps. Wide-mouth glass bottles, 1-quart volume, equipped with PTFE-lined screw-caps may also be used. Prior to use, wash bottles and cap liners with detergent and rinse with tap and distilled water. Allow the bottles and cap liners to air dry, then muffle at 400°C for 1 hour. After cooling, rinse the bottles and cap liners with hexane, seal the bottles, and store in a dust-free environment.

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- 5.1.1** Automatic sampler (optional): Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportional composites.
- 5.2** Kuderna-Danish (K-D) glassware.
- 5.2.1** Synder column: Three-ball macro (Kontes K-503000-0121 or equivalent).
- 5.2.2** Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent) with ground-glass stopper.
- 5.2.3** Evaporative flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- 5.3** Gas chromatography system.
- 5.3.1** The gas chromatograph must be equipped with a glass-lined injection port compatible with the detector to be used. A data system is recommended for measuring peak areas.
- 5.3.1.1** Column 1: 180 cm long by 2 mm ID, glass, packed with 10% OV-11 on Gas Chrom W-HP (100/120 mesh) or equivalent.
- 5.3.1.2** Column 2: 180 cm long by 2 mm ID, Pyrex^R glass, packed with 3% Dexsil 300 on Chromasorb W-HP (80/100 mesh) or equivalent.
- 5.3.1.3** Column 3: 180 cm long by 2mm ID Glass, packed with 3% SP-2100 on Supelcoport (100/120 mesh) or equivalent.
- 5.3.1.4** Column 1 was used to develop the accuracy and precision statements in Section 12. Guidelines for the use of alternative column packings are provided in Section 10.3.1.
- 5.3.1.5** Detector: Nitrogen/phosphorous. This detector has proven effective in the analysis of wastewaters for the parameters listed in Section 1.1 and was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.3.
- 5.4** Chromatographic column: 300 mm long by 10 mm ID Chromaflex, equipped with coarse-fritted bottom plate and PTFE stopcock. (Kontes K-420540-0213 or equivalent).
- 5.5** Drying column: Approximately 400 mm long by 20 mm ID borosilicate glass, equipped with coarse-fritted bottom plate.
- 5.6** Miscellaneous.

- 5.6.1 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 5.6.2 Separatory funnel: 2-L, equipped with PTFE stopcock.
- 5.6.3 Water bath: Heated with concentric ring cover, capable of temperature control ($\pm 2^{\circ}\text{C}$). The bath should be used in a hood.
- 5.6.4 Standard solution storage containers: 15-L bottles with PTFE-lined screw-caps.
- 5.6.5 Boiling chips: Approximately 10/40 mesh. Heat to 400°C for 30 minutes or perform a Soxhlet extraction with methylene chloride.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 Reagents.

- 6.1.1 Acetone, hexane, and methylene chloride: demonstrated to be free of analytes.
- 6.1.2 Florisil: PR grade (60/100 mesh). Purchase activated at 675°C and store in glass containers with glass stoppers or foil-lined screw-caps. Before use, activate each batch overnight at 200°C in foil-covered glass containers. To prepare for use, place the amount necessary for the number of columns to be run in a 500-mL reagent bottle and add 2% by weight of reagent water. Seal and mix thoroughly by shaking or rolling for 10 minutes. Allow to stand for at least 2 hours prior to use. The mixture must be homogeneous. Keep the bottle tightly sealed to ensure proper activity.
- 6.1.3 Reagent water: reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.
- 6.1.4 Sodium hydroxide (NaOH) solution (10N): Dissolve 40 g NaOH in reagent water and dilute to 100 mL.
- 6.1.5 Sodium sulfate: Granular, anhydrous. Condition by heating at 400°C for 4 hours in a shallow tray.
- 6.1.6 Sulfuric acid (H_2SO_4) solution (1+1): Add a measured volume of concentrated H_2SO_4 to an equal volume of reagent water.
- 6.1.7 Sodium thiosulfate: ACS, granular.

6.2 Standard stock solutions (1.00 µg/µL): These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures.

6.2.1 Prepare standard stock solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-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 standard stock.

6.2.2 Store standard stock solutions at 4°C in 15-mL bottles equipped with PTFE-lined screw-caps. Standard stock solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.2.3 Standard stock solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7. *SAMPLE COLLECTION, PRESERVATION, AND STORAGE*

7.1 Collect all samples in duplicate. Grab samples must be collected in glass containers. Conventional sampling practices⁵ should be followed, except that the bottle must not be prewashed with sample before collection.

7.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

7.3 Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid.

7.4 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction⁶.

8. *CALIBRATION AND STANDARDIZATION*

8.1 Calibration.

8.1.1 A set of at least three calibration solutions containing the method analytes is needed. One calibration solution should contain each analyte at a concentration approaching but greater than the estimated detection limit (Tables 1 and 2) for that compound; the other two solutions should contain analytes at concentrations that bracket the range expected in samples. For example, if the detection limit for a particular analyte is 0.2 µg/L, and a sample expected to contain approximately 5 µg/L is analyzed, solutions of standards should be prepared at concentrations representing 0.3 µg/L, 5µg/L, and 10 µg/L for the particular analyte.

- 8.1.2** To prepare a calibration solution, add an appropriate volume of a standard stock solution to a volumetric flask and dilute to volume with hexane.
- 8.1.3** Starting with the standard of lowest concentration, analyze each calibration standard according to Section 10.3 and tabulate peak height or area response versus the mass of analyte injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.
- 8.1.4** The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm 10\%$, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

9. QUALITY CONTROL

9.1 Monitoring for interferences.

- 9.1.1** Analyze a laboratory reagent blank each time a set of samples is extracted. A laboratory reagent blank is a 1-L aliquot of reagent water. If the reagent blank contains a reportable level of any analyte, immediately check the entire analytical system to locate and correct for possible interferences and repeat the test.

9.2 Assessing accuracy.

- 9.2.1** After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and the laboratory control standard may not be used for calibration of the analytical system.
 - 9.2.1.1** Laboratory control standard concentrate: From stock standards prepared as described in Section 6.3, prepare a laboratory control standard concentrate that contains each analyte of interest at a concentration of 2 $\mu\text{g}/\text{mL}$ in acetone or other suitable solvent.
 - 9.2.1.2** Laboratory control standard: Using a pipette, add 1.00 mL of the laboratory control standard concentrate to a 1-L aliquot of reagent water.
 - 9.2.1.3** Analyze the laboratory control standard as described in Section 10. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) with the equation:

Equation 1

$$P_i = \frac{100S_i}{T_i}$$

where

S_i = Analytical results from the laboratory control standard, in $\mu\text{g/L}$

T_i = Known concentration of the spike, in $\mu\text{g/L}$

9.2.2 At least annually, the laboratory should participate in formal performance evaluation studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared.

9.3 Assessing precision

9.3.1 Precision assessments for this method are based upon the analysis of field duplicates (Section 7.1). Analyze both sample bottles for at least 10% of all samples. To the extent practical, the samples for duplication should contain reportable levels of most of the analytes.

9.3.2 For each analyte in each duplicate pair, calculate the relative range⁷ (RR_i) with the equation:

Equation 2

$$RR_i = \frac{100R_i}{X_i}$$

where

R_i = Absolute difference between the duplicate measurements X_1 and X_2 , in $\mu\text{g/L}$

X_i = Average concentration found $\left(\frac{X_1 + X_2}{2} \right)$, in $\mu\text{g/L}$

9.3.3 Individual relative range measurements are pooled to determine average relative range or to develop an expression of relative range as a function of concentration.

10. PROCEDURE

10.1 Sample extraction.

- 10.1.1** Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5 to 9 with sodium hydroxide or sulfuric acid.
- 10.1.2** Add 60 mL of methylene chloride to the sample bottle and shake for 30 seconds to rinse the walls. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the extract in a 250-mL Erlenmeyer flask.
- 10.1.3** Add an additional 60-mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.
- 10.1.4** Perform a third extraction in the same manner. Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect it in a 500-mL K-D flask equipped with a 10-mL concentrator tube. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.
- 10.1.5** Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 85°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride.
- 10.1.6** For Florisil column cleanup or gas chromatography, the extract must be in hexane solution. To exchange the solvent to hexane, add one or two fresh boiling chips to the flask and ampule containing the extract, add 50 mL of hexane, and reattach the Snyder column. Pour about 1 mL of hexane into the top of the Snyder column, and concentrate the extract at 85 to 95°C in the hot water bath as above. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

- 10.1.7** Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Dilute to 10 mL with hexane for analysis by gas chromatography (Section 10.3) if cleanup is not required. If the extract requires cleanup, proceed to Section 10.2. If the extracts will be stored longer than 2 days, they should be transferred to PTFE-sealed screw-cap bottles. Proceed with gas chromatographic analysis.
- 10.1.8** Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.
- 10.2** Cleanup and separation.
- 10.2.1** Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of alachlor, butachlor, diphenamid, and lethane in various clean waters and municipal effluents. The use of Florisil as the cleanup material for fluridone and norflurazon has been demonstrated to yield recoveries of less than 50%, and is not recommended as a cleanup material for these compounds. Use of specific detectors may obviate the necessity for cleanup of relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%.
- 10.2.2** Place the necessary amount of deactivated Florisil into a 20 mm ID chromatographic column and tap the column to settle the Florisil. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the Florisil.
- 10.2.3** Pre-elute the column with 50 to 60 mL of hexane. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, transfer the sample extract onto the column by decantation. Complete the transfer by rinsing with two additional 2-mL volumes of hexane. Alternatively, a measured aliquot of the extract may be taken for cleanup.
- 10.2.4** Just prior to exposure of the sodium sulfate layer to the air, elute the column with 100 mL hexane. Discard the eluate and repeat the elution with 200 mL of 6% (v/v) acetone in hexane. Collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube (Fraction 1). All elutions should be carried out using a flow rate of about 5 mL/min.
- 10.2.5** Perform a second elution with 200 mL of 15% acetone in hexane (Fraction 2). Collect each fraction in a separate K-D apparatus. The elution pattern for these compounds is shown in Table 3.
- 10.2.6** Determine, from Table 3, the fractions of interest and concentrate by standard K-D technique, as indicated in Section 10.1.5, using hexane in place of methylene chloride, to a volume of 10 mL.
- 10.2.7** Analyze the fractions by gas chromatography.

10.3 Gas chromatography analysis.

10.3.1 Recommended columns and detectors and operating conditions for the gas chromatography system are described in Section 5.3. Tables 1 and 2 summarize the recommended operating conditions for the gas chromatograph. Included in these tables are retention times and estimated detection limits that can be achieved by this method. Examples of the separations achieved are shown in Figures 1 through 3. Other packed columns, chromatographic conditions, or detectors may be used if data quality comparable to Table 4 is achieved. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and data quality comparable to Table 4 is achieved.

10.3.2 Inject 2 to 5 μL of the sample extract using the solvent-flush technique.⁸ Record the volume injected to the nearest 0.05 μL , the total extract volume, and the resulting peak size in area or peak height units.

10.3.3 The width of the retention-time window used to make identifications should be based upon measurements of actual retention-time variations of standards over the course of the day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.3.4 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

10.3.5 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

11. CALCULATIONS

11.1 Determine the concentration (C) of individual compounds in the sample in micrograms per liter with the equation:

Equation 3

$$\text{Concentration, } \mu\text{g/L} = \frac{(A) (V_t)}{(V_i) (V_s)}$$

where

A = Amount of analytes injected, in ng

V_i = Volume of extract injected, in μL

V_t = Volume of total extract, in $\mu\text{g/L}$

V_s = Volume of water extracted, in mL

- 11.2 Report the results for the unknown samples in micrograms per liter. Round off the results to the nearest 0.1 $\mu\text{g/L}$ or two significant figures.

12. METHOD PERFORMANCE

- 12.1 Estimated detection limits (EDL) and associated chromatographic conditions are listed in Table 1.⁹ The detection limits were calculated from the minimum detectable response of the EC detector equal to 5 times the GC background noise, assuming a 10-mL final extract volume of a 1-L sample and a GC injection of 5 μL .

- 12.2 Single-laboratory accuracy and precision studies were conducted by Environmental Science and Engineering,⁶ using spiked samples. The results of these studies are presented in Table 2.

13. GC/MS CONFIRMATION

- 13.1 It is recommended that GC/MS techniques be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compounds of interest. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak, but not to exceed 7 scans per peak utilizing a 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all glass or glass-lined materials is recommended. A computer system should be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.
- 13.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices. Chromatographic tailing factors of less than 5.0 must be achieved. The calculation of tailing factors is illustrated in Method 625.¹⁰
- 13.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP performance criteria are achieved.¹¹

- 13.4** To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. It is recommended that at least 25 ng of material be injected into the GC/MS. The criteria below must be met for qualitative confirmation.
- 13.4.1** The molecular ion and other ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to $\pm 10\%$. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20 to 40%.
- 13.4.2** The retention time of the compound in the sample must be within 6 seconds of the same compound in the standard solution.
- 13.4.3** Compounds that have similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.
- 13.5** Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.
- 13.6** Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These may include the use of alternative packed or capillary GC columns or additional cleanup.

References

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8. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).
9. "Evaluation of Ten Pesticide Methods," U.S. Environmental Protection Agency, Contract No. 68-03-1760, Task No. 11, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio (in preparation).
10. "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" EPA-600/4-82-057, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio.
11. Eichelberger, J.W., Harris, L.E., and Budde, W.L. *Analytical Chemistry*, 46, 1912 (1975).

Table 1. Gas Chromatography and Detection Limits of Certain Amines and Lethane

| <i>Parameter</i> | <i>Retention Time (min)</i> | | | <i>Estimated Detection Limit (µg/L)</i> |
|------------------|-----------------------------|-----------------|-----------------|---|
| | <i>Column 1</i> | <i>Column 2</i> | <i>Column 3</i> | |
| Alachlor | 6.9 | -- | -- | 0.2 |
| Butachlor | 10.5 | -- | -- | 0.3 |
| Diphenamide | 10.8 | -- | -- | 0.2 |
| Fluridone | 2.2 | 2.45 | 2.1 | 0.5 |
| Lethane | 2.0 | -- | -- | 0.1 |
| Norflurazon | 18.4 | -- | -- | 0.02 |

Column 1: Glass, 180 cm long by 2 mm ID, packed with 10% OV-11 on Gas Chrom W-HP, 100/120 mesh; nitrogen carrier gas at a flow rate of 30 mL/min. Column temperature is held at 225°C for 4 minutes after injection and then programmed to 275°C at 4°/min and held for 8 minutes.

Column 2: Glass, 180 cm long by 2 mm ID, packed with 3% Dexsil 300 on Chromasorb W-HP, 80/100 mesh; nitrogen carrier gas at a flow rate of 30 mL/min. Column temperature at 300°C isothermal.

Column 3: Glass, 180 cm long by 2 mm ID, packed with 3% SP-2100 on Supelcoport, 100/120 mesh; nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature at 275°C isothermal.

Table 2. Single-Laboratory Accuracy and Precision

| <i>Parameter</i> | <i>Matrix Type*</i> | <i>Spike Range (µg/L)</i> | <i>No. of Replicates</i> | <i>Average Percent Recovery</i> | <i>Relative Standard Deviation (%)</i> |
|------------------|---------------------|-------------------------------|------------------------------|---|--|
| Alachlor | 1 | 255 | 7 | 113 | 9.0 |
| | 1 | 996 | 7 | 104 | 13.3 |
| Butachlor | 1 | 286 | 7 | 93.1 | 8.2 |
| | 1 | 1,420 | 7 | 92.8 | 4.3 |
| Diphenamid | 2 | 9.3 | 7 | 100 | 14.2 |
| | 3 | 740 | 7 | 98.8 | 7.0 |
| Fluridone** | 1 | 20.8 | 7 | 92.0 | 11.5 |
| | 1 | 998 | 7 | 88.4 | 11.4 |
| Lethane | 1 | 167 | 7 | 93.3 | 19.9 |
| | 1 | 576 | 7 | 97.6 | 29.4 |
| Norlurazone** | 1 | 243 | 7 | 89.5 | 7.4 |
| | 3 | 1,048 | 7 | 102 | 6.1 |

* 1 = Manufacturing effluent wastewaters.

2 = Manufacturing effluent wastewater + POTW effluent at a ratio of 1:200.

3 = Manufacturing effluent wastewater + POTW effluent at a ration of 1:1.

** Florisil cleanup not employed.

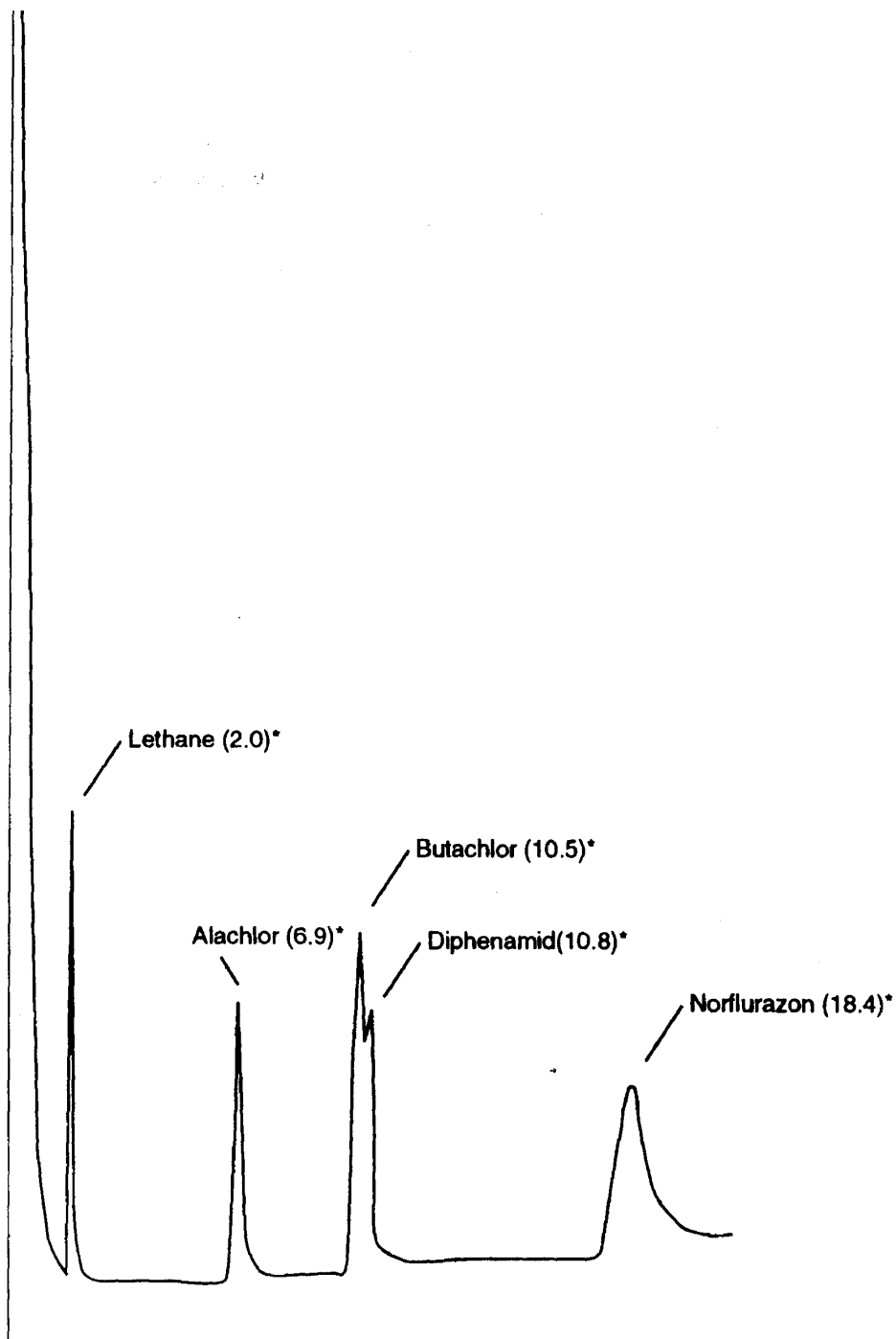
Table 3. Florisil* Cleanup Recoveries

| Solvent Fraction** | Alachlor | Average Percent Butachlor | Recoveries Diphenamid | Lethane |
|-------------------------------|-----------------|--------------------------------------|----------------------------------|----------------|
| 1 | 103 | 95 | | 106 |
| 2 | ND | ND | 96 | ND |

* 2% deactivated.

** 1 = 6% acetone/hexane

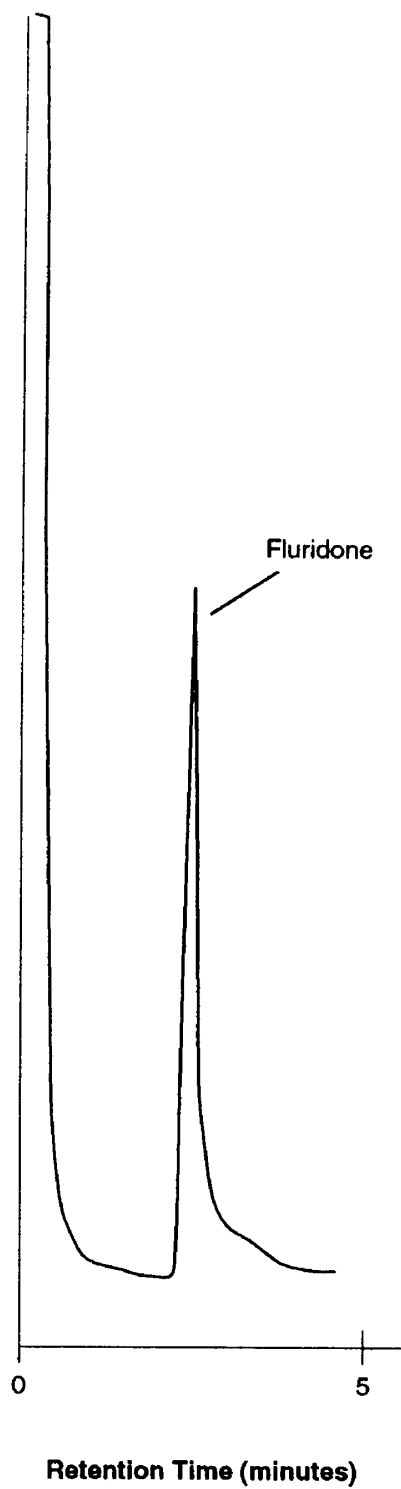
2 = 15% acetone/hexane



*Retention Time in parentheses

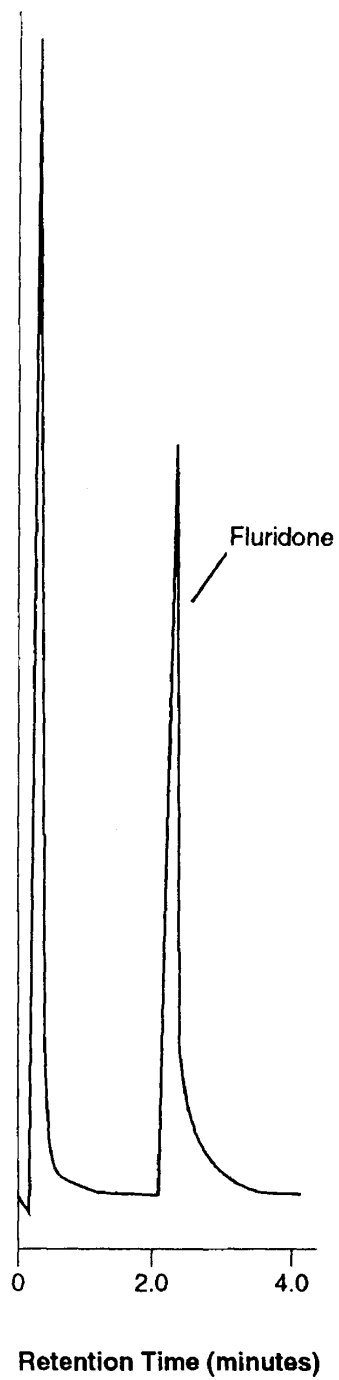
A52-002-73A

Figure 1. Gas Chromatogram of Amines/Lethane (Column 2)



A52-002-74A

Figure 2. Gas Chromatogram of Fluridone (Column 2)



A52-002-75A

Figure 3. Gas Chromatogram of Fluridone (Column 3)