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Office of Pesticides and
Toxic Substances (H-7501C)

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QUALITY ASSURANCE PROJECT PLAN FOR THE NATIONAL PESTICIDE SURVEY OF DRINKING WATER WELLS ANALYTICAL METHOD 1 - NITROGEN/PHOSPHOROUS PESTICIDES AND ANALYTICAL METHOD 3 - CHLORINATED ACID HERBICIDES

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APPROVAL PAGE

U.S. ENVIRONMENTAL PROTECTION AGENCY

Project Officer and Technical Monitor	Date
NPS Quality Assurance Officer	Date

MONTGOMERY LABORATORIES

Quality Assurance	Date
Project Manager	Date
Program Manager	Date

NATIONAL PESTICIDE SURVEY
QUALITY ASSURANCE PROJECT PLAN FOR
ANALYTICAL METHOD 1 - NITROGEN/PHOSPHORUS PESTICIDES AND
ANALYTICAL METHOD 3 - CHLORINATED ACID HERBICIDES

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3. PROJECT DESCRIPTION

Project Summary

Montgomery Laboratories will provide analytical services to the U.S. EPA for analysis of samples collected from well water sites throughout the country to assess the nature and scope of contamination by pesticides and their by-products (National Pesticide Survey or NPS). These data will be used to determine correlations between pesticide contamination and such factors as patterns of pesticide usage and ground water vulnerability.

Background

During the planning stages of the NPS, EPA found that no combination of currently approved methods could satisfy the need of the Survey for analyses of over 100 pesticides, degradation products, and metabolites. A considerable method development effort was therefore initiated in cooperation with the EPA Environmental Monitoring Systems Laboratory (EMSL) in Cincinnati. The lab contracted with Battelle-Columbus for the development of one new method and revisions to five existing EPA methods. Battelle used both real and simulated groundwaters as test matrices during the development effort in order to approximate the type of sample that would be encountered during actual Survey analyses. Prior to the NPS pilot, results of Battelle's efforts were subjected to peer review by the Agency, States, universities, and commercial labs. During the pilot, the performance of the methods was evaluated again and further improvements to the methods were made at this time. Concurrent with the implementation of the Survey, a multilab validation study will be conducted.

Methods

Montgomery Laboratories will utilize the following NPS methods to perform the analyses:

- NPS Method #1 - Determination of Nitrogen- and Phosphorus- Containing Pesticides in Ground Water by Gas Chromatography with a Nitrogen- Phosphorus Detector. (Appendix A)

  Pesticides containing nitrogen and/or phosphorus are extracted from water at neutral pH by methylene chloride and analyzed by capillary column gas chromatography equipped with a nitrogen-phosphorous detector. This method is based on EPA Methods 622 and 633. Table 3.1 lists the pesticides to be analyzed by this method.

  The method involves adding 100 grams of NaCl to one liter of sample (adjusted to pH 7) with 60 ml of methylene chloride. This extraction is performed three times and the extracts are combined. The extract is dried over sodium sulfate. The extract solvent is exchanged to methyl-t-butyl ether (MTBE). The 5 ml final extract is injected into a GC equipped with a 30 M DB-5 fused silica capillary column and the compounds detected with a Nitrogen-Phosphorus detector. The confirmation column will be a 30 M DB-1701 fused silica capillary column. Montgomery will use a single injection, dual column-dual detector setup for automatic dual column confirmation.

- NPS Method #3 - Determination of Chlorinated Acids in Ground Water By Gas Chromatography with an Electron Capture Detector. (Appendix A)

  Certain phenols and chlorophenoxy acid herbicides are extracted from water at an acidic pH by ethyl ether. The extracts are esterified and analyzed by capillary column gas chromatography equipped with an electron capture detector. This method is based on EPA Method 615. Table 3.2 lists the pesticides to be analyzed by this method.

  The method involves adding 250 grams of NaCl to one liter of sample which is then adjusted to pH 12 with 6N NaOH. The sample is periodically shaken for one hour to hydrolyze derivatives. The sample is then extracted three times with 60 ml of methylene chloride. This basic extract contains extraneous organic material and is therefore discarded. The pH is then adjusted to pH 2 or less with H_2SO_4. The sample is then extracted with 120 ml of diethyl ether. The sample is then extracted two additional times with 60 ml of diethyl ether. The ether extracts are combined and dried over sodium sulfate. The extract solvent is then exchanged to Methyl-t-butyl ether (MTBE). This extract is then methylated using diazomethane. Silicic acid is added to the extract to destroy any remaining diazomethane. The 5 ml final extract is injected into a GC equipped with a 30 M DB-5 fused silica capillary column and the compounds detected with a Electron Capture Detector. The confirmation column would be a 30 M DB-1701 fused silica capillary column. Montgomery will use a single injection, dual column-dual detector setup for automatic dual column confirmation. The method contains a special Florsil cleanup procedure to be used on extracts of all samples.

TABLE 3.1

PESTICIDES ANALYZED USING NPS METHOD 1

Alachlor
Ametryn
Atraton
Atrazine
Bromacil
Butachlor
Butylate
Carboxin
Chlorpropham
Cycloate
Diazinon
Dichlorvos
Diphenamid
Disulfoton
Disulfoton sulfone
Disulfoton sulfoxide
EPTC
Ethoprop
Fenamiphos
Fenarimol
Fluridone
Hexazinone
Merphos
Methyl paraoxon
Metolachlor
Metribuzin
Mevinphos
MGK 264
Molinate
Napropamide
Norflurazon
Pebulate
Prometon
Prometryn
Pronamide
Propazine
Simazine
Simetryn
Stirofos
Tebuthiuron
Terbacil
Terbufos
Terbutryn
Triademefon
Tricyclazole
Vernolate

TABLE 3.2

PESTICIDES ANALYZED USING NPS METHOD 3

Acifluorfen
Bentazon
Chloramben
2,4-D
2,4-DB
Dalapon
DCPA Acid metabolites
Dicamba
3,5-Dichlorobenzoic acid (DBA)
Dichlorprop (2,4-DP)
Dinoseb
5-Hydroxydicamba
4-Nitrophenol
PCP
Picloram
2,4,5-T
2,4,5-TP (Silvex)

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

The staff organization and chain of command which Montgomery Laboratories will utilize for this project is shown in Figure 4.1. Details of staff responsibilities and qualifications are summarized in this Section.

PROJECT MANAGER: ANDREW D. EATON, Ph.D

As Laboratory Director, Dr. Eaton will serve as the Project Manager and have full responsibility and authority for the project and serve as liaison with the U.S. EPA Project Officer. Dr. Eaton will review all of the final data generated for the project, oversee any major decisions which must be made, insure that the Program Manager has the necessary resources to accomplish the proposed work within the allotted time and budget, and insure that all laboratory and EPA specified quality control guidelines are being performed and are acceptable. Dr. Eaton will also insure that appropriate corrective action is taken for any out-of-control events that occur. Dr. Eaton can be reached at Montgomery's telephone number: (818) 796-9141.

PROGRAM MANAGER: JULIE ZALIKOWSKI

Julie Zalikowski will serve as the Program Manager and provide daily technical and managerial guidance to insure that the analytical work is performed within EPA specified turn-around times and conforms with the quality control guidelines specified by EPA and this QA Project Plan. Ms. Zalikowski can be reached at Montgomery's telephone number: (818) 796-9141.

QUALITY ASSURANCE OFFICER: RICK A. MEALY

Mr. Mealy will insure that all contract specified and routine internal laboratory quality control procedures are performed by the analysts for this project. He will also insure that all data and supporting quality control parameters are reviewed and approved by an appropriate supervisor or peer before the analyst is allowed to enter the data into the computer system. Approval is granted upon verification that all quality control parameters lie within specified acceptance limits and no analytical or computational errors appear on the analyst's data sheets. Mr. Mealy, as QA officer, reports directly to the laboratory director. Mr. Mealy can be reached at Montgomery's telephone number: (818) 796-9141.

ASSISTANT QUALITY ASSURANCE OFFICER: WAVERLY BRAUNSTEIN

Ms. Braunstein will serve as the Assistant Quality Assurance Officer, performing periodic audits. She is currently the laboratories' Assistant QAO, reporting to Mr. Mealy.

GAS CHROMATOGRAPHY ANALYST: ROOBIK YAGHOUBI

Mr. Yaghoubi is an associate chemist/GC analyst and will perform GC analysis for Method 3. He has been with Montgomery for the past 2 years.

GAS CHROMATOGRAPHY ANALYST: FRANKLIN CONSTANTINE

Mr. Constantine is a chemist/GC analyst and will perform GC analysis for Method 1. Mr. Constantine has performed a wide variety of GC analyses of environmental samples and has over 4 years of experience.

EXTRACTIONS SUPERVISOR: RICHARD HANSEN

Mr. Hansen is the extractions supervisor. Mr. Hansen will supervise the extraction of the samples, insuring that the proper QC samples are performed and that the extractions are performed in the specified holding times. Mr. Hansen has been with Montgomery Laboratories for five years performing extractions, TOC, TOX, THM, EDB/DBCP, pesticide and herbicide analyses on a variety of drinking waters and ground waters.

EXTRACTION TECHNICIANS

The following persons will be performing extractions for Methods 1 and 3: Jeannie Park, Edy Cosio, Lisa Loring, Stanley Kikkert, Enrique Gomez, Francisco Gomez.

SUPERVISING GAS CHROMATOGRAPHY/MASS SPEC ANALYST: CECILIA LEI

Cecilia Lei is the supervisor of the GC/MS group at Montgomery Laboratories. She has over 5 years of experience performing GC/MS analysis of environmental samples. Ms. Lei is proficient at mass spectral interpretation and analysis of compounds in drinking water. Ms. Lei will perform the confirmation of extracts by GC/MS.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYST: DAN HAUN

Mr. Haun has three years of GC/MS experience and was a GC/MS operator at CompuChem Laboratories before coming to Montgomery Laboratories. Mr. Haun will perform the confirmation of extracts by GC/MS.

SAMPLE RECEIVING CLERK

Beverly Gaskins will be the primary Sample Receiving Clerk. The backup Sample Receiving Clerk will be Bruce Havlik, who is Montgomery Laboratories current Sample Receiving Clerk. Both can be reached at Montgomery's phone number during working hours. Montgomery's address for sample

receipt is 555 E. Walnut, Pasadena, CA, 91101. The phone number is (818) 796-9141. Normal working hours are from 8 am to 5 pm local Pacific time.

DATA HANDLING AND REPORTING CLERK

Beverly Gaskins will be the Data Handling and Reporting Clerk. This will be the same person who will be primary contact for sample receipt. Julie Zalikowski will serve as backup.

TECHNICAL MONITOR: ROBERT A. MAXEY

The EPA Technical Monitor for Methods 1 and 3 will be Robert Maxey of the EPA's office in Mississippi. His telephone number is (601) 688-1225. Mr. Maxey will serve as primary contact for the project for all technical matters concerning Methods 1 and 3.

EPA PROJECT OFFICER: ROBERT A. MAXEY

The EPA Project Officer for Methods 1 and 3 will be Bob Maxey of the EPA's office in Mississippi. His telephone number is (601) 688-1225. Mr. Maxey will serve as primary contact for all contractual matters concerning Methods 1 and 3.

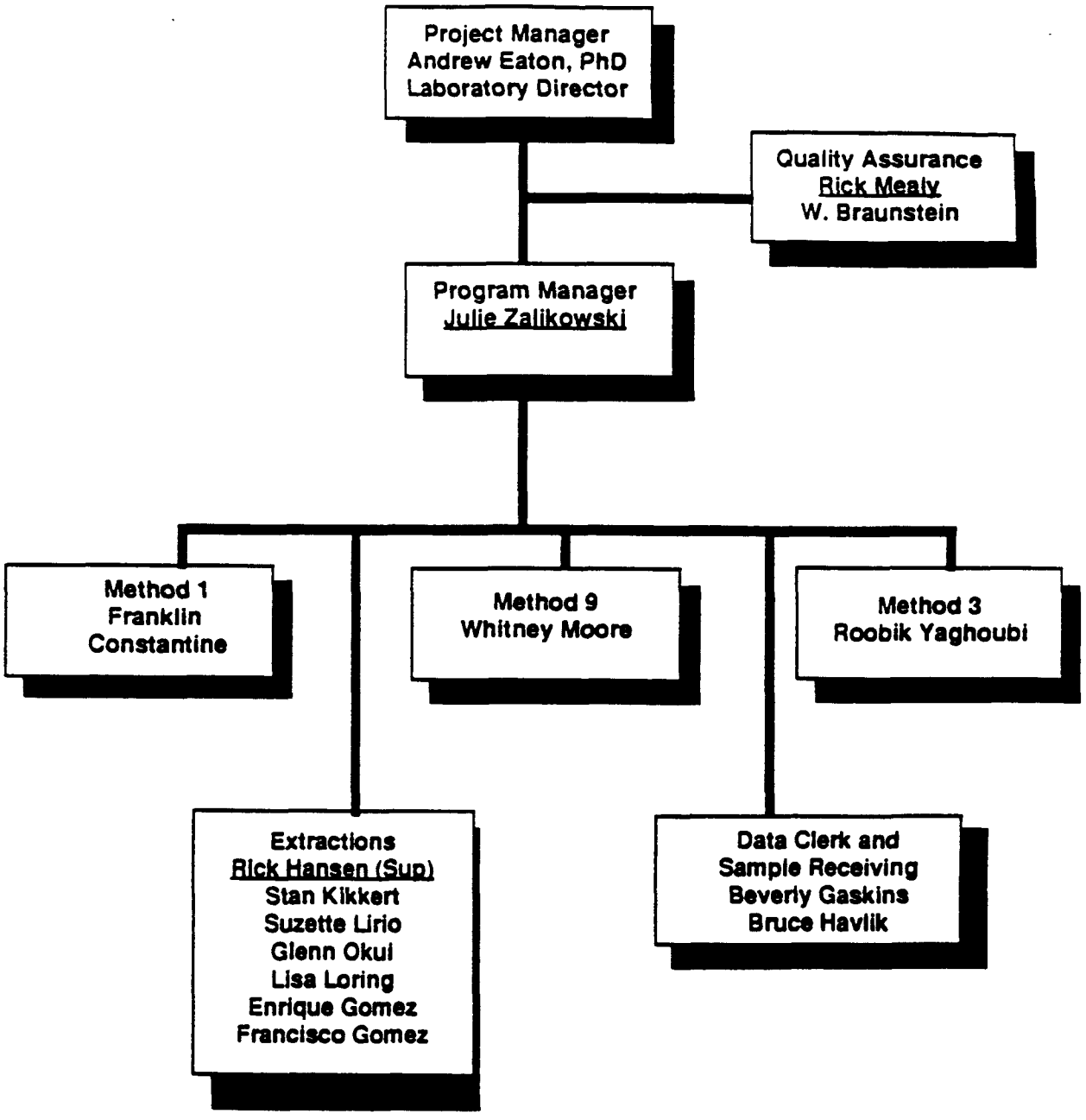
SUMMARY

The following is a summary of the Montgomery Laboratories personnel assigned to this project:

Program Manager:	Julie Zalikowski
QA Oversight:	Rick Mealy Waverly Braunstein
Sample Receipt: Backup:	Beverly Gaskins Bruce Havlik
Sample Preparation:	Rick Hansen (supervisor) Jeannie Park Edy Cosio Lisa Loring Stanley Kikkert Enrique Gomez Francisco Gomez
Sample Analysis:	Roobik Yaghoubi (Method 3) Franklin Constantine (Method 1)
GCMS Confirmation:	Celilia Lei Dan Haun
Data Handling and Reporting: Backup:	Beverly Gaskins Julie Zalikowski

FIGURE 4.1

MONTGOMERY LABS
NPS STAFF ORGANIZATION



5. QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Initial Demonstration of Capabilities: Determining Reporting Limits

The following procedure will be used to determine the estimated detection limits (EDL) and minimum reporting limits (MRL).

1) Determine the concentration of standard necessary to produce an instrument detector response with a 5/1 signal to noise ratio.

2) Spike eight reagent water samples at the concentration determined above, and analyze in a single day.

3) Compute Minimum Detectable Level (MDL) by multiplying the standard deviation by the student's t value, appropriate for a 99% confidence level, and a standard deviation estimated with n-1 degrees of freedom.

4) The EDL equals either the concentration of analyte yielding a detector response with a 5/1 signal to noise ratio, or the calculated MDL, whichever is greater.

5) Determined EDLs must be no greater than twice those determined during methods development.

6) The acceptability of EDLs exceeding the above limits will be determined by the Technical Monitor, based on health effect values.

7) The eight EDL extracts will also be analyzed using the confirmation column. EDLs determined on the confirmation column must equal those determined on the primary column. Again, EDLs exceeding this requirement will be approved on a case by case basis, by the technical monitors.

8) The laboratory will be required to perform up to six analyses per analyte mix by GC/MS, for the appropriate Methods. These analyses will be performed by MID, using the three ions specified by EPA and included as Appendix C. The purpose of these analyses are to determine the concentration at which a 5/1 signal to noise ratio, for the least intense of the three ions, is obtained.

9) The minimum reporting levels (MRLs) found in Table 5.1, are computed with the following multiples of the EDL:

   Method 1 MRL = 4 times EDL
   Method 3 MRL = 5 times EDL

10) Any chromatographic peak occurring at the proper retention time of an NPS analyte, at a concentration level between the EDL and the MRL, is to be reported as an occurrence of that analyte. However, no confirmations or quantifications are to be performed. If this suspect analyte occurs frequently, the proper confirmations and subsequent adjustment of the minimum reporting level may be required. Also, any frequent occurrence of a non-NPS analyte at what appears to be a high concentration, should be noted. Section 11 of this QAPjP contains the requirements for monitoring these occurrences.

11) The lower concentration calibration standard must be prepared at a concentration equal to the minimum reportable level.

Establishment and Use of Control Charts

1) Montgomery Laboratories will be required to demonstrate control of the measurement system via use of control charts. Control must be demonstrated for each analyte for which quantitation is required and for the surrogate at a concentration equal to that spiked into samples.

2) To establish the control charts, following initial demonstration of capability, 5 reagent water samples will be spiked at 10 times the MRL for the method and carried through extraction and analysis. An additional 15 samples will be spiked and analyzed, 5 on each of 3 days. The data from these 20 spiked samples will be used to construct control charts.

3) Criteria for Accuracy and Precision

   1) The Relative Standard Deviation (RSD) for any analyte must be less than or equal to 20%, except where data generated by Battelle at the corresponding level indicated poorer precision. The RSDs exceeding 20% will be evaluated on a case-by-case basis by the Technical Monitor for the method.

   2) The mean recovery of each analyte must lie between Battelles' mean recovery for each analyte (at the corresponding level) and plus or minus 3 times the RSD for that analyte as determined by Battelle during methods development, but no greater than Battelle's recovery plus or minus 30%.

      Example: For an analyte "A"

      Battelle demonstrated recovery of 80% for analyte A with RSD of 5%. Acceptable recoveries will be 80% plus or minus 3 times 5% or 65% - 95%; or,

      Battelle demonstrated recovery of 80% with RSD of 15%. Acceptable recoveries will be limited to 80% plus or minus 30% or 50% - 110%.

   3) Surrogate: In establishing the control chart for the surrogate, criteria in 3(1) and (2) above apply; it follows that one of the spike mixes must contain the surrogate at the concentration spiked into actual samples.

      Surrogate recoveries from samples will be required to be within plus or minus 30% of the mean recovery determined for that surrogate during the initial demonstration of capabilities.

      If the surrogate spiked into the Method Blank or LCS should fail to meet the quality control requirements for the recovery of that surrogate, this Method Blank or LCS must be invalidated. This would result in the invalidation of all samples associated with that Method Blank or LCS. In order to reduce the possibility of this resulting in the loss of otherwise valid data, the following procedures can be used:

      a) A LCS in which the surrogate recovery has failed to meet the quality control limits can be validated if the following conditions are met:

         i) The LCS meets all other required quality control elements.

ii) The surrogate recovery observed for the Method Blank associated with that same sample set meets the quality control limits determined using the control chart for that surrogate.

b) A Method Blank in which the surrogate recovery has failed to meet the plus or minus 30% criteria can be validated if a field sample associated with that same sample set meets all of the quality control requirements for a Method Blank.

4) Warning Limits/Control Limits: The control charts will be drawn so as to depict both warning limits (plus or minus 2 standard deviations (sd)) and control limits (plus or minus 3sd) about the mean.

4) Outliers: Dixon's test will be used to determine outliers. The method for using Dixon's test is included as Appendix D. There can be no more than 3 outliers per analyte from the 20 spiked controls.

5) Out-of-Control Situations: Sections 5(1) and 5(2) below refer to the recovery of analytes in the laboratory control standards (LCS) which are part of each sample set.

1) In the following instances, analytical work must be stopped until an "in-control" situation is established.

a) More than 15% of the analytes of a particular method are outside the control limits.

b) The same analyte is outside the control limit twice in a row, even though more than 85% of the total analytes are in control.

2) An "alert" situation arises when one of the following occurs:

a) Three or more consecutive points for an analyte are outside the warning limits but inside the control limits.

b) A run of 7 consecutive points above or below the mean.

c) A run of 7 points for an analyte in increasing or decreasing order.

An "alert" situation implies a trend toward an "out-of-control" situation. The laboratory is required to evaluate the analytical system before proceeding. If "alert" or "out-of-control" situation occur frequently, re-establishing control charts may be required by the Technical Monitor before analytical work can proceed.

3) Other Factors:

a) Method Blank: If the method blank exhibits a peak within the retention window of any analyte and is greater than or equal to one-half the MRL for that analyte, an "out-of-control" situation has developed.

b) Performance-Evaluation Samples: If the laboratory fails on one of the PE samples, an "out-of-control" situation is present.

6) Updating Control Charts: Following the establishment of the control chart, a Laboratory Control Standard (LCS) will be part of each analytical or "sample set". When 5 such controls have been run, the recoveries of these analytes will be incorporated into the control charts by adding these 5 most recent recoveries to the 20 original points and then deleting the first 5 of the original points. If the chart was generated using only 17 points, only 2 of the first points are discarded. Dixon's test will be applied to the new data to evaluate outliers. The method for using Dixon's test is presented in Appendix D. Accuracy and precision are recalculated and the chart re-drawn. The newly drawn chart will then apply to all data in sample sets subsequent to the last one used to update the chart.

Laboratory QC Requirements For Primary Analyses

1) Laboratory control standard mixes (LCS), which together contain all method analytes, will be analyzed with each set of samples. Method 1 will contain 3 LCS mixes and Method 3 will contain 2 LCS mixes. A list of the compounds for each LCS mix is given in Table 5.2.

2) A set of samples is defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time.

3) The internal standard area checks detailed in the methods will be used as stated (Section 10.5 of the method) with the exception that the allowable limits will be plus or minus 20 percent. However the control limits will be reassessed following completion of the initial demonstration of capabilities.

4) The measurement system is to be evaluated whenever any analyte is observed in a method blank, at a concentration greater than or equal to one-half the MRL. Method blanks are to be analyzed with each sample set.

   A sample set in which the surrogate compound recovery of the Method Blank has failed to meet the plus or minus 30% criteria can be validated by use of a Field Sample, from that sample set, which meets all of the QC requirements for a Method Blank. Note that this is not a procedure to validate the surrogate or the Method Blank, but rather it is a procedure to validate the sample set by use of a Field Sample as a Method Blank.

5) The criteria for monitoring instrument control standards will be utilized as stated in the method (Section 10.9 of the method).

6) Surrogate recoveries from field samples will be required to be within plus or minus 30% of the mean recovery determined for that surrogate during the initial demonstration of capabilities.

7) The requirement for monitoring calibration standard responses will be followed as written in the methods (Section 9.2.3 of the method).

8) Samples failing any QC criteria must be reanalyzed at the contractors expense.

9) Only qualitative analyses will be required for the following Method 1 compounds: Diazinon, Disulfoton, Disulfoton sulfone, Disulfoton sulfoxide, Merphos, Pronamide, and Terbufos. Only qualitative analyses will be required for Acifluorfen, Chloramben, Dalapon, and 4-Nitrophenol in Method 3. While these analytes are to be present in

at least one of the concentration levels of the calibration standards, they are not subject to any of the QC requirements.

10) Each time that new calibration standard dilutions are prepared they must be compared to the existing calibration curve, and the observed concentration must agree within plus or minus 20% of the expected concentration. For Method 1, the Technical Monitor may change this requirement if the standards prove to be unstable.

11) Any deviation from the analytical procedures or QC requirements must be approved by the Technical Monitor and documented in writing.

Laboratory QC Requirements For Second Column Confirmation Analyses

1) Second column confirmation will be required for all compounds detected on the primary column at concentrations above the MRL.

2) Quantitate by comparison to a calibration standard, which is within plus or minus 20% of the concentration of the sample determined using the primary column.

3) The concentration determined on the secondary column must agree within plus or minus 25% of the result determined on the primary column.

4) If the concentration determined on the secondary column does not agree within the limits stated above the laboratory must confer with the Technical Monitor concerning resolution of the discrepancy, if the results on both columns are above the MRL.

Laboratory QC Requirements for Time-Storage

Time storage samples will be collected and analyzed during the NPS study to determine the stability of the compounds in aqueous solution and in the extraction solvent. These samples will be collected at a frequency of 10% over the period of the study.

One time storage site will consist of four aliquots collected for each spiking mixture. Therefore, for Method 1, twelve 1 L bottles will be collected per time storage site and for Method 3, eight 1 L bottles will be collected per time storage site. For each spiking mixture, two of the four replicate aliquots will be spiked, extracted, and analyzed within a four-day time frame. They will then be reanalyzed 10 - 18 days after the first analysis. The remaining two duplicates will be spiked at the same time as the first two duplicated but will be allowed to sit 14 days before extraction. These samples will then be analyzed within four days of extraction.

All time storage samples will be spiked at 10 X MRL. Results of the time storage samples will be reported to EPA along with the corresponding regular sample. Any statistical analysis of time storage data will be conducted by EPA.

Laboratory QC Requirements for Lab Spikes

Lab spikes are duplicate field samples that have been spiked in the lab with known amounts of the analytes of interest in order to monitor spike recoveries from that matrix. The frequency of spiked samples will be 10% of all samples. Samples to be spiked and the concentration to be spiked will be designated on sample receipt material. Montgomery will not make the decision of which samples to spike. All laboratory QC requirements for primary analyses will apply to the analysis of lab spike samples.

GC/MS Confirmation

1) GC/MS confirmation will be required for all compounds confirmed by second column analysis.

2) The sample is to be compared to a standard prepared at the concentration determined for the sample, on either the primary or secondary column, whichever concentration is the lower.

3) If additional sample treatment is performed for GC/MS analysis (blowdown, etc.), the standard and sample must both undergo the same treatment.

4) Results of the GC/MS analysis are simply reported as the presence or absence of the analyte.

5) The sample extract is to be shipped to the referee laboratory for high resolution GC/MS analysis if confirmation of the analyte is not possible using quadrupole GC/MS due to the concentration of the analyte, and if the concentration is equal to or greater than one-half the lowest adverse health effect level for that analyte, or if requested by the Technical Monitor.

   The sample extracts will be shipped in 1 ml screwcap vials, packed in ice and shipped to the EPA Sample Custodian; Gerald Gardner, USEPA, Environmental Chemistry Laboratory, NASA/NSTL, Building 105, NSTL Station, MS 39529. Each vial will have the liquid level marked on it's side to determine if evaporation of extract has occurred during shipment.

Miscellaneous Other QC Notes

1) The results of the Initial Demonstration of Capabilities will be reported to the Technical Monitor for approval and inclusion into this QAPjP

2) Additional samples will be collected at 10% of the samples sites for spiking at the laboratory. The data from these spikes will be used to assess the recovery of the analytes from a variety of matrices. These samples are to be spiked at analyte concentrations equal to 2, 10 or 20 times the minimum reportable level for each analyte. Only one of the standard mixes will be spiked per spike sample. Samples collected for the analyte stability studies are to be spiked at 10 times the minimum reportable level for each analyte.

TABLE 5.1

METHOD 1 MRLs

Compound	MRL ug/l
Alachlor	1.00
Ametryn	0.260
Atraton	0.336
Atrazine	0.240
Bromacil	2.216
Butachlor	1.472
Butylate	0.600
Carboxin	1.032
Chlorpropham	0.700
Cycloate	0.400
Diazinon	0.084
Dichlorvos	0.240
Diphenamid	0.432
Disulfoton	0.200
Disulfoton sulfone	0.200
Dislfoton sulfoxide	0.352
EPTC	0.30
Ethoprop	0.120
Fenamiphos	0.297
Fenarimol	0.404
Fluridone	1.776
Hexazinone	0.268
Merphos	0.420
Methyl paraoxon	0.300
Metolachlor	1.50
Metribuzin	0.364
Mevinphos	0.300
MGK-264	2.08
Molinate	0.360
Napropamide	0.500
Norflurazone	0.356
Pebulate	0.384
Prometon	0.292
Prometryn	0.200
Pronamide	1.34
Propazine	0.196
Simazine	0.752
Simetryn	0.104
Stirofos	0.360
Tebuthiuron	0.448
Terbacil	3.492
Terbufos	0.200
Terbutryn	0.297
Triademefon	0.320
Tricyclazole	1.20
Vernolate	0.368

TABLE 5.1 (continued)

METHOD 3 MRLs

Compound	MRL ug/l
Acifluorfen	0.20
Bentazon	0.50
Chloramben	0.50
2,4-D	0.50
2,4-DB	2.0
Dalapon	5.0
DCPA	0.20
Dicamba	0.20
3,5-Dichlorobenzoic acid	0.60
Dichlorprop (2,4-DP)	0.50
Dinoseb	2.5
5-Hydroxydicamba	0.20
4-Nitrophenol	5.0
Pentachlorophenol	0.20
Picloram	1.0
Silvex (2,4,5-TP)	0.20
2,4,5-T	0.20

TABLE 5.2

METHOD 1 LCS MIXES

MIX A

Bromacil
Carboxin
Chlorpropham
Cycloate
Dichlorvos
Diphenamid
Disulfoton (qual)
Disulfoton sulfone (qual)
Disulfoton sulfoxide (qual)
EPTC
Fenarimol
Fluridone
Hexazinone
Merphos
Metribuzin
Mevinphos
Molinate
Norflurazon
Pebulate
Prometon (qual)
Prometryn
Pronamide (qual)
Propazine
Simetryn
Tebuthiuron
Triademefon
Tricyclazole
Vernolate

MIX B

Alachlor
Atrazine
Butylate
Ethoprop
Fenamiphos
Methyl paraoxon
MGK 264
Striofos
Terbufos (qual)
Terbutryn

MIX C

Ametryn
Atraton
Butachlor
Diazinon (qual)
Metholachlor
Napropamide
Simazine
Terbacil

TABLE 5.2 (continued)

METHOD 3 LCS MIXES

MIX A	MIX B
Acifluorfen	Chloramben (qual)
Bentazon	Dinoseb
2,4-D	4-Nitrophenol
2,4-DB	
Dalapon	
DCPA Acid metabolites	
Dicamba	
3,5-Dichlorobenzoic Acid	
Dichloroprop 2,4 DP	
5-Hydroxy Dicamba	
PCP	
Pichloram	
2,4,5-T	
2,4,5-TP Silvex	

6. SAMPLING PROCEDURES

Sample bottle preparation, sample collection, and sample shipping will be performed by an EPA contractor (ICF). Samples will be shipped iced for overnight delivery to the laboratory.

The containers, preservatives, and maximum holding times specified in the methods for each analytical group required for this contract are listed in Table 6.1. Any work orders supplied by the EPA with the samples are used as a packing slip by the Sample Receiving Clerk to insure that the correct number of bottles have been shipped and have been correctly labelled. Table 6.2 lists the number of bottles to be shipped to Montgomery with each sample type.

TABLE 6.1

SAMPLE CONTAINERS, PRESERVATIVES, AND HOLDING TIMES

ANALYSIS	SIZE	PRESERVATIVE	HOLDING TIME
NPS #1	1 L	HgCl2 - 10 ml	Extract 14 Days Analyze 14 Days
NPS #3	1 L	HgCl2 - 10 ml	Extract 14 Days Analyze 14 Days

All samples will be stored at 4°C
All extracts will be stored at -20°C
Mercuric chloride solution is 1 g/l in deionized water.

Sampling Paperwork

A) Figure 6.1 is a copy of the label to be used on the sample bottles. The label will contain the following information: Sample number, Sample code, Date sampled, and Sampler name. The following codes will be used for the sample number identification:

The example sample number is PD-0415-1-3-6.
- P = National Pesticide Survey Sample
- D = Domestic well
- C = Community well
- R = Resampled well
- B = PE sample
- 0415 = Site number
- 1 = Lab number
- 3 = Method number
- 6 = Analysis scenario

An additional code will be on each sample label. An example of this code is JMM-#3-XXX, where JMM is Montgomery Laboratories, #3 is method 3, and XXX is a code for the exact sample type. The following is a list of possible sample types and their codes:
- FS = Field Sample
- FD = Field Duplicate
- BU = Backup Sample

T/S = Time Storage, t = 14 days
T/S0 = Time Storage dup , t = 0 days
T/S14 = Time Storage dup, t = 14 days
LSS = Laboratory Spike, where
LSS-A1 = Lab spike, Mixture A, Level 1
LSS-B1 = Lab spike, Mixture B, Level 1

(LSS spiked at Level 2 (10 x MRL) will also serve as Time Storage, t=0 days.)

B) Figure 6.2 is a copy of the field sample tracking sheet which will be used.

TABLE 6.2

TOTAL SAMPLE BOTTLES REQUIRED

Kit Type Sample type	JMM #1 Regular			JMM #2 Reg. + L.S.			JMM #3 Reg. + L.S. + T/S		
Bottle size	1000 ml	1000 ml	125 ml	1000 ml	1000 ml	125 ml	1000 ml	1000 ml	125 ml
Method #	1	3	9	1	3	9	1	3	9
Primary	1	1	1	1	1	1	1	1	1
Backup	1	1	1	1	1	1	1	1	1
Lab Spike				1	1	1			
T/S D0							2	2	2
T/S D14							2	2	2
Totals	2	2	2	3	3	3	6	6	6
# sites	825	825	825	450	150	150	225	150	75
TOTAL	1650	1650	1650	1350	1200	1050	1080	870	660

TOTAL BOTTLE REQUIRED:
1000 ml = 7800
125 ml = 3360

7. SAMPLE CUSTODY

Laboratory Notification and Sample Receipt

The EPA implementation contractor (ICF, Inc.) was responsible for maintaining and daily updating of the NPSIS data base (Appendix J). The Sample Receiving Clerk would log-in via modem on a daily basis and print out the sampling schedule. This schedule was utilized by both the Sample Receiving Clerk and the Program Manager to schedule the laboratory work schedules. Upon receipt of the samples at the laboratory, Sample Receiving Clerk will inspect the sample, note the sample condition on the Field Sample Tracking Form. The Sample Receiving Clerk will then via the NPSIS data base notify ICF, Inc. as to the condition of the sample bottles, ice, and discrepancies between the sample labels and the Field Sample Tracking Form. In addition to notifying ICF, Inc. the Sample Receiving Clerk will notify the Program Manager who will then notify the Technical Monitor.

Samples must arrive at the laboratory with ice still remaining in the shipping box. If a sample box arrives at the laboratory without any ice remaining, the laboratory will contact the Technical Monitor immediately.

The sample bottles and boxes will be returned to the EPA implementation contractor (ICF, Inc) as soon as possible after the arrival of the samples. ICF will provide return shipping to their headquarters facility in Fairfax, Virginia via a commercial shipper. The sample bottles and boxes will be returned in bulk and not tracked individually.

Holding Times and Storage

Samples will be held in the dark and in the refrigerator at 4°C until extraction. The extracts will be held in a freezer at -20°C. Only the aliquot needed for analysis (usually 1 ml) will be removed from the freezer. Strict adherence to sample and extract maximum holding times (14 days) is required for both the primary and secondary column analyses. All analyses should be completed as soon as possible, but under extenuating circumstances, the maximum extract holding time may be extended to 28 days for GC/MS analyses only, if approved by the Technical Monitor.

Sample status will be monitored daily by the Data Handling and Reporting Clerk and the Program Manager. This monitoring will insure that the samples are extracted and analyzed within the proper holding times. Items to be checked daily will include: 1) sample holding times to insure that all extraction and extract holding times are met; 2) completeness of data packages to insure that data will be reported in the required amount of time; and 3) status of all outstanding QC problems.

Refrigerator and Freezer temperatures are monitored daily, Monday through Friday of each week by the Sample Control Person. The temperature at the beginning of the day is recorded on the record sheet taped to the front of the unit. Acceptance limits for the refrigerator are 2 to 8°C. Acceptance limits for the freezer are -30 to -10°C. A copy of this form may be found at the back of this section (Figure 7.1).

FIGURE 7.1

Refrigerator #_____

Read daily when the refrigerator is first opened.
Record temperature and initials in the space provided.
Report out-of-control temperatures to Joan Oppenheimer or Carole Lemay.
If the refrigerator is opened on a weekend be sure to read the temp.

Acceptable temp range: 2C - 8C

YEAR:

Date	Jan	Feb	March	April	May	June	Comments
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							
27							
28							
29							

Sample Disposal

Due to the use of mercuric chloride as a preservative, all samples are potentially hazardous. Water samples will be disposed of after the 14 day holding time has been exceeded. The water samples for disposal are first aerated to remove any ether. The pH of the water sample is them adjusted to pH 8-11. After adjusting the pH all water sample are combined in a 55 gallon teflon drum and treated with a 12% solution of sodium borohydride. After treatment the water is analyzed by mercury cold vapor EPA Method 7471), if the mercury concentration is less than 100 ppb the water is dumped and the precipitate is packed as hazardous waste.

Sample extracts will be held until the Technical Monitor approves of their disposal. Extracts will be stored in the dark at -20°C. Extracts will be lab packed and disposed of as a hazardous waste.

Sample Tracking

Sample tracking will be performed by the Program Manager. When samples arrive they will be entered in to a Sample Tracking & Summary File. This file contains all of the information about sampling and shipping needed for the final sample report. ICF will supply much of this information.

The laboratory will use the sample identification number described in Section 6 instead of assigning the sample a laboratory tracking number. The primary means of tracking the samples will be by extraction or analysis set number.

Each extraction set will be assigned a unique number and will be tracked as a set. The number will be in the form #-#### where the first number is the Method number (1, 3 or 9) and the other number is assigned consecutively. The Sample Tracking Form includes spaces to check for the completion of primary, secondary, and confirmation analysis as well as all of the required QC checks. A master list of all extraction sets will be kept to track the progress of all sets (Sample Tracking Form, Figure 7.2 and 7.3). This list will be used for determining when sample disposal can take place.

The Data Handling and Reporting Clerk and the Program Manager will monitor the status of all sample analyses by examination of the Sample Tracking Forms and the Extraction Set Tracking Forms. The Data Handling and Reporting Clerk will check the status of the outstanding extractions and analyses daily by talking to the analysts involved. Any potential problems will be brought to the attention of the Program Manager, who will then contact the appropriate supervisors.

Copies of all of the tracking and reporting forms are included at the back of this section. This includes not only the tracking forms but the data reporting forms (Figure 7.4 and 7.5).

FIGURE 7.2

METHOD 1

SAMPLE TRACKING FORM

Method: 1 Extraction Set Number 1 - _____

Date Extraction Started: ___/___/___ Date Extraction Completed: ___/___/___

Extracted By: _____ Spiked By: _____ Analysed By _____

Standard Number: _____

Sample ID	Date Sample	Date Spiked	Sample Volume	Ext Volume	Date Analysed	Date Confirm	Date GCMS	% Surr Rec	Int Std	QC Comp?	Anal Comp?	Comments
MBLK												
LCSA												
LCSB												
LCSC												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												
PD- PC- -1-1-												

Comments _____

FIGURE 7.3

METHOD 3

SAMPLE TRACKING FORM

Method: 3

Extraction Set number 3 _____

Date Extraction Started: ___/___/___ Date Extraction Completed ___/___/___

Extracted By: _____ Spiked By: _____ Analyzed By _____

Standard Number: _____

Sample ID	Date Sample	Date Spiked	Sample Volume	Ext Volume	Date Analyzed	Date Confirm	Date GCMS	% Surr Rec	Int Std	QC Comp?	Anal Comp?	Comments
MBLK												
LCSA												
LCSB												
PD-PC- -1-3-												
PD-PC- -1-3-												
PD-PC-												
PD-PC-												
PD-PC-												
PD-PC- -1-3-												
PD-PC- -1-3-												
PD-PC- -1-3-												
PD-PC- -1-3-												
PD-PC- -1-3-												

Comments _____

FIGURE 7.4

SAMPLE RESULTS FORM
METHOD 1

Extraction Set Number: 1 -_____ Sample ID:_____

Date Extracted:___/___/___ Date Analyzed:___/___/___

Analyzed By:_____ Analysis: PRIM / CONF / GCMS

GC Run Number:_____

Calibration Run Number:_____ Standard Stock Number:_____

Mix - Compound	Conc.	Mix - Compound	Conc.
B - Alachlor		B - Methyl paraoxon	
C - Ametryn		C - Metolachlor	
C - Atraton		A - Metribuzin	
B - Atrazine		A - Mevinphos	
A - Bromacil		B - MGK 264	
C - Butachlor		A - Molinate	
B - Butylate		C - Napropamide	
A - Carboxin		A - Norflurazon	
A - Chlorpropham		A - Pebulate	
A - Cycloate		A - Prometon	
		A - Prometryn	
C - Diazinon (qual)		A - Pronamide (qual)	
A - Dichlorvos		A - Propazine	
A - Diphenamid		C - Simazine	
A - Disulfoton (qual)		A - Simetryn	
A - Disulfoton sulfone (qual)		B - Stirofos	
A - Disulfoton sulfoxide(qual)		A - Tebuthiuron	
A - EPTC		C - Terbacil	
B - Ethoprop		B - Terbufos (qual)	
B - Fenamiphos		B - Terbutryn	
A - Fenarimol		A - Triademefon	
A - Fluridone		A - Tricyclazole	
A - Hexazinone		A - Vernolate	
A - Merphos (qual)			

Surrogate Recovery:_____% Internal Standard:_____%

Comments: _____

LCSA QC OK? Y/N LCSB QC OK? Y/N LCSC QC OK? Y/N
Surrogate OK? Y/N IS OK? Y/N
Sample Holding time OK? Y/N Extract Holding time OK? Y/N
Analysis Checked By: _____ Need further analysis? Y/N

FIGURE 7.5

SAMPLE RESULTS FORM
METHOD 3

Extraction Set Number: 3 -_____ Sample ID:_____

Date Extracted:___/___/___ Date Analyzed:___/___/___

Analyzed By:_____ Analysis: PRIM / CONF / GCMS

GC Run Number:_____

Calibration Run Number:_____ Standard Stock Number:_____

Mix - Compound	Conc.	Mix - Compound	Conc.
A - Acifluorfen (qual)		A - Dichloroprop	
A - Bentazon		B - Dinoseb	
B - Chloramben (qual)		A - 5-Hydroxy Dicamba	
A - 2,4-D		B - 4-Nitrophenol (qual)	
A - 2,4-DB		A - PCP	
A - Dalapon (qual)		A - Pichloram	
A - DCPA Acid metabolites		A - 2,4,5-T	
A - Dicamba		A - 2,4,5-TP	
A - 3,5-Dichlorobenzoic Acid			

Surrogate Recovery:_____% Internal Standard:_____%

Comments:_____

LCSA QC OK?	Y/N	LCSB QC OK?	Y/N
Surrogate OK?	Y/N	IS OK?	Y/N
Sample Holding time OK?	Y/N	Extract Holding time OK?	Y/N
Analysis Checked By: _____		Need further analysis?	Y/N
QC Checked By: _____		If Y: Which analysis?	Conf/GCMS

8. CALIBRATION PROCEDURES AND FREQUENCY

Calibration Solutions

The EPA will furnish NPS standards at a nominal concentration of 1000 mg/L for Methods 1 and 3 in sealed glass ampules marked with individual batch numbers. Separate dilutions will be made from these stocks for the calibration standards and the laboratory control standards (LCS). The standard dilutions will initially be checked by analyzing the new LCS dilutions compared to the new standard dilutions. If the results of the LCS show the expected recoveries (within control limits, see Section 5, Initial Demonstration, Control Charts) then both dilutions must be correct (or both have the same error). Each time new calibration standard dilutions are prepared they must be compared to the existing calibration curve, and the observed concentration must agree within plus or minus 20% of the expected concentration. If Method 1 cannot meet this criteria the Technical Monitor must be informed.

Records shall be kept in the stock standard notebook indicating how, when, and by whom the dilutions were made. An example page from this book is included at the end of this section (Figure 8.1). Each standard dilution will be assigned a standard number. This number will be recorded with all sample sets analyzed with this standard dilution to provide traceability for the standard used on any given analytical run. This will be the method of tracking each new standard dilution and stock solutions.

The Stock Standard numbers will be assigned as per the following code: NPS#-001-P##-1A; where NPS# is the NPS method number, 001 is the batch number of the NPS standards given to ML by the EPA, P## is the standards notebook page number which describes the preparation of the standard mix preparation, 1 is the level of the dilution (0=low, 1=medium, and 2=high), and A refers to which standard mix. The following example, NPS3-009-P12-3A, refers to NPS3-009 or the lot number 9 NPS stock standard shipped from the EPA. NPS3-009-P12 is a cocktail prepared on page 12 of the standards notebook, and NPS3-009-P12-3A is a high level standard of mix A prepared from cocktail NPS-009-P12.

The stock standard solutions are stored in 3 ml vials with teflon seals and stored in the dark at -20°C. The stock standards will be replaced by new stock standards whenever a new shipment of NPS standard is obtained from the EPA every three to four months. Diluted standards will be prepared as needed, however they will be remade whenever a new NPS standard is obtained. Diluted standards will be stored in 10 ml vials with teflon seals and stored in the dark at -20°C. Standards will be kept in separate freezers from sample extracts.

Calibration Curve

Both Methods 1 and 3 will be calibrated using the Internal Standard Calibration Procedure, Section 9.2 of the Methods. This procedure calls for a minimum of three standards. The lowest calibration standard must be at 2 x MRL and the others should correspond to the range of

concentrations expected in the sample concentrates. One of the other standards must be at a level equivalent to the 10XMRL. After the standards are injected the relative response (RRa) for each analyte to an internal standard will be calculated using the equation:

$$RRa = Aa/Ais$$

where: Aa = area of the analyte

Ais = area of the internal standard

A calibration curve will be generated, RRa versus analyte concentration in the sample in ug/l.

The working calibration curve must be verified each day by measuring one or more calibration standards. If the response for any analyte varies from the predicted response by more than 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

Each time that new calibration standard dilutions are prepared they must be compared to the existing calibration curve, and the observed concentration must agree within plus or minus 20% of the expected concentration. If Method 1 cannot meet this criteria the Technical Monitor must be informed.

Because Montgomery can analyze the sample extract on both the primary and secondary columns simultaneously, a complete standard curve can be generated on the confirmation column.

All calibration curves will be filed separately. The plots of each compound will be hardcopied along with the response factor data. The sample data reports will be cross-referenced to the calibration curve file.

GCMS Analysis

For GCMS confirmation the sample is compared to a standard prepared at the concentration determined for the sample on either the primary or secondary column, whichever concentration is the lower. If additional sample treatment is performed (blowdown, etc.) the standard and sample must both undergo the same treatment. The results of the GCMS confirmation are simply reported as the presence or absence of the analyte, no quantitation.

The GCMS must be shown to be properly tuned during each daily shift prior to analysis. This insures that the masses and abundances which the data system determines are accurate. The compound used for tuning will be Decafluorotriphenylphosphine (DFTPP). The tuning criteria is presented below. An example of the form used to show tuning is presented at the end of this section (Figure 8.2)

Mass	m/e Abundance criteria
51	30 to 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 to 60% of mass 198
197	<1% of mass 198
198	BASE PEAK, 100% RELATIVE ABUNDANCE
199	5 TO 9% OF MASS 198
275	10 TO 30% OF MASS 198
365	1% OF MASS 198
441	Present but less than mass 443
442	>40% of mass 198
443	17 to 23% of mass 442

FIGURE 8.1

Notebook 014 | **SPIKE** | **A in Acetone**
NPS 3-014-P25 | **ROY 11/1/88**
Page 25 | **Stock Mix A un-deriv.**

BATCH	EPA COMPOUNDS IN ACETONE	PURITY	ORIG. CONC.	ACETONE DILUTION WITH PURITY CORRECTION	CONC. STOCK
689	Dalapon	99 2%	1,000 ug/ml	1.26 ml → 25 ml	50 ug/ml
699	3,5-DBA	99.8%	1,000 ug/ml	0.15 ml → 25 ml	6.0 ug/ml
680	Dicamba	99.5%	1,000 ug/ml	0.05 ml → 25 ml	2.0 ug/ml
681	2,4-DP	99.1%	1,000 ug/ml	0.126 ml → 25 ml	5.0 ug/ml
683	2,4-D	99.9%	1,000 ug/ml	0.125 ml → 25 ml	5.0 ug/ml
600	5-Hydroxy dicamba	99.5%	1,000 ug/ml	0.05 ml → 25 ml	2.0 ug/ml
691	PCP	99.2%	1,000 ug/ml	0.05 ml → 25 ml	2.0 ug/ml
693	Silvex	99.3%	1,000 ug/ml	0.05 ml → 25 ml	2.0 ug/ml
682	2,4,5-T	99.5%	1,000 ug/ml	0 50 ml → 25 ml	2.0 ug/ml
679	2,4-DB	99 4%	1,000 ug/ml	0.50 ml → 25 ml	20 ug/ml
687	Bentazon	99.3%	1,000 ug/ml	0.126 ml → 25 ml	5.0 ug/ml
692	Picloram	99.8%	1,000 ug/ml	0.25 ml → 25 ml	10 ug/ml
703	DCPA	95 5%	1,000 ug/ml	0.052 ml → 25 ml	2.0 ug/ml
686	Acifluorfen	99.9%	1,000 ug/ml	0.05 ml → 25 ml	2.0 ug/ml

Notebook 014 | **NPS 3-014-P25** | **B in Acetone**
ROY 11/1/88
Page 25 | **Stock Mix B un-deriv.**

BATCH	EPA COMPOUNDS IN ACETONE	PURITY	ORIG. CONC.	ACETONE DILUTION WITH PURITY CORRECTION	CONC. STOCK
690	PNP	98.7%	1,000 ug/ml	1.27 ml → 25 ml	50 ug/ml
688	Chloramben	91.9%	1,000 ug/ml	0.136 ml → 25 ml	5.0 ug/ml
684	Dinoseb	98.8%	1,000 ug/ml	0.632 ml → 25 ml	25 ug/ml

FIGURE 8.2

GC/MS TUNING AND MASS CALIBRATION

Decafluorotriphenylphosphine

Case Number: Laboratory: Contract:
Inst. ID: FINN Sens. Date: 09/07/89 Sens. Time: 09:29:00
Lab ID: BN407SEP89A Cali Date: Analyst: RLB
Data release authorized by: JAZ 09/07/89

M/E	Ion Abundance Criteria	Spec #581		
51	30 to 60% of mass 198	30.51		
68	less than 2% of mass 69	0.00	(0.00)	1
69	mass 69 relative abundance	37.17		
70	less than 2% of mass 69	0.00	(0.00)	1
127	40 to 60% of mass 198	40.04		
197	less than 1% of mass 198	0.00		
198	base peak, 100% relative abundance	100.00		
199	5 to 9% of mass 198	6.12		
275	10 to 30% of mass 198	24.13		
365	greater than 1% of mass 198	1.58		
441	less than mass 443	11.30		
442	greater than 40% of mass 198	69.53		
443	17 to 23% of mass 442	13.07	(18.80)	2

1 - value in parenthesis is % of mass 69
2 - value in parenthesis is % of mass 442

9. ANALYTICAL PROCEDURES

The following NPS methods will be used for samples analyzed for this contract. The detailed methods are attached to this QAPjP as Appendix A.

METHOD 1

Method Summary

NPS Method 1 is entitled "Determination of Nitrogen- and Phosphorus- Containing Pesticides in Ground Water by Gas Chromatography with a Nitrogen-Phosphorus Detector". Pesticides containing nitrogen and/or phosphorus are extracted from water at neutral pH by methylene chloride and analyzed by capillary column gas chromatography equipped with a nitrogen-phosphorous detector. This method is based on EPA Methods 622 and 633.

The method involves adding 100 grams of NaCl to one liter of sample (adjusted to pH 7) with 60 ml of methylene chloride. This extraction is performed three times and the extracts are combined. The extract is dried over sodium sulfate. The extract solvent is exchanged to methyl-t-butyl ether (MTBE). The 5 ml final extract is injected into a GC equipped with a 30 M DB-5 fused silica capillary column and the compounds detected with a Nitrogen-Phosphorus detector. The confirmation column will be a 30 M DB-1701 fused silica capillary column. Montgomery will use a single injection, dual column-dual detector setup for automatic dual column confirmation.

Equipment

Primary GC: Varian 3500
- Dual Capillary columns with 2 ECD
- Model 8034 autosampler
- Dual channel Nelson 760 series A/D

Backup GC: HP 5980
- Dual capillary columns with 2 ECD
- Model 7673A autosampler
- Dual channel Nelson 760 series A/D

Primary Data System: Nelson model 4430 chromatographic workstation
- 5 dual channel 760 series instrument module A/D's
- 3 Thinkjet printers
- Color monitor
- HP 9000 series 300 computer with floating point hardware
- 20 MB hard disk
- 130 MB hard disk
- Tape Drive for file archival

Backup Data systems: Varian Vista 401

Primary GCMS for confirmations: Finnigan 4021
- Capillary column
- NOVA 4X Incos computer
- 70 MB disk drive
- Dual terminal

Backup GCMS: Finnigan 5100
- Capillary column
- NOVA 4X Incos computer
- 70 MB disk drive
- Dual terminals

Analysis Types

The following table is a list of the analysis types and frequency of analysis for Method 1.

Analysis Type	Frequency
PRIMARY ANALYSIS	
Instrument Control Standards	1/Day
Lab Control Standard (LCS) (one LCS per standard mix)	1/Set
Method Blank	1/Set
Calibration Standards	1/Day
Field Sample	1/Site
Backup Sample	As Needed
Spiked Sample	10%
Day 0 time Storage Sample	10%
Day 14 Time Storage Sample	10%
Day 14 Time Storage Extract	10%
Performance Evaluation Samples	As Requested
CONFIRMATIONAL COLUMN ANALYSIS	
Field Sample	As Needed
Calibration Standards	As Needed
GCMS CONFIRMATION	
Field Sample	As Needed
Calibration Standard	As Needed

Maximum Number of Samples Per Set

Based on the required QC, the maximum number of field samples which could be analyzed per sample set is 10. Note that each "sample set" is defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time.

Method Deviations

There are several deviations from the published method. If the QAPjP differs from the procedures listed in the method, the QAPjP rules. Several of the known deviations are:

10.7.1.1 The method states that the spiking concentration should be 1 to 5 times the background level or 15 times the EDL. This QAPjP states (Section 5) that the samples will be spiked at 2, 5 or 10 times the MRL.

10.8 The method states that a method blank should not contain any peaks within the retention time window of any analyte which is greater than or equal to one half of the EDL for that analyte. This QAPjP changes the EDL to MRL in that statement.

10.6.1 The method defines a sample set as all those samples extracted within a 24 hour period. For the purposes of this QAPjP a sample set has been defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time by the same analyst.

General Because Mercuric chloride is used as a preservative in all of the field samples, 10 mg/l Mercuric chloride is to be added to all LCS, Blanks, etc. prepared in the laboratory.

At this time Montgomery proposes no other method deviations from the published method. Any other proposed deviations will have to be discussed with and approved by the Technical Monitor before use for survey samples.

METHOD 3

Method Summary

NPS Method 3 is entitled "Determination of Chlorinated Acids in Ground Water By Gas Chromatography with an Electron Capture Detector". Certain phenols and chlorophenoxy acid herbicides are extracted from water at an acidic pH by ethyl ether. The extracts are esterified and analyzed by capillary column gas chromatography equipped with an electron capture detector. This method is based on EPA Method 615.

The method involves adding 250 grams of NaCl to one liter of sample which is then adjusted to pH 12 (as measured with pH paper) with 6N NaOH. The sample is periodically shaken for one hour to hydrolyze derivatives. The sample is then extracted three times with 60 ml of methylene chloride. This basic extract contains extraneous organic material and is therefore discarded. The pH is then adjusted to pH 2 (as measured with pH paper) or less with H_2SO_4. The sample is then extracted with 120 ml of diethyl ether. The sample is then extracted two additional times with 60 ml of diethyl ether. The ether extracts are combined and dried over sodium sulfate. The extract solvent is then exchanged to Methyl-t-butyl ether (MTBE). This extract is then methylated using diazomethane. Silicic acid is added to the extract to destroy any remaining diazomethane. The 5 ml final extract is injected into a GC equipped with a 30 M DB-5 fused silica capillary column and the compounds detected with a Electron Capture Detector. The confirmation column would be a 30 M DB-1701 fused silica capillary column. Montgomery will use a single injection, dual column-dual detector setup for automatic dual column confirmation. The method contains a Florisil cleanup procedure to be used on all sample extracts, standards and controls.

Equipment

Primary GC: HP 5890
- Dual capillary columns with 2 ECD
- Model 7673A autosampler
- Dual channel Nelson 760 series A/D

Backup GC: Varian 3500
- Dual capillary columns with 2 ECD
- Model 8000 autosampler
- Dual channel Nelson 760 series A/D

Primary Data System: Nelson model 4430 chromatographic workstation
- 5 dual channel 760 series instrument module A/D's
- 3 Thinkjet printers
- Color monitor
- HP 9000 series 300 computer with floating point hardware
- 20 MB hard disk
- 130 MB hard disk
- Tape Drive for file archival

Backup Data systems: 2 Varian Vista 401's

Primary GCMS for confirmations: Finnigan 4021
- Capillary column
- NOVA 4X Incos computer
- 70 MB disk drive
- Dual terminal

Backup GCMS: Finnigan 5100
- Capillary column
- NOVA 4X Incos computer
- 70 MB disk drive
- Dual terminals

Analysis Types

The following table is a list of the analysis types and frequency of analysis for Method 3.

Analysis Type	Frequency
PRIMARY ANALYSIS	
Instrument Control Standards	1/Day
Lab Control Standard (LCS) (one LCS per standard mix)	1/Set
Method Blank	1/Set
Methylation Blank	1/Batch
Methylation Standards	3/Batch
Florisil Elution Standard	1/Set
Calibration Standards	1/Day
Field Sample	1/Site
Backup Sample	As Needed
Spiked Sample	10%
Day 0 time Storage Sample	10%
Day 14 Time Storage Sample	10%

Day 14 Time Storage Extract	10%
Performance Evaluation Samples	As Requested
CONFIRMATIONAL COLUMN ANALYSIS	
Field Sample	As Needed
Calibration Standards	As Needed
GCMS CONFIRMATION	
Field Sample	As Needed
Calibration Standard	As Needed

Maximum Number of Samples Per Set

Based on the required QC, the maximum number of field samples which could be analyzed per sample set is 9. Note that each "sample set" is defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time.

Method Deviations

There are several deviations from the published method. If the QAPjP differs from the procedures listed in the method the QAPjP rules. Several of the known deviations are:

10.7.1.1	The method states that the spiking concentration should be 1 to 5 times the background level or 15 times the EDL. This QAPjP states (Section 5) that the samples will be spiked at 2, 5 or 10 times the MRL.
10.8	The method states that a method blank should not contain any peaks within the retention time window of any analyte which is greater than or equal to one half of the EDL for that analyte. This QAPjP changes the EDL to MRL in that statement. This QAPjP also allows the compound dalapon to fail this requirement due to its retention time.
10.6.1	The method defines a sample set as all those samples extracted within a 24 hour period. For the purposes of this QAPjP a sample set has been defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time by the same analyst.
General	Because Mercuric chloride is used as a preservative in all of the field samples, 10 mg/l Mercuric chloride is to be added to all LCS, Blanks, etc. prepared in the laboratory.
General	A Methylation Blank will be run with each batch of methylation reagent prepared. This blank should meet the same criteria as the method blank.
General	Three Methylation standards will be run when a new batch of methylation reagent is prepared. These will be non-extracted standards at 5 times the concentration of the LCS and diluted 5 times before analysis. The mean of these must meet the same recovery criteria as the LCS. The Methylation standards will show that the methylation step is working correctly and proper derivitization is occurring.

General — A Florisil Elution Standard will be run whenever a new batch of florisil is activated. This will be used to determine the recovery of the compounds from the Florisil. A non-extracted standard will be placed on the Florisil column at the sample concentration of the LCS. The recovery should fall in the same range as the LCS.

General — There is a portion on each analytical run for Method 3 which is excluded from the integration program. That portion of the chromatogram often has several peaks which result from the extraction solvents. The uniterated portion is from 4.5 min to about 10 min for the primary DB-5 column and 5.5 min to 11.0 min on the confirmation DB 1701 column. Dalapon is eluted in this region and as a result the Technical Monitor removed dalapon as a Method 3 quantitative analyte.

At this time Montgomery proposes no other method deviations from the published method. Any other proposed deviations will have to be discussed with and approved by the Technical Monitor before use for survey samples.

10. DATA REDUCTION, VALIDATION AND REPORTING

Data Reduction

All data for Methods 1 and 3 will be collected by the Nelson 4430 chromatographic workstation through the Nelson 760 series A/D convertors. Standards will be run at the beginning of the day. The analytical run will be calibrated as described in Section 8 of this QAPjP. When samples are run, the software will detect peaks and identify them based on absolute retention times compared to the standards. The area of the peaks will be determined and the concentration calculated from the calibration plots. All outputs of the Nelson software will be filed for the duration of the project, or until the Technical Monitor approves of its disposal. Note: The Nelson data system has been verified by performance on known samples over the last 2 years.

The rounding of numbers and significant figures is addressed in Appendix E. This Appendix was taken from Chapter 7 of EPA publication EPA-600/4-79-019, "Handbook for Analytical Quality Control in Water and Wastewater Laboratories."

Data Verification

The Nelson data will be reviewed and checked by the primary analyst. The primary analyst will review all of the raw data and calculation and insure that the QC criteria was met. Following completion of each analysis set, the analytical raw data, chromatograms, and QC summary sheets are reviewed by a peer analyst. The peer analyst will insure that the data produced by the primary analyst is complete and correct. The completed data and QC are then submitted to the NPS project Data Handling and Reporting Clerk and the Program Manager to verify that all quality control parameters fall within acceptance limits and to review the analytical data for calculation errors or inconsistencies. The Data Handling and Reporting Clerk will then enter the data into the computer data system.

The following items are to be checked for each sample set:

1) Is the instrument control standard's signal to noise ratio greater than the limit the method specifies?

2) Is the instrument control standard's peak symmetry factor within the limits set by the method?

3) Is the instrument control standard's peak geometry factor within the limits set by the method?

4) Is the instrument control standard's resolution within the limits set by the method?

5) Is the date from sampling to receipt within the limits set by the survey requirement (1 day)?

6) Is the date from sampling to extraction within the limits set by the survey (14 days)?

7) Is the date from extraction to analysis within the limits set by the survey requirements (14 days)?

8) Is the percent recovery of the surrogate within the limits set by the survey requirements?

9) Is the internal standard area count within the limits set by the method requirements?

10) Is the concentration of a blank greater than or equal to one-half of the MRL?

11) Is the concentration of a field sample above the reporting limit?

   a) If so, is there a confirmation analysis of the analyte?

   b) Is the concentration of the confirmatory column within the limits set by the survey requirements?

   c) If so, is there a GCMS confirmation analysis?

12) Is the percent recovery of each analyte in the lab control standard within the limits of the appropriate control chart?

13) Is the percent recovery of each analyte in the lab spike sample within the limits of the appropriate control chart?

14) Is the percent recovery of each analyte in the performance evaluation sample within the limits set by the survey requirements?

15) Ensure that the Nelson data computer is correctly identifying each compound within the Retention Time Windows.

16) Is the calibration standard within 20% of the previous calibration curve, or was a new calibration curve run?

17) Were refrigerator and freezer temperatures within acceptable limits during storage of samples and extracts?

Data Validation

Validation of analytical data is dependent on insuring that key procedural steps which impact data quality are followed and that all quality control parameters fall within documented acceptance criteria. The following procedural steps must be adhered to for all of the NPS methods since deviations can have a serious impact on data quality.

- Any data not contained on a QC form will be contained in the analysts' notebook.
- A solvent blank is performed on each new lot of solvent utilized for extractable organic analyses. The solvent cannot be used if the levels of analytes exceed the established method detection limits for these compounds.
- After analysis of a high concentration sample, a reagent water blank or solvent blank should be run until there is no longer a memory effect. A high concentration

is defined as the concentration of the highest standard analyzed, unless data shows that lower concentrations can carryover at a measurable level (one-half the MRL).

- Instrument performance must be checked daily and routine and special maintenance must be documented in the instrument maintenance log (example in Figure 10.1). The data from the Instrument QC Standard (Section 10.9 of the methods) used to examine peak tailing, poor peak geometry, poor resolution, missing peaks, and poor peak response are all indicative of instrumentation problems which must be corrected before samples can be analyzed. A copy of the Instrument QC Standard reporting form is included as Figure 10.2.

- Samples must be warmed to room temperature before performing extraction or analysis.

- For GC analyses, a record of retention times obtained on spikes and standards for each compound is maintained. The average retention time and variance for each compound is calculated daily from each day's run of standards and spikes. The retention times of individual samples must fall within 3 standard deviations of the average retention time for each compound.

All laboratory analysts go through an orientation and training program to insure that they are performing all of the required steps and quality control parameters for their analysis. Training is provided by the appropriate senior analyst and verification of proper training is provided by not allowing the analyst to work on samples until performing acceptably on EPA performance samples which are provided to the analyst by the QA Officer as single blind samples. Once an analyst is trained, his work is continually reviewed by his immediate supervisor and the Manager of Analytical Services. His/her work is always sporadically reviewed by the QA Officer through review of performance on periodic double blind check samples and routine monthly laboratory system audits.

Data Reporting

All data will be reported as sample sets. A sample set is defined as all samples, blanks, spiked samples, LSC, etc. , which are extracted at the same time. When the sample set is completed, an ACSII file in the required format will be produced. A copy of the required format is provided as Appendix B. All data for a sample set are to be reported as a complete data set, including all QC and confirmatory data no later than two months form the date of sample collection. The data files will be sent to Christopher Frebis at the EPA in Cincinnati, Ohio. The files will be on IBM compatible 5. 25 inch floppy disks. Exceptions to the standard reporting procedure are:

- Situations when results from confirmation columns do not agree with results from primary columns within 25 percent are to be reported and discussed with the Technical Monitor.

- Any DCPA on both columns must be reported regardless of differences in quantitation between the primary and confirmation columns.

- Confirmed positives for certain levels of certain analytes. The Rapid Reporting Levels are listed in Tables 10.1 and 10.2. If an analyte listed in the two tables is

observed in the primary analyses at or above the RRL the following actions will be instituted:

1) The appropriate confirmation analyses (GC/MS) should be performed as soon as practical.

2) The laboratory will telephone the Technical Monitor as soon as confirmation is completed.

3) The laboratory will immediately document the observed results in a letter to the Technical Monitor.

Determining and Reporting the Presence of NPS Analytes Below the MRL

The following procedure has been established for determining and reporting the presence of an NPS analyte below the MRL:

1) Only peaks with responses of between one-half the MRL and the MRL on the primary column will be investigated. A response on the secondary column, indicating the presence of the analyte, is also required for additional work.

2) a) The first occurrence of a peak meeting the requirements of (1) will be noted and the peak retention time is verified. Retention time verification requires the calculation of the mean retention time of the three compound standards. A retention time window is then calculated as 3x the standard deviation + the mean of the three standards. If the peak in question falls within this window for both the primary and confirmation column, the presences of the compound is reported to the technical monitor and GCMS confirmation is performed.

b) For responses meeting the requirements of (1) and (2), the laboratory will attempt low-resolution GCMS confirmation if the GC/MS supervisor feels it is within the capability of the instrument. If the confirmation is not within the capability of Montgomery, such extracts will be sent weekly, under iced conditions by next-day air, to the appropriate referee laboratory having high-resolution GC/MS capabilities. Copies of chromatograms and all pertinent sample information must be sent along with the extracts including extracts of the related Method Blank. It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tight seal and do not contribute interferences to the extracts. Volume level must be marked on the outside of the vial or ampule.

3) Whether the identification of the analyte is attempted at Montgomery or the referee laboratory, only analytes positively confirmed by GC/MS will be reported beyond the Technical Monitor for the Method and the Analytical Coordinators. No unconfirmed data will be reported outside the NPS analytical system. Unsuccessful attempts at confirmation will also be reported to the Technical Monitor.

4) Following either the successful GC/MS confirmation of two such responses for the same analyte or two successive failures to confirm the analyte by GC/MS without any prior successful GC/MS confirmation on any samples, discussions with OPP personnel will take place before continuing low level work on that analyte.

Procedure for Determining the Identity of Non-NPS Analytes

It is expected that, over the course of the NPS program, numerous extraneous responses will be evident on chromatograms form the various methods. The laboratory will be required to attempt identification of peaks or responses on the primary column exhibiting the minimal criteria below.

1) If, upon initial analyses, the response of an extraneous peak on the primary column is equal to or greater than the response of the nearest NPS analyte on that column at 10 times MRL, an attempt must be made to identify that unknown peak or response by GC/Ms. Full scan spectra and subsequent library search are expected and must be followed by comparison of the spectra of the unknown compound with those of an authentic standard of the suspected compound.

2) The work in (1) must be attempted by the laboratory on the first such occurrence of such a peak and the results of the attempt reported to the Technical Monitor. If the laboratory feels their instrument is not capable of the confirmatory work, they must send both that extract and that of the related Method Blank to the referee laboratory under iced conditions by next-day air. It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tight seal and do not contribute interferences to the extracts. Volume level must be marked on the outside of the vial or ampule.

   Specific sample and analytical information must accompany each such extract including: Sample ID number, weight of sample matrix contained in the ampule, copies of chromatograms from the primary GC column, identification of the retention time window for the unknown response(s) as defined by the last NPS analyte to elute before the unknown peak or response and the first NPS analyte to elute following the unknown response.

3) Whether the identification of the unknown compound is attempted at Montgomery or the referee laboratory, only compounds positively confirmed by GC/MS will be reported beyond the Technical Monitor and the Analytical Coordinators. No unconfirmed data will be reported outside the NPS analytical system. Unsuccessful attempts at identification will also be reported to the Technical Monitor.

4) Following either the successful confirmation of two such extraneous peaks proving to be the same compound or two failures to identify a response with the same retention time without a prior successful GC/MS confirmation on a sample, discussions with OPP personnel will take place before continuation with identification work on that particular compound.

Storage of Data

All laboratory data and information pertaining to NPS will be stored for the duration of the program. This includes all refrigerator and freezer temperature logs, sample receipt forms, sample tracking forms, extraction logs, GC run logs, instrument control standard forms, chromatograms, sample results forms, GCMS tunes, control charts, instrument maintenance logs, reagents and standard preparation records, calibration data, and data and records related to corrective actions. Note that all of raw data will be stored in hardcopy form. All hardcopy data will be stored in files labeled with the sample set number for the method. The GC calibration runs will be stored in

separate folders. A master log will be kept of all samples with reference to the sample set it was analyzed with. All hardcopy data and backup computer tapes will be stored in locked file cabinets. Only the Program Manager, Data Tracking and Reporting Clerk Operations Manager will have keys to the data. The exact storage system is detailed in the "Montgomery Laboratories Standard Operating Procedure for the Archival of the National Pesticide Survey (NPS) Data" which is included as Appendix L.

TABLE 10.1

METHOD 1 RAPID REPORTING LEVELS

Analyte	Rapid Reporting Level
Alachlor	40 ug/l
Ametryn	300
Atrazine	50
Bromacil	3,000
Butylate	1,000
Carboxin	1,000
Diphenamid	300
Fenamiphos	5.0
Hexazinone	1,000
Metolachlor	500
Metribuzin	300
Propazine	500
Simazine	50
Tebuthiuron	700
Terbacil	300

TABLE 10.2

METHOD 3 RAPID REPORTING LEVELS

Analyte	Rapid Reporting Level
Acifluorfen	100 ug/l
Bentazon	90
2,4-D	100
Dalapon	300
Dicamba	300
Dinoseb	7.0
Pentachlorophenol	300
Picloram	700
2,4,5-T	350
2,4,5-TP	70

FIGURE 10.1

MAINTENANCE ON GC

DATE	MAINTENANCE
3/30/89	Septum Replaced - Injector A
4/10/89	Septum Replaced - Injector A
4/13/89	Septum Replaced - Injector A
4/13/89	Changed the glass insert on Injector A
4/13/89	Septum Replaced
4/20/89	Changed the glass insert on Injector A and Septum Replaced
4/20/89	Changed the glass insert on Injector A and Septum Replaced
6/1/89	New Columns were installed and all the peaks are sharp and change in R.T.
6/5/89	Change the septic and glass insert
6/16/89	New columns were installed
6/20/89	Septum Replaced
6/27/89	Changed the glass insert and Septum Replaced
6/30/89	New columns were installed
7/4/89	Septum Replaced
7/12/89	New columns were installed and changed the glass insert and Septum Replaced
7/18/89	Septum Replaced
7/21/89	New columns and charged the glass insert and Septum Replaced
7/25/89	Column inlet to detector was broken, the whole line which carries N_2 into the detector had to be replaced
8/4/89	New columns and change the glass insert and Septum Replaced
8/21/89	Septum Replaced

FIGURE 10.2

INSTRUMENT QC STANDARD

Method 1

Date: ____/____/____ Analyst: _____

TEST	ANALYTE	REQUIREMENTS	VALUE	QC MET?
Sensitivity	Vernolate	Detection of analyte	Y or N	
		S/N > 5	S/N =	
Chromatographic Performance	Bromacil	0.90 < PSF < 1.10	PSF =	
		0.80 < PGF < 1.20	PGF =	
Column Performance	Prometon Atrazine	Resolution > 0.7	R =	

NOTES:

1) PSF = Peak Symmetry Factor

$$PSF = \frac{w(1/2)}{0.5 \times W(1/2)}$$

Where w(1/2) is the width of the front of the peak at half height assuming the peak is split at its highest point and W(1/2) is the peak width at half height.

2) PGF = Peak Gaussian Factor

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

Where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

3) Resolution is defined as:

$$R = \frac{t}{W}$$

Where t is the difference in elution times between the two peaks and W is the average peak width at the baseline.

4) Concentrations of the Instrument QC Standard:

Vernolate: 0.05 ug/ml
Bromacil: 0.5 ug/ml
Prometon: 0.30 ug/ml
Atrazine: 0.15 ug/ml

FIGURE 10.2 (continued)

INSTRUMENT QC STANDARD

Method 3

Date: ___/___/___ Analyst: _____

TEST	ANALYTE	REQUIREMENTS	VALUE	QC MET?
Sensitivity	Dinoseb	Detection of analyte	Y or N	
		S/N > 5	S/N =	
Chromatographic Performance	4-NP	0.70 < PSF < 1.05	PSF =	
		0.70 < PGF < 1.05	PGF =	
Column Performance	3,5-DCBA 4-NP	Resolution > 0.4	R =	

NOTES:

1) PSF = Peak Symmetry Factor

$$PSF = \frac{w(1/2)}{0.5 \times W(1/2)}$$

Where w(1/2) is the width of the front of the peak at half height assuming the peak is split at its highest point and W(1/2) is the peak width at half height.

2) PGF = Peak Gaussian Factor

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

Where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

3) Resolution is defined as:

$$R = \frac{t}{W}$$

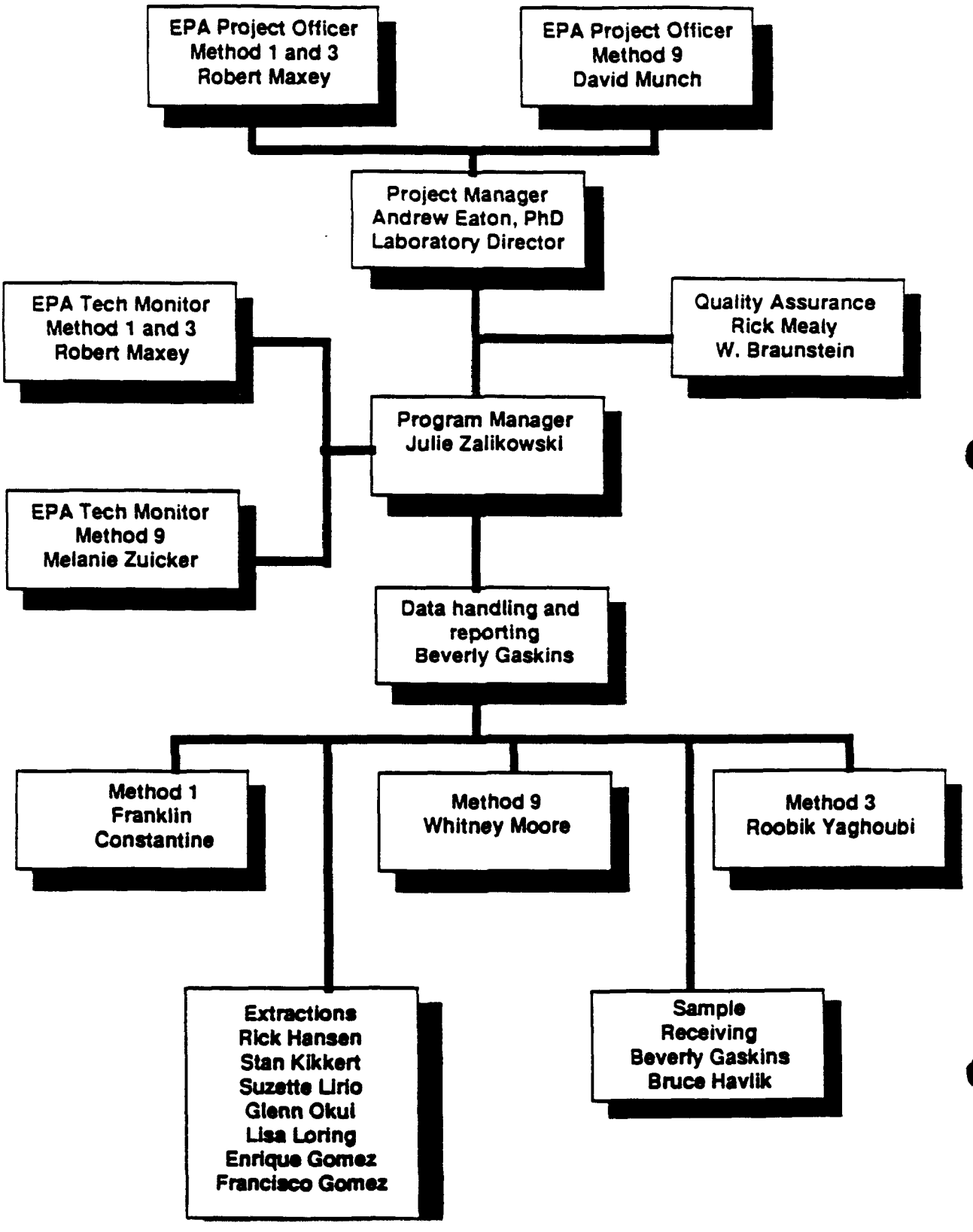
Where t is the difference in elution times between the two peaks and W is the average peak width at the baseline.

4) Concentrations of the Instrument QC Standard:

Dinoseb: 0.004 ug/ml
4-Nitrophenol (4-NP): 1.6 ug/ml
3,5-Dichlorobenzoic acid (3,5-DCBA): 0.6 ug/ml

FIGURE 10.3

MONTGOMERY LABS
NPS STAFF ORGANIZATION
AND WORK FLOW



11. INTERNAL QUALITY CONTROL CHECKS

This sections lists the type and frequency of quality control checks to be done in conjunction with this project. Any time a QC sample analyte falls outside of the acceptance criteria an "out-of-control" situation exists. A corrective form must be filled out stating the appropriate information (Section 15). The Program Manager must be informed and no further samples run until the system is shown to be back in control. Data produced while the system is out-of-control are unacceptable and cannot be used for any purpose. It is imperative that the QC discussed here is followed and the QC results thoroughly documented.

Summary Of QC Requirements

Table 11.1 is a tabular summary of the QC requirements, frequency, criteria and response to QC failure. Most of these points are spelled out in more detail below.

Response To QC Failure

If any QC requirements for a sample set are not met no further analysis of that sample set will be performed until the system is shown to be back in control. Extraction sets extracted after the set in question also can not be analyzed until they are shown to be in control. No further extractions should be performed until the extraction QC samples are shown to be in control by reanalysis of the first set in question or any subsequent sample set which had already been extracted. If the QC samples for a subsequent set are in control then the system is shown to be in control for that set only. It is anticipated that up to 5 sample sets will be between extraction and analysis and therefore could be subject to problems of this type.

Frequency of QC Samples

The following table lists the frequency of field and QC samples to be analyzed for Methods 1 and 3.

Analysis Type	Frequency
PRIMARY ANALYSIS	
Instrument Control Standards	1/Day
Lab Control Standard (LCS) (one LCS per standard mix)	1/Set
Method Blank	1/Set
Calibration Standards	1/Day
Field Sample	1/Site
Backup Sample	As Needed
Spiked Sample	10%
Day 0 Time Storage Sample	10%
Day 14 Time Storage Sample	10%
Day 14 Time Storage Extract	10%
Performance Evaluation Samples	As Requested

CONFIRMATIONAL COLUMN ANALYSIS

Field Sample	As Needed
Calibration Standards	As Needed

GCMS CONFIRMATION

Field Sample	As Needed
Calibration Standard	As Needed

Control Charts

1) Control charts will be kept for all analytes and the surrogate. The initial control charts will be established as in Section 5 of this QAPjP, the Initial Demonstration of Capabilities.

2) Updating Control Charts: Following the establishment of the control chart, an LCS will be part of each analytical or "sample set". When 5 such controls have been run, the recoveries of these analytes will be incorporated into the control charts by adding these 5 most recent recoveries to the 20 original points and then deleting the first 5 of the original points. If the chart was generated using only 17 points, only 2 of the first points are discarded. Dixon's test will be applied to the new data to evaluate outliers. Accuracy and precision are recalculated and the chart re-drawn. The newly drawn chart will then apply to all data in sample sets subsequent to the last one used to update the chart.

3) Out-of-Control Situations: Sections 3(1) and 3(2) below refer to the recovery of analytes in the laboratory control standards (LCS) which are part of each sample set.

   1) In the following instances, analytical work must be stopped until an "in-control" situation is established.

      a) More than 15% of the analytes of a particular method are outside the control limits.

      b) The same analyte is outside the control limit twice in a row, even though more than 85% of the total analytes are in control.

   2) An "alert" situation arises when one of the following occurs:

      a) Three or more consecutive points for an analyte are outside the warning limits but inside the control limits.

      b) A run of 7 consecutive points above or below the mean.

      c) A run of 7 points for an analyte in increasing or decreasing order.

      An "alert" situation implies a trend toward an "out-of-control" situation. The laboratory is required to evaluate the analytical system before proceeding. If an "alert" or "out-of-control" situation occurs frequently, re-establishing control charts may be required by the Technical Monitor before analytical work can proceed.

Laboratory QC Requirements For Primary Analyses

1) Laboratory control standard mixes (LCS), which together contain all method analytes, will be analyzed with each set of samples. Method 1 will have 3 LCS mixes and Method 3 will have 2 LCS mixes. (See Table 5.2) Results of the LCSs are to be reported as a normal sample.

2) A set of samples is defined as all samples, blanks, spiked samples, LCS, etc. , which are extracted at the same time.

3) The internal standard area checks detailed in the methods will be used as stated (Section 10.5 of the method). However the control limits will be reassessed following completion of the initial demonstration of capabilities. The internal standard checks will be reported with each sample set.

4) The measurement system is to be evaluated whenever any analyte is observed in a method blank, at a concentration greater than or equal to one-half the MRL (see Section 5 of this QAPjP). Method blanks are analyzed with each sample set. A corrective action form will be filed whenever this occurs.

5) The criteria for monitoring instrument control standards will be analyzed with each sample set as stated in the method (Section 10.9 of the method). The results of this ICS will be reported with each sample set. If the ICS does not meet the criteria set forth in the method a corrective action form will be filed.

6) Surrogate recoveries will be required to be within plus or minus 30% of the mean recovery determined for that surrogate during the initial demonstration of capabilities.

7) Time storage samples must be extracted within plus or minus 4 days of the proper date, and analyzed within 4 days of extraction. For example, non-stored time storage samples must be spiked within the 14 day holding time for samples and must be analyzed within 4 days of that extraction. A stored time storage sample must be extracted by no sooner than 10 days and no later than 18 days after being spiked, and must be analyzed within 4 days of being extracted.

8) The requirement for monitoring calibration standard responses will be followed as written in the methods (Section 9.2.3 of the method).

9) Samples failing any QC criteria must be reanalyzed at the contractors expense.

10) Only qualitative analyses will be required for the following Method 1 compounds: Diazinon, Disulfoton, Disulfoton sulfone, Disulfoton sulfoxide, Merphos, Pronamide, and Terbufos. There are four qualitative analytes in Method 3; Chloramben, 4-Nitrophenol,Acifluorfen, and Dalpon. While these analytes are to be analyzed in at least one of the concentration levels of the calibration standards, they are not subject to any of the QC requirements.

11) Each time that new calibration standard dilutions are prepared they must be compared to the existing calibration curve, and the observed concentration must agree within plus or minus 20% of the expected concentration. For Method 1, the Technical Monitor may change this requirement if the standards prove to be unstable.

12) Any deviation from the analytical procedures or QC requirements must be approved by the Technical Monitor and documented in writing.

Laboratory QC Requirements For Second Column Confirmation Analyses

1) Second column confirmation will be required for all compounds detected on the primary column at a concentration above the MRL.

2) Quantitate by comparison to a calibration standard, which is within plus or minus 20% of the concentration of the sample determined using the primary column.

3) The concentration determined on the secondary column must agree within plus or minus 25% of the result determined on the primary column.

4) If the concentration determined on the secondary column does not agree within the limits stated above, the laboratory must confer with the Technical Monitor concerning resolution of the discrepancy, if the results on both columns are above the MRL.

GC/MS Confirmation

1) GC/MS confirmation will be required for all compounds confirmed by second column analysis.

2) The sample is to be compared to a standard prepared at the concentration determined for the sample, on either the primary or secondary column, whichever concentration is the lower.

3) If additional sample treatment is performed for GC/MS analysis (blowdown, etc.), the standard and sample must both undergo the same treatment.

4) Results of the GC/MS analysis are simply reported as the presence or absence of the analyte.

5) The sample extract is to be shipped to the referee laboratory for high resolution GC/MS analysis if confirmation of the analyte is not possible using quadrupole GC/MS due to the concentration of the analyte, and if the concentration is equal to or greater than one-half the lowest adverse health effect level for that analyte, or if requested by the Technical Monitor.

Florisil Preparation and Storage

Florisil will be prepared as per section 7. 15 of Method 3. The Florisil will be stored in a desiccator until use. Each batch of activated Florisil will be tested for recovery by spiking a known concentration of standard onto the Florisil and determining the recovery. The recovery should be within LCS limits as determined in Section 5.

Methylation QC Checks

Each batch of Diazomethane will be checked for background contaminants by the methylation of a solvent blank. This solvent blank must meet the same criteria as the Method Blank.

Each batch of Diazomethane will also be tested for recovery by methylating three standards. The recovery of these methylation standards must be the same as for the LCS.

Miscellaneous Other QC Notes

1) Additional samples will be collected at 10% of the samples sites for spiking at the laboratory. The data from these spikes will be used to assess the recovery of the analytes from a variety of matrices. These samples are to be spiked at analyte concentrations equal to 2, 10 or 20 times the minimum reportable level for each analyte. Only one of the standard mixes will be spiked per spike sample. Samples collected for the analyte stability studies are to be spiked at 10 times the minimum reportable level for each analyte.

2) Other "Out-of-Control" events:

   a) Method Blank: If the method blank exhibits a peak within the retention window of any analyte and is greater than or equal to one-half the MRL for that analyte, an "out-of-control" situation has developed.

   b) Performance-Evaluation Samples: If the laboratory fails on one of the PE samples, an "out-of-control" situation is present.

3) Surrogate Monitoring

   a) The surrogate recovery observed for all Field Samples, LSS and Method Blanks must fall within plus or minus 30% of the mean recovery of the surrogate on the control charts. The surrogate recovery for the LCS must fall within the control limits established on the control chart.

   b) A LCS in which the surrogate recovery has failed to meet the quality control limits can be validated, if the following conditions are met:

      i) The LCS meets all other required quality control elements.

      ii) The surrogate recovery observed for the Method Blank associated with that same sample set, meets the quality control limits determined using the control chart for that surrogate.

   c) A Method Blank in which the surrogate recovery has failed to meet the plus or minus 30% criteria can be validated, if a Field Sample associated with that same sample set, meets all of the quality control requirements for a Method Blank.

Internal QC Checks

The NPS Quality Assurance Officer will provide quarterly performance check samples to the laboratory Program Manager. The Program Manager will submit the check sample as a blind to the GC analyst. Results of the quarterly performance check samples will be submitted to the Technical Monitor. The acceptance criteria for the performance evaluation results will be established by the NPS Quality Assurance Officer. The criteria utilized is detailed in Section 12 of this QAPjP.

TABLE 11.1

QA CRITERIA/RESPONSE

QA Check	Frequency	Criteria	Response
Sample Holding Time	Each sample	Sample must be extracted within 14 days of sampling.	If >14 days, do not extract sample - Inform Program Manager and TM.
Sample Extract Holding Time (Primary and Confirmation)	Each sample	Extract must be analyzed within 14 days of extraction (except GCMS)	If > 14 days, do not analyze sample - Inform Program Manager and TM.
Sample Extract Holding Time (GCMS confirmation)	Each sample needing GCMS Confirmation	Extract must be analyzed by GCMS within 28 days of extraction	If > 28 days, inform Program Manager and TM.
Time Storage Sample Holding Time	Time Storage Samples	Time Storage Samples must be extracted within 4 days of specified date.	If >4 days, do not extract sample - Inform Program Manager and TM.
Time Storage Extract Holding Time	Each Time Storage Sample Extract	Time Storage Sample Extracts must be analyzed within 4 days of specified date.	If > 4 days, do not analyze extract, Inform Program Manager and TM.
Instrument Control Std - Sensitivity	Daily	Detection of analyte. S/N > 5	Reevaluate GC/Detector system - Clean detector, Injection port, etc.
Instrument Control Std - Chromatographic Perform. Method 1	Daily	0.90 < PSF < 1.10 0.80 < PGF < 1.20	Reevaluate GC Column system - New column needed?
Instrument Control Std - Chromatographic Perform. Method 3	Daily	0.70 < PSF < 1.05 0.70 < PGF < 1.05	Reevaluate GC Column system - New column needed?
Instrument Control Std - Column Performance Method 1	Daily	Resolution > 0.70	Reevaluate GC Column system - New column needed?
Instrument Control Std - Column Performance Method 3	Daily	Resolution > 0.40	Reevaluate GC Column system - New column needed?
Method Blank	1 per set	No peak greater than 0.5 times MRL	Determine source of contamination prior to processing samples
Solvent Blank	Each new solvent Lot	No peak greater than 0.5 times MRL	Determine whether new lot should be purchased or current lot distilled.
Laboratory Control Standard (LCS) Control Limits "Out-Of-Control"	1 per set for each standard mix	>15% of LCS recoveries outside control limits established as per Section 5 of this QAPP. Or one analyte outside control limits twice in a row.	"Out of Control" Event - no futher analysis to be analyzed until system back "in-control"
Laboratory Control Standard (LCS) "Alert Situations"	1 per set for each standard mix	3 or > points for an analyte outside warning limits. 7 points above or below mean. 7 points inc. or decr.	"Alert" situation exists. Evaluate problem. Can still analyze samples
Laboratory Sample Spikes	10% or as specified	Same as for LCS	If LCS for that set ok - then Matrix problem.

TABLE 11.1 (continued)

QA CRITERIA/RESPONSE

QA Check	Frequency	Criteria	Response
Calibration Standard	1 per day	Must agree within 20% of current calibration curve	Repeat with new calibration std. or repeat calibration curve.
New Calibration Stock Standard	Each new Calib. Standard Stock	Must agree within 20% of old stock.	Remake Stock. If this doesn't work, Inform Program Manager and TM.
Internal Standard Area counts	Each sample	Within 20% of average IS area count for calibration	one time - rerun. Still - mistake Many times - check calibration
Surrogate Standard Recovery	Each sample	Within 30% of average Surrogate Recovery established in Section 5 of this QAPP (Initial Demo of Cap.).	Blanks - Reinject. Still - "Out of Control". Sample - possible Matrix problem
Compound detected on primary column	As needed	A compound is quantified on the primary column when the level is > MRL	Run on confirmation column
Compound confirmed by confirmation column	As needed	A compound is confirmed by the confirmation column if the conc. is within 25% of value on primary column	If concentration high enough - GCMS If not - send to EPA for High Res GCMS analysis
Compound Retention Time	Each sample	Retention time of an analyte in a sample must fall within a window ± times the std. of the RT used to calulate the window	Determine if new window needs to be calculated
EPA Performance Evaluation Samples	When requested by EPA	No criteria established yet	Laboratory analytical system out-of-control until problem resolved No further analyses performed.
Florisil check	Each set	Recovery should be within LCS limits	Check method of preparing Florisil. Or obtain new lot of Florisil.
Internal QC Check Samples	Random	Same as LCS	Same as LCS
Methylation Blank Check	Each batch of Diazomethane	Same as Method Blank	Same as Method Blank
Methylation Efficiency Check Standards	Each batch of Diazomethane	Same as LCS	Same as LCS
Performance Check Samples	Each Quarter	Set by NPS QA Officer See Section 12 QAPjP	At the Discretion of NPS QA Officer

Note: A corrective action form must be filed with the QAO and Program Manager for each of the above occurences.

12. PERFORMANCE AND SYSTEM AUDITS

Performance and System Audits

The Quality Assurance Officer will review this QAPjP with all personnel associated with this project to insure that they have read and understand it. Each analyst will sign a statement saying that they have read and understand the QAPjP and will conduct the analyses in accordance with it. The QA Officer or his assistant will conduct monthly formal system and data audits during which they will track a single sample set throughout the system to insure that the QAPjP is being implemented, that all systems are operating as expected and that data can be verified. These system audits will not be announced to the analytical staff prior to their being carried out. The analytical staff is expected to cooperate fully with the QA Officer during the audit. Any deficiencies will be reported immediately to the Program Manager, the Laboratory Director, the analyst's supervisor, and the Technical Monitor. A corrective action form will be filled out for each deficiency. The QC auditor verifies that the deficiency has been corrected during the next audit. The frequency of system audits will be increased if the frequency of QC problems increase.

A system audit will consist of tracking at least one sample set through every step of analysis and reporting. All steps in the system will be evaluated, even if the sample set did not require their use. For example, the maintenance logs will be checked during each audit, even if they were not needed for this sample set. The content of the system audit will include (but not be limited to):

Sample receipt and recordkeeping
Extraction/Analysis set assignment
Extraction recordkeeping
Sample and extract holding times
LCS and spike assignment
Standards preparation and recordkeeping
Random calculation checks
Check analysis forms for completeness
Instrumental log books
Instrument calibration
Instrument Control Standards and recordkeeping
Method Blank Results
Laboratory Spike sample results
Internal Standard results and recordkeeping
Surrogate Standard results and recordkeeping
Compound confirmation by confirmation column
Compound confirmation by GCMS
Compound Retention time recordkeeping
Internal QC sample results
Florisil check results and recordkeeping
Corrective action reports and followup
Reports to Management
Timeliness of reporting QC problems
Other QC related matters

Performance evaluation (PE) samples will be sent quarterly to the laboratory by the NPS Quality Assurance Officer (QAO). Each quarter the QAO will consult the Technical Monitors for Montgomery

Labs for recommendations on the analytes and on the analyte levels that should be included in the samples. The samples will be prepared in acetonitrile, verified by the EPA referee lab and then shipped to the lab in sealed glass ampules with instructions for analysis. Montgomery will be expected to report their results to the Technical Monitors in memo form by the study deadline as well as in the standard format required for all Survey samples. A minimum of three weeks will be allotted for the analysis and reporting activities associated with participation in the PE study.

The results will be evaluated both qualitatively and quantitatively. Qualitative acceptance criteria will be based on correct identification of all analytes known to be present in the PE sample and no false positives.

Quantitative acceptance criteria for the samples will be based on a statistical comparison of Montgomery's results with those achieved by the referee lab. Specifically, the referee lab will be asked to report seven values for the PE standard, so that using equation 12-1, a 99% confidence interval using the Student's "T" distribution can be constructed around the mean of the referee laboratory's results.

Equation 12-1: $x \pm (((t_{1-\alpha,n-1}) (s))/(n))$

where:
- x = mean
- t = value from Students "T" distribution for an α of . 005 and (n-1) degrees of freedom.
- s = standard deviation
- n = sample size

A confidence interval will likewise be constructed around the single value reported by Montgomery. However, rather than requesting multiple analyses to generate a value for standard deviation (s), the standard deviation will be taken from the control charts that were in effect at the time the PE was analyzed. Since the control charts are kept in terms of percent recovery, the PE results will be converted to a percent recovery based on the theoretical "true" value. The confidence interval based on percent recovery will then be converted to a range of concentrations. Criteria for acceptable performance will be that the confidence intervals generated from the referee analysis must overlap by at least one point with the confidence intervals generated from Montgomery's analysis.

A report of Montgomery's performance will be prepared by the NPS QAO in conjunction with a Survey statistician. Distribution of the report will include the Radian project manager, the Method 1 and 3 technical Monitor, the Survey Director, and the ODW and OPP QAOs.

13. PREVENTIVE MAINTENANCE

GC Analyses

Routine maintenance will be performed on the GC in accordance with the following schedule:

Task	Frequency
Clean detector	Monthly or as required (Method 1,3)
Change detector collector	As required by performance (Method 1)
Change detector bead	As required by performance
Bake out GC column	Daily or as required
Change GC column	As required by performance
Change injection port septa	Weekly or as required
Clean injection port liner	Monthly or as required by performance
Change GC gas filter traps	Every six months or as needed

The laboratory also maintains a service contract with Varian and a service representative is usually on the premises the same day the call for service is placed.

Critical spare parts are also available to minimize downtime and the following list of replacement parts and consumable spares is maintained within the laboratory at all times:

1) Columns (at least one of each type used)
2) Ferrules for columns
3) Syringes
4) Injection port septa
5) Detector collector (Method 1)
6) Detector beads (Method 1)

GCMS Analyses

The following schedule of maintenance tasks and spare parts applies to the Finnigan 5100, the Finnigan 4000, and the Hewlett Packard MSD.

Routine maintenance will be performed on the GCMS and purge and trap units in accordance with the following schedule:

Task	Frequency
Clean source	Monthly or as required by performance
Clean quadrapoles	Monthly or as required by performance
Bake out GC column	Daily or as required
Change GC column	As required by performance
Change injection port septa	Weekly or as required
Clean injection port liner	Monthly or as required by performance
Change GC gas filter traps	Every six months or as needed

Both of the instruments are under maintenance and service contracts which include emergency service and preventive maintenance. Usually the preventive maintenance checks include changing pump oil, source cleaning, disk alignment checks and others.

Critical spare parts are also available to minimize downtime and the following list of replacement parts and consumable spares is maintained within the laboratory at all times:

1) Columns (at least one of each type used)
2) Ferrules for columns
3) Syringes
4) Filaments (at least two of each)
5) Copper gaskets
6) Injection port septa
7) Vacuum pump oil

14. SPECIFIC PROCEDURES FOR ASSESSING MEASUREMENT SYSTEM DATA

The following formulas are used to calculate the data for the QC checks and for statistics related to QC checks.

Percent Recovery (R_i)

$$\text{Percent Recovery } (R_i) = \frac{(100 * \text{Determined Value of Spike or Standard})}{\text{True Value of Spike or Standard}}$$

Average Recovery (R)

$$\text{Average Recovery } (R) = \sum_{i=1}^{n} Ri/n$$

Standard Deviation (S_r)

$$\text{Standard Deviation } (Sr) = \sqrt{\frac{\left(\sum_{i=1}^{n} R - \bar{R}\right)^2}{n-1}}$$

where n = number of measurements for each analyte
R_i = individual percent recovery value
R = average percent recovery value

Control Limits

The control limits for control charts are calculated as follows:

Upper Control Limit (UCL) = $R + 3S_r$

Upper Warning Limit (UWL) = $R + 2S_r$

Lower Warning Limit (LWL) = $R - 2S_r$

Lower Control Limit (LCL) = $R - 3S_r$

Peak Symmetry Factor (PSF)

$$PSF = \frac{w(1/2)}{0.5 * W(1/2)}$$

Where w(1/2) = width of front of peak at half height assuming peak is split at its highest point and W(1/2) is the peak width at half height (see Figure 7 of Method 1).

Peak Gaussian Factor (PGF)

$$PGF = \frac{1.83 * W(1/2)}{W(1/10)}$$

Where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height (see Figure 7 of Method 1).

Resolution (R)

$$R = \frac{t}{W}$$

Where t is the difference in elution times between the two peaks and W is the average peak width at the baseline of the two peaks.

15. CORRECTIVE ACTION

Corrective action is required in response to an out-of-control event. Out-of-control events are signalled whenever a quality control sample or parameter falls outside of acceptance limits. The specific out-of-control events are listed in Section 11 of this QAPjP. Quality control parameters are evaluated for their acceptability on a daily basis according to the established acceptance limits and are monitored with control charts to detect trends in accuracy and variability which are indicative of a shift in the methodology caused by analytical error. The required frequency and acceptance limits for these parameters have been discussed in other sections of this plan. The exact corrective actions are also discussed in Section 11 of this QAPjP.

Any time a QC problem occurs the QC Officer, Program Manager and Sample Tracking and Reporting Clerk must be informed. If the problem is analytical, the supervisor of the section will also be informed.

The analyst or sample receipt clerk is the first to be aware when a QC parameter falls outside of the acceptance limits and has primary responsibility for notifying the QC Officer and the Program Manager and attempting to solve the problem. The analyst must keep the QC Officer and the Project Manager informed of specifically which QC parameter(s) were unacceptable and what area the analyst feels is the probable source of error. The method of notification will usually be by corrective action form. The analyst and the Program Manager then map out a strategy of diagnostic tests to verify whether this assessment is correct. It will be the responsibility of the Program Manager to insure that the QA problem was solved prior to sample analysis proceeding. An example of a corrective action form is included as Figure 15.1.

The corrective action form will include the following information:

- Date of out-of-control event
- Environmental samples impacted
- Brief description of the non-conformance
- Actions taken to resolve the non-conformance
- Conclusion/Disposition of the data

The corrective action form will be submitted to the QA Officer, Data Handling and Reporting Clerk, and the Program Manager. This information is included in the monthly progress reports submitted to the Technical Monitor (see Section 16 of this QAPjP).

FIGURE 15.1

CORRECTIVE ACTION REPORT

General Information:

Analysis Date:	_____	Analysis:	_____
Extraction Date:	_____	Matrix:	_____
Analyst:	_____	Instrument ID:	_____

Environmental samples impacted (Client/JMM ID):

Brief description of the non-conformance: *(Columns 1,2 & 3)*

Actions taken to resolve the non-conformance: *(Refer to Column 4)*

Conclusions/Disposition of the data: *(Refer to Column 5)*

Analyst _____ *Date:* _____

Group Leader _____ *Date:* _____

QA Officer _____ *Date:* _____

FIGURE 15.1 (continued)

IDENTIFICATION AND RESOLUTION OF QA PROBLEM EVENTS

PARAMETER	QA PROBLEM	SUSPECT	CORRECTIVE ACTION	DOCUMENTATION REQUIRED
Holding Times Exceeded				Report to immediate supervisor and the Analytical Services Manager. Complete a CORRECTIVE ACTION REPORT listing the affected sample IDs, and the reason that holding times were not met.
Instrument	Reduced sensitivity	Leaks, septa, bad lamps, columns	Repair/Replace as necessary.	Note any adjustments in the appropriate instrument maintenance log. Unless data have been generated under these conditions, no Corrective Action Report.
Calibration	Linearity	Bad injection: 1 standard.	Reanalyse 1 or more suspect standards.	If this corrects the trouble, simply make a note in the run log. No Corrective Action Report required unless samples run using the questionable curve.
	Daily criteria not met.	Bad standards.	Prepare fresh standards; rerun.	No Corrective Action Record required unless samples are analysed under unacceptable conditions. Note in log.
Blanks	Analytes in method blank.	Sample carryover.	Analyse 2nd blank.	Reanalyse any sample since last blank which contains analytes detected in the blank. If holding times have been exceeded, complete a CORRECTIVE ACTION REPORT.
	Analytes in prep blank.	Carryover.	See above.	See above.
		Extraction/ Digestion.	Re-extract samples.	Complete a CORRECTIVE ACTION REPORT. The data for any samples which cannot be re-extracted must be qualified.
Duplicates	Poor RPD-- Internal dups.	Bad aliquots.	Analyse a 2nd set of duplicates.	If acceptable precision is obtained, assume poor aliquotting. Note in run log; report 2nd set. If precision remains poor, complete a CORRECTIVE ACTION REPORT. Re-extract/analyse samples or qualify data.
	Poor RPD-- Client dups.	Bad aliquots.	See above.	See above.
		Field process.	Verify instrument precision.	Document on a CORRECTIVE ACTION REPORT that duplicate injections/analyses exhibit acceptable precision.
			Evaluate analytical precision.	If holding times permit, reprep/reanalyse samples. Document any samples that cannot be analysed with acceptable precision on a CORRECTIVE ACTION REPORT.
Matrix Spikes	Poor recovery	Spike:Bckgrnd. (5:5)	Note if 5:0 (1.0	Prepare a CORRECTIVE ACTION REPORT noting results relative to spike:background ratio. Accept data if associated LCS met acceptance criteria.
		Sample homogeneity.	Evaluate non-spike compounds RPDs.	If poor precision b/w non-spike compounds, try to document that laboratory & instrument precision are acceptable on a CORRECTIVE ACTION REPORT.
		Interference.	Identify peak/ quant. ion overlap.	Document the interference on a CORRECTIVE ACTION REPORT. Sample data is valid if associated LCS meet acceptance criteria.
LCS	Values outside acceptance criteria.	Extraction. Standards. Analysis.	Reprep/analyse if possible.	If samples cannot be reanalysed, report data with qualifiers. Complete a CORRECTIVE ACTION REPORT form identifying any affected samples.

16. QA REPORTS TO MANAGEMENT

Each day the Program Manager will meet with the Data Handling and Reporting Clerk to discuss the status of all samples sets. This will include the status of shipping, extractions, analysis, QC, data reporting and sample disposal. If needed, the Program Manager will discuss problems with the Laboratory Director, the Quality Assurance Officer and other Laboratory Managers. These problems could include QC problems, turnaround time problems, missing data problems, and personnel problems. It is our intention that these daily meetings will be able to keep all of these problems under control before they can seriously affect the overall project.

QA Audit Reports

The in-house QA audit reports will be written by the QA Officer or the Assistant. The audit report will be forwarded to the Project Manager , the Program Manager, and the Technical Monitor via the monthly report. The audit report will include the deficiencies noted as "major" or "minor". Both the major and minor issues should be resolved immediately in a formal response. The response will come from the Program Manager and will be forwarded to the Project Manager, the QA Officer, and the Technical Monitor.

Monthly Report Format

Six copies of the monthly report are to be provided within 15 calendar days after the end of the period being reported. The copies are to be sent to the appropriate Technical Monitor. The report will be prepared by the Program Manager. The report will be reviewed by the Project Manager and the QC Officer and signed off by the Project Manager and Program Manager.

The report format should contain the following information for the report period:

- Summary of progress
  - -- samples, received, analyses in progress
  - -- status of data processing for analyzed sets of samples
- Reports on standards
  - -- new dilutions and results of check before using
- Summary list of bench-level corrective actions
- Identification of problems about any phase of the project
- Copies of representative and unusual chromatograms
- Information requested by the Technical Monitor because of specific methodology or problems encountered

- Changes in any personnel working on the project
- Results of in-house system audits

APPENDIX A

NPS METHODS 1 AND 3

Method 1. Determination of Nitrogen- and Phosphorus-Containing Pesticides in Ground Water by Gas Chromatography with a Nitrogen-Phosphorus Detector

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain nitrogen- and phosphorus-containing pesticides in ground water. Analytes that can be determined using this method are listed in Table 1.

1.2 This method has been validated in a single laboratory. Estimated detection limits (EDLs) have been determined and are listed in Table 2. Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.2.

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by GC with a nitrogen-phosphorus detector (NPD).

2.2 An alternative manual liquid-liquid extraction method using separatory funnels is also described.

3. DEFINITIONS

3.1 Artificial ground water -- an aqueous matrix designed to mimic a real ground water sample. The artificial ground water should be reproducible for use by others.

3.2 Calibration standard -- a known amount of a pure analyte, dissolved in an organic solvent, analyzed under the same procedures and conditions used to analyze sample extracts containing that analyte.

3.3 Estimated detection limit (EDL) -- the minimum concentration of a substance that can be measured and reported with confidence that the analyte concentration is greater than zero as determined from the analysis of a sample in a given matrix containing the analyte. The EDL is equal to the level calculated by multiplying the standard deviation of replicate measurements times the students' t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom or the level of the compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately five, whichever value is higher.

3.4 Instrument quality control (QC) standard -- a MTBE solution containing specified concentrations of specified analytes. The instrument QC standard is analyzed each working day prior to the analysis of sample extracts and calibration standards. The performing laboratory uses this solution to demonstrate acceptable instrument performance in the areas of sensitivity, column performance, and chromatographic performance.

3.5 Internal standard -- a pure compound added to a sample extract in a known amount and used to calibrate concentration measurements of other analytes that are sample components. The internal standard must be a compound that is not a sample component.

3.6 Laboratory control standard -- a solution of analytes prepared in the laboratory by dissolving known amounts of pure analytes in a known amount of reagent water. In this method, the laboratory control standard is prepared by adding appropriate volumes of the appropriate standard solution to reagent water.

3.7 Laboratory method blank -- a portion of reagent water analyzed as if it were a sample.

3.8 Performance evaluation sample -- A water-soluble solution of method analytes distributed by the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, Ohio. A small measured volume of the solution is added to a known volume of reagent water and analyzed using procedures identical to those used for samples. Analyte true values are unknown to the analyst.

3.9 Quality control check sample -- a water soluble solution containing known concentrations of analytes prepared by a laboratory other than the laboratory performing the analysis. The performing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method. A small measured volume of the solution is added to a known volume of reagent water and analyzed with procedures identical to those used for samples. True values of analytes are known by the analyst.

3.10 Stock standard solution -- a concentrated solution containing a certified standard that is a method analyte, or a concentrated

solution of an analyte prepared in the laboratory with an assayed reference compound.

3.11 Surrogate standard -- a pure compound added to a sample in a known amount and used to detect gross abnormalities during sample preparation. The surrogate standard must be a compound that is not a sample component.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section 10.8.

4.1.1 Glassware must be scrupulously cleaned.[1] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the ground water sampled. Cleanup of sample extracts may be necessary. Positive identifications should be confirmed using the confirmation column specified in Table 3.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must 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 safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[2-4] for the information of the analyst.

6. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in Section 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

6.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Flask, Erlenmeyer -- 500-mL.

6.2.4 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

6.2.5 Evaporative flask, K-D -- 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.6 Snyder column, K-D -- three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.7 Snyder column, K-D -- two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.3 Separatory funnel shaker -- Capable of holding eight 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI).

6.4 Tumbler -- Capable of holding 4 to 6 tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA.).

6.5 Boiling stones -- Carborundum, #12 granules (Arthur H. Thomas Co. #1590-033). Heat at 400°C for 30 min prior to use. Cool and store in desiccator.

6.6 Water bath -- Heated, capable of temperature control (±2°C). The bath should be used in a hood.

6.7 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 GAS CHROMATOGRAPH -- Analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

6.8.1 Primary column -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 um film thickness (available from J&W). Validation data presented in this method were obtained using this column. Alternative columns may be used in accordance with the provisions described in Section 10.3.

6.8.2 Confirmation column -- 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 um film thickness (available from J&W).

6.8.3 Detector -- Nitrogen-phosphorus (NPD). A NPD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Section 10.3.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Acetone, methylene chloride, MTBE -- Distilled-in-glass quality or equivalent.

7.2 Phosphate buffer, pH7 -- Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

7.3 Sodium sulfate, granular, anhydrous, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.4 Sodium chloride (NaCl), crystal, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.5 o-Nitrotoluene -- >98% purity, for use as an internal standard (available from Aldrich Chemical Co.).

7.6 Triphenyl phosphate (TPP) -- >98% purity, for use as internal standard (available from Aldrich Chemical Co.).

7.7 1,3-Dimethyl-2-nitrobenzene -- >98% purity, for use as surrogate standard (available from Aldrich Chemical Co.).

7.8 9-Nitroanthracene -- >98% purity, for use as a surrogate standard (available from Aldrich Chemical Co.).

7.9 Reagent water -- Reagent water is defined as a water in which an interferent is not observed at or above the EDL of any analyte. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.10 STOCK STANDARD SOLUTIONS (1.00 ug/uL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.10.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. The stock solution for simazine should be prepared in methanol. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.10.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.

7.10.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.

7.11 INTERNAL STANDARD SPIKING SOLUTION -- Prepare the internal standard spiking solution by accurately weighing approximately 0.0150 g of pure o-nitrotoluene and 0.0500 g of pure TPP. Dissolve the o-nitrotoluene and TPP in MTBE and dilute to volume in a 100-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 uL of the internal standard spiking solution to 5 mL of sample extract results in final o-nitrotolene and TPP concentrations of 0.3 ug/mL and 5.0 ug/mL. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

7.12 SURROGATE STANDARD SPIKING SOLUTION -- Prepare the surrogate standard spiking solution by accurately weighing approximately 0.0250 g of pure 1,3-dimethyl-2-nitrobenzene and 0.0010 g of 9-nitroanthracene. Dissolve the 1,3-dimethyl-2-nitrobenzene and 9-nitroanthracene in MTBE and dilute to volume in a 100-mL volumetric flask. Transfer the surrogate standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 uL of the surrogate standard spiking solution to a 1-L sample prior to extraction results in 1,3-dimethyl-2-nitrobenzene and 9-nitroanthracene concentrations in the sample of 12.5 ug/L and 0.5 ug/L, respectively. Assuming quantitative surrogate recovery, addition of 50 uL of the surrogate standard spiking solution to a sample results in 1,3-dimethyl-2-nitrobenzene and 9-nitroanthracene concentrations in the final extract of 2.5 ug/mL and 0.1 ug/mL, respectively. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

7.13 INSTRUMENT QC STANDARD -- Prepare the instrument QC standard by adding 5 uL of the vernolate stock solution, 0.5 mL of the bromacil stock solution, 30 uL of the prometon stock solution, 15 uL of the atrazine stock solution, 1.0 mL of the surrogate spiking solution, and 500 uL of the internal standard spiking solution to a 100-mL volumetric flask. Dilute to volume with MTBE and thoroughly mix the solution. Transfer the instrument QC standard to a TFE-fluorocarbon-sealed screw cao bottle and store at room temperature. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices[5] should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling

site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.2.2 After the sample is collected in a bottle containing preservative, seal the bottle and shake vigorously for 1 min.

8.2.3 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results presented in Table 11 indicate that most of the target analytes present in samples are stable for 14 days when stored under these conditions. However, analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.3 EXTRACT STORAGE

8.3.1 Extracts should be stored at 4°C away from light. Preservation study results given in Table 11 indicate that most analytes are stable for 28 days; however, a 14-day maximum extract storage time is recommended. The analyst should verify appropriate extract holding times applicable to the samples under study.

9. CALIBRATION

9.1 Establish GC operating parameters equivalent to those indicated in Table 3. The GC system must be calibrated using the internal standard technique (Section 9.2).

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. TPP has been identified as a suitable internal standard.

9.2.1 Prepare calibration standards at a minimum of three (suggested five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with MTBE. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

9.2.2 Inject 2 uL of each calibration standard and tabulate the relative response for each analyte (RR_a) to an internal standard using the equation:

$$RR_a = A_a/A_{is}$$

where: A_a = the peak area of the analyte, and
A_{is} = the peak area of the internal standard.

Generate a calibration curve of analyte relative response, RR_a, versus analyte concentration in the sample in ug/L. Data presented in this report were generated using TPP for quantification calculations.

9.2.3 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a quality control (QC) program. The minimum requirements of this program consist of the following: an initial demonstration of laboratory capability; the analysis of surrogate standards in each and every sample as a continuing check on sample preparation; the monitoring of internal standard area counts or peak heights in each and every sample as a continuing check on system performance; the analysis of laboratory control standards, QC samples, and performance evaluation (PE) samples as continuing checks on laboratory performance; the analysis of spiked samples as a continuing check on recovery performance; the analysis of method blanks as a continuing check on contamination; and frequent analysis of the instrument QC standard to assure acceptable instrument performance.

10.2 INITIAL DEMONSTRATION OF CAPABILITY -- To establish the ability to perform this method, the analyst must perform the following operations.

10.2.1 Select a representative spike concentration (suggest 15 times the EDL) for each of the target analytes. Using a stock standard that differs from calibration standard, prepare a laboratory control (LC) check sample concentrate in methanol 1000 times more concentrated than the selected spike concentration.

10.2.2 Using a syringe, add 1 mL of the LC sample concentrate to each of a minimum of four 1-L aliquots of reagent water. A representative ground water may be used in place of the reagent water, but one or more unspiked

aliquots must be analyzed to determine background levels, and the spike level must, at a minimum, exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 11.

10.2.3 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (S_R), for the results. Ground water background corrections must be made before R and S_R calculations are performed.

10.2.4 Table 2 and Tables 4-9 provide single laboratory recovery and precision data obtained for the method analytes from reagent and artificial ground waters, respectively. Similar results from dosed reagent and artificial ground waters should be expected by any experienced laboratory. Compare results obtained in Section 10.2.3 to the single laboratory recovery and precision data. If the results are not comparable, review potential problem areas and repeat the test. Results are comparable if the calculated percent relative standard deviation (RSD) does not exceed 2.6 times the single laboratory RSD or 20 percent, whichever is greater, and your mean recovery lies within the interval $R \pm 3S$ or $R \pm 30\%$ whichever is greater.

10.3 In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.4 ASSESSING SURROGATE RECOVERY

10.4.1 All samples and blanks must be fortified with the surrogate spiking compound before extraction. A surrogate standard determination must be performed on all samples (including matrix spikes) and blanks.

10.4.2 Determine whether the measured surrogate concentration (expressed as percent recovery) falls between 70 and 130 percent.

10.4.3 When the surrogate recovery for a laboratory method blank is less than 70 or greater than 130 percent, the laboratory must take the following actions:

(1) Check calculations to make sure there are no errors.

(2) Check internal standard and surrogate standard spiking solutions for degradation, contamination, or other obvious abnormalities.

(3) Check instrument performance.

Reinject the laboratory method blank extract. If the reanalysis fails the 70 to 130 percent recovery criteria, the analytical system must be considered "out of control." The problem must be identified and corrected before continuing.

10.4.4 When the surrogate recovery for a sample is less than 70 percent or greater than 130 percent, the laboratory must establish that the deviation is not due to laboratory problems. The laboratory shall document deviations by taking the following actions:

(1) Check calculations to make sure there are no errors.

(2) Check internal standard and surrogate standard spiking solutions for degradation, contamination, or other obvious abnormalities.

(3) Check instrument performance.

Recalculate or reanalyze the extract if the above steps fail to reveal the cause of the noncompliant surrogate recoveries. If reanalysis of the sample or extract solves the problem, only submit the sample data from the analysis with surrogate spike recoveries within the required limits. If reanalysis of the sample or extract fails to solve the problem, then report all data for that sample as suspect.

10.5 ASSESSING THE INTERNAL STANDARD

10.5.1 An internal standard peak area or peak height check must be performed on all samples. All sample extracts must be fortified with the internal standard.

10.5.2 Internal standard recovery must be evaluated for acceptance by determining whether the measured peak area or peak height for the internal standard in any sample deviates by more than 30 percent from the average peak area or height for the internal standard in the calibration standards.

10.5.3 When the internal standard peak area or height for any sample is outside the limit specified in 10.5.2, the laboratory must investigate.

10.5.3.1 Single occurrence -- Reinject an aliquot of the extract to ensure proper sample injection. If the reinjected sample extract aliquot displays an internal standard peak area or height within specified limits, quan-

tify and report results. If the reinjected sample extract aliquot displays an internal standard peak area or height outside the specified limits, but extract aliquots from other samples continue to give the proper area or height for the internal standard, assume an error was made during addition of the internal standard to the failed sample extract. Repeat the analysis of that sample.

10.5.3.2 Multiple Occurrence -- If the internal standard peak areas or heights for successive samples fail the specified criteria (10.5.2), check the instrument for proper performance. After optimizing instrument performance, check the calibration curve using a calibration check standard (Section 9). If the calibration curve is still applicable and if the calibration check standard internal standard peak area or height is within ±30% of the average internal standard peak area or height for the calibration standards, re-analyze those sample extracts whose internal standard failed the specified criteria. If the internal standard peak areas or heights now fall within the specified limits, report the results. If the internal standard peak areas or heights still fail to fall within the specified limits or if the calibration curve is no longer applicable, then generate a new calibration curve (Section 9) and reanalyze those sample extracts whose internal standard failed the peak area or height criteria.

10.6 ASSESSING LABORATORY PERFORMANCE

10.6.1 The laboratory must, on an ongoing basis, analyze at least one laboratory control standard per sample set (a sample set is all those samples extracted within a 24-hour period).

10.6.1.1 The spiking concentration in the laboratory control standard should be 15 times the EDL.

10.6.1.2 Spike a 1-L aliquot of reagent water with a laboratory control (LC) sample concentrate (the volume of the spike should be kept to a minimum so the solubility of the analytes of interest in water will not be affected) and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (R_i) as (100xA)%/T,

where T is the known true concentration of the spike.

10.6.1.3 Compare the percent recovery (R_i) for each analyte with established QC acceptance criteria. QC criteria are established by initially analyzing five laboratory control standards and calculating the average percent recovery (R) and the standard deviation of the percent recovery (S_R) using the following equations:

$$R = \sum_{i=1}^{n} R_i/n$$

and

$$S_R = \frac{1}{n-1} \sum_{i=1}^{n} R_i^2 - \frac{\left(\sum_{i=1}^{n} R_i\right)^2}{n}$$

where: n = number of measurements for each analyte, and
R_i = individual percent recovery value.

Calculate QC acceptance criteria as follows:

Upper Control Limit (UCL) = $R + 3S_R$
Lower Control Limit (LCL) = $R - 3S_R$

Alternatively, the data generated during the initial demonstration of capability (Section 10.2) can be used to set the initial upper and lower control limits.

Update the performance criteria on a continuous basis. After each five to ten new recovery measurements (R_is), recalculate R and S_R using all the data, and construct new control limits. When the total number of data points reach twenty, update the control limits by calculating R and S_R using only the most recent twenty data points.

Monitor all data from laboratory control standards. Analyte recoveries must fall within the established control limits.

If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the source of the problem must be immediately identified and resolved before continuing the analyses. The analytical result for that analyte in samples is suspect and must be so labeled. All results for that analyte in that sample set must also be labeled suspect.

10.6.2 Each quarter, it is essential that the laboratory analyze (if available) QC check standards. If the criteria established by the U.S. Environmental Protection Agency (USEPA) and provided with the QC standards are not met, corrective action needs to be taken and documented.

10.6.3 The laboratory must analyze an unknown performance evaluation sample (when available) at least once a year. Results for each of the target analytes need to be within acceptable limits established by USEPA.

10.7 ASSESSING ANALYTE RECOVERY

10.7.1 The laboratory must, on an ongoing basis, spike each of the target analytes into ten percent of the samples.

10.7.1.1 The spiking concentration in the sample should be one to five times the background concentration, or, if it is impractical to determine background levels before spiking, 15 times the EDL.

10.7.1.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. Spike a second sample aliquot with a laboratory control (LC) sample concentrate (the volume of the spike should be kept to a minimum so the solubility of the analytes of interest in water will not be affected) and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (R_i) as $100(A-B)\%/T$, where T is the known true concentration of the spike.

10.7.1.3 Compare the percent recovery (R_i) for each analyte with QC acceptance criteria established from the analyses of laboratory control standards.

Monitor all data from dosed samples. Analyte recoveries must fall within the established control limits.

10.7.1.4 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is judged to be in control, the recovery problem encountered with the dosed sample is judged to be matrix-related, not system-related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

10.8 ASSESSING LABORATORY CONTAMINATION (METHOD BLANKS) -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. This is accomplished by the analysis of a laboratory method blank. A laboratory method blank is a 1-L aliquot of reagent water analyzed as if it was a sample. Each time a set of samples is extracted or there is a change in reagents, a laboratory method blank must be processed to assess laboratory contamination. If the method blank exhibits a peak within the retention time window of any analyte which is greater than or equal to one-half the EDL for that analyte, determine the source of contamination before processing samples and eliminate the interference problem.

10.9 ASSESSING INSTRUMENT PERFORMANCE (INSTRUMENT QC STANDARD) -- Instrument performance should be monitored on a daily basis by analysis of the instrument QC standard. The instrument QC standard contains compounds designed to indicate appropriate instrument sensitivity, column performance and chromatographic performance. Instrument QC standard components and performance criteria are listed in Table 10. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the GC-NPD system. A GC-NPD chromatogram generated from the analysis of the instrument QC standard is shown in Figure 1. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs. An instrument QC standard should be analyzed with each sample set.

10.10 ANALYTE CONFIRMATION - When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry or a second gas chromatography column must be used. A suggested confirmation column is described in Table 3.

10.11 ADDITIONAL QC - 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.

11. PROCEDURE

11.1 AUTOMATED EXTRACTION METHOD -- Validation data presented in this method were generated using the automated extraction procedure with the mechanical tumbler.

11.1.1 Add preservative to samples not previously preserved (Section 8.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike the sample with 50 uL of the surrogate standard spiking solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.1.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer.

11.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.1.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. 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 upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask containing approximately 5 g anhydrous sodium sulfate. Swirl flask to dry extract; allow flask to sit for 15 min.

11.1.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 MANUAL EXTRACTION METHOD -- Alternative procedure.

11.2.1 Add preservative to samples not previously preserved (Section 8.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike the sample with 50 uL of the surrogate standard spiking solution. Pour the entire sample into a 2-L separatory funnel.

11.2.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer.

11.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. 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 upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask containing approximately 5 g anhydrous sodium sulfate.

11.2.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Swirl flask to dry extract; allow flask to sit for 15 min.

11.2.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Decant the methylene chloride extract into the K-D concentrator. Rinse the remaining sodium sulfate with two 25-mL portions of methylene chloride and decant the rinses into the K-D concentrator.

11.3.2 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 65 to 70°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. 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 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

11.3.4 Add 50 uL of the internal standard spiking solution to the sample extract, seal, and shake to distribute the internal standard. Transfer extract to an appropriate-sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-NPD.

11.5 GAS CHROMATOGRAPHY

11.5.1 Table 3 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 3 are retention times observed using this method. Examples of the separations achieved using these conditions are shown in Figures 2-6. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.3 are met.

11.5.2 Calibrate the system daily as described in Section 9. The standards and extracts must be in MTBE.

11.5.3 Inject 2 uL of the sample extract. Record the resulting peak size in area units.

11.5.4 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 a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

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

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the relative response for the analyte to the internal standard (RR_a) using the calibration curve described in Section 9.2.2.

12.2 For samples processed as part of a set where the laboratory control standard recovery falls outside of the control limits in Section 10, data for the affected analytes must be labeled as suspect.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range. Analytes were divided into five spiking groups (A-E) for recovery studies. EDL data are given in Table 2. Method range data are given in Tables 4-7.

13.2 In a single laboratory, analyte recoveries from two artificial ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analytes were divided into five spiking groups (A-E) for recovery studies. Analyte recoveries from the two artificial matrices are given in Tables 8 and 9.

13.3 In a single laboratory, analyte recoveries from a ground water preserved with mercuric chloride were determined 0, 14, and 28 days after sample preparation. Sample extracts were also reanalyzed after they were stored for 28 days at -4°C and protected from light. Results were used to predict expected analyte stability in ground water samples and sample extracts. Analytes were divided into five spiking groups (A-E) for recovery studies. Analyte recoveries from the preserved, spiked ground water samples and stored sample extracts are given in Table 11.

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TABLE 1. METHOD ANALYTES

Analyte	CAS No. (a)	Ident. Code (b)
Alachlor	15972-60-8	D7
Ametryn	834-12-8	A7
Aspon (c)	3244-90-4	D9
Atraton	111-44-4	D5
Atrazine	1912-24-9	B3
Azinphos methyl (c)	86-50-0	D14
Bolstar (c)	35400-46-4	E10
Bromacil	314-40-9	D8
Butachlor	23184-66-9	C10
Butylate	2008-41-5	D2
Carboxin	5234-68-5	C11
Chlorpropham	101-21-3	D4
Cycloate	1134-23-2	A3
Demeton-O (c)	298-03-3	A2
Demeton-S	126-75-0	C3
Diazinon	333-41-5	C1
Dichlofenthion (c)	97-17-6	C5
Dichlorvos	62-73-7	E1
Diphenamid	957-51-7	B11
Disulfoton	298-04-4	A5
Disulfoton sulfone	2497-06-5	B12
Disulfoton sulfoxide (c)	2497-07-6	D1
EPN (c)	2104-64-5	E12
EPTC	759-94-4	B1
Ethion (c)	563-12-2	A10
Ethoprop	13194-48-4	B2
Ethyl parathion (c)	56-38-2	A9
Famphur (c)	52-85-7	A12
Fenamiphos	22224-92-6	A10
Fenarimol	60168-88-9	E13
Fenitrothion (c)	122-14-5	A8
Fensulfothion (c)	115-90-2	D12
Fenthion (c)	55-38-9	C8
Fonofos (c)	944-22-9	B5
Fluridone	59756-60-4	E14
Hexazinone	51235-04-2	D13
Malathion (c)	121-75-5	E8
Merphos	150-50-5	B13
Methyl paraoxon	950-35-6	B6
Methyl parathion (c)	298-00-0	B7
Metolachlor	51218-45-2	C7
Metribuzin	21087-64-9	C6
Mevinphos	7786-34-7	A1

TABLE 1. METHOD ANALYTES (continued)

Analyte	CAS No. (a)	Ident. Code (b)
MGK 264	113-48-4	C9
MGK 326 (c)	136-45-8	A6
Molinate	2212-67-1	D3
Napropamide	15299-99-7	E9
Norflurazon	27314-13-2	C12
Pebulate	1114-71-2	E2
Phorate (c)	298-02-2	E4
Phosmet (c)	732-11-6	E11
Prometon (c)	1610-18-0	A4
Prometryn	7287-19-6	B8
Pronamide (c)	23950-58-5	D6
Propazine	139-40-2	B4
Simazine	122-34-9	E5
Simetryn	1014-70-6	E7
Stirofos	22248-79-9	D10
Tebuthiuron	34014-18-1	E3
Terbacil	5902-51-2	E6
Terbufos (c)	13071-79-9	C4
Terbutryn	886-50-0	B9
Triademefon	43121-43-3	B10
Tricyclazole	41814-78-2	D11
Vernolate	1929-77-7	C2

(a) CAS No. = Chemical Abstracts Service registry number.

(b) Code used for identification of peaks in figures; letter indicates spiking mixture which contained each analyte; IS = TPP internal standard; SUR = 1,3-dimethyl-3-nitrobenzene surrogate standard.

(c) Compound shows aqueous instability.

TABLE 2. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 1) AND EDLs (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)	EDL(f)
Alachlor	0.38	ND (g)	8	119	0.0468	10	0.38
Ametryn	2.0	ND	8	100	0.0678	3	2.0
Aspon	0.25	ND	8	131	0.0288	9	0.25
Atraton	0.60	ND	8	120	0.0580	8	0.60
Atrazine	0.13	ND	8	101	0.00505	4	0.13
Azinphos methyl	2.2	ND	8	110	0.158	6	2.2
Bolstar	0.13	ND	8	107	0.0131	9	0.13
Bromacil	2.5	0.00182	8	113	0.229	8	2.5
Butachlor	0.38	ND	8	99	0.0407	11	0.38
Butylate	0.15	ND	8	93	0.0178	13	0.15
Carboxin	0.60	ND	8	101	0.0584	10	0.60
Chlorpropham	0.50	0.0842	8	124	0.0669	11	0.50
Cycloate	0.25	ND	8	101	0.00725	3	0.25
Demeton-O	0.60	ND	8	35	0 0360	17	0.60
Demeton-S	0.25	ND	8	90	0 0129	6	0.25
Diazinon	0.25	ND	8	94	0.0433	18	0.25
Dichlofenthion	0.10	ND	8	100	0.0145	14	0.1
Dichlorvos	2.5	ND	8	78	0.0933	5	2.5
Diphenamid	0.60	ND	8	84	0.0273	5	0.60
Disulfoton	0.30	ND	8	100	0.00955	3	0.30
Disulfoton sulfone (h)	3.8	ND	7	94	0.202	6	3.8
Disulfoton sulfoxide	0.38	ND	7	110	0.0261	6	0.38
EPN	0.050	ND	8	92	0.0136	29	0.050
EPTC	0.25	ND	8	87	0.0266	12	0.25
Ethion	0.30	ND	8	96	0.0167	7	0.30
Ethoprop	0.19	ND	8	108	0.00699	3	0.19
Ethyl parathion	0.45	0.217	8	80	0.0317	9	0.45
Famphur	0.60	ND	8	94	0.0273	5	0.60
Fenamiphos	1.0	ND	8	91	0.0386	4	1.0
Fenarimol	0.38	ND	8	92	0.0681	19	0.38
Fenitrothion	0.45	ND	8	119	0.0244	5	0.45
Fensulfothion	2.5	ND	8	111	0.191	7	2.5
Fenthion	0.10	ND	8	82	0.00570	7	0.10
Fluridone	3.8	ND	7	78	0.882	30	3.8
Fonofos	0.65	ND	8	95	0.0581	9	0.65
Hexazinone	0.76	ND	8	127	0.0508	5	0.76
Malathion	0.38	ND	8	98	0.0343	9	0.38
Merphos	0.25	ND	8	101	0.0135	5	0.25
Methyl paraoxon	2.5	ND	8	100	0.101	4	2.5
Methyl parathion	0.19	ND	8	96	0.00582	3	0.19
Metolachlor	0.75	ND	8	94	0.0619	9	0.75
Metribuzin	0.15	ND	8	114	0.00964	6	0.15

TABLE 2. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 1) AND EDLs (a) (continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)	EDL(f)
Mevinphos	5.0	ND	8	92	0.291	6	5.0
MGK 264	0.50	ND	8	101	0.0628	12	0.50
MGK 326	0.15	ND	8	90	0.0121	9	0.15
Molinate	0.15	ND	8	117	0.0202	12	0.15
Napropamide	0.25	ND	8	97	0.0230	9	0.25
Norflurazon	0.50	0.0585	8	86	0.0326	8	0.50
Pebulate	0.13	ND	8	84	0.00719	7	0.13
Phorate	0.30	ND	8	87	0.0279	11	0.30
Phosmet	0.75	ND	8	101	0.0485	6	0.75
Prometon	0.30	ND	7	48	0.0129	9	0.30
Prometryn	0.19	ND	8	88	0.00801	5	0.19
Pronamide	0.76	ND	8	123	0.0934	10	0.76
Propazine	0.13	ND	8	93	0.00455	4	0.13
Simazine	0.075	ND	8	99	0.00467	6	0.075
Simetryn	0.25	ND	8	97	0.0118	5	0.25
Stirofos	0.76	0.0132	8	121	0.0604	7	0.76
Tebuthiuron	1.3	ND	8	101	0.193	15	1.3
Terbacil	4.5	ND	8	100	0.186	4	4.5
Terbufos	0.50	ND	8	91	0.0190	4	0.50
Terbutryn	0.25	ND	8	91	0.0102	4	0.25
Triademefon	0.65	ND	8	95	0.0311	5	0.65
Tricyclazole	1.0	ND	8	216	0.0716	3	1.0
Vernolate	0.13	ND	8	100	0.0184	14	0.13

(a) Data corrected for amount detected in blank; average recovery of 1,3-dimethyl-2-nitrobenzene surrogate standard from eight spiked reagent water samples was 93% (6.3 percent relative standard deviation).

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) EDL = estimated detection limit in sample in ug/L; calculated by multiplying standard deviation (S) times the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

(g) ND = interference not detected in blank.

(h) EDL calculated using spiking level 2; analyte was not detected at spiking level 1.

TABLE 3. PRIMARY AND CONFIRMATION ANALYSIS CONDITIONS

Analyte	Relative or Absolute Retention Time	
	Primary (a,d)	Confirmation (b,e)
Alachlor	0.765	34.10
Ametryn	0.766	34.52
Aspon	0.797	35.10
Atraton	0.665	29.97
Atrazine	0.676	31.23
Azinphos methyl	1.066	49.58
Bolstar	0.958	(c)
Bromacil	0.792	40.00
Butachlor	0.882	39.00
Butylate	0.478	18.47
Carboxin	0.910	42.05
Chlorpropham	0.619	(c)
Cycloate	0.608	29.67
Demeton-O	0.576	24.88
Demeton-S	0.663	(c)
Diazinon	0.707	(c)
Dichlofenthion	0.733	32.28
Dichlorvos	0.352	15.35
1,3-Dimethyl-2-nitrobenzene (SUR1)	0.308	(c)
Diphenamid	0.827	37.97
Disulfoton	0.711	30.90
Disulfoton sulfone	0.879	42.42
Disulfoton sulfoxide	0.406	(c)
EPN	1.031	47.42
EPTC	0.427	16.57
Ethion	0.948	42.65
Ethoprop	0.608	26.42
Ethyl parathion	0.799	37.13
Famphur	0.967	46.38
Fenamiphos	0.889	41.00
Fenarimol	1.092	50.02
Fenitrothion	0.774	36.22
Fensulfothion	0.937	44.42
Fenthion	0.796	35.90
Fluridone	1.206	59.07
Fonofos	0.677	30.25
Hexazinone	0.991	47.80
Malathion	0.789	36.12
Merphos (f)	0.901	39.28
Methyl paraoxon	0.757	34.10
Methyl parathion	0.742	35.10
Metolachlor	0.803	35.70

TABLE 3. PRIMARY AND CONFIRMATION ANALYSIS CONDITIONS (continued)

Analyte	Relative or Absolute Retention Time	
	Primary (a,d)	Confirmation (b,e)
Metribuzin	0.749	34.73
Mevinphos	0.479	21.92
MGK 264 (g)	0.824	36.73
MGK 326	0.695	33.53
Molinate	0.546	22.47
Napropamide	0.890	(c)
9-Nitroanthracene (SUR2)	0.872	(c)
o-Nitrotoluene (IS1)	0.255	(c)
Norflurazon	0.977	47.58
Pebulate	0.498	19.73
Phorate	0.625	27.73
Phosmet	1.027	47.93
Prometon	0.672	30.00
Prometryn	0.769	34.23
Pronamide	0.697	32.63
Propazine	0.681	31.13
Simazine	0.670	31.32
Simetryn	0.760	34.55
Stirofos	0.878	39.65
Tebuthiuron	0.535	42.77
Terbacil	0.719	(c)
Terbufos	0.693	(c)
Terbutryn	0.783	34.80
Triademefon	0.811	37.00
Tricyclazole	0.899	44.33
Vernolate	0.488	19.25

TABLE 3. PRIMARY AND CONFIRMATION ANALYSIS CONDITIONS (continued)

FOOTNOTES

(a) Retention time relative to TPP internal standard (IS2) which elutes at approximately 47 min.

(b) Absolute retention time in minutes.

(c) Data not available.

(d) Primary conditions:

Column:	30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 um film thickness (J&W).
Injection volume:	2 uL splitless with 45 second delay
Carrier gas:	He @ 30 cm/sec linear velocity
Injector temp:	250°C
Detector temp:	300°C
Oven temp:	Program from 60°C to 300°C at 4°C/min
Detector:	NPD

(e) Confirmation conditions:

Column:	30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 um film thickness (J&W).
Injection volume:	2 uL splitless with 45 second delay
Carrier gas:	He @ 30 cm/sec linear velocity
Injector temp:	250°C
Detector temp:	300°C
Oven temp:	Program from 60°C to 300°C at 4°C/min
Detector:	NPD

(f) Merphos is converted to S,S,S-tributyl phosphorotrithioate (DEF) in the hot GC injection port; DEF is actually detected using these analyses conditions.

(g) MGK 264 gives two peaks; peak identified in this table used for quantification.

TABLE 4. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 2) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	1.9	ND (f)	7	95	0.118	6
Ametryn	10	ND	7	44	1.16	13
Aspon	1.3	ND	8	98	0.0774	6
Atraton	3.0	ND	7	85	0.158	6
Atrazine	0.63	ND	8	93	0.0305	5
Azinphos methyl	11	ND	8	96	0.411	4
Bolstar	0.63	ND	7	85	0.0282	5
Bromacil	13	ND	7	86	0.494	5
Butachlor	3.8	ND	8	96	0.149	4
Butylate	0.76	ND	7	92	0.112	16
Carboxin	6.0	ND	8	102	0.274	4
Chlorpropham	2.5	ND	7	96	0.178	7
Cycloate	1.3	ND	6	80	0.114	11
Demeton-O	3.0	ND	6	67	0.365	18
Demeton-S	2.5	ND	8	114	0.141	5
Diazinon	2.5	ND	8	115	0.183	6
Dichlofenthion	1.0	ND	8	101	0.0470	5
Dichlorvos	13	ND	7	87	0.866	8
Diphenamid	3.0	ND	8	93	0.156	6
Disulfoton	1.5	ND	7	85	0.155	12
Disulfoton sulfone	3.8	ND	7	94	0.202	6
Disulfoton sulfoxide	1.9	ND	7	110	0.230	11
EPN	0.25	ND	7	96	0.0206	9
EPTC	1.3	ND	7	83	0.104	10
Ethion	1.5	ND	7	75	0.381	34
Ethoprop	1.0	ND	7	94	0.0798	8
Ethyl parathion	2.3	ND	7	87	0.285	14
Famphur	3.0	ND	7	90	0.382	14
Fenamiphos	5.0	ND	7	88	0.610	14
Fenarimol	1.9	ND	7	97	0.0956	5
Fenitrothion	2.3	ND	7	87	0.280	14
Fensulfothion	13	ND	8	95	0.833	7
Fenthion	1.0	ND	7	97	0.0632	7
Fluridone	19	ND	7	107	1.132	6
Fonofos	3.3	ND	8	98	0.239	7
Hexazinone	3.8	ND	7	90	0.0968	3
Malathion	1.9	ND	7	94	0.110	6
Merphos	1.3	ND	8	91	0.0647	5
Methyl paraoxon	13	ND	8	99	1.33	10
Methyl parathion	1.0	ND	8	92	0.0912	10
Metolachlor	7.5	ND	8	93	0.287	4
Metribuzin	1.5	ND	8	101	0.0703	5

TABLE 4. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 2) (a)
(continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Mevinphos	25	ND	7	93	3.20	14
MGK 264	5.0	ND	8	100	0.220	4
MGK 326	1.5	ND	7	38	0.108	19
Molinate	0.76	ND	7	99	0.0622	8
Napropamide	1.3	ND	7	94	0.0569	5
Norflurazon	5.0	ND	8	94	0.232	5
Pebulate	0.63	ND	7	81	0.0398	8
Phorate	1.5	ND	7	92	0.101	7
Phosmet	3.8	ND	7	99	0.212	6
Prometon	1.5	ND	7	63	0.158	17
Prometryn	1.0	ND	7	90	0.0441	5
Pronamide	3.8	ND	7	87	0.203	6
Propazine	0.63	ND	8	100	0.0492	8
Simazine	0.38	ND	7	89	0.0221	6
Simetryn	1.3	ND	7	89	0.0676	6
Stirofos	3.8	ND	7	82	0.146	5
Tebuthiuron	6.3	ND	7	111	0.705	10
Terbacil	23	ND	7	88	1.89	9
Terbufos	2.5	ND	8	97	0.179	4
Terbutryn	1.3	ND	7	93	0.0530	4
Triademefon	3.3	ND	8	93	0.180	6
Tricyclazole	5.0	ND	7	83	0.157	4
Vernolate	1.3	ND	8	93	0.0702	6

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 5. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 3)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	3.8	ND (f)	8	95	0.390	11
Ametryn	20	ND	8	91	1.91	11
Aspon	2.5	ND	8	97	0.147	6
Atraton	6.0	ND	8	91	0.640	12
Atrazine	1.3	ND	8	92	0.103	9
Azinphos methyl	22	ND	8	94	1.87	9
Bolstar	1.3	ND	8	77	0.0900	9
Bromacil	25	ND	8	91	2.26	10
Butachlor	3.8	ND	8	96	0.149	4
Butylate	1.5	ND	6	97	0.321	22
Carboxin	6.0	ND	8	102	0.274	4
Chlorpropham	5.0	ND	8	93	0.554	12
Cycloate	2.5	ND	8	89	0.234	10
Demeton-O	6.0	ND	8	78	0.523	11
Demeton-S	2.5	ND	8	114	0.141	5
Diazinon	2.5	ND	8	115	0.183	6
Dichlofenthion	1.0	ND	8	101	0.0470	5
Dichlorvos	25	ND	8	97	1.39	6
Diphenamid	6.0	ND	8	93	0.501	9
Disulfoton	3.0	ND	8	89	0.287	11
Disulfoton sulfone	7.5	ND	8	98	0.722	10
Disulfoton sulfoxide	3.8	ND	8	87	0.441	13
EPN	0.50	ND	8	90	0.0201	4
EPTC	2.5	ND	8	85	0.230	11
Ethion	3.0	ND	8	91	0.262	10
Ethoprop	1.9	ND	8	103	0.0889	5
Ethyl parathion	4.5	ND	8	92	0.392	9
Famphur	6.0	ND	8	93	0.510	9
Fenamiphos	10	ND	8	90	0.840	9
Fenarimol	3.8	ND	8	99	0.185	5
Fenitrothion	4.5	ND	8	94	0.407	10
Fensulfothion	25	ND	8	97	1.17	5
Fenthion	1.0	ND	8	96	0.0680	7
Fluridone	38	ND	8	87	3.28	10
Fonofos	6.5	ND	8	89	0.534	9
Hexazinone	7.6	ND	8	90	0.532	8
Malathion	3.8	ND	8	84	0.189	6
Merphos	2.5	ND	8	96	0.201	8
Methyl paraoxon	25	ND	8	98	2.47	10
Methyl parathion	1.9	ND	8	97	0.177	10
Metolachlor	7.5	ND	8	93	0.287	4
Metribuzin	1.5	ND	8	101	0.0703	5

TABLE 5. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 3) (continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Mevinphos	50	ND	8	95	5.04	11
MGK 264	5.0	ND	8	100	0.220	4
MGK 326	1.5	ND	8	87	0.146	11
Molinate	1.5	ND	8	98	0.259	18
Napropamide	2.5	ND	8	101	0.143	6
Norflurazon	5.0	ND	8	94	0.232	5
Pebulate	1.3	ND	8	94	0.104	9
Phorate	3.0	ND	8	78	0.173	7
Phosmet	7.5	ND	8	86	0.310	5
Prometon	3.0	ND	8	78	0.267	11
Prometryn	1.9	ND	8	93	0.165	9
Pronamide	7.6	ND	8	91	0.776	11
Propazine	1.3	ND	8	92	0.103	9
Simazine	0.75	ND	8	100	0.0508	7
Simetryn	2.5	ND	8	99	0.131	5
Stirofos	7.6	ND	8	98	0.459	6
Tebuthiuron	13	ND	8	84	1.15	11
Terbacil	45	ND	8	97	2.41	6
Terbufos	5.0	ND	8	97	0.179	4
Terbutryn	2.5	ND	8	94	0.214	9
Triademefon	6.5	ND	8	93	0.539	9
Tricyclazole	10	ND	8	86	0.675	8
Vernolate	1.3	ND	8	93	0.0673	6

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 6. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 4)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	9.4	ND (f)	8	95	0.531	6
Ametryn	50	ND	8	104	5.69	11
Aspon	6.3	ND	8	90	0.356	6
Atraton	15	ND	8	94	0.727	5
Atrazine	3.1	ND	7	96	0.158	5
Azinphos methyl	56	ND	8	105	4.53	8
Bolstar	3.1	ND	7	100	0.400	13
Bromacil	63	ND	8	94	3.00	5
Butachlor	9.4	ND	7	96	0.261	3
Butylate	3.8	ND	8	62	0.341	15
Carboxin	15	ND	7	89	0.598	4
Chlorpropham	13	ND	8	92	0.668	6
Cycloate	6.3	ND	8	104	0.724	11
Demeton-O	15	ND	8	93	1.89	14
Demeton-S	6.3	ND	7	96	0.394	7
Diazinon	6.3	ND	7	97	0.350	6
Dichlofenthion	2.5	ND	7	91	0.124	5
Dichlorvos	63	ND	8	92	5.31	9
Diphenamid	15	ND	7	93	0.607	4
Disulfoton	7.5	ND	8	105	0.879	11
Disulfoton sulfone	19	ND	7	91	0.669	4
Disulfoton sulfoxide	9.4	ND	8	104	1.48	15
EPN	1.3	ND	8	99	0.162	13
EPTC	6.3	ND	7	90	0.414	7
Ethion	7.5	ND	8	106	0.762	10
Ethoprop	4.8	ND	7	88	0.457	11
Ethyl parathion	11	ND	8	108	1.22	10
Famphur	15	ND	8	103	1.54	10
Fenamiphos	25	ND	8	102	2.60	10
Fenarimol	9.4	ND	8	84	1.09	14
Fenitrothion	11	ND	8	107	1.18	10
Fensulfothion	63	ND	8	101	5.26	8
Fenthion	2.5	ND	6	88	8.47	10
Fluridone	94	ND	7	88	8.47	10
Fonofos	16	ND	7	89	1.18	8
Hexazinone	19	ND	8	96	1.22	7
Malathion	9.4	ND	7	105	1.16	12
Merphos	6.3	ND	7	95	0.350	6
Methyl paraoxon	63	ND	7	90	2.93	5
Methyl parathion	4.8	ND	7	89	0.232	5
Metolachlor	19	ND	7	98	1.28	7
Metribuzin	3.8	ND	7	97	0.259	7

TABLE 6. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 4)
(continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Mevinphos	125	ND	8	99	12.0	10
MGK 264	13	ND	7	95	0.275	2
MGK 326	3.8	ND	8	107	0.379	9
Molinate	3.8	ND	8	101	0.478	12
Napropamide	6.3	ND	8	84	0.479	9
Norflurazon	13	ND	7	85	0.772	7
Pebulate	3.1	ND	8	86	0.288	11
Phorate	7.5	ND	7	91	1.02	15
Phosmet	19	ND	8	103	2.46	13
Prometon	7.5	ND	8	102	0.815	11
Prometryn	4.8	0.582	7	129	0.277	4
Pronamide	19	ND	8	96	1.12	6
Propazine	3.1	ND	7	92	0.194	7
Simazine	1.9	ND	8	86	0.115	7
Simetryn	6.3	ND	8	84	0.435	8
Stirofos	19	ND	8	91	1.12	7
Tebuthiuron	31	ND	8	82	1.34	5
Terbacil	113	ND	8	82	11.8	13
Terbufos	13	ND	7	94	0.544	4
Terbutryn	6.3	ND	7	91	0.221	4
Triademefon	16	ND	7	92	0.595	4
Tricyclazole	25	ND	8	92	1.61	7
Vernolate	3.1	ND	7	83	0.124	5

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 7. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 5)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	38	ND (f)	8	94	2.35	7
Ametryn	200	ND	8	98	5.81	3
Aspon	25	ND	8	93	1.31	6
Atraton	60	ND	8	90	3.76	7
Atrazine	13	ND	8	93	0.548	5
Azinphos methyl	224	ND	7	64	23.3	16
Bolstar	13	ND	8	95	0.878	7
Bromacil	250	ND	8	93	16.5	7
Butachlor	38	ND	8	90	2.25	7
Butylate	15	ND	8	78	1.01	9
Carboxin	60	ND	8	96	5.38	9
Chlorpropham	50	ND	8	93	3.21	7
Cycloate	25	ND	8	100	0.725	3
Demeton-O	60	ND	7	85	3.29	6
Demeton-S	25	ND	8	86	1.51	7
Diazinon	25	ND	8	88	2.07	9
Dichlofenthion	10	ND	8	90	0.458	5
Dichlorvos	250	ND	8	96	14.5	6
Diphenamid	60	ND	8	94	2.01	4
Disulfoton	30	ND	8	99	0.851	3
Disulfoton sulfone	75	ND	8	88	2.09	3
Disulfoton sulfoxide	38	ND	8	84	3.02	9
EPN	5.0	ND	8	95	0.307	6
EPTC	25	ND	8	88	1.46	7
Ethion	30	ND	7	94	2.00	7
Ethoprop	19	ND	8	93	0.973	5
Ethyl parathion	45	ND	7	93	2.64	6
Famphur	60	ND	7	99	1.75	3
Fenamiphos	100	ND	8	98	2.72	3
Fenarimol	38	ND	8	104	3.18	8
Fenitrothion	45	ND	7	96	1.87	4
Fensulfothion	250	ND	8	91	9.31	4
Fenthion	10	ND	8	89	0.726	8
Fluridone	375	ND	8	98	28.8	8
Fonofos	65	ND	8	94	2.92	5
Hexazinone	76	ND	8	93	3.52	5
Malathion	38	ND	8	97	2.28	6
Merphos	25	ND	8	101	1.00	4
Methyl paraoxon	250	ND	8	92	10.0	4
Methyl parathion	19	ND	8	94	0.712	4
Metolachlor	75	ND	8	92	4.44	6
Metribuzin	15	ND	8	91	0.885	7

TABLE 7. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 5) (continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Mevinphos	500	ND	8	89	17.9	4
MGK 264	50	ND	8	90	3.76	8
MGK 326	15	ND	7	94	0.794	6
Molinate	15	ND	8	87	0.912	7
Napropamide	25	ND	8	102	2.39	9
Norflurazon	50	ND	8	101	3.75	7
Pebulate	13	ND	8	88	1.04	9
Phorate	30	ND	8	95	3.35	12
Phosmet	75	ND	8	98	4.64	6
Prometon	30	ND	8	85	1.68	7
Prometryn	19	ND	8	94	0.710	4
Pronamide	76	ND	8	93	4.70	7
Propazine	16	ND	8	73	0.604	5
Simazine	8	ND	8	101	0.594	8
Simetryn	25	ND	8	103	1.99	8
Stirofos	76	ND	8	97	6.64	9
Tebuthiuron	125	ND	8	87	10.5	10
Terbacil	450	ND	8	101	34.7	8
Terbufos	50	ND	8	93	3.79	8
Terbutryn	25	ND	8	93	0.909	4
Triademefon	65	ND	8	98	2.41	4
Tricyclazole	100	ND	8	89	4.18	5
Vernolate	13	ND	8	88	0.797	7

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 8. RECOVERY OF ANALYTES FROM HARD ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	3.8	ND (f)	7	82	0.214	7
Ametryn	20	ND	7	102	2.30	11
Aspon	2.5	ND	7	81	0.261	13
Atraton	6.0	ND	7	84	0.382	8
Atrazine	1.3	ND	8	89	0.0787	7
Azinphos methyl	22	ND	7	87	2.27	12
Bolstar	1.3	ND	8	85	0.0778	7
Bromacil	25	ND	7	81	1.29	6
Butachlor	3.8	ND	8	93	0.551	16
Butylate	1.5	ND	7	36	0.115	21
Carboxin	6.0	ND	8	98	0.771	13
Chlorpropham	5.0	ND	7	82	0.353	9
Cycloate	2.5	ND	7	97	0.345	14
Demeton-O	6.0	ND	7	82	0.334	7
Demeton-S	2.5	ND	8	81	0.151	7
Diazinon	2.5	ND	8	83	0.210	10
Dichlofenthion	1.0	ND	8	78	0.0647	8
Dichlorvos	25	ND	8	86	1.57	7
Diphenamid	6.0	ND	8	88	0.279	5
Disulfoton	3.0	ND	7	107	0.352	11
Disulfoton sulfone	7.5	ND	8	92	0.324	5
Disulfoton sulfoxide	3.8	ND	7	88	0.835	25
EPN	0.50	ND	8	87	0.0365	8
EPTC	2.5	ND	8	83	0.132	6
Ethion	3.0	ND	7	97	0.165	6
Ethoprop	1.9	ND	8	91	0.134	8
Ethyl parathion	4.5	ND	7	97	0.282	6
Famphur	6.0	ND	7	91	0.254	5
Fenamiphos	10	ND	7	87	0.509	6
Fenarimol	3.8	ND	8	89	0.244	7
Fenitrothion	4.5	ND	7	96	0.247	6
Fensulfothion	25	ND	7	87	2.36	11
Fenthion	1.0	ND	8	79	0.380	5
Fluridone	38	ND	8	91	4.10	12
Fonofos	6.5	ND	8	87	0.292	5
Hexazinone	7.6	ND	7	86	0.436	7
Malathion	3.8	ND	8	88	0.268	8
Merphos	2.5	ND	8	90	0.0972	4
Methyl paraoxon	25	ND	8	97	1.87	8
Methyl parathion	1.9	ND	8	89	0.0915	5
Metolachlor	7.5	ND	8	92	0.765	11

TABLE 8. RECOVERY OF ANALYTES FROM HARD ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a) (continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Metribuzin	1.5	ND	8	99	0.142	10
Mevinphos	50	ND	7	93	2.76	6
MGK 264	5.0	ND	8	91	0.555	12
MGK 326	1.5	ND	7	96	0.0561	4
Molinate	1.5	ND	7	83	0.116	9
Napropamide	2.5	ND	8	89	0.126	6
Norflurazon	5.0	ND	8	101	0.781	15
Pebulate	1.3	ND	8	80	0.0774	7
Phorate	3.0	ND	8	90	0.188	7
Phosmet	7.5	ND	8	90	0.449	7
Prometon	3.0	ND	7	89	0.154	6
Prometryn	1.9	ND	8	91	0.149	9
Pronamide	7.6	ND	7	84	0.502	8
Propazine	1.3	ND	8	89	0.0787	7
Simazine	0.75	ND	8	86	0.0393	6
Simetryn	2.5	ND	8	88	0.119	5
Stirofos	7.6	ND	7	84	0.469	7
Tebuthiuron	13	ND	8	85	1.28	12
Terbacil	45	ND	8	86	2.20	6
Terbufos	5.0	ND	8	80	0.301	8
Terbutryn	2.5	ND	8	91	0.197	9
Triademefon	6.5	ND	8	94	0.301	5
Tricyclazole	10	ND	7	90	0.586	7
Vernolate	1.3	ND	8	79	0.108	11

(a) Corrected for amount found in blank; artificial ground water was Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

(b) n = number of data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 9. RECOVERY OF ANALYTES FROM ORGANIC-CONTAMINATED ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Alachlor	3.8	ND (f)	8	90	0.312	9
Ametryn	20	ND	8	96	0.710	4
Aspon	2.5	ND	8	93	0.302	13
Atraton	6.0	ND	8	91	0.486	9
Atrazine	1.3	ND	7	92	0.0621	5
Azinphos methyl	22	ND	8	97	2.79	13
Bolstar	1.3	ND	8	106	0.221	16
Bromacil	25	ND	8	88	2.09	9
Butachlor	3.8	ND	8	84	0.204	6
Butylate	1.5	ND	8	83	0.110	9
Carboxin	6.0	ND	8	87	0.292	6
Chlorpropham	5.0	ND	8	93	0.428	9
Cycloate	2.5	ND	8	93	0.0815	3
Demeton-O	6.0	ND	8	61	0.255	7
Demeton-S	2.5	ND	8	83	0.130	6
Diazinon	2.5	ND	8	84	0.0813	4
Dichlofenthion	1.0	ND	8	75	0.0747	10
Dichlorvos	25	ND	8	106	3.99	15
Diphenamid	6.0	ND	7	93	0.253	5
Disulfoton	3.0	ND	8	95	0.135	5
Disulfoton sulfone	7.5	ND	7	96	0.242	3
Disulfoton sulfoxide	3.8	ND	7	54	0.733	36
EPN	0.50	ND	8	110	0.0735	13
EPTC	2.5	ND	7	86	0.105	5
Ethion	3.0	ND	8	97	0.130	4
Ethoprop	1.9	ND	7	79	0.0582	4
Ethyl parathion	4.5	ND	8	90	0.112	3
Famphur	6.0	ND	8	94	0.160	3
Fenamiphos	10	ND	8	89	0.247	3
Fenarimol	3.8	ND	8	89	0.236	7
Fenitrothion	4.5	ND	8	92	0.131	3
Fensulfothion	25	ND	8	94	2.86	12
Fenthion	1.0	ND	8	81	0.0509	6
Fluridone	38	ND	8	86	3.58	11
Fonofos	6.5	ND	7	88	0.253	4
Hexazinone	7.6	ND	8	95	0.665	9
Malathion	3.8	ND	8	109	0.605	15
Merphos	2.5	ND	7	92	0.0845	4
Methyl paraoxon	25	ND	7	94	0.973	4
Methyl parathion	1.9	ND	7	85	0.0596	4
Metolachlor	7.5	ND	8	84	0.322	5

TABLE 9. RECOVERY OF ANALYTES FROM ORGANIC-CONTAMINATED ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a) (continued)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Metribuzin	1.5	ND	8	86	0.0627	5
Mevinphos	50	ND	8	92	1.86	4
MGK 264	5.0	ND	8	83	0.270	7
MGK 326	1.5	ND	8	76	0.507	4
Molinate	1.5	ND	8	89	0.131	10
Napropamide	2.5	ND	8	104	0.434	17
Norflurazon	5.0	ND	8	87	0.219	5
Pebulate	1.3	ND	8	98	0.197	15
Phorate	3.0	ND	8	106	0.509	16
Phosmet	7.5	ND	8	107	0.958	12
Prometon	3.0	ND	8	63	0.0947	3
Prometryn	1.9	ND	7	93	0.0740	4
Pronamide	7.6	ND	8	92	0.617	9
Propazine	1.3	ND	7	92	0.0621	5
Simazine	0.75	ND	8	103	0.110	14
Simetryn	2.5	ND	8	103	0.354	14
Stirofos	7.6	ND	8	95	0.699	10
Tebuthiuron	13	ND	8	98	1.64	13
Terbacil	45	ND	8	102	5.35	12
Terbufos	5.0	ND	8	77	0.353	9
Terbutryn	2.5	ND	7	92	0.0971	4
Triademefon	6.5	ND	7	95	0.285	5
Tricyclazole	10	ND	8	90	1.05	12
Vernolate	1.3	ND	8	81	0.0299	3

(a) Corrected for amount found in blank; artificial ground water was reagent water spiked with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

(b) n = number of data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

TABLE 10. INSTRUMENT QC STANDARD

Test	Analyte	Conc, g/mL	Requirements
Sensitivity	Dichlofenthion	0.01	Detection of analyte; S/N >3
	Sulprofos	0.01	Detection of analyte; S/N >3
	Vernolate	0.01	Detection of analyte; S/N >3
Chromatographic performance	Cycloate	5	0.95 < PSF < 1.05; 0.95 < PGF < 1.05 (a)
	Fenitrothion	3	0.95 < PSF < 1.05; 0.95 < PGF < 1.05 (a)
	Triphenylphosphate	1	0.95 < PSF < 1.05; 0.95 < PGF < 1.05 (a)
Column performance	Pronamide	0.15	Resolution > 1.4 (b)
	Fonofos	0.025	

(a) PSF = peak symmetry factor. Calculated using the equation:

$$PSF = \frac{w(1/2)}{0.5 \times W(1/2)}$$

where w(1/2) is the width of the front of the peak at half height assuming the peak is split at its highest point and W(1/2) is the peak width at half height (see Figure 7).

PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height (see Figure 7).

(b) Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

TABLE 11. PRESERVATION STUDY RESULTS

Day Extracted		0		0		14		28	
Day Analyzed		0		28		14		28	
Analyte	Amount, ug/L	R(b)	RD(c)	R	RSD	R	RSD	R	RSD
Alachlor	3.8	76	0 7	73	2.0	84	0.2	65	0.0
Ametryn	20	95	1.9	86	1.1	70	7.8	74	1.5
Aspon	2.5	76	0 4	134	0 8	5	0.2	16	0.1
Atraton	6.0	76	1.1	82	2.3	85	0.3	67	0.1
Atrazine	1.3	79	0.1	83	0.2	86	0.1	80	0 1
Azinphos methyl	22	78	3.4	108	9.0	ND(a)	-	ND	-
Bolstar	1.3	82	0.0	72	0 1	ND	-	ND	-
Bromacil	25	74	4 2	72	11.8	89	2.3	33	0.5
Butachlor	3.8	75	0.3	72	0.2	60	1.6	53	0.4
Butylate	1.5	51	0.3	18	1.7	85	0.1	66	0.0
Carboxin	6.0	81	0.3	97	1.6	97	0.8	57	0.6
Chlorpropham	5.0	76	1 0	73	2.2	84	0.3	68	0.0
Cycloate	2.5	91	0 3	83	0 2	86	0.2	82	0 1
Demeton-O	6.0	72	0.4	95	0 2	ND	-	ND	-
Demeton-S	2.5	81	0.1	85	0.1	73	0.5	27	0.8
Diazinon	2.5	79	0.2	76	0.1	93	0.4	57	0.3
Dichlofenthion	1.0	74	0.0	80	0.1	1	0.7	ND	-
Dichlorvos	25	78	3.2	60	2.2	93	1.1	41	17.7
Diphenamid	6.0	82	0.6	92	0.6	90	0.3	85	0.5
Disulfoton	3.0	98	0.2	83	0.1	87	0.2	79	0.2
Disulfoton sulfone	7.5	83	0.9	88	1.0	97	0.4	83	0.6
Disulfoton sulfoxide	3.8	83	0.7	72	1.4	8	0.9	ND	-
EPN	0.50	84	0.0	63	0.0	ND	-	ND	-
EPTC	2.5	80	0.3	85	0.3	89	0.2	83	0.2
Ethion	3.0	66	0.3	92	0.2	ND	-	ND	-
Ethoprop	1.9	82	0.2	86	0.3	92	0.1	85	0.1
Ethyl parathion	4.5	78	0.3	91	0.1	5	2.8	ND	-
Famphur	6.0	87	0.4	91	0.3	7	3.1	ND	-
Fenamiphos	10	92	0.5	92	0.6	94	0.7	82	1.0
Fenarimol	3.8	82	0.1	54	0.1	101	0.3	60	2.7
Fenitrothion	4.5	80	0.3	88	0.1	7	2.0	ND	-
Fensulfothion	25	78	3.6	101	7 7	12	2.8	18	0.3
Fenthion	1.0	76	0.0	81	0.1	29	0.2	ND	-
Fluridone	38	90	1.5	62	0.9	94	2.8	58	27
Fonofos	6.5	81	0.7	106	0.9	ND	-	ND	-
Hexazinone	7.6	78	1.2	99	2.7	86	0.4	71	0.2
Malathion	3.8	83	0.1	58	0.2	ND	-	ND	-
Merphos	2.5	82	0.3	87	0.3	93	0.1	84	0.2
Methyl paraoxon	25	85	2.5	81	3.3	93	1.0	83	1.7
Methyl parathion	1.9	84	0.2	82	0.3	10	0.1	14	0.0

TABLE 11. PRESERVATION STUDY RESULTS (continued)

Day Extracted		0		0		14		28	
Day Analyzed		0		28		14		28	
Analyte	Amount, ug/L	R(a)	RSD(b)	R	RSD	R	RSD	R	RSD
Metolachlor	7.5	76	0.6	76	0.2	95	1.1	61	1.0
Metribuzin	1.5	79	0.1	79	0.1	95	0.2	59	0.2
Mevinphos	50	88	3.5	92	1.8	86	4.2	74	2.6
MGK 264	5.0	77	0.4	76	0.1	94	0.8	58	0.7
MGK 326	1.5	72	0.2	97	0.1	ND	-	ND	-
Molinate	1.5	76	0.3	76	0.7	86	0.1	66	0.0
Napropamide	2.5	81	0.1	81	0.1	85	0.4	62	1.8
Norflurazon	5.0	82	0.4	77	0.1	100	0.8	63	0.6
Pebulate	1.3	76	0.1	60	0.0	100	0.1	58	0.9
Phorate	3.0	71	0.3	74	0.1	ND	-	ND	-
Phosmet	7.5	84	0.7	63	0.5	ND	-	ND	-
Prometon	3.0	60	0.4	99	0.2	21	0.5	11	1.6
Prometryn	1.9	81	0.2	61	0.3	84	0.1	48	0.3
Pronamide	7.6	71	1.5	59	4.5	4	1.8	ND	-
Propazine	1.3	80	0.1	86	0.1	99	0.1	86	0.1
Simazine	0.75	81	0.0	60	0.0	99	0.0	62	0.5
Simetryn	2.5	81	0.1	81	0.0	100	0.1	60	1.8
Stirofos	7.6	78	1.3	91	4.9	83	0.4	61	0.2
Tebuthiuron	13	91	0.2	58	3.4	101	0.7	54	9.2
Terbacil	45	74	3.1	59	0.7	99	2.3	60	31.8
Terbufos	5.0	72	0.2	77	0.5	ND	-	ND	-
Terbutryn	2.5	82	0.3	84	0.3	90	0.2	85	0.2
Triademefon	6.5	84	0.7	82	0.6	100	0.4	83	0.5
Tricyclazole	10	72	1.5	92	2.5	99	1.6	68	0.3
Vernolate	1.3	70	0.1	72	0.1	91	0.2	57	0.2

(a) ND = not detected.

(b) R = average percent recovery.

(c) RSD = percent relative standard deviation.

TABLE 1. METHOD 1 ANALYTES INCLUDED IN PHASE III STUDIES

Alachlor	Fenthion
Ametryn	Fluridone
Aspon	Fonofos
Atraton	Hexazinone
Atrazine	Malathion
Azinphos methyl	Merphos
Bromacil	Methyl paraoxon
Butachlor	Methyl parathion
Butylate	Metolachlor
Carboxin	Metribuzin
Chlorpropham	Mevinphos
Chlorpyrifos	MGK 264
Coumaphos	MGK 326
Cycloate	Molinate
Demeton-O	Napropamide
Demeton-S	Norflurazon
Diazinon	Pebulate
Dichlofenthion	Phorate
Dichlorvos	Phosmet
Dioxathion	Prometon
Diphenamid	Prometryn
Disulfoton	Pronamide
Disulfoton sulfone	Propazine
Disulfoton sulfoxide	Simazine
EPN	Simetryn
EPTC	Stirofos
Ethion	Tebuthiuron
Ethoprop	Terbacil
Ethyl parathion	Terbufos
Famphur	Terbutryn
Fenarimol	Triademefon
Fenitrothion	Tricycloazole
Fensulfathion	Vernolate

TABLE 2. METHOD 1 IDLs AND PROPOSED VALIDATION SPIKING LEVELS

Analyte	Spiking Mix	Spiking Mix Conc, µg/mL(a)	IDL, µg/mL	EMDL, µg/L	Validation Spiking Levels, µg/L (b) 1	2	3	4	5
Alachlor	D	10	0.08	0.38	0.38	1.9	3.8	9.4	19
Ametryn	A	100	0.40	2.0	2.0	10	20	50	200
Aspon	D	6.3	0.05	0.25	0.25	1.3	2.5	6.3	25
Atraton	D	30	0.12	0.60	0.60	3.0	6.0	15	60
Atrazine	B	6.3	0.025	0.13	0.13	0.63	1.3	3.1	13
Azinphos methyl	D	110	0.45	2.2	2.2	11	22	55	220
Bolstar	E	6.3	0.025	0.13	0.13	0.63	1.3	3.1	13
Bromacil	D	130	0.50	2.5	2.5	13	25	63	250
Butachlor	C	19	0.075	0.38	0.38	1.9	3.8	9.4	38
Butylate	D	7.6	0.030	0.15	0.15	0.76	1.5	3.8	15
Carboxin	C	30	0.12	0.60	0.60	3.0	6.0	15	60
Chlorpropham	D	25	0.10	0.50	0.50	2.5	5.0	13	50
Coumophos	C	12	0.050	0.23	0.23	1.1	2.3	5.7	23
Cycloate	A	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Demeton-O	A	30	0.12	0.60	0.60	3.0	6.0	15	60
Demeton-S	C	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Diazinon	C	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Dichlofenthion	C	5.0	0.020	0.10	0.10	0.50	1.0	2.5	10
Dichlorvos	E	125	0.50	2.5	2.5	13	25	63	250
Diphenamid	B	30	0.12	0.60	0.60	3.0	6.0	15	60
Disulfoton	A	15	0.060	0.30	0.30	1.5	3.0	7.5	30
Disulfoton sulfone	B	38	0.15	0.75	0.75	3.8	7.5	19	75
Disulfoton sulfoxide	D	19	0.075	0.38	0.38	1.9	3.8	9.4	38
EPN	E	2.5	0.010	0.050	0.050	0.25	0.50	1.3	5.0
EPTC	B	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Ethion	A	15	0.060	0.30	0.30	1.5	3.0	7.5	30
Ethoprop	B	10	0.038	0.19	0.19	1.0	1.9	4.8	19
Ethyl parathion	A	23	0.090	0.45	0.45	2.3	4.5	11	45
Famphur	A	30	0.12	0.60	0.60	3.0	6.0	15	60
Fenamiphos	A	50	0.20	1.0	1.0	5.0	10	25	100

TABLE 2. METHOD 1 IDLs AND PROPOSED VALIDATION SPIKING LEVELS (continued)

Analyte	Spiking Mix	Spiking Mix Conc, µg/mL(a)	IDL, µg/mL	EMDL, µg/L	Validation Spiking Levels, µg/L (b) 1	2	3	4	5
Fenarimol	E	19	0.075	0.38	0.38	1.9	3.8	9.4	38
Fenitrothion	A	23	0.090	0.45	0.45	2.3	4.5	11	45
Fensulfothion	D	130	0.50	2.5	2.5	13	25	63	250
Fenthion	C	5.0	0.020	0.10	0.10	0.50	1.0	2.5	10
Fluridone	E	190	0.75	3.8	3.8	19	38	94	380
Fonofos	B	33	0.13	0.65	0.65	3.3	6.5	16	65
Hexazinone	D	38	0.15	0.76	0.76	3.8	7.6	19	76
Malathion	E	19	0.075	0.38	0.38	1.9	3.8	9.4	38
Merphos	B	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Methyl paraoxon	B	130	0.50	2.5	2.5	13	25	63	250
Methyl parathion	B	10	0.038	0.19	0.19	1.0	1.9	4.8	19
Metolachlor	C	38	0.15	0.75	0.75	3.8	7.5	19	75
Metribuzin	C	7.5	0.030	0.15	0.15	0.75	1.5	3.8	15
Mevinphos	A	250	1.0	5.0	5.0	25	50	125	500
MGK 264	C	25	0.10	0.50	0.50	2.5	5.0	13	50
MGK 326	A	7.5	0.030	0.15	0.15	0.75	1.5	3.8	15
Molinate	D	7.6	0.030	0.15	0.15	0.76	1.5	0.76	15
Napropamide	E	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Norflurazon	C	25	0.10	0.50	0.50	2.5	5.0	13	50
Pebulate	E	6.3	0.025	0.13	0.13	0.63	1.3	3.1	13
Phorate	E	15	0.060	0.30	0.30	1.5	3.0	7.5	30
Phosmet	E	38	0.15	0.75	0.75	3.8	7.5	19	75
Prometon	A	15	0.060	0.30	0.30	1.5	3.0	7.5	30
Prometryn	B	10	0.038	0.19	0.19	1.0	1.9	4.8	19
Pronamide	D	38	0.15	0.76	0.76	3.8	7.6	19	76
Propazine	B	6.3	0.025	0.13	0.13	0.63	1.3	3.1	13
Simazine	E	3.8	0.015	0.075	0.075	0.38	0.75	1.9	7.5
Simetryn	E	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Stirofos	D	38	0.15	0.76	0.76	3.8	7.6	19	76
Tebuthiuron	E	63	0.25	1.3	1.3	6.3	13	31	125

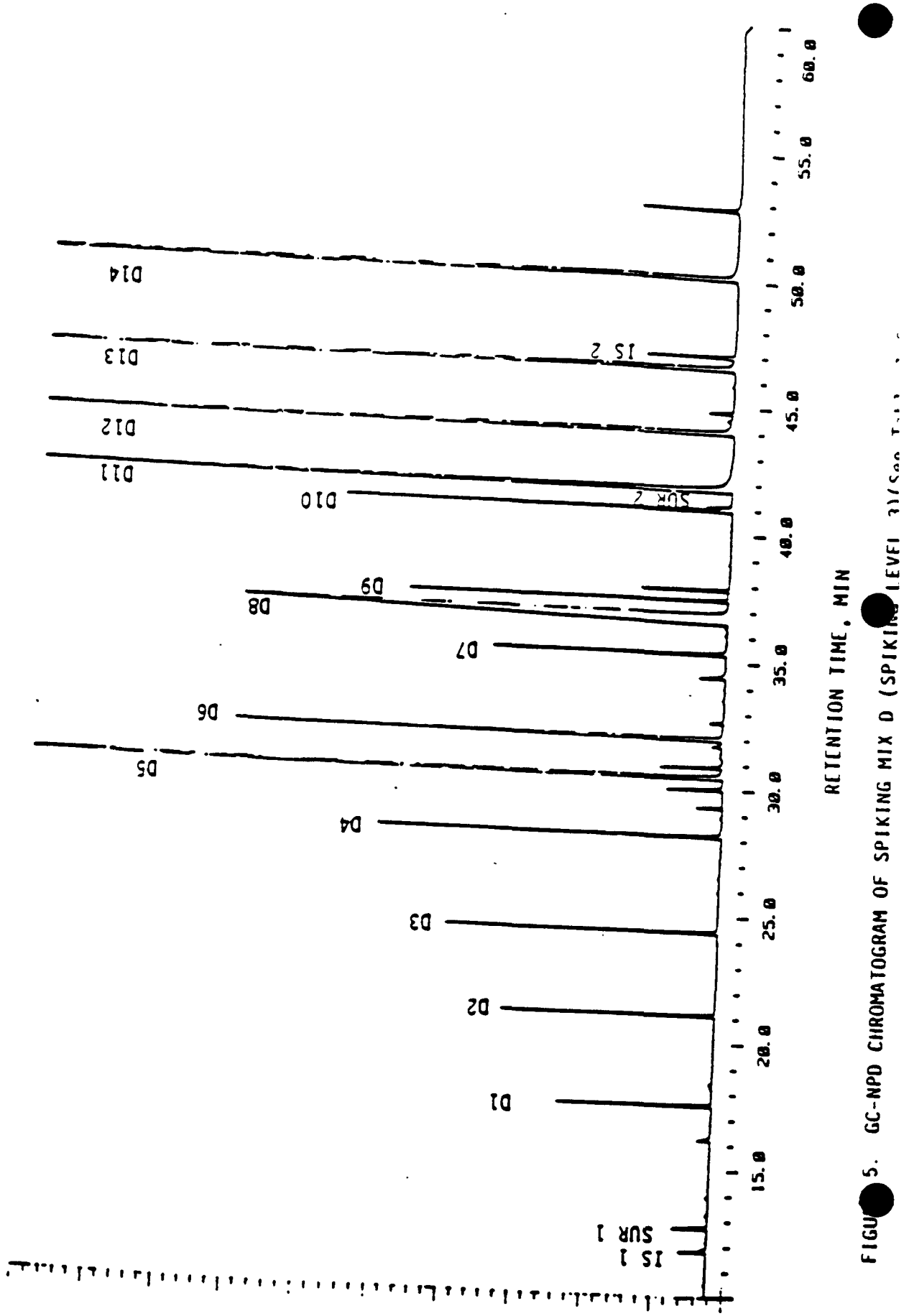
TABLE 2. METHOD 1 IDLs AND PROPOSED VALIDATION SPIKING LEVELS (continued)

Analyte	Spiking Mix	Spiking Mix Conc, µg/mL(a)	IDL, µg/mL	EMDL, µg/L	Validation Spiking Levels, µg/L (b) 1	2	3	4	5
Terbacil	E	230	0.90	4.5	4.5	23	45	113	450
Terbufos	C	25	0.10	0.50	0.50	2.5	5.0	13	50
Terbutryn	B	13	0.050	0.25	0.25	1.3	2.5	6.3	25
Triademefon	B	33	0.13	0.65	0.65	3.3	6.5	16	65
Tricyclazole	D	50	0.20	1.0	1.0	5.0	10	40	100
Vernolate	C	6.3	0.025	0.13	0.13	0.63	1.3	3.1	13

(a) Spiking mixture prepared in MTBE; 20 µL of spiking mix was added to samples to achieve spiking level 1.

(b) Spiking level 3 used for matrix validation and preservation studies.

Figure 5



FIGU 5. GC-NPD CHROMATOGRAM OF SPIKING MIX D (SPIKI LEVEL

Figure 4

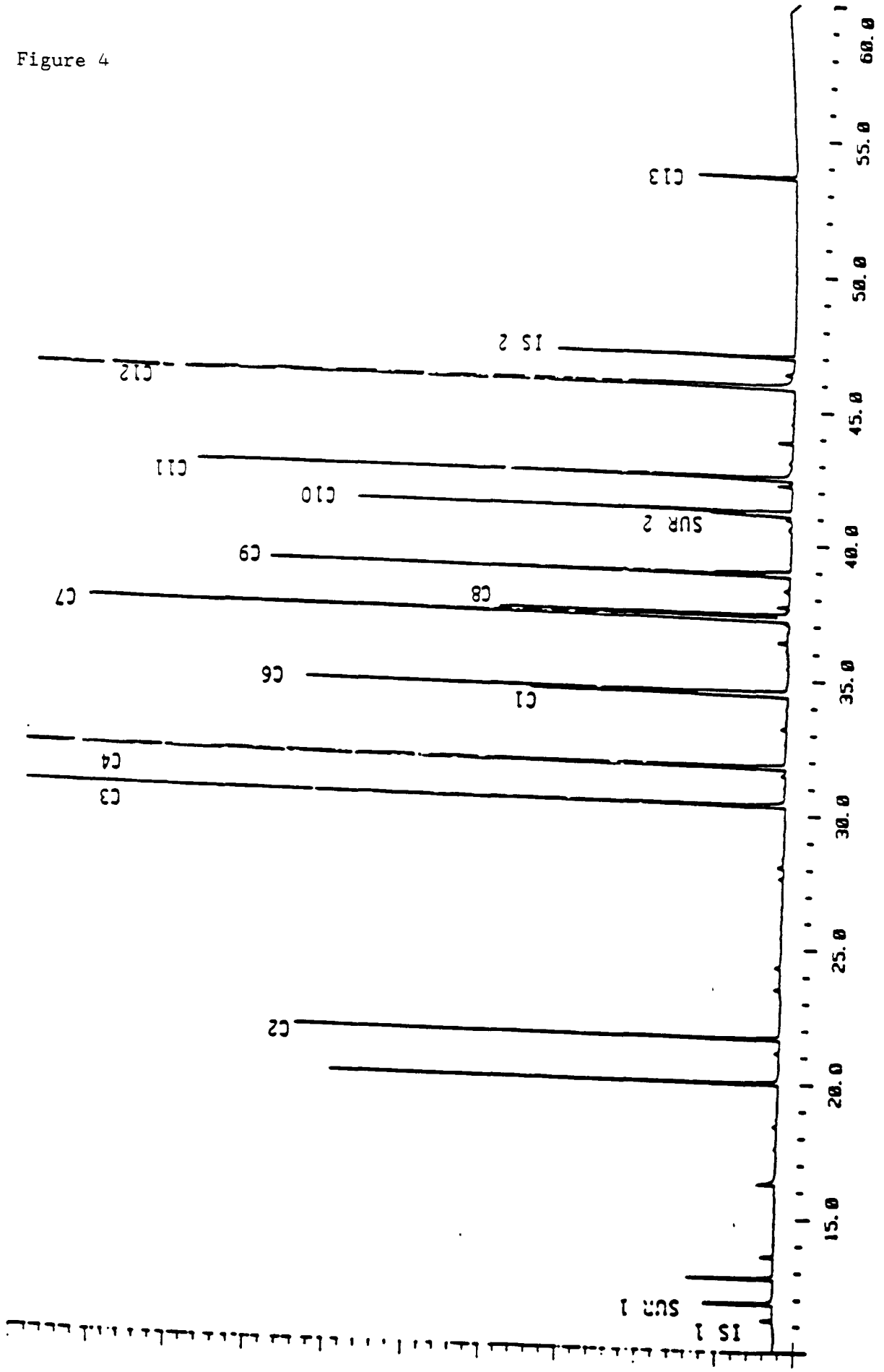


FIGURE 4. GC-NPD CHROMATOGRAM OF SPIKING MIX C (SPIKING LEVEL 3)(See Table 1 for peak identifications)

Figure 3

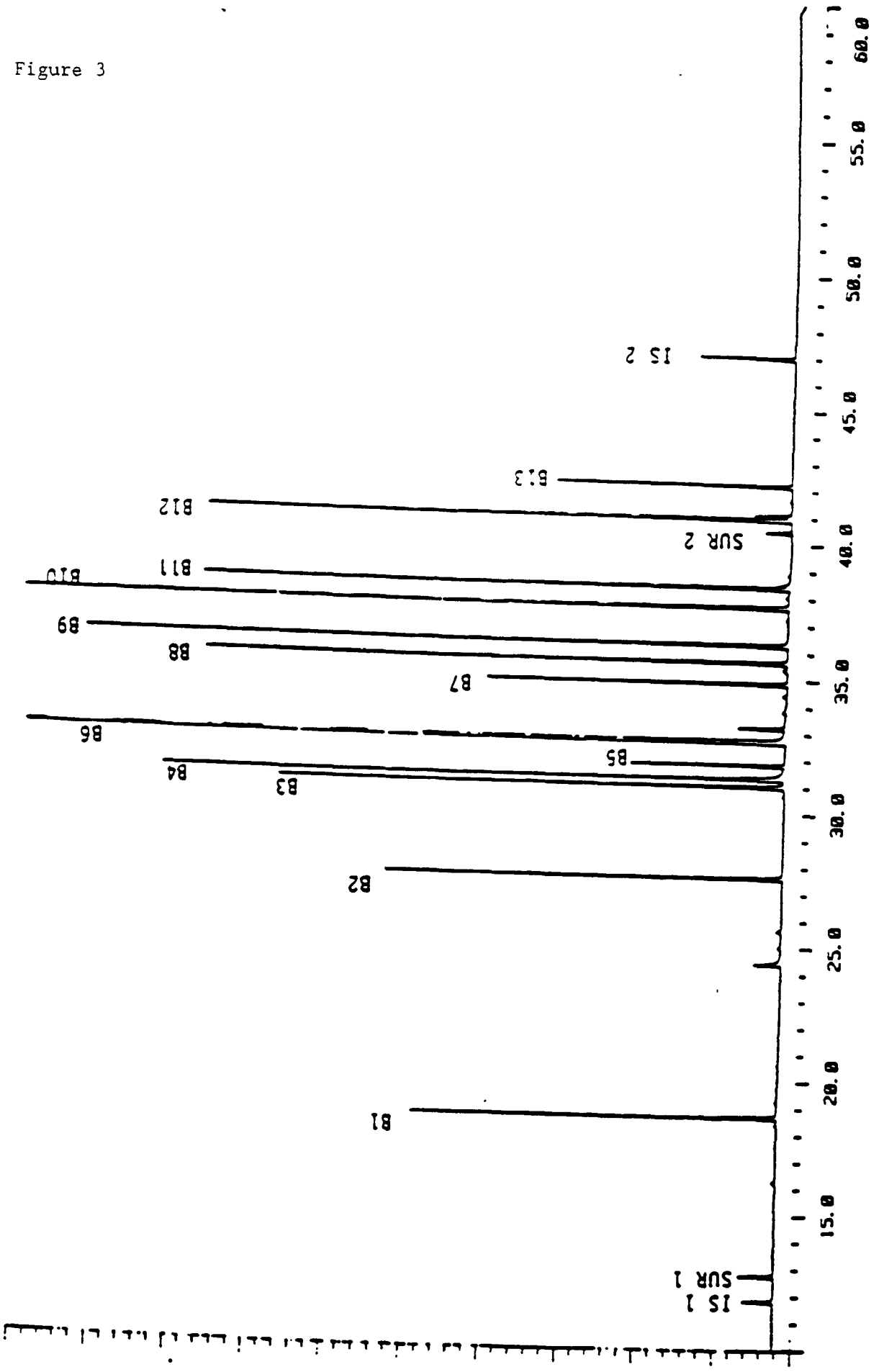


FIGURE 3. GC-NPD CHROMATOGRAM OF SPIKING MIX B (SPIKING LEVEL 3)(See Table 1 for peak identifications)

Figure 2

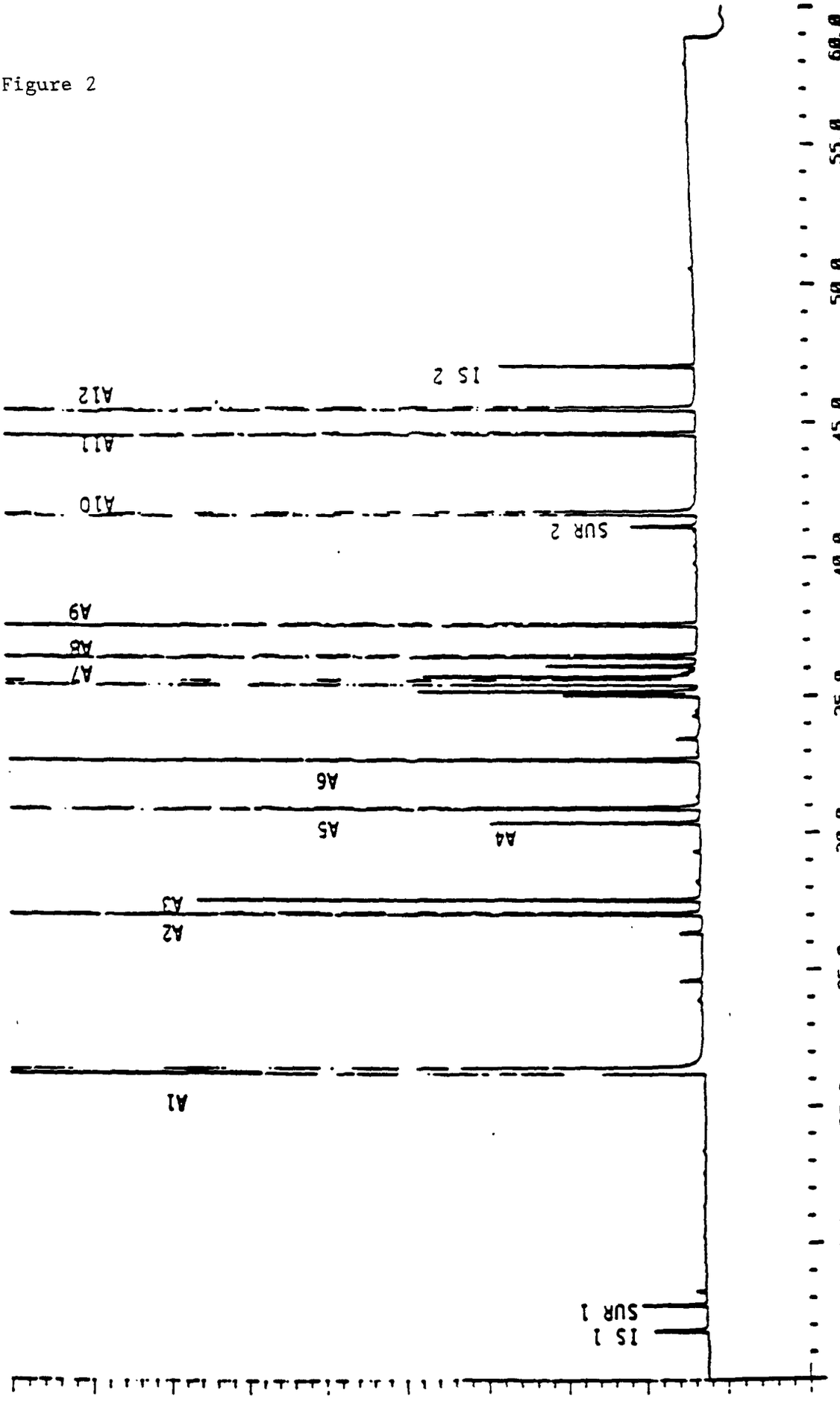


FIGURE 2. GC-NPD CHROMATOGRAM OF SPIKING MIX A (SPIKING LEVEL 3)(See Table 1 for peak identifications)

Figure 1

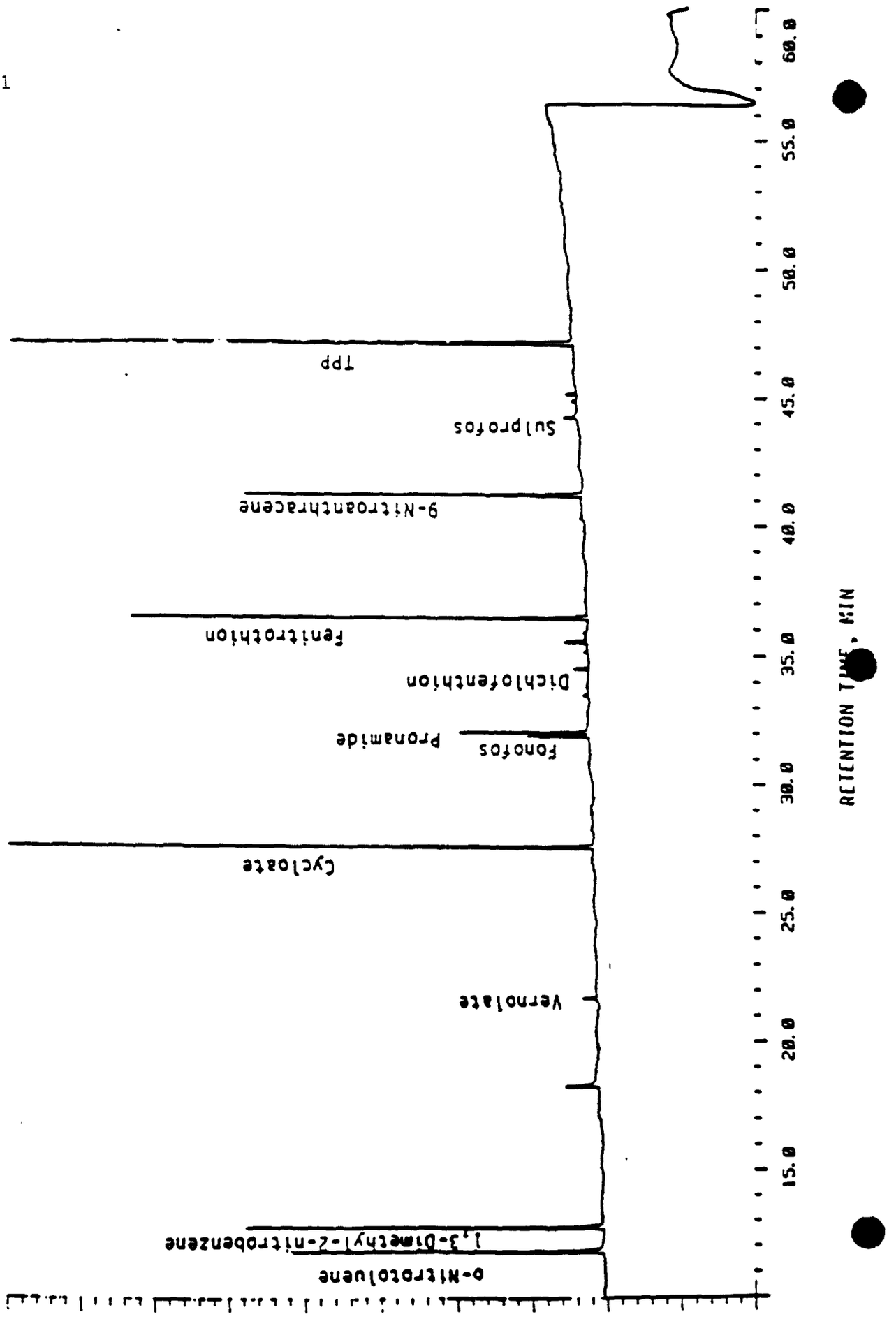

o-Nitrotoluene
1,3-Dimethyl-2-nitrobenzene
Vernolate
Cycloate
Fonofos
Pronamide
Dichlofenthion
Fenitrothion
9-Nitroanthracene
Sulprofos
TPP
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
RETENTION TIME, MIN

TABLE 4. METHOD 1 ANALYTES DISPLAYING AQUEOUS INSTABILITY

Priority	Nonpriority
Fonofos	Aspon
Methyl parathion	Azinphos methyl
Prometon	Bolstar
Pronamide	Demeton-O
	Dichlofenthion
	Disulfoton sulfoxide
	EPN
	Ethion
	Ethyl parathion
	Famphur
	Fenitrothion
	Fensulfothion
	Fenthion
	Malathion
	MGK 326
	Phorate
	Phosmet
	Terbufos

Figure 6

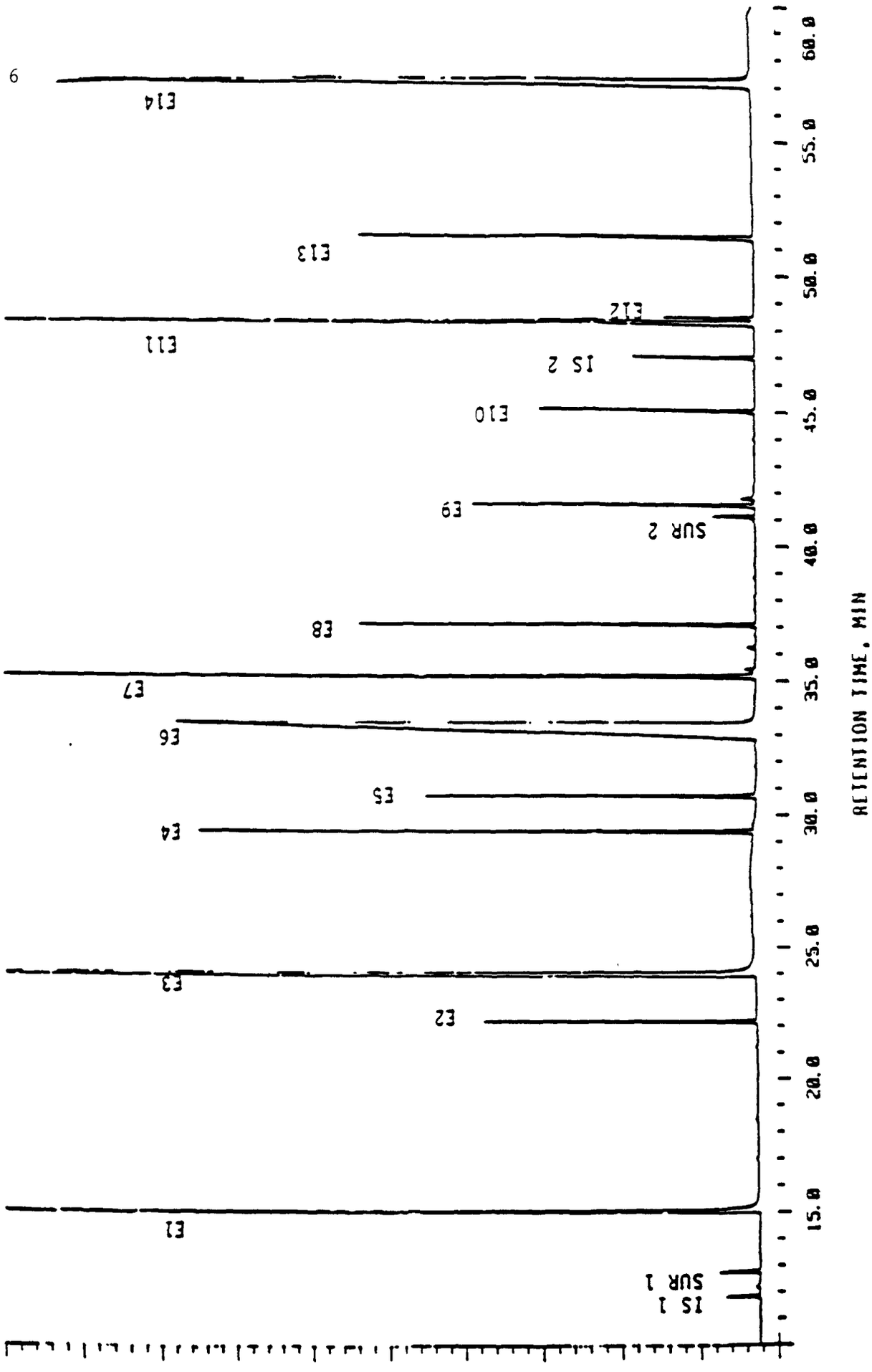

IS 1
SUR 1
E1
E2
E3
E4
E5
E6
E7
E8
SUR 2
E9
E10
IS 2
E11
E12
E13
E14
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
RETENTION TIME, MIN

Figure 7

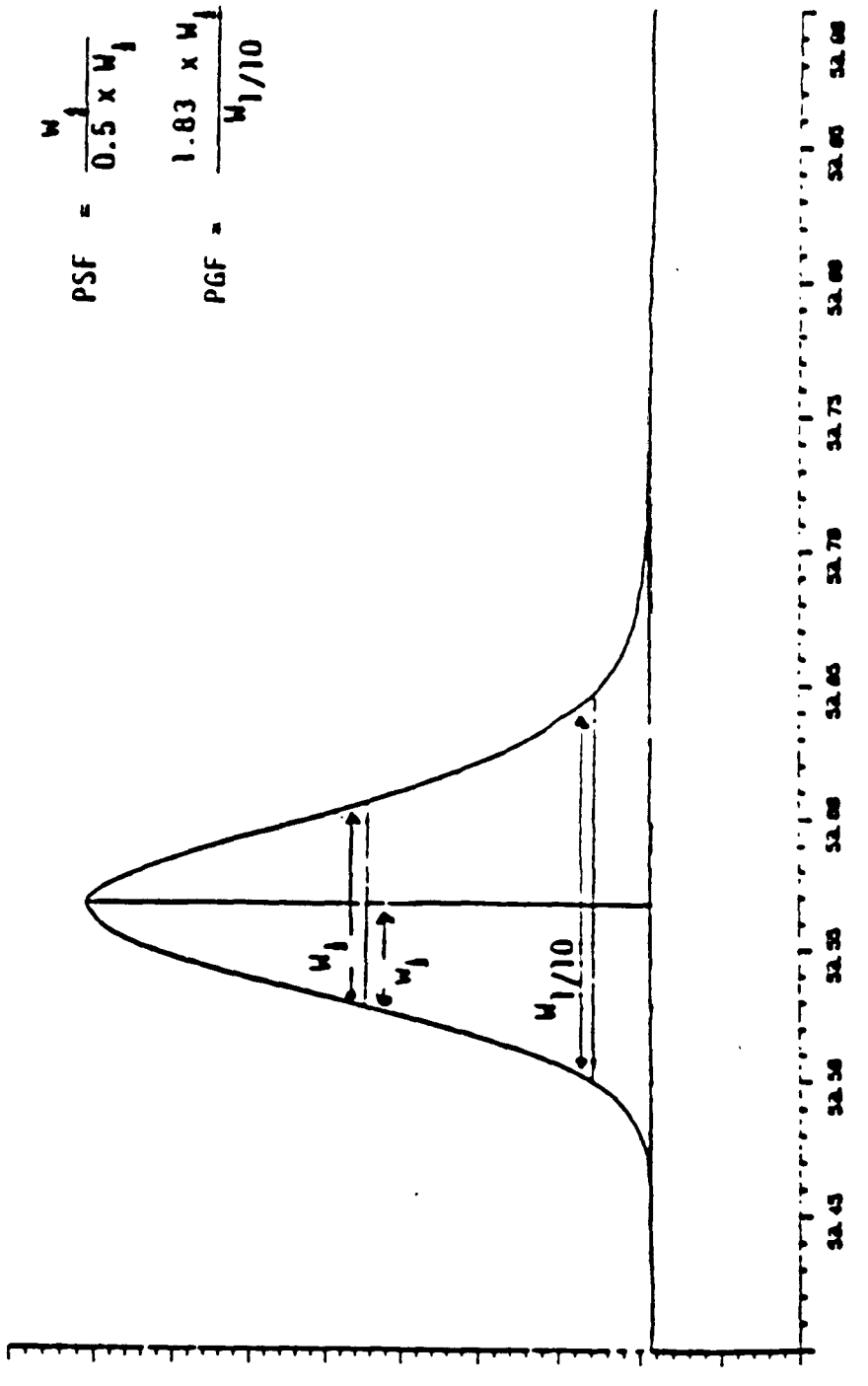


FIGURE 7. EQUATIONS USED TO CALCULATE PEAK SYMMETRY FACTOR (PSF) AND PEAK GAUSSIAN FACTOR (PGF)

Method 3. Determination of Chlorinated Acids in Ground Water by Gas Chromatography with an Electron Capture Detector

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water. Analytes that can be determined by this method are listed in Table 1.

1.2 This method may be applicable to the determination of salts and esters of analyte acids. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid.

1.3 This method has been validated in a single laboratory. Estimated detection limits (EDLs) have been determined and are listed in Table 2. Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.2.

1.5 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is adjusted to 0.1 N sodium hydroxide and shaken for 1 hour to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed, and the esters are determined by GC using an electron capture detector (ECD).[1]

2.2 The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered.

3. DEFINITIONS

3.1 Artificial ground water -- an aqueous matrix designed to mimic a real ground water sample. The artificial ground water should be reproducible for use by others.

3.2 Calibration standard -- a known amount of a pure analyte, dissolved in an organic solvent, analyzed under the same procedures and conditions used to analyze sample extracts containing that analyte.

3.3 Estimated detection limit (EDL) -- the minimum concentration of a substance that can be measured and reported with confidence that the analyte concentration is greater than zero as determined from the analysis of a sample in a given matrix containing the analyte. The EDL is equal to the level calculated by multiplying the standard deviation of replicate measurements times the students' t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom or the level of the compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately five, whichever value is higher.

3.4 Internal standard -- a pure compound added to a sample extract in a known amount and used to calibrate concentration measurements of other analytes that are sample components. The internal standard must be a compound that is not a sample component.

3.5 Instrument quality control (QC) standard -- a methyl tert-butyl ether (MTBE) solution containing specified concentrations of specified analytes. The instrument QC standard is analyzed each working day prior to the analysis of sample extracts and calibration standards. The performing laboratory uses this solution to demonstrate acceptable instrument performance in the areas of sensitivity, column performance, and chromatographic performance.

3.6 Laboratory control (LC) standard -- a solution of analytes prepared in the laboratory by dissolving known amounts of pure analytes in a known amount of reagent water. In this method, the LC standard is prepared by adding appropriate volumes of the appropriate standard solution to reagent water.

3.7 Laboratory method blank -- an aliquot of reagent water analyzed as if it were a sample.

3.8 Quality control check sample -- a water soluble solution containing known concentrations of analytes prepared by a laboratory other than the laboratory performing the analysis. The performing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method. A small measured volume of the solution is added to a known volume of reagent water and analyzed with procedures identical to those used for samples. True values of analytes are known by the analyst.

3.9 Stock standard solution -- a concentrated solution containing a certified standard that is a method analyte, or a concentrated solution of an analyte prepared in the laboratory with an assayed reference compound.

3.10 Surrogate standard -- a pure compound added to a sample in a known amount and used to detect gross abnormalities during sample preparation. The surrogate standard must be a compound that is not a sample component.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section 10.7.

4.1.1 Glassware must be scrupulously cleaned.[2] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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.

4.2 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with (1+9) hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when sol-

vent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.[3,4]

4.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the ground water sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences. Positive identifications should be confirmed using the confirmation column specified in Table 3.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must 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 identified[5-7] for the information of the analyst.

5.2 Diazomethane is a toxic carcinogen and can explode under certain conditions. The following precautions must be followed:

5.2.1 Use only a well ventilated hood -- do not breath vapors.

5.2.2 Use a safety screen.

5.2.3 Use mechanical pipetting aides.

5.2.4 Do not heat above 90°C -- EXPLOSION may result.

5.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.

5.2.6 Store away from alkali metals -- EXPLOSION may result.

5.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5.3 Ethyl ether is an extremely flammable solvent. If a mechanical device is used for sample extraction, the device should be equipped with an explosion-proof motor and/or placed in a hood to avoid possible damage and injury due to an explosion.

6. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed, rinsed with acetone, and dried before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcocks, ground glass or TFE-fluorocarbon stoppers.

6.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

6.2.4 Evaporative flask, K-D -- 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.5 Snyder column, K-D -- three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.6 Snyder column, K-D -- two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.7 Flask, round-bottom -- 500-mL with 24/40 ground glass joint.

6.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.2.9 Disposable pipets -- sterile plugged borosilicate glass, 5-mL capacity (Corning 7078-5N or equivalent).

6.3 Separatory funnel shaker -- Capable of holding eight 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI).

6.4 Tumbler -- Capable of holding 4 to 6 tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA).

6.5 Boiling stones -- Teflon, CHEMWARE (Norton Performance Plastics No. 015021).

6.6 Water bath -- Heated, capable of temperature control (±2°C). The bath should be used in a hood.

6.7 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 Diazomethane generator -- Diazomethane generator assembly as shown in Figure 1.

6.9 Glass wool -- Acid washed (Supelco 2-0383 or equivalent) and heated at 450°C for 4 hours.

6.10 GAS CHROMATOGRAPH -- Analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

6.10.1 Primary column -- 30 m long x 0.25 mm I.D. SPB-5 bonded fused silica column, 0.25 um film thickness (available from Supelco). Validation data presented in this method were obtained using this column. Alternative columns may be used in accordance with the provisions described in Section 10.3.

6.10.2 Confirmation column -- 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 um film thickness (available from J&W).

6.10.3 Detector -- Electron capture. This detector has proven effective in the analysis of spiked reagent and artificial ground waters. An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Section 10.3.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Acetone, methanol, methylene chloride, MTBE --'Pesticide quality or equivalent.

7.2 Ethyl ether, unpreserved -- Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

7.3 Sodium sulfate, granular, anhydrous, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances. Acidify by slurrying 100 g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.1 mL concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. The pH must be below pH 4. Store at 130°C.

7.4 Sodium hydroxide (NaOH), pellets -- ACS grade.

7.4.1 NaOH, 6 N -- Dissolve 216 g NaOH in 900 mL reagent water.

7.5 Sulfuric acid (H_2SO_4), concentrated, ACS grade -- sp. gr. 1.84.

7.5.1 H_2SO_4, 12 N -- Slowly add 335 mL concentrated H_2SO_4 to 665 mL of reagent water.

7.6 Carbitol, ACS grade -- available from Aldrich Chemical Co.

7.7 Diazald, ACS grade -- available from Aldrich Chemical Co.

7.8 Sodium chloride (NaCl), crystal, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.9 4,4'-Dibromooctafluorobiphenyl (DBOB) -- >99% purity, for use as internal standard (available from Aldrich Chemical Co).

7.10 2,4-Dichlorophenylacetic acid (DCAA) -- >99% purity, for use as surrogate standard (available from Aldrich Chemical Co).

7.11 Reagent water -- Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.12 STOCK STANDARD SOLUTIONS (1.00 ug/uL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.12.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the conven-

ience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.12.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.

7.12.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.

7.13 INTERNAL STANDARD SPIKING SOLUTION -- Prepare an internal standard spiking solution by accurately weighing approximately 0.0010 g of pure DBOB. Dissolve the DBOB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 25 uL of the internal standard spiking solution to 10 mL of sample results in a final internal standard concentration of 0.25 ug/L.

7.14 SURROGATE STANDARD SPIKING SOLUTION -- Prepare a surrogate standard spiking solution by accurately weighing approximately 0.0010 g of pure DCAA. Dissolve the DCAA in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 uL of the surrogate standard spiking solution to a sample prior to extraction results in a surrogate standard concentration in the sample of 5 ug/L and, assuming quantitative recovery of DCAA, a surrogate standard concentration in the final extract of 0.5 ug/mL.

7.15 INSTRUMENT QC STANDARD -- Prepare a diluted dinoseb solution by adding 10 uL of the 1000 ug/mL dinoseb stock solution to MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the instrument QC standard, add 40 uL of the diluted dinoseb solution, 16 uL of the 4-nitrophenol stock solution, 6 uL of the 3,5-dichlorobenzoic acid stock solution, 50 uL of the surrogate standard spiking solution, 25 uL of the internal standard spiking solution, and 250 uL of methanol to a 5-mL volumetric flask and diluting to volume with MTBE. Methylate sample as described in Section 11.3. Dilute the sample to 10 mL in MTBE. Transfer the instrument QC standard to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature.

7.16 Florisil -- 60-100/PR mesh (Sigma No. F-9127). Activate by heating in a shallow container at 150°C for at least 24 and not more than 48 hours.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices[8] should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 The samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results given in Table 11 indicate that samples stored under these conditions are stable for at least 28 days after collection.

8.2.2 Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a 10 mg/mL solution of mercuric chloride in water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.2.3 After the sample is collected in the bottle containing preservative, seal the bottle and shake vigorously for 1 min.

8.3 EXTRACT STORAGE

8.3.1 Sample extracts should be stored at 4°C away from light. Preservation study results given in Table 11 indicate that sample extracts stored under these conditions are stable for at least 28 days.

9. CALIBRATION

9.1 Establish GC operating parameters equivalent to those indicated in Table 3. The GC system must be calibrated using the internal standard technique (Section 9.2).

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

9.2.1 Prepare calibration standards at a minimum of three (suggested five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and 250 uL methanol, and dilute to volume with MTBE. Esterify acids with diazomethane as

described in Section 11.3. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

9.2.2 Inject 2 uL of each calibration standard and tabulate the relative response for each analyte (RR_a) to the internal standard using the equation:

$$RR_a = A_a/A_{is}$$

where: A_a = the peak area of the analyte, and
A_{is} = the peak area of the internal standard.

Generate a calibration curve of RR_a versus analyte concentration in the sample in ug/L.

9.2.3 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a quality control (QC) program. The minimum requirements of this program consist of the following: an initial demonstration of laboratory capability; the analysis of surrogate standards in each and every sample as a continuing check on sample preparation; the monitoring of internal standard area counts or peak heights in each and every sample as a continuing check on system performance; the analysis of QC samples, performance evaluation (PE) samples, and spiked samples as a continuing check on recovery performance; the analysis of method blanks as a continuing check on contamination; and frequent analysis of the instrument QC standard to assure acceptable instrument performance.

10.2 INITIAL DEMONSTRATION OF CAPABILITY -- To establish the ability to perform this method, the analyst must perform the following operations.

10.2.1 Select a representative spike concentration (suggest 15 times the EDL) for each of the target analytes. Using a stock standard that differs from calibration standard, prepare a laboratory control (LC) check sample concentrate in methanol 1000 times more concentrated than the selected spike concentration.

10.2.2 Using a syringe, add 1 mL of the LC sample concentrate to each of a minimum of four 1-L aliquots of reagent water. A representative ground water may be used in place of the reagent water, but one or more unspiked aliquots must be analyzed to determine background levels, and the spike level must, at a minimum, exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 11.

10.2.3 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (S_R), for the results. Ground water background corrections must be made before R and S_R calculations are performed.

10.2.4 Table 2 and Tables 4-9 provide single laboratory recovery and precision data obtained for the method analytes from reagent and artificial ground waters, respectively. Similar results from dosed reagent and artificial ground waters should be expected by any experienced laboratory. Compare your laboratory results (obtained in Section 10.2.3) to the single laboratory recovery and precision data. If the results are not comparable, review potential problem areas and repeat the test. Your laboratory results are comparable if your calculated percent relative standard deviation (RSD) does not exceed 2.6 times the single laboratory RSD or 20 percent, whichever is greater, and your mean recovery lies within the interval $R \pm 3S$ or $R \pm 30\%$, whichever is greater.

10.3 In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.4 ASSESSING SURROGATE RECOVERY

10.4.1 All samples and blanks must be fortified with the surrogate spiking compound before extraction. A surrogate standard determination must be performed on all samples (including matrix spikes) and blanks.

10.4.2 Determine whether the measured surrogate concentration (expressed as percent recovery) falls between 70 and 120 percent.

10.4.3 When the surrogate recovery for a laboratory method blank is less than 70 or greater than 120 percent, the laboratory must take the following actions:

(1) Check calculations to make sure there are no errors.

(2) Check internal standard and surrogate standard spiking solutions for degradation, contamination, or other obvious abnormalities.

(3) Check instrument performance.

Reinject the laboratory method blank extract. If the reanalysis fails the 70 to 120 percent recovery criteria, the analytical system must be considered "out of control." The problem must be identified and corrected before continuing.

10.4.5 When the surrogate recovery for a sample is less than 70 percent or greater than 120 percent, the laboratory must establish that the deviation is not due to laboratory problems. The laboratory shall document deviations by taking the following actions:

(1) Check calculations to make sure there are no errors.

(2) Check internal standard and surrogate standard spiking solutions for degradation, contamination, or other obvious abnormalities.

(3) Check instrument performance.

Recalculate or reanalyze the extract if the above steps fail to reveal the cause of the noncompliant surrogate recoveries. If reanalysis of the sample or extract solves the problem, only submit the sample data from the analysis with surrogate spike recoveries within the required limits. If reanalysis of the sample or extract fails to solve the problem, then report all data for that sample as suspect.

10.5 ASSESSING THE INTERNAL STANDARD

10.5.1 An internal standard peak area or peak height check must be performed on all samples. All sample extracts must be fortified with the internal standard.

10.5.2 Internal standard recovery must be evaluated for acceptance by determining whether the measured peak area or peak height for the internal standard in any sample deviates by more than 30 percent from the average peak area or height for the internal standard in the calibration standards.

10.5.3 When the internal standard peak area or height for any sample is outside the limit specified in 10.5.2, the laboratory must investigate.

10.5.3.1 Single occurrence -- Reinject an aliquot of the extract to ensure proper sample injection. If the reinjected sample extract aliquot displays an internal standard peak area or height within specified limits, quantify and report results. If the reinjected sample extract aliquot displays an internal standard peak area or height outside the specified limits, but extract aliquots from other samples continue to give the proper area or height for the internal standard, assume an error was made during addition of the internal standard to the failed sample extract. Repeat the analysis of that sample.

10.5.3.2 Multiple Occurrence -- If the internal standard peak areas or heights for successive samples fail the specified criteria (10.5.2), check the instrument for proper performance. After optimizing instrument performance, check the calibration curve using a calibration check standard (Section 9). If the calibration curve is still applicable and if the calibration check standard internal standard peak area or height is within ±30% of the average internal standard peak area or height for the calibration standards, reanalyze those sample extracts whose internal standard failed the specified criteria. If the internal standard peak areas or heights now fall within the specified limits, report the results. If the internal standard peak areas or heights still fail to fall within the specified limits or if the calibration curve is no longer applicable, then generate a new calibration curve (Section 9) and reanalyze those sample extracts whose internal standard failed the peak area or height criteria.

10.6 ASSESSING ANALYTE RECOVERY

10.6.1 The laboratory must, on an ongoing basis, spike each of the target analytes into one sample per sample set (a sample set is all those samples extracted within a 24-hour period) or ten percent of the samples, whichever is of greater frequency.

10.6.1.1 The spiking concentration in the sample should be one to five times the background

concentration, or, if it is impractical to determine background levels before spiking, 15 times the EDL.

10.6.1.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. Spike a second sample aliquot with a laboratory control (LC) sample concentrate (the volume of the spike should be kept to a minimum so the solubility of the analytes of interest in water will not be affected) and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (R_i) as 100(A-B)%/T, where T is the known true concentration of the spike.

10.6.1.3 Compare the percent recovery (R_i) for each parameter with established QC acceptance criteria. QC criteria are established by initially analyzing five spiked samples as in Section 10.6.2, calculating the average percent recovery (R) and the standard deviation of the percent recovery (S_R) using the following equations:

$$R = \sum_{i=1}^{n} R_i/n$$

and

$$S_R = \frac{1}{n-1}\sum_{i=1}^{n} R_i^2 - \frac{\left(\sum_{i=1}^{n} R_i\right)^2}{n}$$

where: n = number of measurements for each analyte, and
R_i = individual percent recovery value.

Calculate QC acceptance criteria as follows:

Upper Control Limit (UCL) = $R + 3S_R$
Lower Control Limit (LCL) = $R - 3S_R$

Alternatively, the data generated during the initial demonstration of capability (Section 10.2) can be used to set the initial upper and lower control limits.

Monitor all data from dosed samples. Analyte recoveries must fall within the established control limits.

Update the method performance criteria on a continuous basis. After each five to ten new recovery measurements (R_is), recalculate R and S_R using all the data, and construct new control limits. When the total number of data points reach twenty, update the control limits by calculating R and S_R using only the most recent twenty data points.

10.6.2 Each quarter, it is essential that the laboratory analyze (if available) QC check standards. If the criteria established by the U.S. Environmental Protection Agency (USEPA) and provided with the QC standards are not met, corrective action needs to be taken and documented.

10.6.3 If any parameter fails the acceptance criteria for recovery in Section 10.6.1.3, a LC check standard containing each parameter that failed must be prepared and analyzed.

10.6.3.1 Prepare the LC check standard by adding 1 mL of LC check sample concentrate to a 1-L aliquot of reagent water. The LC check standard needs only to contain the parameters that failed the criteria in Section 10.6.1.3.

10.6.3.2 Analyze the LC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (R_i) as 100(A/T)%, where T is the true value of the standard concentration.

10.6.3.3 Compare the percent recovery (R_i) for each parameter with the QC acceptance criteria found on your control chart. Only parameters that failed the test in Section 10.6.2.4 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the source of the problem must be immediately identified and resolved before continuing the analyses. The analytical result for that parameter in the unspiked sample is suspect and must be so labeled. All results reported since the last dosed sample shown to be in control must also be labeled suspect.

If the recovery of any such parameter falls within the designated range, the laboratory performance for that parameter is judged to be in control, and the recovery problem encountered with the dosed sample is judged to be matrix-related, not system-related. The result for that parameter in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

10.6.4 The laboratory must analyze an unknown performance evaluation sample (when available) at least once a year. Results for each of the target analytes need to be within acceptable limits established by USEPA.

10.7 ASSESSING LABORATORY CONTAMINATION (METHOD BLANKS) -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. This is accomplished by the analysis of a laboratory method blank. A laboratory method blank is a 1-L aliquot of reagent water analyzed as if it was a sample. Each time a set of samples is extracted or there is a change in reagents, a laboratory method blank must be processed to assess laboratory contamination. If the method blank exhibits a peak within the retention time window of any analyte which is greater than or equal to one-half the EDL for that analyte, determine the source of contamination before processing samples and eliminate the interference problem.

10.8 ASSESSING INSTRUMENT PERFORMANCE (INSTRUMENT QC STANDARD) -- Instrument performance should be monitored on a daily basis by analysis of the instrument QC standard. The instrument QC standard contains compounds designed to indicate appropriate instrument sensitivity, column performance and chromatographic performance. Instrument QC standard components and performance criteria are listed in Table 10. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the GC-ECD system. A GC-ECD chromatogram generated from the analysis of the instrument QC standard is shown in Figure 2. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs. An instrument QC standard should be analyzed with each sample set.

10.9 ANALYTE CONFIRMATION - When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry or a second gas chromatography column must be used. A suggested confirmation column is described in Table 2.

10.10 ADDITIONAL QC - 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.

11. PROCEDURE - Validation data presented in this method were generated using the mechanical separatory funnel shaker.

11.1 HYDROLYSIS AND CLEANUP

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike sample with 50 uL of the surrogate standard spiking solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.1.2 Add 17 mL of 6 N NaOH to the sample, seal, and shake for 1 hour using the appropriate mechanical mixing device.

11.1.3 Add 300 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble the sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.1.4 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. 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 upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the organic phase. If the tumbler is used, return the aqueous phase to the tumbler bottle.

11.1.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 EXTRACTION AND CONCENTRATION

11.2.1 Add 17 mL of 12 N H_2SO_4 to the sample, seal, and shake to mix.

11.2.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.3 Add 300 mL ethyl ether to the sample, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.2.4 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. 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 upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the aqueous phase. Collect the extract in a 500-mL round-bottom flask containing about 5 g of acidified anhydrous sodium sulfate. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

11.2.5 Assemble a K-D concentrator by attaching a concentrator tube to a 500-mL evaporative flask.

11.2.6 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D in concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom flask and funnel with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

11.2.7 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. 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 min.

11.2.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether. Add 2 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 250 uL of methanol. Rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

11.3 ESTERIFICATION OF ACIDS

11.3.1 Assemble the diazomethane generator (Figure 1) in a hood.

11.3.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.2 grams Diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 1 min. Immediately remove first sample and replace with second sample. Bubble diazomethane through the second sample extract for 1 min. Diazomethane reaction mixture should be used to esterify only two samples; prepare new reaction mixture in Tube 2 to esterify each two additional samples.

11.3.3 Seal concentrator tubes with Teflon stoppers. Store at room temperature in a hood for 30 min.

11.3.4 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 5.0 mL with MTBE.

11.4 FLORISIL CLEANUP

11.4.1 Place a small plug of glass wool into a 5-mL disposable glass pipet. Tare the pipet, and measure 1 g of activated Florisil into the pipet.

11.4.2 Apply 5 mL of 5 percent methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the

Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.

11.4.3 Apply 5 mL methylated sample to the Florisil. Collect eluate in K-D tube.

11.4.4 Add 1 mL of 5 percent methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column. Collect eluate in a K-D tube. Repeat with 1-mL and 3-mL aliquots of 5 percent methanol in MTBE, collecting eluates in K-D tube.

11.4.5 If necessary, dilute eluate to 10 mL with 5 percent methanol in MTBE. Spike with 25 uL of internal standard solution. Thoroughly mix sample and place aliquot in a GC vial for subsequent analysis.

11.4.6 Seal the vial and store in a refrigerator if further processing will not be performed immediately. Analyze by GC-ECD.

11.5 GAS CHROMATOGRAPHY

11.5.1 Table 3 summarizes the recommended operating conditions for the GC. Included in Table 3 are retention times observed using this method. Examples of the separations achieved using these conditions are shown in Figures 2-4. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.3 are met.

11.5.2 Calibrate the system daily as described in Section 9. The standards and extracts must be in MTBE.

11.5.3 Inject 2 uL of the sample extract. Record the resulting peak size in area units.

11.5.4 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 a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

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

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the relative response for the analyte to the internal standard (RR_a) using the equation for the calibration curve described in Section 9.2.2.

12.2 For samples processed as part of a set where the laboratory control standard recovery falls outside of the control limits in Section 10, results for the affected analytes must be labeled as suspect.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range. In cases where analytes coeluted using primary analytical conditions, results from confirmatory GC conditions were used. EDL results are given in Table 2. Method range results are given in Tables 4-7.

13.2 In a single laboratory, analyte recoveries from two artificial ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two artificial matrices are given in Tables 8 and 9.

13.3 In a single laboratory, analyte recoveries from a ground water preserved with mercuric chloride were determined 0, 14, and 28 days after sample preparation. Analyte recoveries were also determined from sample extracts stored at 4°C for 14 and 28 days. Results were used to predict expected analyte stability in ground water samples and sample extracts. Analyte recoveries from the preserved, spiked ground water samples and stored sample extracts are given in Table 11.

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TABLE 1. METHOD ANALYTES

Analyte	CAS No. (a)	Ident. Code (b)
Acifluorfen	50594-66-6	17
Bentazon	25057-89-0	14
Chloramben	133-90-4	9
2,4-D	94-75-7	6
Dalapon	75-99-0	1
2,4-DB	94-82-6	12
DCPA acid metabolites (c)	--	16
Dicamba	1918-00-9	4
3,5-Dichlorobenzoic acid	51-36-5	2
Dichlorprop	120-36-5	5
Dinoseb	88-85-7	13
5-Hydroxydicamba	7600-50-2	10
4-Nitrophenol	100-02-7	3
PCP	87-86-5	7
Picloram	1918-02-1	15
2,4,5-T	93-76-5	11
2,4,5-TP	93-72-1	8

(a) CAS No. = Chemical Abstracts Service Registry Number.

(b) Code used for identification of peaks in figures; IS = 4,4'-dibromooctafluorobiphenyl internal standard; SUR = 2,4-dichlorophenylacetic acid surrogate standard.

(c) DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies.

TABLE 2. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 1) AND EDLs (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)	EDL(f)
Acifluorfen	0.020	ND(f)	6	139	0.0306	110	0.096
Bentazon (i)	0.20	ND	7	92	0.0346	19	0.20
Chloramben (h,i)	0.080	ND	7	118	0.0310	33	0.093
2,4-D (i)	0.20	ND	7	90	0.0248	14	0.20
Dalapon	1.0	ND	6	90	0.400	45	1.3
2,4-DB (h,i)	0.80	ND	7	37	0.229	78	0.80
DCPA diacid metabolite	0.020	ND	6	50	0.0052	53	0.020
Dicamba (i)	0.080	ND	7	155	0.0269	22	0.081
2,4-Dichlorobenzoic acid	0.060	0.00906	6	69	0.0194	38	0.061
Dichlorprop	0.20	ND	6	77	0.0814	53	0.26
Dinoseb (h,i)	0.080	ND	7	118	0.0623	66	0.19
5-Hydroxydicamba (i)	0.040	ND	7	49	0.00547	28	0.040
4-Nitrophenol	0.10	ND	6	89	0.0399	45	0.13
PCP (j)	0.040	0.0500	6	130	0.0242	24	0.076
Picloram (i)	0.12	ND	7	166	0.0468	24	0.14
2,4,5-T (i)	0.080	ND	7	87	0.0144	21	0.080
2,4,5-TP (h,i)	0.040	ND	7	140	0.0249	44	0.075

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) EDL = the level calculated by multipyling the standard deviation of replicate measurements times the students' t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom or the level of the compound in a sample yielding a peak in a final extract with signal-to-noise ratio of approximately five, whichever value is greater.

(h) Results from confirmatory analysis conditions.

(i) Results from spiking level 2.

(j) Results from spiking level 3.

TABLE 3. PRIMARY AND CONFIRMATION CHROMATOGRAPHIC CONDITIONS

Analyte	Relative or Absolute Retention Time for Given Conditions	
	Primary (a)(c)	Confirmation (b)(d)
Acifluorfen	1.52	43.2
Bentazon	1.21	34.6
Chloramben	1.08	(e)
2,4-D	0.927	27.0
Dalapon	0.123	(e)
2,4-DB	1.17	32.2
DCPA acid metabolites (c)	1.29	37.4
Dicamba	0.802	22.6
3,5-Dichlorobenzoic acid	0.676	17.7
Dichlorprop	0.909	25.6
Dinoseb	1.18	34.1
5-Hydroxydicamba	1.09	30.7
4-Nitrophenol	0.678	20.5
PCP	1.03	27.0
Picloram	1.23	35.6
2,4,5-T	1.11	30.9
2,4,5-TP	1.08	29.5

(a) Retention time relative to DBOB internal standard which elutes at approximately 27.5 min.

(b) Absolute retention time in minutes.

(c) Primary conditions:

Column:	30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 um film thickness (J&W)
Injection volume:	2 uL splitless with 45 second delay
Carrier gas:	He @30 cm/sec linear velocity
Injector temp:	250°C
Detector temp:	320°C
Oven temp:	Program from 60°C to 300°C at 4°C/min
Detector:	ECD

(d) Confirmation conditions:

Column:	30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 um film thickness (J&W)
Injection volume:	2 uL splitless with 45 second delay
Carrier gas:	He @30 cm/sec linear velocity
Injector temp:	250°C
Detector temp:	320°C
Oven temp:	Program from 60°C to 300°C at 4°C/min
Detector:	ECD

(e) Data not available.

TABLE 4. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 2) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.040	ND(f)	7	88	0.00826	23
Bentazon	0.20	ND	7	92	0.0346	19
Chloramben (g)	0.080	ND	7	118	0.0310	33
2,4-D	0.20	ND	7	90	0.0248	14
Dalapon	2.0	ND	6	107	0.457	21
2,4-DB (g)	0.80	ND	7	37	0.229	78
DCPA diacid metabolite	0.040	ND	7	89	0.0318	89
Dicamba	0.080	ND	7	155	0.0269	22
3,5-Dichlorobenzoic acid	0.12	ND	7	85	0.0117	11
Dichlorprop	0.40	ND	7	110	0.0689	16
Dinoseb (g)	0.080	ND	7	118	0.0623	66
5-Hydroxydicamba	0.040	ND	7	49	0.00547	28
4-Nitrophenol	0.20	ND	7	148	0.0450	15
PCP (h)	0.0080	ND	-	-	-	-
Picloram	0.12	ND	7	166	0.0468	24
2,4,5-T	0.080	ND	7	87	0.0144	21
2,4,5-TP (g)	0.040	ND	7	140	0.0249	44

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

(h) Analyte not detected at this spiking level.

TABLE 5. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.20	0.00171	6	121	0.0318	13
Bentazon	1.0	ND(f)	4	120	0.163	14
Chloramben (g)	0.40	0.0222	6	111	0.0615	13
2,4-D	1.0	0.00943	6	131	0.274	21
Dalapon	10	1.17	6	100	2.24	20
2,4-DB (g)	4.0	ND	6	87	0.5182	15
DCPA diacid metabolite	0.20	ND	6	74	0.0200	13
Dicamba	0.40	ND	6	135	0.129	24
3,5-Dichlorobenzoic acid	0.60	0.00500	6	102	0.098	16
Dichlorprop	2.0	0.0847	6	107	0.418	19
Dinoseb (g)	0.40	0.113	6	42	0.0971	34
5-Hydroxydicamba	0.20	ND	6	103	0.0325	16
4-Nitrophenol	1.0	ND	6	131	0.234	18
PCP	0.040	0.0500	6	130	0.0242	24
Picloram	0.60	0.308	6	91	0.149	17
2,4,5-T	0.40	0.00218	6	117	0.0639	14
2,4,5-TP (g)	0.20	0.00455	6	134	0.0631	23

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

TABLE 6. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 4) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.50	ND(f)	6	89	0.0525	12
Bentazon	2.5	ND	6	90	0.500	22
Chloramben (g)	1.0	0.0373	6	89	0.137	15
2,4-D	2.5	ND	6	94	0.307	13
Dalapon	25	1.33	6	82	2.69	12
2,4-DB (g)	10	ND	6	55	0.657	12
DCPA diacid metabolite	0.50	ND	6	50	0.0652	26
Dicamba	1.0	ND	6	87	0.0683	8
3,5-Dichlorobenzoic acid	1.5	0.0130	6	101	0.139	9
Dichlorprop	5.0	ND	6	90	0.525	12
Dinoseb (g)	1.0	ND	5	31	0.123	40
5-Hydroxydicamba	0.50	ND	6	85	0.0567	13
4-Nitrophenol	2.5	0.121	6	93	0.267	11
PCP	0.10	0.0227	6	82	0.00950	9
Picloram	1.5	0.0313	6	82	0.200	16
2,4,5-T	1.0	0.0207	6	90	0.0948	10
2,4,5-TP (g)	0.50	0.0132	6	90	0.0587	13

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

TABLE 7. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 5) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	2.0	ND(f)	6	90	0.0676	4
Bentazon	10	ND	6	80	1.02	13
Chloramben (g)	4.0	ND	6	55	0.0888	4
2,4-D	10	ND	6	74	0.481	6
Dalapon	100	1.77	6	81	4.28	5
2,4-DB (g)	40	ND	6	59	1.30	5
DCPA diacid metabolite	2.0	ND	6	23	0.338	74
Dicamba	4.0	ND	6	79	0.126	4
3,5-Dichlorobenzoic acid	6.0	ND	6	88	0.340	6
Dichlorprop	20	ND	6	78	0.623	4
Dinoseb (g)	4.0	ND	6	74	0.267	9
5-Hydroxydicamba	2.0	ND	6	67	0.170	13
4-Nitrophenol	10	ND	6	73	0.387	5
PCP	0.40	0.0664	6	73	0.0208	6
Picloram	6.0	ND	5	73	0.518	12
2,4,5-T	4.0	ND	6	77	0.181	6
2,4,5-TP (g)	2.0	ND	6	84	0.0861	5

(a) Data corrected for amount detected in blank.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

TABLE 8. RECOVERY OF ANALYTES FROM HARD ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.20	ND(f)	5	103	0.040	20
Bentazon	1.0	ND	5	82	0.378	46
Chloramben (g)	0.40	0.0157	7	112	0.043	9
2,4-D	1.0	0.0100	5	110	0.051	5
Dalapon	10	ND	5	128	3.027	24
2,4-DB (g)	4.0	ND	7	(h)	-	-
DCPA diacid metabolite	0.20	0.0200	5	81	0.048	27
Dicamba	0.40	ND	6	92	0.068	19
3,5-Dichlorobenzoic acid	0.60	0.0650	6	82	0.049	9
Dichlorprop	2.0	0.0251	5	106	0.099	5
Dinoseb (g)	0.40	ND	5	89	0.054	15
5-Hydroxydicamba	0.20	0.0224	5	88	0.012	6
4-Nitrophenol	1.0	0.100	7	127	0.374	27
PCP	0.040	0.0177	7	84	0.006	11
Picloram	0.60	ND	5	97	0.139	24
2,4,5-T	0.40	0.0419	5	96	0.017	4
2,4,5-TP (g)	0.20	ND	6	105	0.014	6

(a) Data corrected for amount detected in blank; hard artificial ground water used to generate these results was Absopure Natural Artesian spring Water obtained from the Absopure Water Company in Plymouth, Michigan.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

(h) Analyte not recovered from hard artificial ground water.

TABLE 9. RECOVERY OF ANALYTES FROM ORGANIC-CONTAMINATED ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.20	ND(f)	7	110	0.024	11
Bentazon	1.0	ND	7	111	0.089	8
Chloramben (g)	0.40	ND	7	104	0.049	12
2,4-D	1.0	ND	7	112	0.093	8
Dalapon	10	ND	7	109	1.140	11
2,4-DB (g)	4.0	ND	7	79	0.583	19
DCPA diacid metabolite	0.20	0.00857	7	78	0.018	11
Dicamba	0.40	0.0740	7	107	0.026	5
3,5-Dichlorobenzoic acid	0.60	ND	7	96	0.029	5
Dichlorprop	2.0	ND	7	106	0.105	5
Dinoseb (g)	0.40	ND	5	71	0.035	13
5-Hydroxydicamba	0.20	ND	7	102	0.013	6
4-Nitrophenol	1.0	0.0380	7	118	0.102	9
PCP	0.040	0.0137	5	133	0.004	6
Picloram	0.60	0.197	7	86	0.044	6
2,4,5-T	0.40	0.00343	7	108	0.027	6
2,4,5-TP (g)	0.20	ND	5	108	0.028	13

(a) Data corrected for amount detected in blank; organic-contaminated artificial ground water used to generate these results was reagent water spiked with humic acid at the 1 mg/L concentration level. Humic acid (sodium salt) obtained from Aldrich (H1,675-2) was used.

(b) n = number of recovery data points.

(c) R = average percent recovery.

(d) S = standard deviation.

(e) RSD = percent relative standard deviation.

(f) ND = interference not detected in blank.

(g) Results from confirmatory analysis conditions.

TABLE 10. QUALITY CONTROL STANDARD

Test	Analyte	Conc, g/L	Requirements
Sensitivity	Dinoseb	0.004	Detection of analyte; S/N > 3
Chromatographic performance	4-Nitrophenol	1.0	0.90 <PSF<1.05 (a) 0.90 <PGF<1.05 (b)
Column performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 0.4	Resolution >0.95 (c)

(a) PSF = peak symmetry factor. Calculated using the equation:

$$PSF = \frac{w(1/2)}{0.5 \times W(1/2)}$$

where w(1/2) is the width of the front of the peak at half height assuming the peak is split at the highest point and W(1/2) is the peak width at half height.

(b) PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

(c) Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

TABLE 11. PRESERVATION STUDY RESULTS

Day Extracted		0		0		0		14		28	
Day Analyzed	Spiking Level,	0		14		28		14		28	
Analyte	g/L	R(a)	RSD(b)	R	RSD	R	RSD	R	RSD	R	RSD
Acifluorfen	0.20	90	7	109	6	94	9	98	9	96	17
Bentazon	1.0	104	7	114	5	75	5	102	6	76	10
Chloramben(c)	0.40	111	7	108	6	117	1	95	22	118	8
2,4-D	1.0	122	14	118	12	130	20	112	9	111	14
Dalapon	10	78	33	68	26	90	23	84	11	123	7
2,4-DB(c)	4.0	52	30	58	32	31	31	57	6	45	48
DCPA diacid metabolite	0.20	80	8	91	15	56	13	112	27	56	10
Dicamba	0.40	106	7	106	4	121	5	107	6	117	11
3,5-Dichlorobenzoic acid	0.60	82	26	110	17	112	2	97	9	115	8
Dichlorprop	2.0	129	17	114	3	129	9	111	3	119	8
Dinoseb(c)	0.40	100	6	76	1	120	8	36	47	128	6
5-Hydroxydicamba	0.20	75	19	85	7	87	6	65	10	86	6
4-Nitrophenol	1.0	121	12	102	11	129	16	92	16	153	7
PCP	0.040	125	9	130	9	119	9	57	2	56	10
Picloram	0.60	121	6	134	4	83	8	135	5	75	16
2,4,5-T	0.40	120	13	115	3	103	11	103	2	89	7
2,4,5-TP(c)	0.20	103	4	98	3	99	11	60	1	95	4

(a) R = average percent recovery from triplicate analyses.

(b) RSD = percent relative standard deviation.

(c) Calculated using confirmatory analytical conditions.

Figure 1

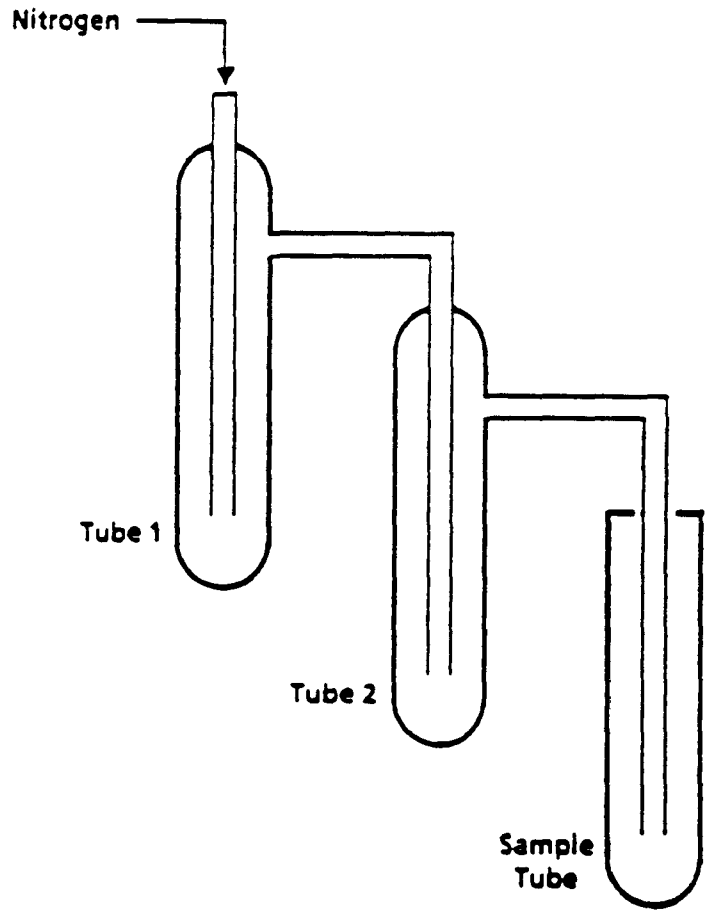


Figure 2

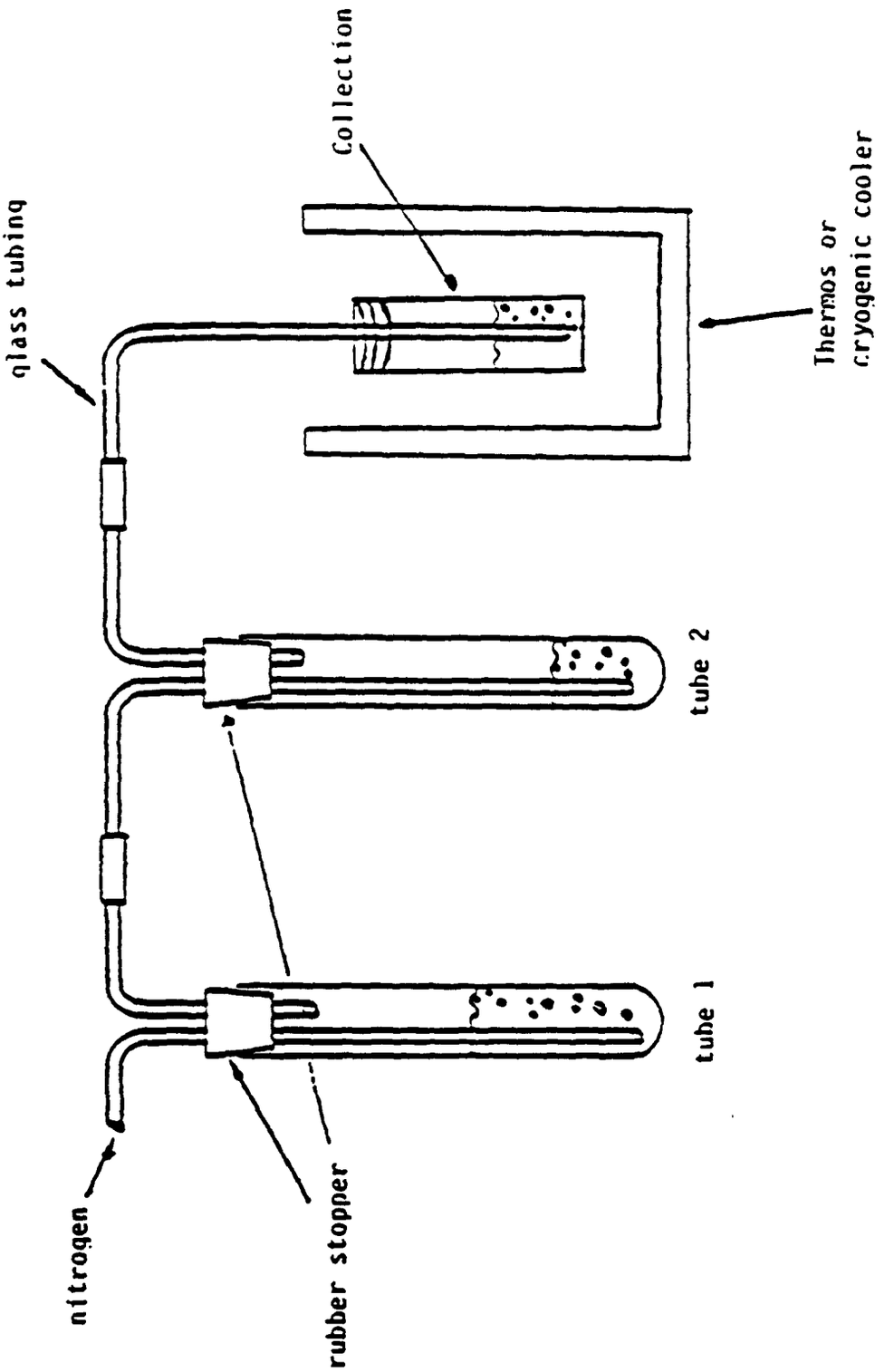
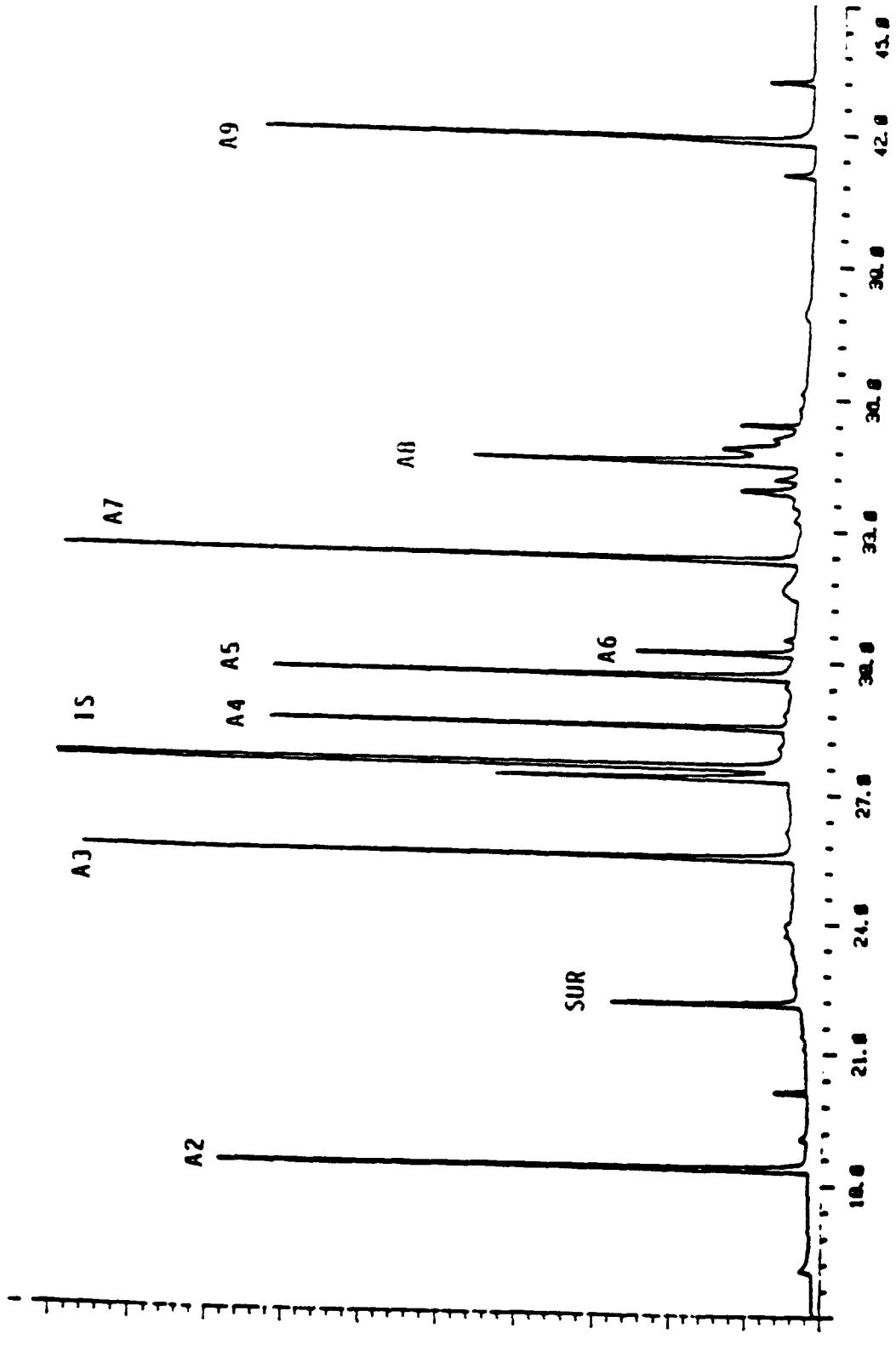

Collection
glass tubing
Thermos or
cryogenic cooler
tube 2
tube 1
nitrogen
rubber stopper

Figure 3



GC-ECD CHROMATOGRAM OF [illegible]IKING MIX A (SPIKING LEVEL 5)

Figure 4

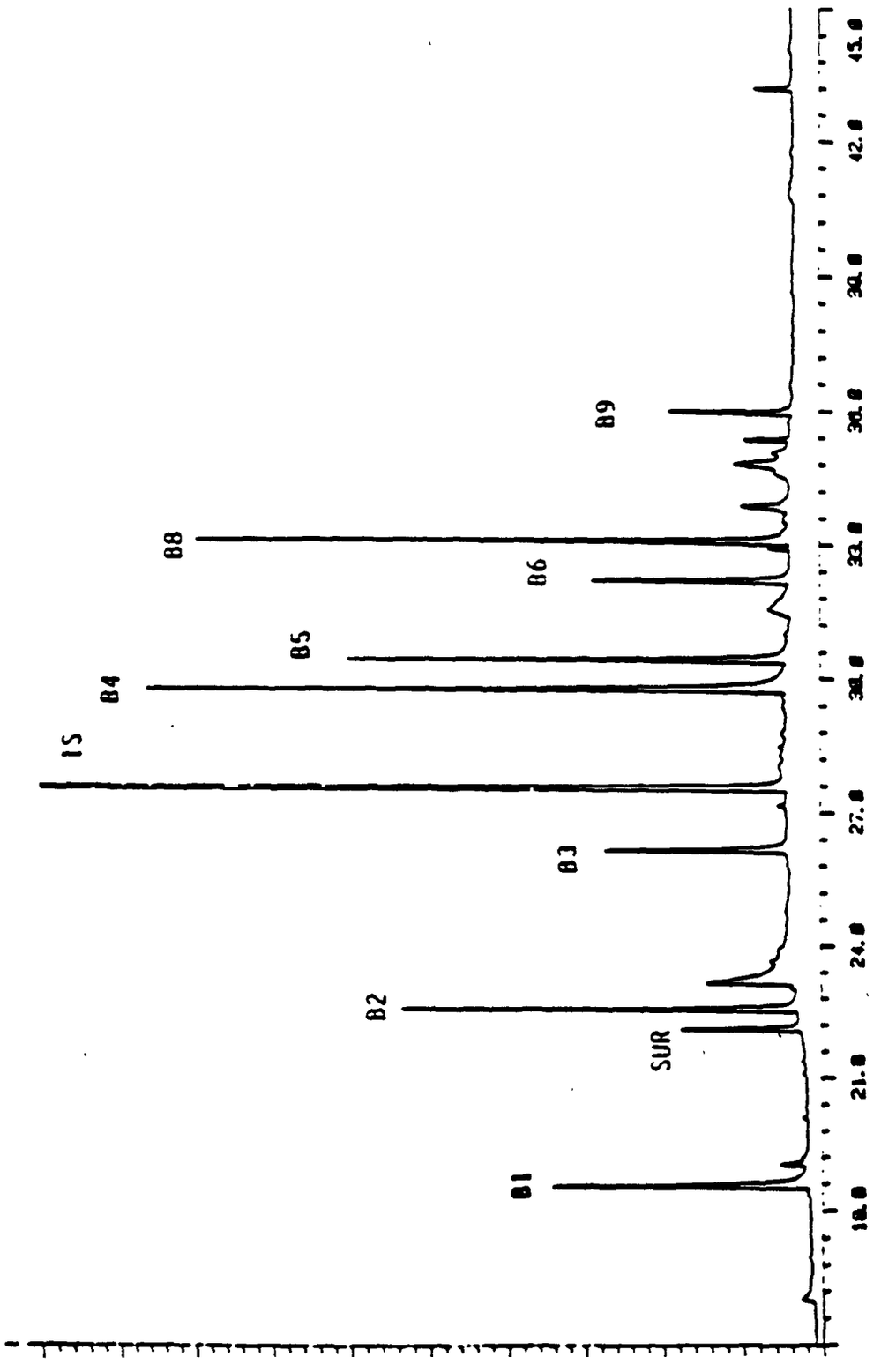
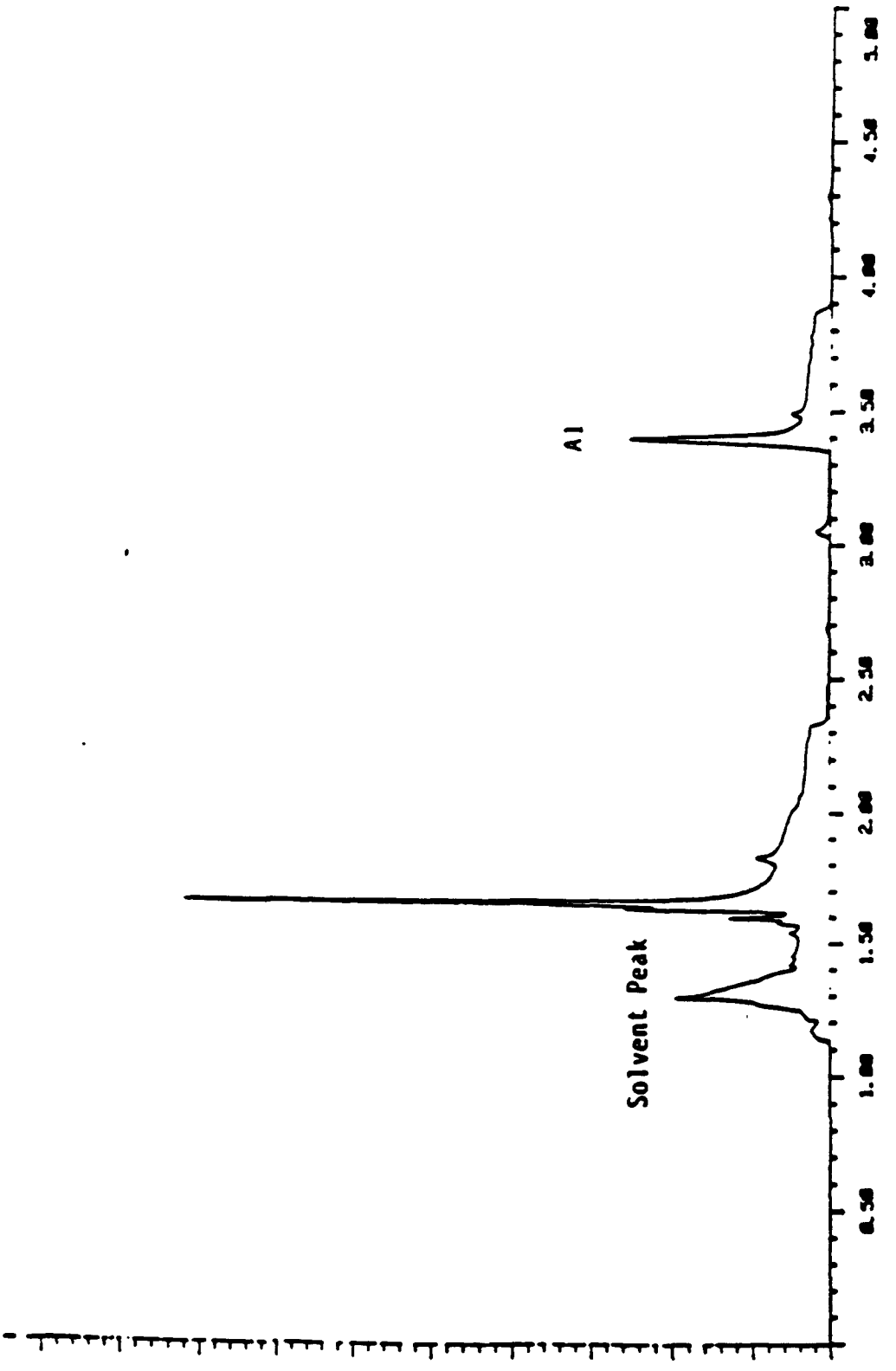
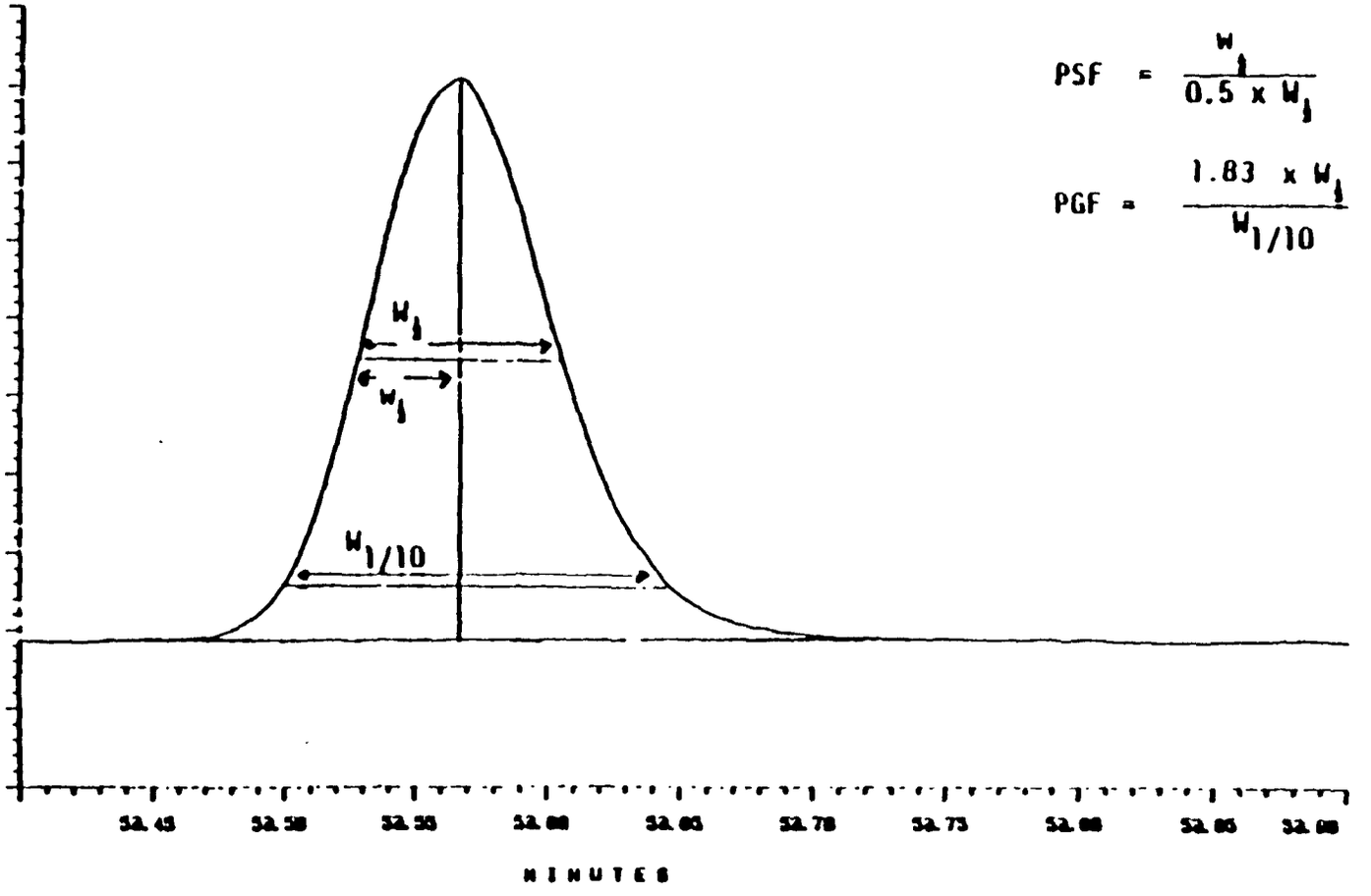


FIGURE 4. GC-ECD CHROMATOGRAM OF SPIKING MIX B (SPIKING LEVEL 5)
(Peak identification codes given in Table 1 of Appendix A)

Figure 5



GC-ECD CHROMATOGRAM OF DALAPON (A1) FROM SPIKING MIX A (SPIKING LEVEL 3)



EQUATIONS USED TO CALCULATE PEAK SYMMETRY FACTOR (PSF) AND PEAK GAUSSIAN FACTOR (PGF)

APPENDIX B

FORMAT FOR NPS DATA FILES

FORMAT FOR NPS INSTRUMENT CONTROL DATA

LINE	COLUMNS	DESCRIPTION
1	1-3	Lab
	6-11	Method
	14-21	Date_Ana
	24-30	Analyst
	35-37	S/N
	42-44	PSF
	49-51	PGF
	55-58	Res.
2	BLANK	
3-??	1-3	enter LAB ABBREVIATION (JMM)
	6-11	enter METHOD NUMBER
	14-21	enter DATE ANALYZED
	24-30	enter ANALIST'S INITIALS
	33-37	enter SIGNAL TO NOISE RATIO
	40-44	enter PEAK SYMMETRY FACTOR
	47-51	enter PEAK GEOMETRY FACTOR
	54-58	enter RESOLUTION

Format for National Pesticide Survey (NPS) Data
(cont.)

LINE	COLUMNS	DESCRIPTION
10	1-4	Type
	8-13	Spiker
	16-22	Extract
	25-31	Analyst
	34-40	Sam_Vol
	43-49	Ext_Vol
	52-60	Int. Std.
	65-70	% Surr
11	1-5	enter SAMPLE TYPE
	8-13	enter SPIKER'S INITIALS
	16-22	enter EXTRACTOR'S INITIALS
	25-31	enter ANALYST'S INITIALS
	34-40	enter VOLUME OF SAMPLE
	43-49	enter VOLUME OF EXTRACT
	52-62	enter INTERNAL STANDARD
	65-70	enter PERCENT RECOVERY OF SURROGATE
12	BLANK	
13	1-8	Comments
14	1-80	enter ANY PERTINENT COMMENTS ON SAMPLE AND ANALYSIS
15	BLANK	
16	1-7	Analyte
	29-33	Conc.
	39-45	Analyte
	67-71	Conc.
17-??	1-25	enter ANALYTE'S NAME
	28-34	enter CONCENTRATION OR PERCENT RECOVERY
	39-63	enter ANALYTE'S NAME
	66-72	enter CONCENTRATION OR PERCENT RECOVERY

NOTES ON NPS FORM.T

1) The format for any date is mm/dd/yy. A m ssing date should be entered as 01/01/60.

2) The format for any time is hh:mm is 24 hou. format. A missing time should be 00:00.

3) Any other data that is missing should be e: tered with a period (.).

4) The number of decimal places should be as ollovs:

Concentration	3	(significa: t figures)
Percent Recovery	1	
Internal Standard	1	(percent r· covery)
Instrument Controls	2	
pH	1	(method 9 · nly)
Temperature	0	
Volumes	0	

5) The code for columns is as follovs:

Primary	PRIM
Confirmatory	CONF
Third	GCMS

6) The laboratory code for Montgomery is JMM

7) The codes for Type are as follovs:

Field sample	SAMP
Shipping blank	SBLK
Method blank	MBLK
Lab control standard	LCS@
Lab spike sample	LSS@#
Time storage extract day 14	HTE@
Time storage sample day 14	HTS@
Time storage sample day 0	DTS@

where @ is the mix letter (A, B, C)
and # is the spiking level (0, 1, ,or 3)

8) There should be at least one blank line between samples in the NPS data file.

9) The codes for Concentration and Percent Re·overies are as follovs:

Not Analyzed	. (period)
Not Detected (< 1/2 MRL)	-999
Saturated	-777
Compound failed LCS but positive by GC: S	-666
Compound failed LCS but negative	-444
Compound failed LCS but postive, no confirmation needed (spiked)	-333
> 1/2 MRL but < MRL, not conf	-222
> 1/2 MRL but < MRL, conf not needed	-222
> 1/2 MRL but < MRL, conf by GCMS	-111
Above MRL but not quantified (as for GCMS or qualitative cmpds)	888

10) If a reported value is greater the (>) s·me number in the NPS instrument control data, then use a minus sign (-) in. tead of >.

APPENDIX C

MASS IONS FOR GCMS CONFIRMATION

TABLE 1 EI AND CI MS CHARACTERISTIC IONS FOR METHODS 1-3 ANALYTES

ANALYTE	METHOD NUMBER	AMOUNT INJECTED, NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
ALACHLOR	1	20	269.8	1808	160	269	188	A5	238	270	240	B60
AMETRYN	1	10	227.4	1833	227	212	170	A92	228	229	256	B43
ASPON	1	20	378.5	1932	211	253	115	A38	379	337	407	B94
ATRATON	1	10	211.3	1546	196	211	169	A103	212	213	240	B54
ATRAZINE	1	20	215.7	1580	200	215	173	A61	216	180	244	B11
AZINPHOS METHYL	1	40	317.3	2647	160	132	77	A79	160	134	127	B30
BROMACIL	1	40	261.2	1914	205	207	190	A93	261	263	205	B44
BUTACHLOR	1	10	311.9	2147	176	160	57	A72	238	240	312	B23
BUTYLATE	1	10	217.4	1017	156	217	146	A53	218	156	246	B3
CARBOXIN	1	20	235.3	2207	143	235	87	A99	236	143	94	B50
CHLORPROPHAM (A)	1		-	-	-	-	-	-	-	-	-	-
CHLORPYRIFOS	1	20	349.0	1936	197	198	314	A70	350	352	121	B19
CHLORPYRIFOS METHYL	1	40	322.5	1778	286	288	125	A37	324	322	111	B93
COUMAPHOS	1	60	362.8	2854	109	362	364	A81	363	365	195	B32
CYCLOATE	1	10	215.4	1371	83	215	154	A58	216	154	244	B8
DEMETON O	1	20	258.4	1349	88	171	60	A57	197	259	139	B7
DEMETON-S	1	10	258.4	1333	88	170	60	A60	139	259	197	B10
DIAZINON (A)	1	10	304.4	-	-	-	-	-	-	-	-	-
DICHLOFENTHION	1	20	314.2	1757	281	281	223	A90	315	317	153	B41
DICHLORVOS	1	40	220.0	685	109	220	185	A51	221	223	185	B1
DIOXATHION (A)	1	80	456.6	-	-	-	-	-	-	-	-	-
DIPHENAMID	1	10	239.3	1984	72	239	167	A96	240	241	268	B47
DISULFOTON	1	20	274.4	1660	88	186	274	A63	91	275	213	B13
DISULFOTON SULFONE	1	40	306.4	2127	(C)	-	-	-	307	121	155	B22
DISULFOTON SULFOXIDE (A)	1	40	290.4	-	-	-	-	-	-	-	-	-
EPN	1	20	323.3	2552	157	169	185	A101	324	294	110	B52
EPTC	1	20	189.4	880	128	189	86	A52	190	128	218	B2
ETHION	1	40	384.5	2337	231	153	384	A74	199	385	155	B25
ETHOPROP	1	10	242.4	1374	158	242	200	A86	241	167	93	B37

TABLE I (continued)

ANALYTE	METHOD NUMBER	AMOUNT INJECTED, NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
ETHYL PARATHION	1	10	291 3	1934	97	291	109	A21	292	262	276	B77
FAMPHUR	1	40	325 4	2382	218	125	93	A100	326	186	111	B51
FENAMIPHOS	1	10	303 4	2169	303	217	154	A98	304	139	167	B49
FENARIMOL	1	20	330 2	2719	139	219	330	A80	331	333	219	B31
FENITRITHION	1	20	277 2	1871	125	277	260	A94	278	248	262	B45
FENSULFOTHION	1	10	308 4	2304	293	308	141	A73	293	309	213	B24
FENTHION	1	20	278 3	1926	278	125	169	A95	279	247	215	B46
FLURIDONE	1	20	329 3	3059	328	329	310	A82	330	310	358	B33
FONOFOS	1	10	246 3	1611	109	246	137	A1	247	137	111	B56
HEXAZINONE	1	40	252.4	2453	171	128	83	A77	253	171	199	B28
LETHANE	1	20	-	1196	57	86	101	A56	148	204	101	B6
MALATHION	1	40	330 4	1920	173	158	127	A69	129	331	285	B18
MERPHOS	1	40	298 5	2199	57	169	202	A8	91	315	225	B63
METHYL PARAOXON	1	40	-	1664	109	247	230	A2	248	218	232	B57
METHYL PARATHION	1	20	263 2	1783	109	263	125	A3	264	234	248	B59
METOLACHLOR	1	20	283 8	1912	162	238	240	A7	284	286	250	B62
METRIBUZIN	1	10	214 3	1775	198	144	214	A64	215	200	115	B14
MEVINPHOS	1	40	224 2	1030	127	192	109	A83	193	225	127	B34
MGK 264	1	10	275 0	2011	164	210	275	A71	276	210	304	B21
MGK 326	1	20	251 0	1798	165	192	179	A65	252	210	238	B15
MOLINATE	1	10	187 3	1187	126	187	55	A84	188	126	216	B35
NAPROPAMIDE (A)	1		-	-	-	-	-	-	-	-	-	-
NORFLURAZON	1	20	303 7	2421	145	303	305	A76	304	306	284	B27
PEBULATE	1	10	203 4	1074	128	203	72	A55	204	128	148	B5
PHORATE	1	20	260 4	1475	75	260	121	A59	261	199	155	B9
PHOSMET	1	20	317 3	2543	160	77	93	A78	160	318	162	B29
PROMETON	1	10	225 4	1578	58	225	210	A104	226	227	254	B55
PROMETRYN	1	10	241 4	1841	241	184	226	A66	242	196	270	B16
PRONAMIDE	1	10	256 1	1626	173	255	175	A89	256	258	190	B40

TABLE 1 (continued)

ANALYTE	METHOD NUMBER	AMOUNT INJECTED, NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
PROPAZINE	1	10	230.0	1588	214	229	231	A88	230	232	194	B39
RONNEL	1	40	321.5	1824	285	287	125	A6	323	321	111	B61
SECBUMETON	1	40	225.3	1685	196	225	169	A3	226	196	254	B58
SIMAZINE	1	20	201.7	1554	201	203	186	A87	202	204	166	B38
SIMETRYN	1	20	213.3	1810	213	155	198	A91	214	168	242	B42
STIROFOS	1	10	366.0	2130	(C)	-	-	-	127	367	365	B107
SULPROVOS	1	20	322.5	2363	156	322	140	A75	323	141	169	B26
TEBUTHIURON (A)	1	80	228.3	-	-	-		-	-	-	-	-
TERBACIL (A)	1	20	216.7	-	-	-	-	-	-	-	-	-
TERBUFOS (A)	1		-	-	-	-	-	-	-	-	-	-
TERBUTHYLAZINE	1	20	229.8	1623	214	229	216	A62	230	232	194	B12
TERBUTRYN	1	20	241.4	1873	185	241	226	A67	242	196	186	B17
THIONAZIN	1	20	248.2	1331	97	248	107	A85	249	97	277	B36
TOKUTHION	1	40	344.0		113	309	311	A106	345	347	163	B108
TRIADEMEFON	1	40	293.8	1944	57	208	85	A97	294	296	168	B48
TRICHLORFATE	1	10	332.6	1966	109	297	299	A105	333	335	337	B20
TRICYCLAZOLE	1	40	189.2	2161	189	162	135	A9	190	165	218	B64
VERNOLATE	1	10	203.3	1048	128	203	86	A54	204	128	232	B4
ALDRIN	2	20	364.9	1875	66	263	265	A20	329	331	293	B76
A-BHC	2	40	290.8	1461	219	217	181	A32	219	217	255	B88
B-BHC	2	40	290.8	1557	219	217	181	A16	219	217	147	B72
D-BHC	2	40	290.8	1651	219	217	181	A17	219	217	147	B73
G-BHC	2	40	290.8	1565	219	217	181	A34	219	217	255	B90
A-CHLORDANE	2	40	409.8	2109	373	375	272	A40	101	373	375	B96
G-CHLORDANE	2	20	409.8	2067	373	375	272	A23	101	373	375	B79
CHLOROBENZILATE	2	10	325.2	2286	251	253	139	A11	307	325	309	B66
CHLOROPROPYLATE (A)	2		-	-	-	-	-	-	-	-	-	-
CHLORONEB	2	20	207.1	1154	206	208	191	A13	207	209	192	B68

TABLE 1 (cont.)

ANALYTE	METHOD NUMBER	AMOUNT INJECTED NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
CHLORTHALONIL	2	40	265.9	1666	266	264	231	A18	267	265	231	B74
DCPA	2	10	332.0	1936	301	332	330	A39	333	331	299	B95
4,4'-DDD	2	20	320.0	2209	235	237	165	A25	207	283	285	B81
4,4'-DDE	2	20	318	2188	246	318	316	A10	319	317	283	B45
4,4'-DDT	2	40	354.5	2404	235	237	165	A28	243	319	317	B84
DICHLORAN (A)	2		-	-	-	-	-	-	-	-	-	-
DIELDRIN	2	40	380.9	2171	79	108	263	A41	345	347	309	B97
ENDOSULFAN I	2	80	406.9	2100	195	339	341	A24	407	409	373	B80
ENDOSULFAN II	2	40	406.9	2263	195	339	341	A26	277	407	409	B82
ENDOSULFAN SULFATE (A)	2		-	-	-	-	-	-	-	-	-	-
ENDRIN	2	40	380.9	2227	81	263	265	A42	345	347	381	B98
ENDRIN ALDEHYDE	2	40	381.9	2315	67	345	347	A27	345	381	383	B83
ETRIDIAZOLE	2	10	247.5	-	211	248	213	A68	211	247	249	B70
HEPTACHLOR	2	20	373.3	1778	100	272	274	A19	337	339	267	B75
HEPTACHLOR EPOXIDE	2	20	389.3	1999	81	353	355	A22	353	355	117	B78
METHOXYCHLOR	2	40	345.7	2573	227	228	114	A29	239	345	347	B85
PROPACHLOR	2	10	211.7	1331	120	211	176	A102	212	214	178	B53
TRANS-PERMETHRIN	2	2	391.3	2841	183	163	-	A30	183	213		B86
TREFLAN	2	40	335.3	1675	306	264	290	A15	336	316	232	B71
ACIFLUORFEN	3	80	374.6	2590	75	375	223	A50	346	376	244	B106
BENTAZON	3	60	254.3	2072	212	254	105	A48	255	213	241	B104
CHLORAMBEN (A)	3		-	-	-	-	-	-	-	-	-	-
2,4-D METHYL ESTER	3	40	235.0	1374	199	234	236	A14	235	237	175	B69
DALAPON (D)	3	80	157.0	-	-	-	-	-	-	-	-	-
2,4-DB	3	20	263.1	1932	101	162	59	A47	101	263	231	B103
DCPA DIACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DCPA MONOACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DICAMBA	3	40	235.0	1165	203	236	205	A31	203	235	205	B87

APPENDIX D

DIXON'S TEST

DIXON'S TEST

Dixon's test is used to confirm the suspicion of outliers of a set of data (for example, control chart data points). It is based on ranking the data points and testing the extreme values for credibility. Dixon's test is based on the ratios of differences between observations and does not involve the calculation of standard deviations.

The procedure for Dixon's test is as follows (from Taylor, 1987):

1) The data is ranked in order of increasing numerical value. For example:

$$X_1 < X_2 < X_3 < \ldots < X_{n-1} < X_n$$

2) Decide whether the smallest, X_1, or the largest, X_n, is suspected to be an outlier.

3) Select the risk you are willing to take for false rejection. For use in this QAPP we will be using a 5% risk of false rejection.

4) Compute one of the ratios in Table 1. For use in this QAPP we will be using ratio r_{22}, since we will be using between 20 and 17 points for the control charts.

5) Compare the ratio calculated in Step 4 with the appropriate values in Table 2. If the calculated ratio is greater than the tabulated value, rejection may be made with the tbulated risk. Fort his QAPP we will be using the 5% risk values (bolded).

Example (from Taylor)

Given the following set of ranked data:

10.45, 10.47, 10.47, 10.48, 10.49, 10.50, 10.50, 10.53, 10.58

The value 10.58 is suspected of being an outlier.

1) Calculate r_{11}

$$r_{11} = \frac{10.58 - 10.53}{10.58 - 10.47} = \frac{0.05}{0.11} = 0.454$$

2) A 5% risk of false rejection (Table 2), $r_{11} = 0.477$

3) Therefore there is no reason to reject the value 10.58.

4) Note that at a 10% risk of false rejection $r_{11} = 0.409$, and the value 10.58 would be rejected.

TABLE 1

CALCULATION OF RATIOS

Ratio	For use if n is between	if X_n is suspect	if X_1 is suspect
r_{10}	3 - 7	$\frac{(X_n - X_{n-1})}{(X_n - X_1)}$	$\frac{(X_2 - X_1)}{(X_n - X_1)}$
r_{11}	8 - 10	$\frac{(X_n - X_{n-1})}{(X_n - X_2)}$	$\frac{(X_2 - X_1)}{(X_{n-1} - X_1)}$
r_{21}	11 - 13	$\frac{(X_n - X_{n-2})}{(X_n - X_2)}$	$\frac{(X_3 - X_1)}{(X_{n-1} - X_1)}$
r_{22}	14 - 25	$\frac{(X_n - X_{n-2})}{(X_n - X_3)}$	$\frac{(X_3 - X_1)}{(X_{n-2} - X_1)}$

Note that for use in this QAPjP ratio r_{22} will be used.

TABLE 2

VALUES FOR USE WITH THE DIXON TEST FOR OUTLIERS

		Risk of False Rejection			
Ratio	n	0.5%	1%	5%	10%
	3	0.994	0.988	0.941	0.806
	4	0.926	0.889	0.765	0.679
r_{10}	5	0.821	0.780	0.642	0.557
	6	0.740	0.698	0.560	0.482
	7	0.080	0.637	0.507	0.434
	8	0.725	0.683	0.554	0.479
r_{11}	9	0.677	0.635	0.512	0.441
	10	0.639	0.597	0.477	0.409
	11	0.713	0.679	0.576	0.517
r_{21}	12	0.675	0.642	0.546	0.490
	13	0.649	0.615	0.521	0.467
	14	0.674	0.641	0.546	0.492
	15	0.647	0.616	0.525	0.472
	16	0.624	0.595	0.507	0.454
	17	0.605	0.577	0.490	0.438
	18	0.589	0.561	0.475	0.424
	19	0.575	0.547	0.462	0.412
r_{22}	20	0.562	0.535	0.450	0.401
	21		0.524	0.440	0.391
	22		0.514	0.430	0.382
	23		0.505	0.421	0.374
	24		0.497	0.413	0.367
	25		0.489	0.406	0.360

Note that for this QAPjP the 5% risk level will be used for ratio r_{22}.

Reference:

John K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI, 1987.

Chapter 7

DATA HANDLING AND REPORTING

7.1 Introduction

To obtain meaningful data on water quality, the sample collector must obtain representative sample and then deliver it unchanged for analysis. The analyst must perfor the proper analysis in the prescribed fashion, complete calculations, and convert results final form for permanent recording of the analytical data in meaningful, exact terms. The results are transferred to a storage facility for future interpretation and use.

The following sections discuss processing of actual values, recording and reporting of data the proper way, some means of quality control of data, and the storage and retrieval of dat

7.2 The Analytical Value

7.2.1 Significant Figures

The term "significant figure" is used, sometimes rather loosely, to describe a judgment the reportable digits in a result. When the judgment is not soundly based, meaningful digi are lost or meaningless digits are reported. On the other hand, proper use of significa figures gives an indication of the reliability of the analytical method used.

The following discussion describes the process of retention of significant figures.

A number is an expression of quantity. A figure or digit is any of the characters 0, 1, 2, 3, 5, 6, 7, 8, 9, which, alone or in combination, serve to express a number. A significant figu is a digit that denotes the amount of the quantity in the particular decimal place in which stands. Reported analytical values should contain only significant figures. A value is ma up of significant figures when it contains all digits known to be true and one last digit doubt. For example, if a value is reported as 18.8 mg/l, the 18 must be firm while the 0.8 somewhat uncertain, but presumably better than one of the values 0.7 or 0.9 would be.

The number zero may or may not be a significant figure depending on the situation.

Final zeros after a decimal point are always meant to be significant figures. For example, the nearest milligram, 9.8 g is reported as 9.800 g.

Zeros before a decimal point with nonzero digits preceding them are significant. With preceding nonzero digit, a zero before the decimal point is not significant.

If there are no nonzero digits preceding a decimal point, the zeros after the decimal po but preceding other nonzero digits are not significant. These zeros only indicate the positi of the decimal point.

Final zeros in a whole number may or may not be significant. In a conductiv measurement of 1,000 μmho/cm, there is no implication by convention that the conduct ity is 1,000 ± 1 μmho. Rather, the zeros only indicate the magnitude of the number.

APPENDIX E

ROUNDING AND SIGNIFICANT FIGURES

APPENDIX F

EXTRACTION SOP FOR METHOD 1

When one number is subtracted from another, rounding off should be completed after the subtraction operation, to avoid possible invalidation of the operation.

When two numbers are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the multiplier with the fewer significant digits.

When two numbers are to be divided, the division is carried out on the two numbers using all digits. Then the quotient is rounded off to the number of significant digits of the divisor or dividend, whichever has the fewer.

When a number contains n significant digits, its root can be relied on for n digits, but its power can rarely be relied on for n digits.

7.2.2.3 Rounding Off the Results of a Series of Arithmetic Operations

The preceding rules for rounding off are reasonable for most calculations; however, when dealing with two nearly equal numbers, there is a danger of loss of all significance when applied to a series of computations that rely on a relatively small difference in two values. Examples are calculation of variance and standard deviation. The recommended procedure is to carry several extra figures through the calculations and then to round off the final answer to the proper number of significant figures.

7.3 Glossary of Statistical Terms

To clarify the meanings of statistical reports and evaluations of water quality data, the following statistical terms are introduced. They are derived in part from usage (1,2) of the American Society for Quality Control.

Accuracy—The difference between an average value and the true value when the latter is known or assumed.

Arithmetic mean—The arithmetic mean (or average) of a set of n values is the sum of the values divided by n:

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Bias—A systematic error due to the experimental method that causes the measured values to deviate from the true value.

Confidence limit, 95 percent—The limits of the range of analytical values within which a single analysis will be included 95 percent of the time.

$$95 \text{ percent CL} = \bar{X} \pm 1.96S$$

where CL is the confidence level and S is the estimate of the standard deviation.

EXTRACTION NPS-1
LIQUID-LIQUID EXTRACTION

Scope and Application

This procedure can be used to measure certain nitrogen- and phosphorous-containing pesticides. The following compounds can be determined using this method:

Alachlor
Ametryn
Atraton
Atrazine
Bromacil
Butachlor
Butylate
Carboxin
Chlorpropham
Cycloate
Demeton-S
Diazinon
Dichlorvos
Diphenamid
Disulfoton
Disulfoton sulfone
Disulfoton sulfoxide (c)
EPTC
Ethoprop
Fenamiphos
Fenarimol
Fluridone
Hexazinone
Merphos
Methyl paraoxon
Metolachlor
Metribuzin
Mevinphos
MGK 264
Molinate
Napropamide
Norflurazon
Pebulate
Prometon
Prometryn
Pronamide
Propazine
Simazine
Simetryn
Stirofos
Tebuthiuron
Terbacil
Terbufos
Terbutryn
Triademefon
Tricyclazole
Vernolate

This is a capillary gas chromotographic method.

Method Summary

A measured volume of approximately 1 L is solvent extracted with three portions of methylene chloride. The methylene chloride extract is isolated, dried, and concentrated to 5 ml after solvent substitution with MTBE. Separation and measurement of the analytes is done by capillary GC with a nitrogen-phosphorous detector.

EXTRACTION NPS-1

Page	Revision #	Revision Date
1	2	March 5. 1990
2	2	March 5. 1990
3	1	October 31. 1989
4	1	October 31. 1989
5	2	March 5. 1990
6	1	October 31. 1989
7	1	October 31. 1989
8	1	October 31. 1989
9 (last)	1	October 31. 1989

Approved:

Group Leader: _____

Operations Manager: _____

QA Officer: _____

Laboratory Director: _____

Reagents and Standards

1) Reagent water, organic-free
2) Sodium Sulfate - Anhydrous. ACS Certified. Baked @ 400°C for four hours.
3) Acetone - Burdick and Jackson or equivalent
4) HCl - ACS certified. Make 0.1 N HCl by slowly adding 8.3 ml concentrated HCl to 900 ml DI and diluting to 1 L with DI.
5) Dipotassium phosphate - ACS grade. Make 0.1 M K_2PO_4 by diluting 17.42 g K_2PO_4 to 1 L with DI.
6) Phosphate buffer, pH 7 - Prepare by mixing enough solution at a ratio of 29.6 ml 0.1 N HCl to 50 ml 0.1 M dipotassium phosphate to make a total of 50 ml per sample (for example, for 14 samples use 266 ml 0.1 N HCl and 450 ml 0.1 M K_2PO_4).
7) 2-Nitrotoluene - Aldrich neat - internal standard
8) MTBE (methyl-tert-butyl-ether) - 99.9% EM Science
9) Methylene chloride - Pesticide quality or equivalent
10) 1,3-Dimethyl-2-nitro-m-benzene - Aldrich neat - surrogate standard.
11) Sodium Chloride, crystal, ACS certified. Baked @ 400°C for four hours.

New spike solutions should be compared to old ones by the analyst. Values should agree within 10%. If not, prepare new standards and compare all three. If the two new ones agree the old solution may have been incorrect or may have deteriorated. If the last solution agrees with the old one use it and discard the other.

Sample Collection, Handling and Preservation

1) Samples are collected in 1 L amber glass bottles with Teflon septa.
2) Samples should be packed in ice and shipped to the laboratory for next day delivery.
3) Samples should be extracted within 14 days of collection and analyzed within 14 days of extraction.

Calibration Procedure

1) Reagent and extraction blanks are included in each analytical run.
2) An LCS standard for each of the three mixes is extracted each day with each set of samples.

Extraction Summary

Aqueous samples are extracted three times with 60 ml portions of methylene chloride at a pH of 7. The extract is dried with sodium sulfate and concentrated to 5 mls with a Kuderna-Danish apparatus. The extract is solvent exchanged twice with MTBE and taken to a final volume of 5 mls.

Interferences

Method interferences may be caused by contaminants in solvents, reagents, and glassware: laboratory reagent blanks must be run in order to demonstrate that these materials are free from interference.

Matrix interferences may be caused by contaminants that are co-extracted from the sample.

Methylene Chloride enhances detector response of internal standard: the procedure for the solvent exchange must be followed carefully.

Do not use PVC or rubber gloves.

Use only baked glassware and teflon screw caps: do not use plastic or rubber materials.

Safety Considerations

The extent of toxicity or carcinogenicity of all of the reagents used has not yet been precisely determined: however, each compound should be treated as hazardous. There is a file of material safety data sheets (MSDS) in the lab available to all. The technician must familiarize him/herself with these before beginning the extraction.

Apparatus

1) Sample container - 1 L glass bottle with Teflon faced septum and open top screw cap.
2) Separatory funnel - 2 L, with teflon stopcock.
3) Water bath - heated, with concenetric ring cover, capable of temperature control within 2°C. Should be in a hood.
4) Volumetric flask - 5 ml with glass stopper
5) 5 ml vial, with teflon-lined screw cap
6) 500 ml Erlenmeyer flask.
7) 500 ml Kuderna-Danish concentration apparatus
8) 1 L graduated cylinder.
9) 100 ml graduated cylinder.

Extraction Procedure

See special notes before beginning extraction procedure.

1) Prepare the log book. recording the following:
   a) Sample number
   b) Spike & Surrogate:
      1)Amount 4)ID Numbers
      2)Preparers 5)Injector's initials
      3)Date prepared
   c) Weights(Initial.final.& net) of each sample
   d) Lot # of chemicals used
   e) NPS Set #
   f) Date extracted
   g) Initials of ones performing the extraction
2) Prepare the labels. recording on each the following:
   a) NPS Set #
   b) Sample #
   c) Net weight
   d) Final volume in MTBE
   e) Date extracted
   f) Initials of ones performing the extraction
3) Prepare a blank by adding 1000 ml DI to a 2 L separatory funnel with a 1 L graduated cylinder: in a similar method. prepare one of each type (a.b.& c) of LCS (laboratory control sample) for every set tested.
4) Dry the sample bottle; weigh and record the full bottle.
5) Check the pH of each sample: record in the log book if not pH 7.
6) Add 100 g NaCl and 50 ml phosphate buffer to each sep funnel.
7) Add 50 ul surrogate into each bottle (funnel for LCS and blank): record the solution in the log book. including the number. amount used. preparer. and the person adding the surrogate.
8) Add the spike solutions to the LCS standards and spike samples (see Special Notes for amounts). Record the solutions in the log book. including the number. amount used. preparer. and the person who added the spike standards.
9) Add the sample to a 2 L separatory funnel: mix.
10) Check the pH. Adjust to pH 7 if necessary. Record all adjustments in the log book.
11) Add 60 ml methylene chloride to each sample bottle. seal. and shake for 30 seconds. Pour the methylene chloride into the funnel. seal. and swirl vent. Extract the sample by shaking for 2 min. Allow the layers to separate for at least 10 min: drain the methylene chloride layer into a 500 ml erlenmeyer flask. If there is an emulsion more than 1/3 the volume of the solvent layer. the separation should be completed by mechanical techniques such as re-sep funneling. Record any emulsions or extraction difficulties.

12) After allowing the methylene chloride to evaporate re-weigh the sample bottle and record the weight.
13) Repeat the extraction procedure a second and third time. shaking for only one minute. A minute before the third drain. swirl the funnel in an upright position in order to ensure that all the $MeCl_2$ is in the lower layer. Collect the extracts in a 500 ml erlenmeyer flask.
14) Add ~20 g anhydrous sodium sulfate to the extract and let sit for 20 min.
15) Assemble a K-D apparatus. Add 15 ml MTBE into the receiver.
16) Decant the extract into the K-D apparatus. Rinse the flask with two 30-ml portions of methylene chloride.
17) Add a boiling chip to the flask and attach a Snyder column. Place the apparatus on a hot water bath @ 75-76°C so that the tube is partially in the water. Concentrate to 3 ml and allow to drain and cool for 10 min. Rinse the lower joint of the K-D with 0.5 ml MTBE.
18) Add a new boiling chip. 10 ml MTBE and attach a micro-snyder column. Pre-wet the column and boil down to 1 ml at 75-76°C. gently tapping the column until smooth boiling is attained to prevent bumping. Let cool for 10 minutes.
19) Add a new boiling chip and 15 ml MTBE. Concentrate to 1 ml at 75-76°C. remembering to gently tap the column until there is smooth boiling in order to prevent bumping.
20) Cool 10 minutes.
21) Rinse a 5 ml volumetric 3 times with acetone. 3 times with methylene chloride. and 4 times with MTBE. Transfer the extract to the solvent-cleaned 5 ml volumetric. Rinse the receiver with MTBE and transfer to the volumetric while adjusting the final volume to 5 mls. Mix thoroughly with a pipette and transfer to a 5 ml vial with a teflon liner.

Quality Control Requirements

1) The LCS. spike. and surrogate recovery should be within control limits. If not. investigate.
2) A blank and one of each LCS should be prepared for each set of samples.
3) Surrogate standard must be added to all samples.

Calculations see GC protocol

Special Notes

1) Spike levels: There are three spike levels used in this method:

Level 0 - 200 ul
Level 1 - 500 ul
Level 2 - 1.0 ml

Each LCS sample receives 1 ml spike solution (level 2).

2) Time Storage Samples (TS) : 5 duplicates of a sample are made. There is one original and two spikes (DTS) extracted the same day; the other two samples are spiked and stored 14 days before extracting (HTS). All are spiked with the same amount and type of mix. **Always add surrogate on the day of extraction.**

3) 50 ul surrogate is added to all samples, blank, and LCS.

4) Abbreviations:

MRL	mimimum reporting level
LCS	laboratory control std.
LSS	laboratory spike sample
TS	time storage
DTS	day 0 time storage dup.
HTS	holding time storage
ETS	Extract time storage

5) Numbering Convention for Samples:

Public comm. Public domes.	Site #	Lab # (JMM=1)	Method num.	Type*
PC	- 2497 -	1 -	3 -	01

* Types:

a) 01	Field sample	d) 13	T.S. 0 day dup.
b) 03	Backup sample	e) 14	T.S. 14 day(HTS)
c) 04-12	Spike sample	f) 15	T.S. 14 day dup (HTS dup)

6) Make sure that the septa of the vials is turned so that the teflon side is on the inside of the cap!

7) A florisil(R) check is a comparison of a florisiled DMS A and B with an unflorisiled DMS A and B. Do a florisil(R) check in the following method:

a) Activate the florisil(R) by baking @ 150°C for 24-48 hrs prior to the day of extraction. Record the activation date on the label and in the standards book. Store in a dessicator, and reactivate every 2 weeks. When a new batch of florisil(R) is activated, a florisil(R) check is required.

b) Prepare an unflorisiled DMS A and B by spiking 0.5 ml standard into a receiver for each DMS. Prepare a DMS A and B for florisiling by spiking 0.5 ml standard into two other receivers. Add 250 ul high purity methanol to each receiver. Add 0.5 ml diazomethane, and dilute to 3 ml with MTBE, and mix well.

c) Cover each receiver with foil and allow to react for 1 hour. If not yellow after 10 minutes, remethylate by adding diazomethane in 0.5 ml increments until it does stay yellow for 10 minutes. Note the remethylation in the log book.

d) Slowly blow off the diazomethane with a gentle stream of nitrogen.

e) Adjust the DMS's to 4 ml with 99.9% MTBE.

f) Assemble two columns to florisil two DMS's. Place a small plug of acidified glass wool into a 5 ml pipette. Tare the pipette and add 1 g activated florisil(R) into the pipette. Record the florisil(R) test in the extraction log book, stating the lot number and activation date of the florisil(R). Also record the DMS standard numbers, preparation date, amount used, and initials of the injector

g) Add 5-10 ml of 5% MeOH in MTBE to each column. Do not let the column go dry. Discard the eluate.
h) Apply each DMS to be florisiled (one of A and one of B) to a column. Collect the eluate in a 10 ml volumetric. Do not let the column go dry.
i) Rinse the receiver with 1 ml 5% MeOH in MTBE. and transfer to the florisil(R) column. Repeat with another 1 ml 5% MeOH in MTBE: again repeat. this time with 3 ml 5% MeOH in MTBE.
j) Dilute to 10 ml with 5% MeOH in MTBE. mix with a pipette. and transfer to a 10 ml vial with a teflon(R) septum.

8) The glassware must be acid-washed in the following manner:

a) Clean the glassware by rinsing once with the last solvent used in it and washing with hot water and detergent.
b) Dip once in a bath of 0.8 N HCl.
c) Rinse three times with tap water.
d) Rinse three times with reagent water. Drain dry.
e) Seal with foil. and bake @ 400°C for 4 hours. Allow to cool.

9) Spike solution testing:

New spike solutions should have been compared to old ones by an analyst before they are used as standards. These standards should be methylated by the following procedure:

a) Obtain 2 acid-washed. baked receivers for each standard to be tested.
b) Spike 1 ml of the old standard into one receiver; into the other spike 1 ml of the new standard. Label the receivers with the correct solution. amount. date. preparer. and tester.
c) Add 250 ul high purity MeOH into each receiver.
d) Add 0.5 ml diazomethane: dilute to 3 ml with 99.9% MTBE. Mix well. cover with foil. and allow to react for one hour.
e) Blow off the yellow solution with a gentle stream of nitrogen.
f) Adjust the volume to 4 ml with 99.9% MTBE.
g) Florisil(R) the sample by following the procedure in Step 27 of **Extraction Procedure**.
h) Dilute to 10 ml with 5% MeOH in MTBE. mix with a pipette. and transfer to a 10 ml vial with a teflon(R) septum.
i) Record the lot numbers and preparation dates of all chemicals used in the log book. and send the samples to the analyst to be tested.

The analyst should compare the old and new solutions. The values should agree within 20%. If not. the analyst should prepare new standards and compare all three. If the two new ones agree. the old solution may have been incorrect or may have deteriorated. If the last solution agrees with the old one use it and discard the other.

10) DMS Testing

New DMS standards should have been compared to old ones by an analyst before they are used as standards. These standards should be methylated by the following procedure:

a) Obtain 2 acid-washed, baked receivers for each standard to be tested.
b) Spike 0.5 ml of the old standard into one receiver; into the other spike 0.5 ml of the new standard. Label the receivers with the correct solution, amount, date, preparer, and tester.
c) Add 250 ul high purity MeOH into each receiver.
d) Add 0.5 ml diazomethane; dilute to 3 ml with 99.9% MTBE. Mix well, cover with foil, and allow to react for one hour.
e) Blow off the yellow solution with a gentle stream of nitrogen.
f) Adjust the volume to 4 ml with 99.9% MTBE.
g) Dilute to 10 ml with 5% MeOH in MTBE, mix with a pipette, and transfer to a 10 ml vial with a teflon(R) septum.
h) Record the lot numbers and preparation dates of all chemicals used in the log book, and send the samples to the analyst to be tested.

The analyst should compare the old and new solutions. The values should agree within 20%. If not, the analyst should prepare new standards and compare all three. If the two new ones agree, the old solution may have been incorrect or may have deteriorated. If the last solution agrees with the old one use it and discard the other.

11) Diazomethane check:

1) Obtain four acid-washed receivers free of scratches or cracks. Label one "blank", and the others "PNP 1","PNP 2", and "PNP 3".
2) Add 1 ml MTBE to each receiver
3) To each PNP sample, add 25 ul PNP standard; to all samples, add 250 ul high-purity MeOH.
4) Add 0.5 ml newly-made diazomethane to each sample. Adjust the volume to 3 ml with 99.9% MTBE.
5) Mix, cover, and allow to react for one hour. Record all lot numbers of solutions used, PNP standard information, diazomethane preparation date, and preparer's initials in the NPS 3 log book.
6) Blow off the diazomethane with a gentle stream of nitrogen until the solution is clear.
7) Adjust the volume to 4 ml with 99.9% MTBE.
8) Bottle each sample, taking them to 10 ml with 5% MeOH in MTBE.

QUICK SUMMARY

PREPARATION Dry the sample bottles: weigh and record full weights.

Add **50 ul surrogate** into each sample: spike LCS and recovery.

Add **100 g** NaCl: mix.

Add **50 ml phosphate buffer. pH 7.**

Pour the sample into a 2 L separatory funnel.

Remove stopper and rinse with DI.

EXTRACTION Extract **3X** with **60 ml** $MeCl_2$ (2 min first shake. 1 min other shakes. Add $MeCl_2$ to sample bottle. rinse walls. and transfer to sep funnel.

Remove stopper. rinse with DI.

Dry extract with ~**20 g** Na_2SO_4 for **20 min.**

Weigh empty bottle: record empty and net weights.

CONCENTRATION Add **10 ml MTBE** into the receiver as a keeper. Decant extract into K-D. Rinse flask and Na_2SO_4 twice with 30 ml portions of $MeCl_2$.

Prewet and concentrate to 3 **ml @ 75°C.**

Cool 10 minutes: rinse joint with **1 ml MTBE.**

Add **10 ml MTBE** and 1 boiling chip. Attach micro-snyder. prewet with **MTBE.** and concentrate to **1 ml @ 75°C.** Remove and cool for 10 minutes.

Add **15 ml MTBE.** prewet. and concentrate to **1 ml.** Cool for 10 minutes. and rinse joint with 0.5 ml MTBE.

Transfer to a 5 ml volumetric. Mix and transfer to a 5 ml vial.

SOLUTIONS

0.1 N HCl: 8.3 ml HCL to 1 L with DI

0.1 M Dipotassium Phosphate: 17.42 g K_2PO_4 to 1 L with DI

Buffer:

# of samples:	10	12	14	16	18	20
0.1 M K_2PO_4:	350	400	450	550	600	700
0.1 N HCl:	207	237	266	325	355	414

APPENDIX G

EXTRACTION SOP FOR METHOD 3

EXTRACTION - NPS 3

Page	Revision #	Revision Date
1	2	March 5, 1990
2	2	March 5, 1990
3	1	November 6, 1989
4	1	November 6, 1989
5	1	November 6, 1989
6	2	March 5, 1990
7	1	November 6, 1989
8	1	November 6, 1989
9	1	November 6, 1989
10	1	November 6, 1989
11	1	November 6, 1989
12	1	November 6, 1989
13	1	November 6, 1989
14	1	November 6, 1989
15 (last)	1	November 6, 1989

Approved:

Group Leader: _____

Operations Manager: _____

QA Officer: _____

Laboratory Director: _____

EXTRACTION NPS-3

LIQUID-LIQUID EXTRACTION

Scope and Application

This procedure can be used to measure certain chlorinated acids in ground water. The following compounds can be determined using this method:

Acifluorfen
Bentazon
Chloramben
2,4-D
Dalapon
2,4-DB
DCPA acid metabolites
Dicamba
3,5-Dichlorobenzoic acid
Dichlorprop
Dinoseb
5-Hydroxydicamba
4-Nitrophenol
PCP
Picloram
2,4,5-T
2,4,5-TP

This method may be used to determine the salts and esters of the above acids. The acid derivatives are indistinguishable from each other; results are listed as the total free acid.

This is a capillary gas chromatographic method.

Method Summary

Aqueous samples of approximately 1L are made basic with 6N NaOH and allowed to sit for 1 hr to hydrolyze derivatives. They are then extracted with methylene chloride in order to remove extraneous material. The samples are acidified, concentrated, and then extracted with ethyl ether. The acids are dried and converted to their methyl esters with the use of diazomethane. Excess diazomethane is removed, and the esters are determined by capillary GC using an electron capture detector.

Interferences

Method interferences may be caused by contaminants in solvents, reagents, and glassware; laboratory reagent blanks must be run in order to demonstrate that these materials are free from interference.

Matrix interferences may be caused by contaminants that are co-extracted from the sample; florisil cleanup may be used to remove many of these interferences.

Do not use PVC or rubber gloves. Let no plastic or rubber materials be used in the procedure. Use acid-washed, baked glassware and teflon(R) caps only.

Safety Considerations

The extent of toxicity or carcinogenicity of all of the reagents used has not yet been precisely determined; however, each compound should be treated as hazardous. There is a file of material safety data sheets (MSDS) in the lab available to all.

Diazomethane is a toxic carcinogen which is explosive. Use only in a well-ventilated hood with a safety screen. Do not heat above 70°C, avoid contact with ground or scratched glass surfaces, and do not store with alkali metals, for an explosion may result. Always keep refrigerated; it is more stable at cool temperatures.

Ethyl ether is extremely flammable and forms explosive peroxides.

Apparatus

All glassware must be acid-washed and baked. See Note 8 in Special Notes for directions.

1) Sample container - 1L glass bottle with Teflon(R) - faced septum and open top screw cap.

2) Separatory funnel - 2L, with teflon(R) stopcock.

3) Water bath - heated, with concentric ring cover, capable of temperature control within 2°C. Should be in a hood.

4) Volumetric flask - 10 ml.

5) Capillary column gas chromatograph with linearized electron capture detector and a split/splitless injector.

6) Capillary column - Primary column: DB5, 30M x 0.24 mm i.d., 0.25 um film thickness.

7) Secondary column: DB1701, 30M x 0.24 mm i.d., 0.25 um film thickness.

8) 10 ml vial, with teflon(R)-lined screw cap.

9) 250 ml Erlenmeyer flask.

10) 500 ml Erlenmeyer flask.

11) 1L Erlenmeyer flask.

12) 500 ml Kuderna-Danish concentration apparatus.

13) Disposable transfer pipettes, with 2 ml bulbs.

14) Glass wool - Acid washed and heated @ 400°C for 4 hours.

15) Alumina column - Solvent washed or baked @ 400°C for 4 hrs; for cleaning ether.

16) 5 ml serological pipettes.

17) 1L graduated cylinder.

18) 100 ml graduated cylinder.

19) 25 ml graduated cylinder.

20) Ring stand.

Reagents and Standards

1) Reagent water, organic-free.

2) Sodium Sulfate - Anhydrous, ACS Certified. Acidify by baking @ 400°C in a shallow glass tray for four hours in the following manner:

   a) For each 2 kg Na_2SO_4, slowly add 20 ml concentrated sulfuric acid to 600 ml ethyl ether.

   b) Add the acidified ether to cover the sodium sulfate and mix thoroughly with a glass rod.

   c) Air dry, and bake @ 400°C for four hours.

   d) Mix 1g of the solid with 5 ml DI and test the pH.

   The pH must be below pH 4. Record the pH in the reagent log book.

3) Sodium hydroxide pellets - ACS certified. Make 6 N NaOH by dissolving 240g NaOH into a total volume of 1L with reagent water.

4) Sulfuric acid - ACS certified. Make 12 N H_2SO_4 by slowly diluting 333.3 ml H_2SO_4 into 1L with reagent water in a 1L volumetric flask.

5) Ethyl ether, unpreserved - Nanograde, free of peroxides by cleaning with alumina. Test a 4L container of ethyl ether for peroxides with a test strip; notify the lab safety officer if the peroxide content is greater than 5 ppm. If the alumina column is not baked, solvent-rinse it with acetone and alumina-cleaned ether. To clean the ether, place a plug of glass wool (which has been baked at 400°C for 4 hours and stored at 150°C) in the bottom of an alumina column. Add a stopcock, making sure that the rubber O-ring is not exposed, and a florisil(R) tip. Into the tip of the column place 37g alumina (which has been baked at 400°C for 4 hours, stored at 150°C, cooled and desiccated before use). Add ether to fill the reservoir and allow 50 ml to elute; discard the eluate. Place an empty 4L jug under the column. Tie tissue along the narrow stem of the column in order to absorb spillage during transfer of ether to the column; cover the open spaces with foil in order to prevent evaporation and contamination, and collect the rest of the 4L ethyl ether. Record the lot number, date cleaned, and preparer's initials on the bottle; indicate that the ether is aluminized by writing (AL) on the bottle. Test the cleaned ether for peroxides with a test strip; if peroxides are present at a level greater than or equal to 2 ppm, do not use, and notify the lab safety officer.

6) Diazald(R) - ACS Certified. See "Diazomethane Preparation" protocol for instructions on preparation of diazomethane. Solution should be prepared and tested before the day of extraction. This solution is stable for 1 month when stored at 0°C.

7) Sodium chloride - crystal, ACS grade. Bake @ 400°C in a shallow glass tray for 4 hours to remove interfering organics.

8) 4,4'-Dibromooctafluorobiphenyl (DBOB) - > 99% purity, for use as an internal standard.

9) 2,4-Dichlorophenylacetic acid (DCAA) - > 99% purity, for use as a surrogate standard.

10) Florisil(R) - 60-100/PR mesh. Activate by heating @ 150°C for 24-48 hours; store in desiccator. Reactivate after two weeks.

11) Acetone - Pesticide quality or equivalent.

12) Methanol - Pesticide quality or equivalent.

13) Methylene chloride - Pesticide quality or equivalent.

14) MTBE (methyl-tert-butyl-ether) - 99.9%, EM Science. VWR Cat # EM-MX0826-1.

15) Basic alumina oxide, activity grade Super 1 (type w 200) - available from Fisher Scientific, catalog # UA4571.

16) Methanol (high purity, purge & trap grade) - B&J Cat # 232-1DK. for methylation of samples.

All spike solutions must be replaced after 90 days or earlier if a problem arises.

Sample Collection, Handling and Preservation

1) Samples are collected in 1L amber glass bottles with Teflon(R) septa.

2) Enough mercuric chloride must be added to the sample bottle to produce a concentration of 10 mg/L. Add 1 ml of a 10 mg/ml solution of mercuric chloride to the sample.

3) Samples should be packed in ice and shipped to the laboratory for next day delivery.

4) The samples must be stored at 4°C away from light from the time of collection until extraction.

5) Samples should be extracted within 14 days of collection and analyzed within 14 days of extraction.

Calibration Procedure

See GC protocol

Extraction Summary

Aqueous samples of approximately 1L are adjusted to pH 14 with 6N sodium hydroxide and shaken a few times over a period of one hour to the hydrolyze derivatives. The samples are extracted 3 times with 60 ml portions of methylene chloride in order to remove extraneous organic material. The samples are then acidified to pH 0 with 12 N H_2SO_4 and extracted 3 times with ethyl ether; the ether extracts are then dried with sodium sulfate and concentrated to 4 ml with a Kuderna-Danish apparatus. The extract is solvent exchanged with MTBE and concentrated with a micro-snyder column to a final volume of 0.5-1 ml.

DMS standards are prepared by spiking 0.5 mls each of DMS standards A and B into separate vials and diluted to 3 ml with 99.9% MTBE. The samples are then derivatized with 250 ul MeOH and 0.5 ml diazomethane, brought to a volume of 4 ml with 99.9% MTBE, and cleaned with a florisil(R) column. They are then taken to a final volume of 10 mls.

Extraction Procedure

See special notes before beginning extraction procedure.

Acid wash all glassware before use. See Note 8 in Special Notes for this procedure.

1) Write up the book, noting the following:
   a) Sample numbers
   b) Spike & Surrogate:
      a) Number
      b) Date prepped
      c) Preparer
      d) Amount used
      e) Initials of injector
   c) Weights (Initial, final, & Net) of each sample
   d) Lot # of each chemical used
   e) NPS Set #
   f) Date extracted
   g) Initials of ones performing the extraction

2) Prepare labels, indicating the following:
   a) NPS Set #
   b) Sample number
   c) Initial weight
   d) Final volume in 5% MeOH/MTBE
   e) Date extracted
   f) Preparers' initials

3) Dry the sample bottle; weigh and record the full bottle.

4) Prepare a blank by adding 1000 ml DI to a 2 L separatory funnel with a 1L graduated cylinder; in a similar method prepare one of each type (a & b) of LCS (laboratory control sample) for every set tested.

5) Add the correct amount of spike standard to the appropriate samples (1 ml into each of LCS A and B).

6) Add 50 ul surrogate into the water of each sample bottle (Spike into the sep funnels for LCS samples and blank). Cap immediately and invert the samples (Note: check to make sure that the caps are teflon(R)-lined.

7) Add the sample to a 2 L separatory funnel.

8) Add 250 g NaCl to the funnel.

9) Adjust the sample to pH 14 by adding 17 ml 6N NaOH; mix well and check the pH. Allow the samples to sit for an hour, shaking periodically during that time.

10) Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 sec. Pour the methylene chloride into the funnel, seal, and swirl vent. Extract the sample by shaking for 2 min. Allow the layers to separate for at least 10 min; drain the methylene chloride into a waste container.

11) After allowing the methylene chloride to evaporate from the sample bottle, re-weigh the sample bottle and record the weight.

12) Repeat the extraction procedure a second and third time, shaking for only one minute. Discard the MeCl2 extracts. Swirl the funnel after the third shake to make sure that all the methylene chloride is in the organic layer. Make sure that all the methylene chloride is drained after the third shake.

13) Adjust the sample to pH 0 by adding 17 ml 12N H_2SO_4; mix well and check the pH.

14) Add 120 ml alumina-cleaned ethyl ether to the sample. Seal, and swirl vent. Extract the sample by shaking for 2 min. Allow the layers to separate for at least 10 min. Remove the aqueous (lower) phase to a 1L and a 250 ml Erlenmeyer flask; collect the ether in a 500 ml flask.

15) Return the aqueous phase to the separatory funnel. Add a 60 ml portion of AL ether and extract the sample a second time by shaking for one minute. Combine the ether in the same flask as before. Perform a third extraction with 60 ml AL ether in the same manner.

16) Add ~20g anhydrous acidified sodium sulfate to the extract, making sure to contact the sides of the flask with the solid, and let sit for 2 hours.

17) Weigh the capped empty bottle; record the empty and net weights.

18) Assemble a K-D apparatus.

19) Decant the extract into the K-D apparatus. Rinse the flask with two 30-ml portions of AL ethyl ether.

20) Add a boiling chip to the flask and attach a Snyder column. Place the apparatus on a hot water bath @60-65°C so that the tube is partially in the water. Concentrate to 4 ml and allow to drain and cool for 10 min. Rinse the lower joint of the K-D with 1-2 ml AL ethyl ether. Add 2 ml MTBE.

21) Add another boiling chip and attach a micro-snyder column. Pre-wet the column with MTBE and boil down to 0.5 ml at 60°C. Lightly tap the receiver until the sample begins to boil to prevent bumping. Let cool for 10 minutes.

22) Prepare Direct Methylated Standards (DMS standards). Both DMS standard A and B must be prepared; they are spiked into separate receivers.

a) DMS A: Spike 0.5 ml (NPS3 underivatized calib. DMS standard A).
b) DMS B: Spike 0.5 ml (NPS3 underivatized calib. DMS standard B).

A florisil(R) check is required of these DMS standards when a new batch of florisil(R) is activated. In a florisil(R) check, the normal DMS standards are compared to florisiled DMS standards (both A & B). See Note 7 under Special Notes.

23) Add 250 ul high purity methanol to all samples.

24) Add 0.5 ml diazomethane solution to each sample; record the solution. Adjust the volume to 3 ml with 99.9% MTBE. Mix well.

25) Cover with foil and allow to react for 1 hour. If not yellow after ~10 minutes, remethylate and note the remethylation in the log book.

26) Slowly blow off the diazomethane with a gentle stream of nitrogen.

27) Adjust the samples to 4 ml with 99.9% MTBE.

28) Florisil(R) all samples except the DMS standards by following this procedure:

a) Assemble the florisil(R) columns. Place a small plug of acidified glass wool into a 5 ml pipette. Tare the pipette and add 1.0 g activated florisil into the pipette. Record the florisil(R) lot number and activation date.

b) Add 5-10 ml of 5% MeOH in MTBE to each column. Do not let the column go dry. Discard the eluate.

c) Apply the sample to the column. Collect the eluate in a 10 ml volumetric. Do not let the column go dry.

d) Rinse the receiver with 1 ml 5% MeOH in MTBE, and transfer to the florisil column. Repeat with another 1 ml 5% MeOH in MTBE; again repeat, this time with 3 ml 5% MeOH in MTBE.

29) Dilute to 10 ml with 5% MeOH in MTBE, mix with a pipette and transfer to a 10 ml vial with a teflon(R) septum. Record the lot numbers and preparation dates of all chemicals used.

Quality Control Requirements

1) The LCS, spike, and surrogate recovery should be within control limits. If not, investigate.

2) A blank and 1 of each LCS should be prepared with each set of samples.

3) Surrogate standard must be added to all samples.

Calculations

See GC protocol.

Special Notes

1) Spike levels: There are three spike levels used in this method:

Level 0 - 200 ul
Level 1 - 500 ul
Level 2 - 1.0 ml

Each LCS sample receives 1 ml spike solution (level 2).

2) Time Storage Samples (TS): 5 duplicates of a sample are made. There is one original and two spikes (DTS) extracted the same day; the other two samples are spiked and stored 14 days before extracting (HTS). All are spiked with the same amount and type of mix. Always add surrogate on the day of extraction.

3) 50 ul surrogate is added to all samples, blank, and LCS.

4) Abbreviations:

MRL	minimum reporting level
LCS	laboratory control std.
LSS	laboratory spike sample
TS	time storage
DTS	day 0 time storage dup.
HTS	holding time storage
ETS	Extract time storage

5) Numbering Convention for Samples:

Public comm./ Public domes.	Site # (JMM=1)	Lab #	Method num.	Type*
PC	2497	1	3	01

* Types:

a)	01	Field sample	d)	13 T.S.	0 day dup.
b)	03	Backup sample	e)	14 T.S.	14 day (HTS)
c)	04-12	Spike sample	f)	15 T.S.	14 day dup (HTS dup)

6) Make sure that the septa of the vials is turned so that the teflon side is on the inside of the cap!

7) A florisil(R) check is a comparison of a florisiled DMS A and B with an unflorisiled DMS A and B. Do a florisil(R) check in the following method:

a) Activate the florisil(R) by baking @ 150°C for 24-48 hrs prior to the day of extraction. Record the activation date on the label and in the standards book. Store in a desiccator, and reactivate every 2 weeks. When a new batch of florisil(R) is activated, a florisil(R) check is required.

b) Prepare an unflorisiled DMS A and B by spiking 0.5 ml standard into a receiver for each DMS. Prepare a DMS A and B for florisiling by spiking 0.5 ml standard into two other receivers. Add 250 ul high purity methanol to each receiver. Add 0.5 ml diazomethane, and dilute to 3 ml with MTBE, and mix well.

c) Cover each receiver with foil and allow to react for 1 hour. If not yellow after ~10 minutes, remethylate by adding diazomethane in 0.5 ml increments until it does stay yellow for 10 minutes. Note the remethylation in the log book.

d) Slowly blow off the diazomethane with a gentle stream of nitrogen.

e) Adjust the DMS's to 4 ml with 99.9% MTBE.

f) Assemble two columns to florisil two DMS's. Place a small plug of acidified glass wool into a 5 ml pipette. Tare the pipette and add 1g activated florisil(R) into the pipette. Record the florisil(R) test in the extraction log book, stating the lot number and activation date of the florisil(R). Also record the DMS standard numbers, preparation date, amount used, and initials of the injector.

g) Add 5-10 ml of 5% MeOH in MTBE to each column. Do not let the column go dry. Discard the eluate.

h) Apply each DMS to be florisiled (one of A and one of B) to a column. Collect the eluate in a 10 ml volumetric. Do not let the column go dry.

i) Rinse the receiver with 1 ml 5% MeOH in MTBE, and transfer to the florisil(R) column. Repeat with another 1 ml 5% MeOH in MTBE; again repeat, this time with 3 ml 5% MeOH in MTBE.

j) Dilute to 10 ml with 5% MeOH in MTBE, mix with a pipette, and transfer to a 10 ml vial with a teflon(R) septum.

8) The glassware must be acid-washed in the following manner:

a) Clean the glassware by rinsing once with the last solvent used in it and washing with hot water and detergent.

b) Dip once in a bath of 0.8 N HCl.

c) Rinse three times with tap water.

d) Rinse three times with reagent water. Drain dry.

e) Seal with foil, and bake @ 400°C for 4 hours. Allow to cool.

9) Spike solution testing: New spike solutions should have been compared to old ones by an analyst before they are used as standards. These standards should be methylated by the following procedure:

a) Obtain 2 acid-washed, baked receivers for each standard to be tested.

b) Spike 1 ml of the old standard into one receiver; into the other spike 1 ml of the new standard. Label the receivers with the correct solution, amount, date, preparer, and tester.

c) Add 250 ul high purity MeOH into each receiver.

d) Add 0.5 ml diazomethane; dilute to 3 ml with 99.9% MTBE. Mix well, cover with foil, and allow to react for one hour.

e) Blow off the yellow solution with a gentle stream of nitrogen.

f) Adjust the volume to 4 ml with 99.9% MTBE.

g) Florisil(R) the sample by following the procedure in Step 27 of Extraction Procedure.

h) Dilute to 10 ml with 5% MeOH in MTBE, mix with a pipette, and transfer to a 10 ml vial with a teflon(R) septum.

i) Record the lot numbers and preparation dates of all chemicals used in the log book, and send the samples to the analyst to be tested.

The analyst should compare the old and new solutions. The values should agree within 20%. If not, the analyst should prepare new standards and compare all three. If the two new ones agree, the old solution may have been incorrect or may have deteriorated. If the last solution agrees with the old one use it and discard the other.

10) DMS Testing: New DMS standards should have been compared to old ones by an analyst before they are used as standards. These standards should be methylated by the following procedure:

a) Obtain 2 acid-washed, baked receivers for each standard to be tested.

b) Spike 0.5 ml of the old standard into one receiver; into the other spike 0.5 ml of the new standard. Label the receivers with the correct solution, amount, date, preparer, and tester.

c) Add 250 ul high purity MeOH into each receiver.

d) Add 0.5 ml diazomethane; dilute to 3 ml with 99.9% MTBE.

Mix well, cover with foil, and allow to react for one hour.

e) Blow off the yellow solution with a gentle stream of nitrogen.

f) Adjust the volume to 4 ml with 99.9% MTBE.

g) Dilute to 10 ml with 5% MeOH in MTBE, mix with a pipette, and transfer to a 10 ml vial with a teflon(R) septum.

h) Record the lot numbers and preparation dates of all chemicals used in the log book, and send the samples to the analyst to be tested.

The analyst should compare the old and new solutions. The values should agree within 20%. If not, the analyst should prepare new standards and compare all three. If the two new ones agree, the old solution may have been incorrect or may have deteriorated. If the last solution agrees with the old one use it and discard the other.

11) Diazomethane check:

1) Obtain four acid-washed receivers free of scratches or cracks. Label one "blank", and the others "PNP 1","PNP 2", and "PNP 3".

2) Add 1 ml MTBE to each receiver.

3) To each PNP sample, add 25 ul PNP standard; to all samples, add 250 ul high-purity MeOH.

4) Add 0.5 ml newly-made diazomethane to each sample. Adjust the volume to 3 ml with 99.9% MTBE.

5) Mix, cover, and allow to react for one hour. Record all lot numbers of solutions used, PNP standard information, diazomethane preparation date, and preparer's initials in the NPS 3 log book.

6) Blow off the diazomethane with a gentle stream of nitrogen until the solution is clear.

7) Adjust the volume to 4 ml with 99.9% MTBE.

8) Bottle each sample, taking them to 10 ml with 5% MeOH in MTBE.

QUICK SUMMARY

ACID-WASH ALL GLASSWARE

PREPARATION	Dry and weigh bottle. Add 50 ul (DCAA) surrogate. Invert the bottle and mix. Spike the LCS and spike samples. Record all solutions.
	Pour sample into sep funnel.
	Add 250.5+0.4 g NaCl.
	Add 17 ml 6 N NaOH to pH 14. Record solution. Mix well.
	Shake periodically for 1 hour.
BASIC CLEANUP	Extract 3X with 60 ml MeCl2. Record lot #. Add MeCl2 to bottle, rinse walls 30 seconds and transfer to the sep funnel. Shake 2 min.
	Discard MeCl2 layer.
EXTRACTION	Add 17 ml 12 N H2SO4. Record solution. Mix and check that pH<2.
	Extract 3X with 120, 60, and 60 ml Al Ethyl Ether. Record lot # date cleaned, and AL lot #.
	Dry extract with ~20 g H+ Na2SO4 for 2 hours.
	Weigh empty bottle; determine and record empty and net weights.
CONCENTRATION	Decant into K-D. Crush and rinse Na2SO4 twice with 30 ml ether.
	Prewet and concentrate to 1 ml @ 60°C.
	Cool 10 minutes; rinse joints with ether.
	Add 2 ml MTBE, attach micro-snyder, prewet with ether, concentrate to 0.5-1.0 ml @ 60°C. Remove and cool 10 minutes.
DMS's	An unflorisiled DMS A and DMS B is required for every set; when a new batch of florisil is activated, two florisiled DMS's are compared to the unflorisiled DMS's.
	DMS A - Spike 0.5 ml (NPS 3 underivatized calib. std. A) into a receiver. Record the spike solution in the book.
	DMS B - Spike 0.5 ml (NPS 3 underivatized calib. std. B) into a receiver. Record the spike solution in the log book.
	Derivatize the DMS standards along with the rest of the samples. Final volume is 10 ml.

DERIVATIZATION	Add 250 ul High Purity MeOH to the samples and DMS.
	Add 0.5 ml Diazomethane. Adjust to 3 ml with 99.9% MTBE. Record solution. Cover with foil, mix and allow to react for 1 hour. Must remain yellow for 10 min.
	Slowly blow off diazomethane with nitrogen.
	Adjust samples to ~4 ml with MTBE.
	Bottle unflorisiled DMS's at 10 ml with 5% MeOH/MTBE and transfer to vial.
FLORISIL	Add H+ glass wool to 5 ml pipette. Tare, and add 1 g activated Florisil. Record lot # and date activated.
	Rinse florisil with 5-10 ml 5% MeOH/MTBE; discard eluate.
	Without letting column go dry, add sample; collect in a clean 10 ml volumetric.
	Rinse receiver with 1 ml 5% MeOH/MTBE; transfer to column. Repeat with another 1 ml and a 3 ml 5% MeOH/MTBE. Collect all.
	Dilute to 10 ml in volumetric with 5% MeOH/MTBE; mix and transfer to vial.

APPENDIX H

SOP FOR PREPARATION OF DIAZOMETHANE

DIAZOMETHANE PREPARATION

Page	Revision #	Revision Date
1	1	December 4, 1989
2	1	December 4, 1989
3	1	December 4, 1989
4	1	December 4, 1989
5	1	December 4, 1989
6	1	December 4, 1989
7 (last)	1	December 4, 1989

Approved:

Group Leader: _____

Operations Manager: _____

QA Officer: _____

Laboratory Director: _____

DIAZOMETHANE PREPARATION

Scope and Application

This procedure can be used to prepare diazomethane, a chemical used in the NPS-3 and 615 herbicide extractions. Diazomethane is used to convert organic acids to their methyl esters.

Method Summary

A mixture of diazald(R) and aluminized ethyl ether is allowed to react in a reaction flask with 6g potassium hydroxide, 10 ml DI, and 35 ml EtOH in a heated water bath. The vapor product of diazomethane is allowed to condense and drip into a cooled collection flask; it is then transferred to an amber bottle; it is then stored in a freezer.

Safety Considerations

Diazald(R) is a highly carcinogenic compound. Gloves must be worn at all times when preparing diazomethane. Any spill must be immediately cleaned and disposed in a sealed bag marked "Hazardous - diazald(R)".

Prepare the diazomethane in a well-ventilated, explosion-proof hood. Ensure that the hood is in correct operation.

Use a large safety shield to cover the apparatus as much as possible.

Diazomethane is highly explosive. All glassware used must be free of scratches, cracks, salts, and ground glass joints. The diazomethane must never be heated above 70°C. Failure to do either will result in an explosion of the diazomethane. If crystals are seen (especially at the collection end of the condenser), an explosion is imminent; either remove the stopper on the top of the condensor and flood with ethyl ether or prepare for the explosion.

Store below 0°C immediately after using.

Only an experienced technician familiar with the hazards of safety techniques to follow should use diazomethane.

Apparatus

1) Diazomethane generation kit - Aldrich chemical company. Contains the following:

Claisen adapter	Round-bottom flask, 50 ml
Connecting adapter	Round-bottom flask, 100 ml
Thermometer adapter	Round-bottom flask, 250 ml
Vacuum distilling adapter	Round-bottom flask, 500 ml
West condenser, 200 mm	125 ml Sep funnel
Distilling column, 200 mm	Teflon(R) stopper
Round-bottom flask, 25 ml	Gas inlet tubes (12)

2) Magnetic heating pad

3) Amber bottle - 250 ml, with teflon(R)-lined screw cap.

4) Three 2L glass beakers.

5) Ring stand

6) Thermometer

7) Safety shield

8) 500 ml erlenmeyer flask

Reagents and Standards

1) Reagent water, organic-free

2) Redistilled EtOH - ACS Certified

3) Potassium hydroxide pellets - ACS certified.

4) Ethyl ether, unpreserved - Nanograde, free of peroxides by cleaning with alumina. Test a 4L container of ethyl ether for peroxides with a test strip; notify the lab safety officer if the peroxide content is greater than 5 ppm. Solvent-rinse an alumina column with acetone and alumina-cleaned ethyl ether. To clean the ether, place a plug of glass wool (which has been baked @ 400°C for 4 hours and stored at 150°C) in the tip of the alumina column. Add a stopcock - making sure that the rubber O ring is not exposed - and a florisil(R) tip. Into the bottom of the column place 37g alumina (which has been baked at 400°C for 4 hours and stored at 150°C). Add ether to fill the reservoir and allow 50 ml to elute; discard the eluate. Place an empty 4L jug under the column. Tie tissue along the narrow stem of the column to absorb spillage during transfer of the ether to the column; cover the open spaces with foil in order to prevent evaporation and contamination. Collect the rest of the 4L of ethyl ether. Record the lot number and date on the bottle; indicate that the ether is aluminized by writing (AL) on the bottle. Test the cleaned ether for peroxides with a test strip; if peroxides are present at a level greater than or equal to 2 ppm, do not use; notify the lab safety officer.

5) Diazald(R) powder - ACS Certified.

6) Ice.

Generation Procedure

All glassware must be free of internal scratches/cracks; it must be kept behind a safety shield at all times.

1) In a flammable, explosion-proof hood, set up the stand and a large safety shield.

2) Set up the glassware carefully, being sure to inspect and replace any scratched or cracked materials.

3) If necessary, redistill 50-100 ml Ethanol. To do this, put the water bath at 95°C. Set up distillation apparatus, making sure to turn on the condensor water. Distill the

EtOH into a collection flask; transfer the EtOH to an amber bottle with a teflon(R)-lined screw cap. Label the bottle "REDISTILLED" with the date and preparer's initials.

4) Into the round-bottom flask weigh 6g KOH. Add 10 ml reagent water, 35 ml redistilled ethanol, and 20 ml aluminized ethyl ether.

5) Prepare the water bath on top of the magnetic stirrer. The bath temperature should be 55-60°C; the rheostat on the heating pad should be set between 2 and 2.2.

6) Prepare diazald(R) solution by weighing 21.4g diazold powder into a clean 500 ml erlenmeyer flask and dissolving with 150 ml aluminized ethyl ether.

7) To the separatory funnel add ~20 ml diazald(R) solution (don't add more since the diazald(R) will precipitate out of solution by collecting on the outside glass joints; this will be kept to a minimum by keeping the joints tight).

8) Attach the reaction flask to the assembled apparatus so that it is immersed 3/4 in the bath.

9) Immediately add the diazald(R) solution slowly to the round-bottom flask so that the rate it enters the flask is the same as that in which it leaves.

10) Place the safety shield in front of the set-up. Close the hood, and allow distillation to take place, making sure that the reaction is not vigorous. Carefully monitor the water temperature.

11) When each portion has been transferred, close the stopcock on the 125 ml separatory funnel. Continue adding the diazald(R) solution to the separatory funnel in this manner until used up.

12) Rinse the solid diazald(R) from the 500 ml flask with 50 ml aluminized ethyl ether.

13) Transfer the solution to the separatory funnel and continue to add it until gone.

14) Allow the reaction to take place until the distillation of the diazomethane is complete (20-30 minutes, or no more solution entering the collection flask).

15) When the distillation is complete, transfer the distillate to two 125 ml amber bottles free of cracks or scratches while wearing a full face shield. On the label, record the solution, date, lot numbers, and preparer's initials; also indicate the intended use (NPS or regular extractions). Write "NPS-1" on one and "NPS-2" on the other.

16) Write up the book, indicating lot numbers of reagents used and the intended use. In the solution notebook, write the procedure including the lot number and amount of each chemical (diazald(R), EtOH, and ethyl ether) used. Indicate the intended use (NPS or regular extractions). The diazomethane must be tested - see the procedure below.

17) Make sure that the cap on the amber bottle is tight and store in the freezer until needed.

18) Clean the apparatus. Wash the apparatus with aluminized ether and then with deionized water, making sure to dump the waste into the red solvent drums. Place

the glassware in a salt tray and cover with foil to prevent breakage. Bake at 400oC overnight.

19) After baking, wrap the internal joints in foil and the external joints with tissue.

20) Carefully place the glassware back into its case.

Diazomethane Test

1) Obtain four acid-washed receivers free of scratches or cracks. Label one "blank", and the others "PNP 1","PNP 2", and "PNP 3".

2) Add 1 ml MTBE to each receiver.

3) To each PNP sample, add 25 ul PNP standard (2000 ug/ml 4 nitrophenol); to all samples, add 250 ul high-purity MeOH.

4) Add 0.5 ml newly-made diazomethane to each sample. Adjust the volume to 3 ml with 99.9% MTBE. Mix, cover, and allow to react for one hour. Record all lot numbers of solutions used, PNP standard information, diazomethane preparation date, and preparer's initials in the NPS 3 log book.

6) Blow off the diazomethane with a gentle stream of nitrogen until the solution is clear.

7) Adjust the volume to 4 ml with 99.9% MTBE.

8) Bottle each sample, taking them to 10 ml with 5% MeOH in MTBE.

QUICK SUMMARY

PREPARATION:

Set up in an explosion-proof hood the stand and a large safety shield.

Set up the glassware; inspect and replace any scratched or cracked materials.

Redistill 50-100 ml EtOH at 95°C. Label the bottle "redistilled" with the date and preparer's initials.

Prepare the water bath @ 55-60°C; the rheostat should be set @ 2-2.2.

GENERATION:

Add 6g KOH, 10 ml DI, 35 ml redistilled EtOH, and 20 ml AL ethyl ether to a round-bottom flask.

Prepare diazold solution by adding 21.4 g Diazold powder and 150 ml Al ethyl ether to a clean 500 ml flask.

Place the shield in front of the apparatus, close the hood, and allow to distill. Carefully watch the temperature; keep the reaction non-vigorous.

Rinse the solid diazald from the 500 ml flask with 50 ml aluminized ethyl ether. Transfer the solution to the sep funnel; add until gone. Allow the reaction to proceed until complete.

Transfer the distillate into 2 125 ml amber glass bottles free of scratches. Record solution, date lot numbers, preparer's units., intended use (NPS or regular extractions), and #1 and #2 on the bottles.

CLEAN-UP:

Write up the book and the solution notebook. Indicate lot numbers and intended use.

Clean the apparatus by washing once with AL ether and once with DI. Dump the waste into the solvent drums. Bake the glassware at 400°C overnight.

Wrap internal joints in foil, external joints in tissue.

DIAZOMETHANE TEST:

Label 4 acid-washed receivers - "BLK","PNP 1","PNP 2","PNP 3". Add 1 ml MTBE to each.

Add 25 ul PNP standard to each PNP receiver.

Add 250 ul High-purity MeOH and 0.5 ml diazomethane (new) to each receiver; dilute to 3 ml with 99.9% MTBE. Mix, cover, and react for 1 hour. Record lot numbers, PNP std. info, diazomethane prep date, and preparer's initials in the NPS 3 log book.

Blow off diazomethane with a gentle stream of nitrogen.

Adjust to 4 ml with 99.9% MTBE. Bottle at 10 ml with 5% MeOH in MTBE.

APPENDIX I

SOP FOR PREPARATION OF SODIUM SULFATE

ACIDIFIED SODIUM SULFATE

4 December 1989

Scope and Application

This procedure is used for the acidification of sodium sulfate, a drying agent used in the process of preparing aqueous samples for gas chromatography. The acidified product is used in the herbicide and phenol tests.

Method Summary

Sodium sulfate is weighed and poured into a clean shallow glass tray. A mixture of ethyl ether with 10 ml H_2SO_4 per each kg Na_2SO_4 is prepared and added to cover the solid. The slurry is mixed, allowed to dry under a hood, triple-wrapped with foil, and baked @ 400°C for 4 hours. The sample is cooled and broken into a fine powder with a clean mortar. It is then tested for acidification by determining the pH of a mixture of 1g solid with 5 ml H_2O; if the pH is below 4, it is then stored in a large amber glass jar with a teflon-lined screw cap for use in extraction of herbicides or phenols.

Safety

Concentrated sulfuric acid is highly corrosive. Wear gloves at all times when handling acid. Clean all spills with an acid spill kit; discard the waste in a method congruent with EPA standards.

Sulfuric acid reacts violently with ether. Pour slowly, and wear gloves and safety glasses during the transfer.

Apparatus

1) A shallow glass tray, capable of holding up to 2 kg sodium sulfate.
2) A glass stirring rod.
3) A balance, capable of weighing up to 2 kg to 0.1 g.
4) A mortar with a teflon tip.
5) A large amber glass jar with a teflon-lined cap.

Reagents

1) Ethyl ether, ACS certified.
2) Sulfuric Acid, ACS certified.
3) Sodium Sulfate, ACS certified.
4) Aluminum foil.

Procedure

1) Weigh out 2 kg sodium sulfate. Pour into a shallow glass tray.

2) Into ~600 ml ethyl ether slowly pour 20 ml concentrated sulfuric acid. Wear gloves and safety glasses, as sulfuric acid reacts violently with ether. Mix well.

3) Pour the ether/acid mixture on top of the salt. Mix well with a glass rod, making sure to break up any chunks.

4) Add enough ether to cover the salt. Let the solvent evaporate in the hood.

5) Triple wrap the tray with aluminum foil.

6) Label the foil and bake in a muffle furnace @ 400°C for 4 hours.

7) Allow to cool. Test for acidification by mixing 1g solid with 5 ml H2O and measuring the pH. The pH must be less than pH 4.

8) Store in a large amber glass jar with a teflon-lined screw cap. Label "H+ Na2SO4", with the date, lot number, and preparer's initials.

9) In the gray book mark the lot numbers and amounts of each solution, date, pH when tested, and preparer's initials.

APPENDIX J

NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

MEMORANDUM 4/5/88

TO: ANDREW EASTON, JAMES M. MONTGOMERY CONSULTANTS

FROM: CHIP LESTER, ICF INC.

RE: NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

ICF's National Pesticide Survey Information System (NPSIS) is ready to collect information from you regarding the receipt of well water samples an their condition. Please find enclosed the following items: 1) A users memo containing all operating instructions, and 2) A copy of Carbon Copy softwar which is necessary to establish communications with NPSIS over phone lines. As mentioned previously, the software allows you to report the receipt of a one or more sample kits. It also prompts you for details regarding the condition of the samples. Additional features include; a bulletin board wh allows you to interactively send messages to ICF staff via your computer keyboard, file transfer, and access to the ICF computerized mail system for sending memos. It is also possible for you to speak over the phone to an I staff member during your session.

It is important that you test the communications link between the NPSI computer and yours. We have experienced trouble when using Carbon Copy software with a computer which has a Manzana 3.5 inch disk drive, and also with computers which have a non-Hercules or non-EGA compatible graphics car

For testing purposes, your sample kit identification numbers and FedEx airbill numbers (respectively) are: PD-0000-151 and 1111111111, PD-0000-152 and 2222222222, and PD-0000-153 and 3333333333. Use these sample kit identification numbers when trying out the NPSIS Sample Receipts Program. (Note to Chip: these will be different for each lab.)

We feel that it would be helpful to both parties if you could call us when you are ready to test the NPSIS system, and we will assist you over the phone during your session. If you would like to do this, please call Beth Estrada at (703) 934-3431. NPSIS will be available for access 24-hours a d seven days a week. We appreciate hearing any comments you have regarding NPSIS.

THE NPSIS SAMPLE RECEIPT PROGRAM

NPSIS is designed to keep track of the day to day operations of the National Pesticide Survey. You play an important role in NPS and your time notification of receiving a kit of samples is essential to the success of ! We have designed the Sample Receipt Program with your busy schedule in mind NPSIS will obtain the minimum amount of information necessary while still maintaining a secure system. You will be entering data into the NPSIS personal computer via your own computer, modem, and Carbon Copy software.

1.1 Hardware and Software Requirements.

The NPSIS Sample Receipt Program has a minimum hardware and software requirement. Here is a list of items you will need:

Hardware:

- One (1) IBM PC, XT, AT, or Personal System model with at least 640K memory.
- One (1) 2400 or 1200 baud Hayes or Hayes compatible mode with cables. (See Carbon Copy guide for cabling requirements and a description of usable modems)
- One (1) data transmission phone line.

Software:

- NPSIS Sample Receipt Program access provided for you by ICF.
- One (1) copy Carbon Copy software which is provided to y by ICF for the duration of NPS.

1.2 Initial Installation Steps.

Before you can access and use NPSIS, you must first load the Carbon Co software onto your PC. The directions are provided in the Carbon Copy manu One item you will want to include is an entry into the "Call Table". This entry will include a name, telephone number, and password for the NPSIS computer. To enter these items into the Call Table, press "2" from the Carl Copy Parameters' Screen. The information you must enter consists of the following:

- Name: NPS
- Telephone Number: 703-961-0629
- Password: NPS

1.3 Parameters for Communications.

NPSIS will maintain a set configuration throughout operation. Any changes due to updates in equipment or the system which will affect your ability to communicate through Carbon Copy will be forwarded to you. The parameters which will be maintained at this time are:

- 2400 baud modem speed.
- Answer ring count equal to one.
- Re-boot on exit after 5 minutes. (If there is a power failure or some other type of interruption, you can log back on to NPSIS and resume your session.)
- Five minute inactivity time constraint.
- Two password attempts.

2 REPORTING A SAMPLE RECEIPT TO NPSIS.

2.1 Establishing a Communications Link.

Once you have installed Carbon Copy and have all of the necessary hardware, you are ready to "log on" to the NPSIS computer at NPF. To do this

Type: C:> CCHELP NPS in your directory containing Carbon Copy.

This command will automatically dial the NPSIS computer, send your password for verification, and establish a data link between the two computers. You will be able to discern what is taking place by messages to your screen.

2.2 Entering A Sample Receipt Into NPSIS.

Once you have established a data link, (e.g., are "logged on"), you w see on the screen exactly what is on the screen of the NPSIS computer. Thi screen you are viewing is the main menu for the Sample Receipt Program. Remember that you are controlling the NPSIS computer via a 2400 baud phone line and your typing will appear on the screen at a much slower rate than y are accustomed to. A few tips on how to use the system are outlined in the next section.

2.2.1 Useful Tips on How to Use NPSIS.

Before you start, a few things to remember are:

- Pressing the "Esc" key will cancel all changes for the screen you are currently in and return you to the previous screen. Pressing "Esc" at the Searching Screen returns you to the main menu.

- Pressing "PgDn" or "PgUp" will save the items you have entered in the current screen and place you in the next or previous screen, respectively. This feature is handy to use when you only have a f items to enter in a screen which prompts for several items.

- Pressing "Enter", "arrow up", or "arrow down" will move the cursor from field to field in each screen. Remember that using the sideways arrows will not work.

- Pressing the "Alt" and "Right Shift" keys together will place the Carbon Copy Control Screen over the NPSIS Sample Receipt Program. You can then use the communications features in Carbon Copy. Pressing "F10" again when you are through will replace the NPSIS Sample Receipt Program screen you were currently in back on your screen, and

- Because you will are most likely to be entering information regarding a number of kits at one time, after you save or cancel your entries for one kit, you will be placed at the initial Sample Searching Screen for a new kit. If you are finished with your dat entry, simply press "Esc" to exit the Sample Searching screen and placed in the main menu.

2.3 A Basic Outline of the Sample Receipt Program.

The NPSIS Sample Receipt Program has three basic features:

- Initial reporting of a NPS sample kit of sample bottles.

- Ability to edit or re-edit an existing report of a kit receipt, and

- Access to ICFs computerized mail system which provides ability to send memoranda to ICF staff.

The information obtained in an entry for a kit of bottles is:

- The kit identification number, the FedEx airbill number and the last name of the person making the entry.

- Any damage to the kit as a whole such as melted ice or breakage of the cooler.

- Verification of which bottles belong in a kit or cooler, notification of any missing bottles or any additional bottles, and

- Any damage to each sample bottle which renders it unusab for analysis and testing.

2.4 NPSIS Sample Receipt Program Screens.

When you have completed the logon procedure, you will see the following main menu on your computer screen:

NATIONAL PESTICIDE SURVEY INFORMATION SYSTEM

SELECTION MENU FOR REPORTING SAMPLE RECEIPTS 04/05/88

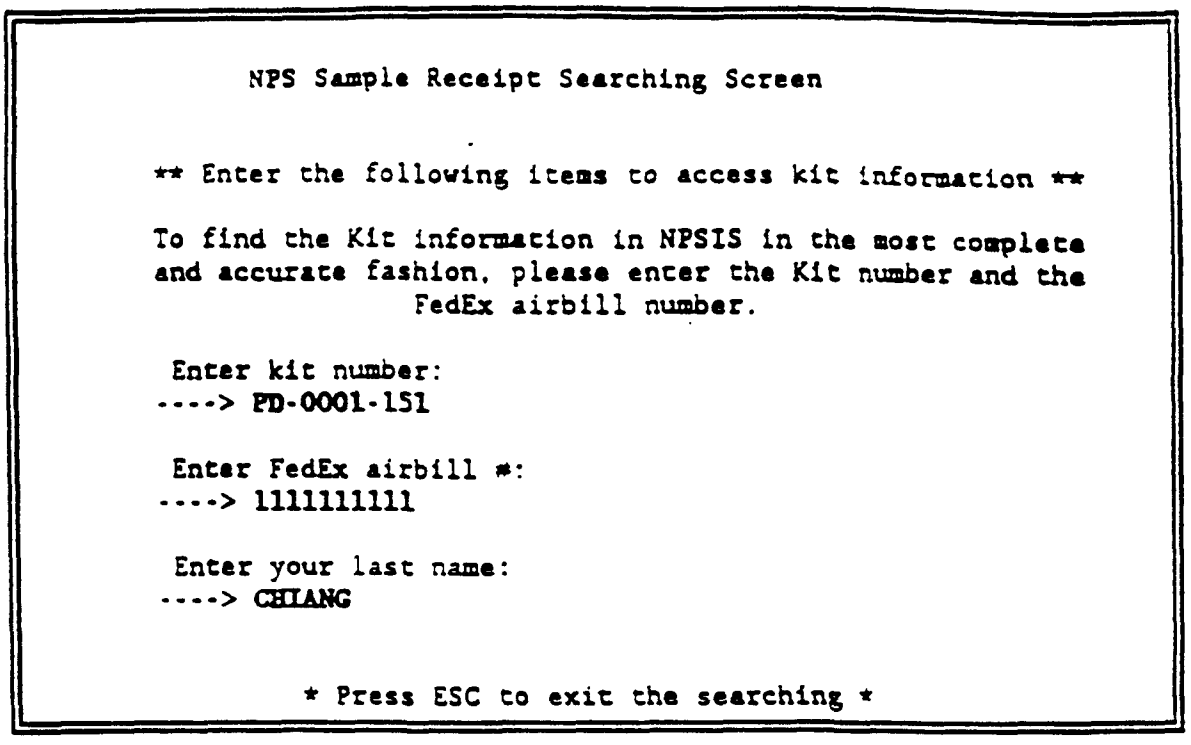
Report \ Edit a Sample Receipt
Send a Memo

Press <Alt><Right-Shift> to Logoff

use ↑ ↓ and ↵ to select option.

The screens provided in this memo will show all of the screens available and thus represent the maximum number of screens you will encounter with NPSIS. It is most likely that you will not have the need to enter informatic reporting damaged kits or samples. Therefore, not all of the screens depicte below will appear in your normal session.

If you choose the first item on the menu, "Report \ Edit a Sample Receipt", you will then be prompted for the kit identification number and the FedEx airbill number associated with the specified kit. The screen will appear like this:



If the kit number you have entered is incorrect, or if the kit number a FedEx airbill number combination is incorrect, NPSIS will prompt you to try enter these number again, as illustrated on the next page. It is possible that the FedEx airbill number on the kit is not the same as the FedEx airbil number which was entered into the NPSIS system. This could happen if the field team loses or damages the airbill.

ERROR!! The kit you entered cannot be found. . .

Kit number: PD-0001-151
AND
FedEx airbill number: 1111111111

Please check these numbers and try again!

****
NPSIS is designed to track Kits and FedEx airbill numbers.
The Kit and FedEx airbill number combination you have entered
does not match what is currently in the system. Please enter
the correct combination. If you still have problems, try
leaving the FedEx airbill # BLANK. Only enter the Kit number.
****

Press any key to continue...

Then, you will encounter this screen insuring that you have entered the FedEx airbill number:

Kit No.: PD-0001-151

Did you enter the correct Kit number and FedEx airbill number?

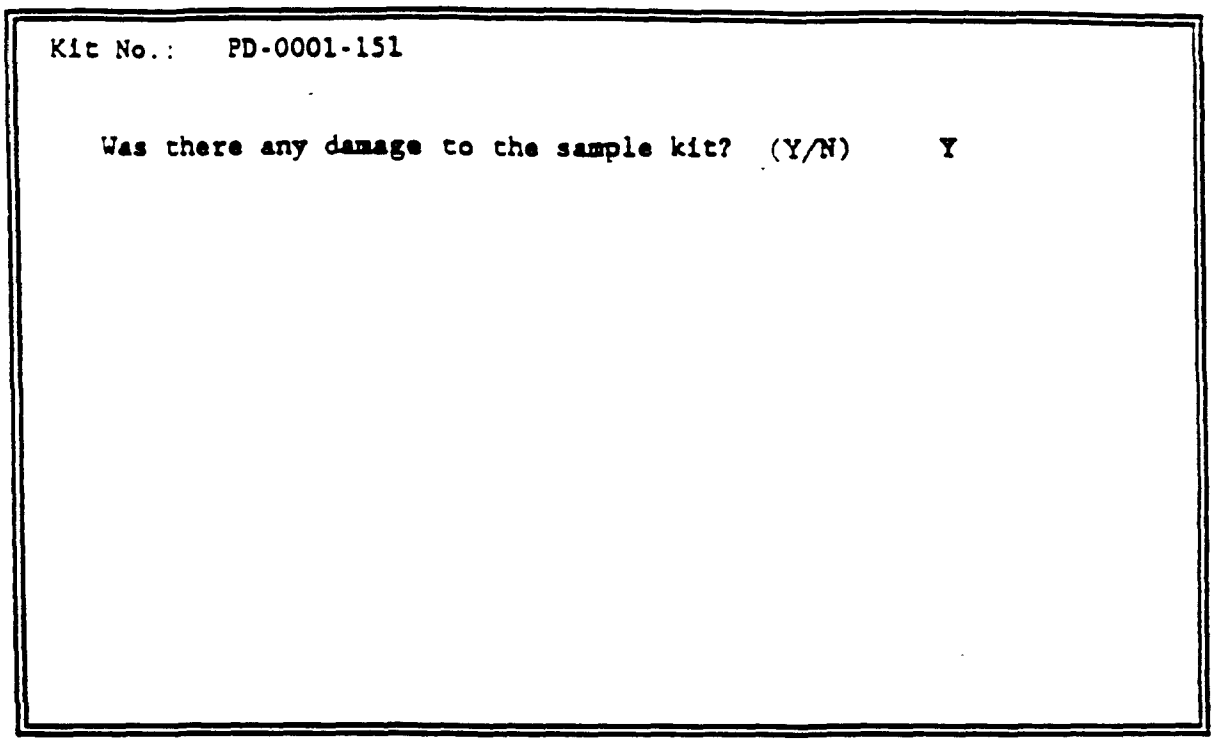
NPSIS is designed to store and track all FedEx airbill numbers.
This Kit may have a different FedEx airbill number than the
system, please enter the new FedEx airbill number:

---->

Note: if the correct airbill number was entered before, hit ENTER.

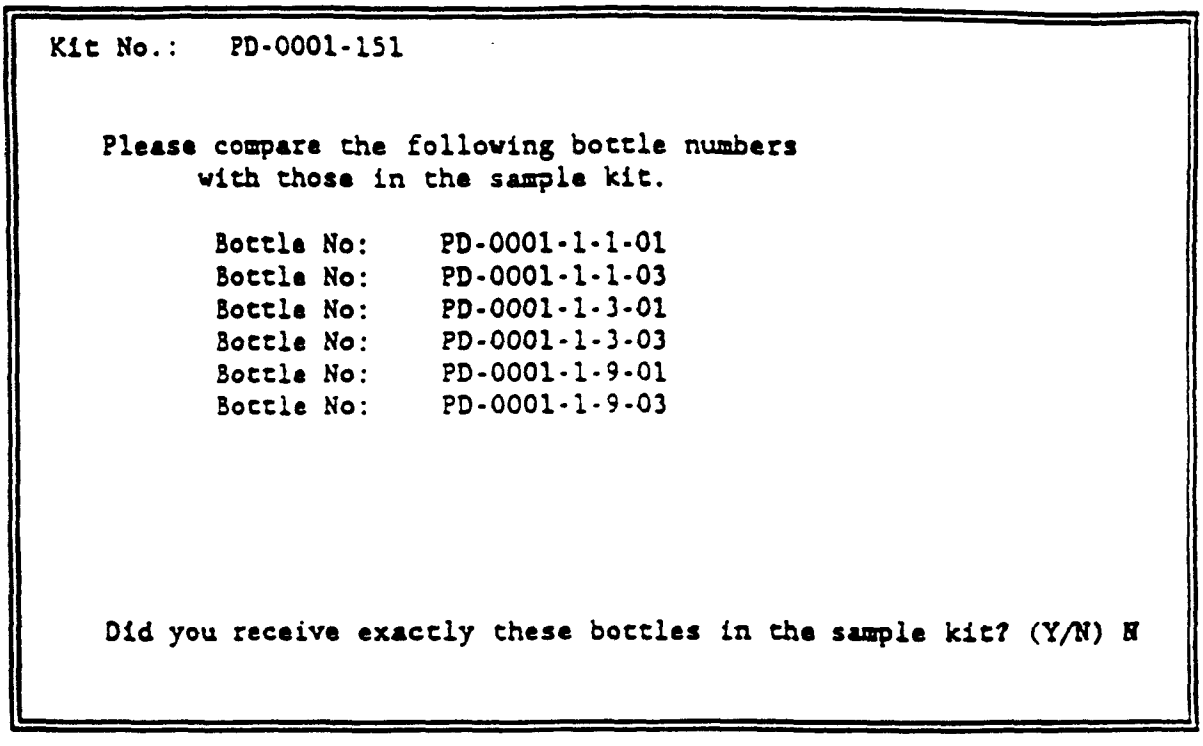
PgDn (Next page), PgUp (Previous page), Esc (Exit)

Once you have correctly identified the sample kit, NPSIS will ask you if there is any damage to the kit as a whole:



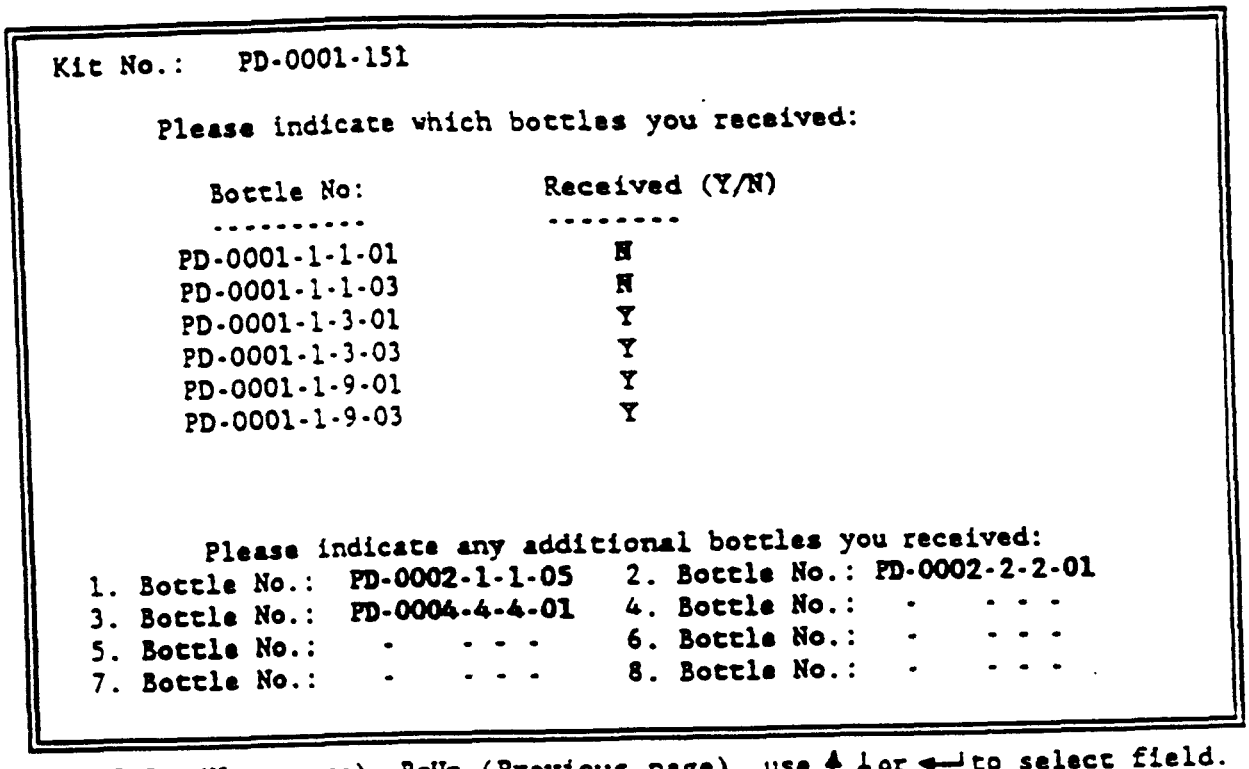
PgDn (Next page), PgUp (Previous page), Esc (Exit)

Next, NPSIS will ask you to survey the contents of the kit and check that which bottles are contained within the kit. You should then look at the bottle labels and determine if any are missing. Don't forget to check and determine if any bottles have been included in the kit which do not appear on the list provided by NPSIS on this screen:



PgDn (Next page), PgUp (Previous page), Esc (Exit)

If you have pressed "N", indicating that you did not receive exactly what NPSIS assumes you have received, you will be prompted to enter the appropriate information. This information includes pressing a "Y" or a "N" beside each bottle, and entering the bottle number found on the labels of any additional bottles you have received:



Kit No.: PD-0001-151

Please indicate which bottles you received:

Bottle No:	Received (Y/N)
PD-0001-1-1-01	N
PD-0001-1-1-03	N
PD-0001-1-3-01	Y
PD-0001-1-3-03	Y
PD-0001-1-9-01	Y
PD-0001-1-9-03	Y

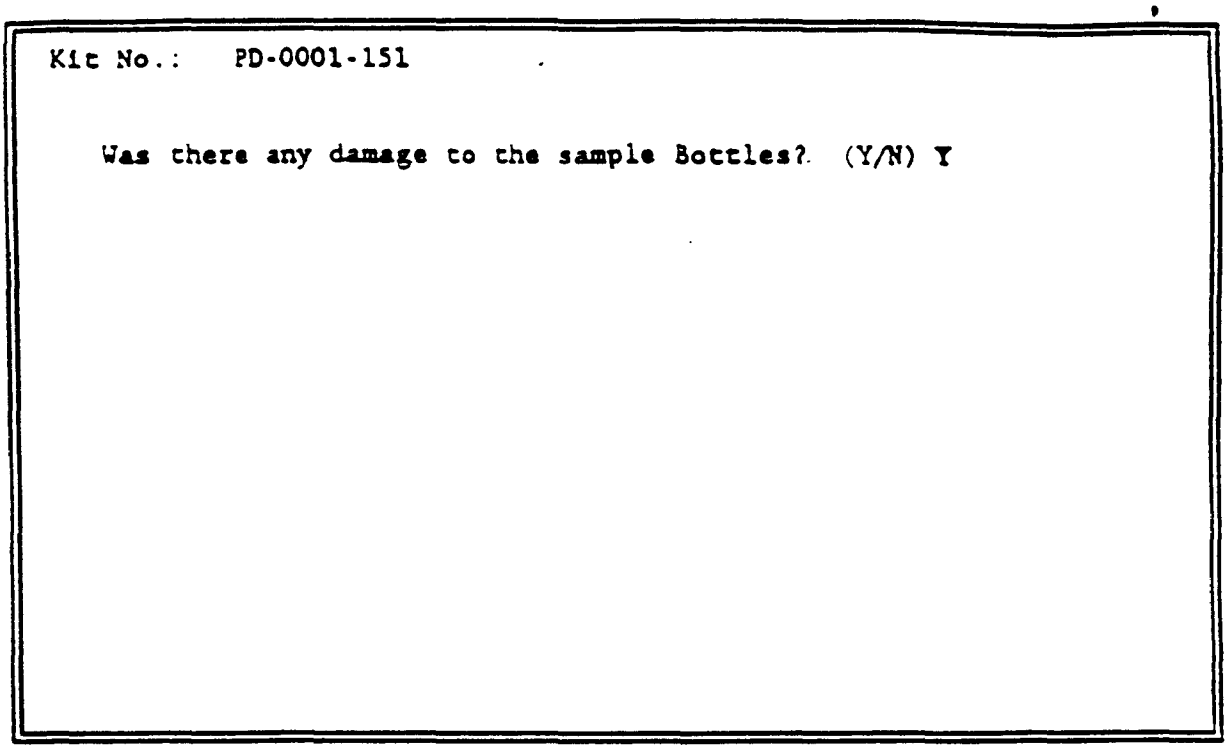
Please indicate any additional bottles you received:

1. Bottle No.: PD-0002-1-1-05		2. Bottle No.: PD-0002-2-2-01	
3. Bottle No.: PD-0004-4-4-01		4. Bottle No.:	- - - -
5. Bottle No.:	- - - -	6. Bottle No.:	- - - -
7. Bottle No.:	- - - -	8. Bottle No.:	- - - -

PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ←┘ to select field.

Notice that the user has indicated that he did not receive the first two bottles on the list. Also note that the user has indicated additional bottles which have come in the sample kit, but which were not on the list.

Next, NPSIS prompts you to indicate if any of the individual bottles ha
been damaged and rendered unusable for analysis:



PgDn (Next page), PgUp (Previous page), Esc (Exit)

In order to complete the appropriate information on damaged samples, you must first press a "Y" or a "N" in the field labeled "Damaged Y/N". If you have entered a "Y" in this field, you must then identify what the cause of the damage is, to the best of your abilities. As noted on the computer screen below, the "Other" category should be used if the sample is unusable but is not broken. Please try to comment whenever possible.

Kit No.: PD-0001-151

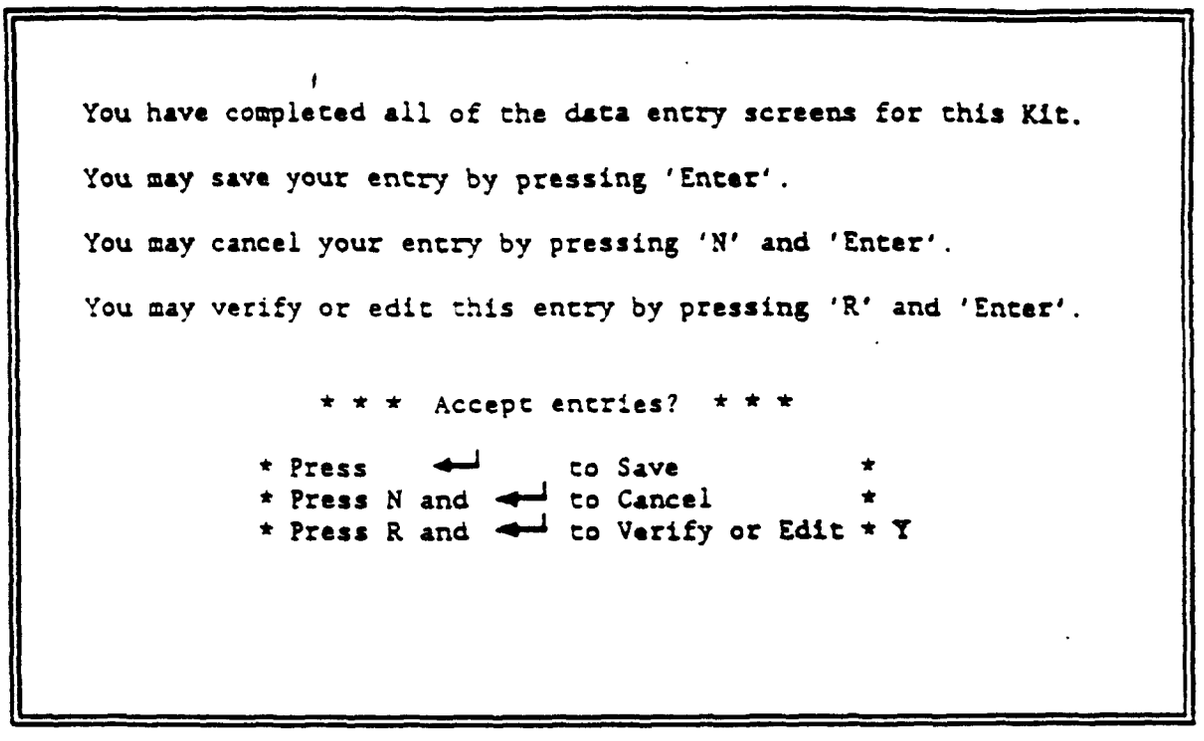
Please indicate which bottles are damaged by entering Y or N, and for those which are damaged, indicate the cause of damage.

Bottle No:	Damaged (Y/N)	--- C A U S E --- Broken (Y/N)	Other (Y/N)	Comment
PD-0001-1-3-01	N			
PD-0001-1-3-03	N			
PD-0001-1-9-01	N			
PD-0001-1-9-03	N			
PD-0002-1-1-05	N			
PD-0002-2-2-01	Y	Y		
PD-0004-4-4-01	N			

The 'Other' cause category is for reporting contamination of a sample, e.g. contamination noted on the Sample Tracking Form, air bubbles, or other reasons a sample is unusable.

PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ↵ to select field.

Now you have completed all of the necessary information needed to verify that the proper samples have reached their final destination in usable condition. You may save your kit entry by pressing "Enter". If you wish to cancel your kit entry and try again, press "N" and "Enter". If you wish to view or edit the current kit entry, press "R" and "Enter" and NPSIS will plac you back at the beginning of your entry.



By pressing "Enter" , you have saved all of the information necessary fc a particular sample kit. NPSIS assumes that you will enter more than one kit entry per session. Therefore, you will be placed at the initial "Searching Screen". If you are finished, press 'Esc' and you will be returned to the main menu. You can then log off of NPSIS by pressing "Alt" and "Right shift" at the same time. You may also send a memo through the ICF computerized mai system. To do this, cursor down to the second menu choice and press "Enter"

The next two pages of this memo describe how to use the ICF electronic mail system. Note that the password for you is NPS. The mail system softwa program will prompt you for this password before it will allow access to the system. Also, when you are selecting the recipients of your memo, please press the space bar beside the initials "NPS". This will send your memo to all ICF staff involved in the NPS project. If you wish to send memos to a particular ICF staff member, please call Beth Estrada for the identification number of the desired ICF employee.

ELECTRONIC MAIL

Function
Augment office communications with electronic transfer of notes and files.

Summary
Electronic Mail (E-Mail) allows you to send, receive, read, and subsequently save or discard notes and attached files.

When you power up your workstation you will automatically enter E-Mail if you have received any mail. Enter your password to check your mail, or press <ESC> twice to avoid E-Mail and continue to the Assist main menu.

Instructions
Operation of E-Mail is similar to Lotus 1-2-3. Press the F1 key to receive help at any time during operation. If any more help is needed contact workstation support to receive a manual.

For more information on any feature of electronic mail, use Network Courier's on-line help or refer to the User's Manual.

Passwords

Your password will be "password" until you change it yourself. Once you have given your password and entered E-Mail, you can change your password by selecting Options, then Password.

Reading Mail

1. Select "Read" from your men Highlight read, then pre <ENTER>.
2. Select the note to read:
   a. Highlight the note (using the arrow keys); and press <ENTER>.
   B. To save the note, select "Storage", then "Save". Enter the name of the file to which the note should be saved.
3. Press <ESC> to select another note.

Writing Mail

1. Select "Compose", then "edit".
2. Press <ENTER> when the highlig moves to "TO".
3. Select the recipients(s):
   a. Move the highlight to the first recipient's initials.
   b. Press the space bar. A small mark will appear.
   c. Repeat steps a and b for all recipients. Press the space b twice to "de-select" recipient The small mark will disappe
   d. Press <ESC> to cancel the entire list.
4. Select the initials of those who w receive copies:
   a. Press the down arrow to t to "CC".
   b. Select recipients as instruct above (step 3, a-d)

Writing Mail, continued

5. Enter a subject and priority. (optional)
6. Select attachments (optional):
   a. Press <ENTER> and type the path for the document(s).
   b. Press <ENTER> and select the document(s) to be attached.
   c. Repeat steps a and b for documents in another directory.
7. Enter the text of your message.
8. Press <ESC> when finished.
9. Select "Transmit" to post the note and attachments.

Quitting the Mail Program

1. Press <ESC> from the menu.
2. Select "YES".

APPENDIX K

NELSON DATA SYSTEM CALCULATIONS

Data System Calculations for NPS Method 1

1) The area response for a given compound is divided by the area response for the internal standard to obtain the area response.

2) The area ratio for a given compound is then plotted against the concentration for each calibration level.

A) Area ratio is plotted on the vertical (y) axis.
B) Concentration is plotted on the horizontal (x) axis.
C) Concentration is in units of ug/ml.

3) The data system then fits the data to a linear regression equation. ($y = mx + b$). for each compound, and calculates the slope and the intercept.

A) The slope, usually designated as "m", is designated C1.
B) The y-intercept, usually designated as "b", is designated C0.
C) Therefore, the form of the equation is now "$y = C1x + C0$".

4) The concentration "x" is then determined by rearranging the equation to get "$x = (y - C0)/C1$".

5) Since "x" represents the concentration of the extract in ug/ml, it is necessary to convert to ug/L to obtain the concentration in the original sample. This is accomplished through the use of a multiplier.

A) The default multiplier is 5 ml/L. This is used whenever exactly one liter of sample is extracted.

B) If a volume other than one liter is extracted, the multiplier is determined by dividing the final extract volume (which is always 5 ml) by the volume, in liters, of the original sample.

- For example, if 1123 ml of original sample are extracted, the multiplier is 5 ml/1.123 L, which is 4.4524 ml/L.

C) Therefore, the concentration "x" is then multiplied by the multiplier to obtain the concentration of a given compound in the original water sample in ug/L.

6) If the sample required dilution, the dilution factor is entered into the data sytem. The data system then multiplies the number obtained in step 5C by this factor to obtain the final concentration.

Example

Mevinphos. Set 1-0144

Area	Area (IS)	Area Ratio	Concentration
224303	1781233	0.1259256	0.132 ug/ml
616550	1783185	0.3457577	0.302 ug/ml
1290078	1747338	0.7383105	0.604 ug/ml

Fitting the data to the equation $y = C1x + C0$. (see Step 3C. previous page). where:

y = Area Ratio
x = Concentration.

the data system provides:

C1 = 1.298
C0 = -0.046.

This information will now be used to determine the concentration of Mevinphos in LCS A.

Area	Area (IS)	Area Ratio
1072000	1731722	0.6190372

Therefore. the concentration of Mevinphos in the extract (x) is:

$x = [0.6190372 - (-0.046)]/1.298 = 0.5123553$ ug/ml.

To obtain the concentration in the original sample:

0.5123553 ug/ml X 5 ml/L = 2.5617765 ug/L. (Note that the default multiplier was used since exactly 1 L of sample was extracted.)

The data system reported the concentration as 2.5611 ug/L. The difference in the 4th decimal place can be attributed to the difference in the number of significant figures used by the computer vs. the number of significant figures used in the manual calculation.

APPENDIX L

SOP FOR ARCHIVAL OF NPS DATA

NPS Method 3 Quantitation Algorithm

The calibration protocol for NPS method 3 involves the use of a 2nd order polynomial fit of the data generated from the analysis of the calibration standards, which makes it much more difficult to ascertain the exact algorithm that is used for sample quantitation.

Initially, a calibration plot of instrument response (in this case the ratio of analyte area to the area of the internal standard [A/Ais]) vs. concentration (in units of ug/mL) is prepared. The datastation then calculates the curve that best fits the data using a standard 2nd order polynomial fit function. The subsequent equation is in the form of:

$$Y = C_2x^2 + C_1x + C_\emptyset$$ where Y= response (A/Ais), and X= concentration (ug/mL)

This equation can be converted into the standard form for a quadratic equation ($Ax^2 + Bx + C = \emptyset$) as follows:

$$\emptyset = C_2x^2 + C_1x + (C_\emptyset - Y)$$

From here, the equation can be solved for X (concentration) for any given Y (A/Ais), using the following formula:

$$X = \frac{-C_1 \pm \sqrt{C_1 2 - (4 * C_2 * (C_\emptyset - Y))}}{2C_2}$$

We have independently verified the Nelson polynomial coefficients using a commercial software program for the Macintosh computer. Consequently, we have assurance that the calibration equation is generated using a 2nd order polynomial fit of the data. Figures 1 represents the calibration data for the three compounds that were detected in a sample in set 0145, as well as the surrogate and the internal standard. The first set of polynomial coefficients were taken directly from the Nelson printout using the number of significant figures provided on the printout. The next set of coefficients represents the coefficients obtained using the independent software package, and serve as verification that this program duplicates the algorithm used by the Nelson system. The final set of coefficients were obtained by plotting concentration vs. area ratio (A/Ais) using the software program. By inverting the plot, these coefficients can be used directly to convert area ratio to concentration.

MONTGOMERY LABORATORIES STANDARD OPERATING PROCEDURE FOR THE ARCHIVAL OF THE NATIONAL PESTICIDE SURVEY (NPS) DATA

Introduction

A Standard Operating Procedure has been developed to allow Montgomery Laboratories (ML) to retrieve all documentation necessary to technically defend NPS analytical results. The documents will be located on the first floor on ML premises in a locked data storage room.

All data that have been collected in support of the National Pesticide Survey will be stored until October of 1992 in a systematic manner such that data may be retrieved in a timely fashion for reference purposes.

The NPS project manager, Julie Zalikowski, will be the primary manager for all archived documents. Ms. Zalikowski and Dr. Eaton, the program manager, will maintain keys to the storage room.

Materials to Archive

1) Method 1 Initial demonstration of capabilities.

2) Since samples are filed by sets, a cross-reference list from sample ID to set ID has been developed. The cross-reference list includes:
   - Sample ID
   - Sample type
   - Date sampled
   - Date received
   - Date extracted
   - Set numbers
   - Date analyzed

3) **Method 1 chromatograms listed in chronological order 1 - 0001 through 1 - 0196**

4) Method 1 Quantitation reports listed in numerical order.
1 - 0001 through 1 - 0196

For each Quantitation report the following materials are available, as appropriate to a given method and /or set:

- Set completion form
- Method Blank (MBLK)
- Corrective Action Forms
- Lab control standards (LCS's)
- Lab spike samples (LSS's)
- Instrument control samples (ICS's)
- Field samples
- Time - storage samples
- Control chart
- GC/MS data (Extract shipping forms and spectras)
- Extraction summary sheet
- Sample tracking
- Dbase hard copy
- Analytical run sheet

5) Method 1 control charts
1 - 1 through 1 - 37

6) Method 3 Initial demonstration of capabilities

7) Method 3 Sample ID to set ID cross-reference list

8) Method 3 chromatograms
3 - 0002 through 3 - 0198

9) Method 3 Quantitation reports
3 - 0002 through 3 - 0198

10) Method 3 Control Charts
3 - 1 through 3 - 39

11) Method 9 Initial demonstration of capabilities

12) Method 9 sample ID to set ID cross-reference list

13) Method 9 Quantitation reports
9 - 01 through 9 - 36

14) ICF sample receipt forms

15) Monthly status reports/Internal QA audit reports

16) Statement of qualification for personnel who participated in the project

17) Log books
   a. Extractions log book
   b. Standards log book (Method 1 & Method 3)
      - Spiking Standards log
      - Internal Standards log
      - Surrogate log
      - Calibration standards log
   c. Method 9 log book
      - Daily log
      - Standard & Reagent log book
   d. Instrument Maintenance log book
   e. GCMS log book
   f. Telephone log book and notes (M1, M3 & M9)

18) Forms and records
   - A Copy of the QAPjP M1, M3, M9
   - Temperature log
   - GCMS Extract shipping form
   - GCMS Reports
   - Copy of NPS formatted disc
   - Hardcopy of any specialized computer programs
   - Time storage extraction and analysis summary

19) Correspondence received from Technical Monitor

20) Performance evaluation results

21) NPS Contract

22) ICF Daily Sampling Schedules

23) General NPS Information

ORGANIZATION OF NPS MATERIALS ACCORDING TO FILE CABINET NUMBER

****

1. a. Method 1 Initial Demonstration of capabilities
   b. Method 1 Sample Cross Reference List
      Method 1 Chromatograms 1-0001 thru 1-0020
   c. Method 1 Chromatograms 1-0021 thru 1-0038
   d. Method 1 Chromatograms 1-0039 thru 1-0054

2. a. Method 1 Chromatograms 1-0055 thru 1-0070
      $MeCl_2$ test
   b. Method 1 Chromatograms 1-0071 thru 1-0084
   c. Method 1 Chromatograms 1-0085 thru 1-0103
   d. Method 1 Chromatograms 1-0104 thru 1-0117

3. a. Method 1 Chromatograms 1-0118 thru 1-0132
   b. Method 1 Chromatograms 1-0133 thru 1-0150
   c. Method 1 Chromatograms 1-0151 thru 1-0169
   d. Method 1 Chromatograms 1-0170 thru 1-0185

4. a. Method 1 Chromatograms 1-0186 thru 1-0196
   b. Method 1 Quantitation Reports 1-0001 thru 1-0095
   c. Method 1 Quantitation Reports 1-0096 thru 1-0196
   d. Method 1 Control Charts 1-1 thru 1-37

5. a. Method 3 Initial Demonstration of Capabilities
      Method 3 Sample cross-reference list
      Method 3 Chromatograms 3-0002 thru 3-0018
   b. Method 3 Chromatograms 3-0019 thru 3-0046
   c. Method 3 Chromatograms 3-0047 thru 3-0072
   d. Method 3 Chromatograms 3-0073 thru 3-0095

6. a. Method 3 Chromatograms 3-0096 thru 3-0120
   b. Method 3 Chromatograms 3-0121 thru 3-0143
   c. Method 3 Chromatograms 3-0144 thru 3-0169
      DCPA Study
   d. Method 3 Chromatograms 3-0170 thru 3-0195

7. a. Method 3 Chromatograms 3-0196 thru 3-0198
      Method 3 Quantitation Reports 3-0002 thru 3-0113

7.(con't.)

b. Method 3 Quantitation Reports 3-0114 thru 3-0198
c. Method 9 Initial Demonstration of Capabilities
Method 9 Sample Cross-reference list
Method 9 Quantitation Reports 9-0002 thru 9-0036
ICF Sample Tracking Forms
d. Monthly Status Reports/Internal QA Reports
NPS Personnel
NPS Method 1, 3 & 9 Log Books
GCMS Log Book
Telephone Log Books & Notes (M1, M3 & M9)

8. a. Copy of QAPP (M1, M3 & M9)
Temperature Log
Copy of NPS Formatted Disc
Specialized Computer Program
Time Storage Summary
Correspondence from Technical Monitor
Performance Evaluation Results
NPS Contract
ICF Daily Sampling Schedules
General NPS information

APPENDIX M

SOP FOR NPS WASTE TREATMENT

NPS WASTE TREATMENT

Page	Revision #	Revision Date
1	1	October 3, 1989
2	1	October 3, 1989
3	1	October 3, 1989
4 (last)	1	October 3, 1989

Approved:

Group Leader: _____

Operations Manager: _____

QA Officer: _____

Laboratory Director: _____

NPS WASTE TREATMENT

Scope and Application

This procedure is used to treat wastewater containing 10-50 mg/l $HgCl_2$ in order to precipitate the salt out of solution.

This is applicable to all treating water from all samples which have been preserved with mercuric chloride.

Method Summary

Sample waste containing $HgCl_2$ is aerated completely to remove any peroxides from ether. The waste is adjusted to pH 8-11 by adding either 25% NaOH or 1 M H_2SO_4 to 15-20 liters of wastewater. The pH'd wastewater is then poured into a 55-gallon teflon drum.

When the drum is 90% full, the salts in it are reduced by adding a sodium borohydride solution. The water is mixed and allowed to sit.

A sample is tested for mercuric chloride; if it passes, the drum is pumped dry and the precipitate poured into the solid waste drum.

Safety Considerations

Mercuric chloride is a neurotoxin and a nephrotoxin. Care must be taken to avoid inhalation of dust; gloves must be worn as $HgCl_2$ may be absorbed through the skin.

When opening the 55 gallon drums, be careful not to inhale ether or methylene chloride fumes; the use of a respirator is recommended.

Material Safety Data Sheets (MSDS) are located in the lab and available for any to use. These sheets describe the hazards of each chemical used and give the method required to treat any injury or spill of such chemicals.

Apparatus

1) 500 ml Erlenmeyer flask.
2) 250 ml graduated cylinder.
3) Analytical balance.
4) Aeration apparatus - a teflon tube with an aeration stone on the end of it.
5) 55 gallon teflon drum, capped.
6) 10 ml pipette.
7) 10 ml glass vial, with teflon screw cap.
8) Pump, with a glass wool filter. Clean the filter by replacing the glass wool once a month.

Reagents and Standards

1) Reagent water, organic-free.

2) Sodium hydroxide pellets - ACS certified. Make 25% NaOH by mixing 250g NaOH with enough reagent water to make 1L solution.

3) Sodium borohydride - ACS certified. Make 12% $NaBH_4$ in 5% NaOH in the following manner:

   1) Weigh 7.5g NaOH into a 500 ml erlenmeyer flask.
   2) Add ~ 50 ml DI to dissolve the NaOH.
   3) Add 18 g $NaBH_4$ into the flask; mix well.

4) Pour the solution into a 250 ml graduated cylinder.

5) Rinse the flask with ~20 ml DI. Pour the rinse into the cylinder to complete the transfer.

6) Add enough DI to the cylinder to dilute the solution to 150 ml. Mix well, and transfer to a 250 ml amber bottle.

Waste Removal Procedure

1) In a hood, aerate NPS-3 waste ~1 day or until any ether has evaporated; aerate NPS-1 waste ~2 hours.

2) Ph the waste to pH 8-11. Use 25% NaOH as the base to pH the waste; if the resulting solution is too basic, use 1 NH_2SO_4 to acidify it.

3) Make 12% sodium borohydride solution in 5% NaOH by following the directions in Reagents.

4) Pour the waste into a 55 gallon teflon drum. When the drum is ~90% full, add the 150 ml sodium borohydride solution. Cap the barrel and shake to ensure dissolution.

5) Let the barrel sit at least 3 days to allow settling of the precipitate.

6) On the fourth day, obtain a 10 ml sample and pour into a 10 ml glass vial with a teflon screw cap. Label the sample "NPS WASTE" with the barrel number, date, and preparer's initials.

7) Take the sample to a metals analyst so that the amt Hg^{++} ions may be tested. Record the sample on the sheet provided.

8) If the sample passes, the supernatant in the drum can be drained by a pump with a glass wool filter; if not, repeat steps 2-7. If the second sample fails, pump the supernatant into a new drum and leave the solid; repeat steps 2-7 with the supernatant and pour the solid into a solid waste drum.

9) Pour the solid into a solid waste drum.

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