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**QUALITY ASSURANCE PROJECT PLAN
FOR THE
NATIONAL PESTICIDE SURVEY OF DRINKING WATER WELLS
ANALYTICAL METHOD 2 - CHLORINATED PESTICIDES**

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**NATIONAL PESTICIDE SURVEY
QUALITY ASSURANCE PROJECT PLAN FOR
ANALYTICAL METHOD 2 - CHLORINATED PESTICIDES**

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3.0 PROJECT DESCRIPTION

Clean Harbors, Inc. (Clean Harbors) has been contracted by the USEPA Office of Pesticide Programs and Technical Support Division to provide analytical services in support of the National Pesticide Survey (NPS). The NPS has been designed to meet two major objectives: (1) to determine the degree to which the drinking water wells of the nation are contaminated by pesticides; and (2) to better understand how pesticide concentrations in drinking water wells are associated with patterns of pesticide usage and the vulnerability of ground water to pollution. Clean Harbors will analyze 750 samples from community water systems and 750 samples from domestic wells for the presence of chlorinated pesticides using gas chromatography with an electron capture detector by Method 2 (revised Oct. 27, 1987).

This Quality Assurance Project Plan (QAPjP) has been prepared to ensure sample analysis and reporting in accordance with Method 2 and contractual reports of work.

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

Figure 4-1 represents Clean Harbors's organization chart for this program. As program manager, Mr. Louis Macri will be responsible for technical and administrative direction of the overall program. Mr. John Verban will coordinate and review all sample preparation and gas chromatographic work. He will also be responsible for initiation of bench level corrective actions.

The key individual responsible for QA is the Director of Quality Assurance, Dr. Richard Fix, who will serve as Program QA Officer. Dr. Fix reports directly to the President of Clean Harbors. The key individual responsible for Analytical QC activities is Christine Johnson, Analytical QC Coordinator, who reports directly to the QA Director. Ms. Johnson is thus independent of the technical groups generating measurement data. The responsibilities of these key QA/QC individuals on this program are briefly described below.

4.1 QA OFFICER'S RESPONSIBILITIES

The Division QA Director, Dr. Richard Fix, is the responsible Quality Assurance Officer for this project. He will review and approve the proposed Project Plan for this contract. He will ensure that any necessary revisions are made and will check on implementation of the QA Plan during the course of this project, scheduling performance and/or system audits as necessary. Dr. Fix will initiate and/or followup on corrective actions. He will aid in preparation of a section of each Monthly Report summarizing QA/QC activities which include estimates of precision, accuracy, and completeness of the required data. Audits conducted, quality problems identified, and corrective actions taken will be described.

4.2 ANALYTICAL QC COORDINATOR'S RESPONSIBILITIES

Ms. Christine Johnson, the Analytical QC Coordinator, oversees and implements the ongoing QC program. She will be responsible for the implementation of the analytical QC measures specified in this Plan. She will review all QC sample results and incorporate them in the appropriate monthly Analytical Results report. She will have overall responsibility for preparing the QC section of these reports.

4.3 LABORATORY STAFF RESPONSIBILITIES

The Program Manager, Louis Macri, will have responsibility for meeting budget and schedule commitments, as well as the technical quality of the work. He will also be the Laboratory contact for the EPA Technical Monitor, Mikki Bolyard ((513) 569-7939). Working directly with Mr. Macri will be John Verban. Mr. Verban will be responsible for coordinating sample extraction with Mr. Doug Buffington and analysis by GC. Mr. Verban will also be responsible for primary data review and

initiation of bench level corrective action as well as being backup analyst for Ms. Kate Duffy who will perform the majority of the analysis and data reduction.

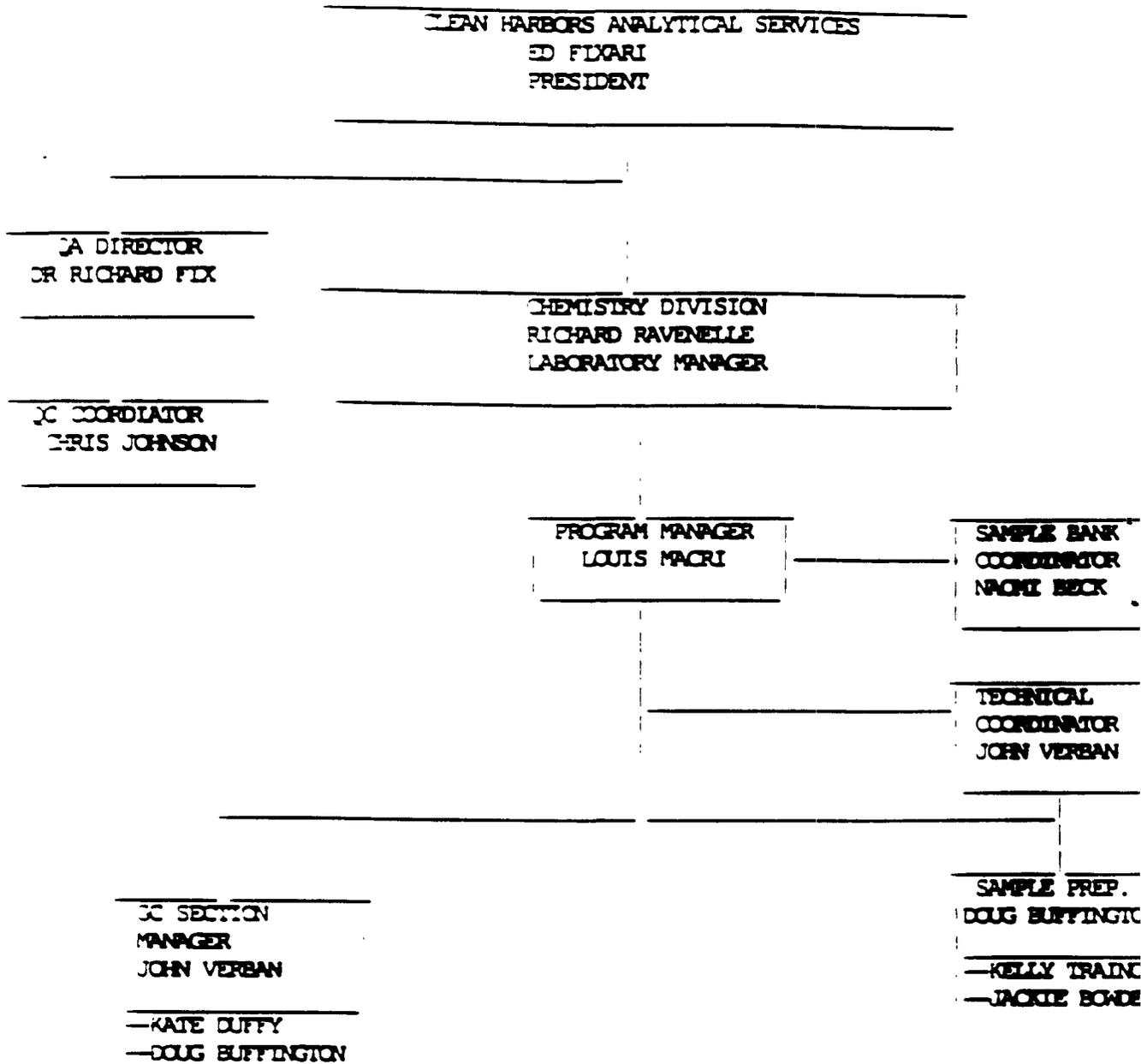
Ms. Naomi Beck is responsible for sample receipt. The shipping address for samples is:

Clean Harbors Analytical Services, Inc.
213 Burlington Road
Bedford, Massachusetts 01730

Ms. Beck can be reached at (617) 275-6111.

Steve Cappello will be acting project coordinator, assuming the responsibilities previously assigned to John Verban, from March 3, 1990 until the close of the project.

FIGURE 4-1
PROGRAM ORGANIZATIONAL CHART



5. QA OBJECTIVES FOR MEASUREMENT DATA

5.1 DETERMINATION OF ESTIMATED DETECTION LIMIT (EDL)

A determination will be made of the standard concentration necessary to produce an ECD response with a 5/1 signal to noise ratio. Two analyte mixes will then be prepared and used to spike eight (8) pairs of reagent water samples. These samples will be prepared and analyzed as a batch.

The standard deviation (SD) will then be calculated using the following equation.

$$SD = \sqrt{\frac{1}{n-1} \left(\sum_{i=1}^n x - \bar{x} \right)^2}$$

where: n = the number of measurements for each analyte
 X = individual measured value in $\mu\text{g/L}$, and
 \bar{x} = average measured value in $\mu\text{g/L}$.

The minimum detection level (MDL) will then be computed by the following equation:

$$MDL = SD \times 3.500 \text{ (Student's } t \text{ value).}$$

The estimated detection limit (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. The EDLs, determined in this manner, must be no greater than two times those determined during methods development, as listed in Appendix A, Table 2.

The minimum reportable level, MRL, will be calculated using the following equation:

$$MRL = 5 \times EDL$$

5.2 DETERMINATION OF GC/MS DETECTION LIMITS

Six analyses of each analyte mix will be performed by Multiple-ion detection (MID) GC/MS, using the three ions specified by EPA (Appendix B). The results of these analyses will be used to determine the concentration at which a 5/1 signal to noise ratio, for the least intense of the ions, is obtained.

5.3 CONSTRUCTION OF CONTROL CHARTS

Control charts will be used to demonstrate control of the measurement system. Control charts will be generated upon completion of the initial determination of reporting limits. To establish the control charts, 5 reagent water samples for each of the two analyte mixes will be spiked at ten times the MRL and carried through the Method 2 extraction and analysis procedure. An additional 3 sets of 5 spiked reagent water samples will be similarly generated and analyzed on each of 3 days. The data from all 20 samples will be used to construct the control chart. The mean recovery (R) and standard deviation (SD) will be calculated as follows:

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

where: R_i = the individual recovery value,
 R = average recovery value, and
 n = the number of measurements.

ACCEPTANCE CRITERIA FOR ACCURACY AND PRECISION WILL BE THE FOLLOWING:

- The RSD for analytes must be less than or equal to 20%, except where data, listed in Appendix A, Table 2, indicates that poorer precision was obtained by Battelle in the method validation. Technical monitors will determine action to be taken if criteria are not met.
- The mean recovery (\bar{R}) of each analyte must be within R plus or minus $3x$ SDs as determined by Battelle, but no greater than plus or minus 30 percent.
- Initial surrogate recovery control will also be demonstrated on 20 samples. Surrogate control charts will be generated to provide control limits for surrogate recovery in samples.
- Warning limits of 2 standard deviations and control limits of 3 standard deviations will be depicted on control charts for both laboratory control standards and surrogates.

Dixon's test will be used to determine a maximum of three outliers per analyte from the 20 spiked reagent waters. Appendix C provides a discussion of Dixon's test.

Established control charts will be updated with spiked samples prepared with sets of spiked reagent waters when data from 5 spikes are available. Data from the 5 earliest spiked samples will be deleted, the precision and accuracy recalculated and the control chart redrawn.

5.4 FREQUENCY AND PROCEDURE FOR MATRIX SPIKING

During the survey, EPA will provide field samples from 10% of the sites for the laboratory to assess the recoveries of spiked analytes from a variety of matrices. These samples are to be spiked at analyte concentrations equal to 2, 5 or 10 times the MRL for each analyte. The required spiking level will be specified on the sample label.

6. SAMPLING PROCEDURES

All sampling for the National Pesticide Survey will be performed under the direction of ICF. Clean Harbors will receive 1-liter water samples, preserved with 10 mg/L of mercuric chloride preservative. Sample bottles will be shipped, iced, to the Clean Harbors laboratory in Bedford, Massachusetts for analysis by Method 2. Clean Harbors will be responsible for notifying the Technical Monitor if a sample box arrives without any ice remaining.

ICF will be responsible for the collection of duplicate samples at 10% of the sites for spiking at Clean Harbors. All samples will be clearly labelled to differentiate field samples (FS), backup samples (BU), lab spikes (LS), and time storage samples (T/S). The field label is reproduced in Figure 6-1. All samples will be accompanied by a field sample tracking sheet, depicted in Figure 6-2.

FIGURE 6-1

NATIONAL PESTICIDE SURVEY

SAMPLE #: PC-2226-1-9-03

JMM - METHOD# 9 KIT: 111
BACKUP SAMPLE
PRESERVATIVE: H2SO4

<u>DATE</u>	<u>TIME</u>	<u>SAMPLER</u>

NATIONAL PESTICIDE SURVEY

SAMPLE #: PC-2226-1-9-01

JMM - METHOD# 9 KIT: 111
FIELD SAMPLE
PRESERVATIVE: H2SO4

<u>DATE</u>	<u>TIME</u>	<u>SAMPLER</u>

FIGURE 6-2

NPS FIELD SAMPLE TRACKING SHEET

WELL I.D. NO.: 0000

FRDS I.D. No. (CNS WELL ONLY): _____

SAMPLE COLLECTION DATE: / /

TRACKING FORM COMPLETED BY: _____

LAB: BSL
 SCENARIO: 1

KIT NO.: PD-0000-611
 EQ1 1 of 1

TO BE COMPLETED BY:

ICF			FIELD TEAM			LAB	
SAMPLE NUMBER	BOTTLE SIZE	SAMPLE DESCRIPTION	SAMPLER (INITIAL)	TIME SAMPLED	COMMENTS (1)	RECEIVED:	COMMENTS
PD-0000-6-1-01	1000	FIELD SAMPLE				N:	
PD-0000-6-3-01	1000	FIELD SAMPLE				N:	
PD-0000-6-6-01	60	FIELD SAMPLE				N:	
PE-0000-6-1-03	1000	BACKUP SAMPLE				N:	

CHLORINE TEST: _____

SHIPPED BY: _____ DATE _____ TIME _____ SENT TO: _____ _____ _____	LAB ADDRESS: <u>BAY ST. LOUIS EPA-ENVIRONMENTAL</u> <u>CHEMISTRY LAB, 3036 N. 11th</u> <u>ST. LOUIS, MO 63109</u>	RECEIVED AT LAB BY: _____ DATE _____ TIME _____ CONDITION (3): _____ _____ _____
--	--	--

(1) FOR EXAMPLE: BOTTLE BROKEN, BOTTLE MISSING, OVERFILLED BOTTLE, CAP WAS DROPPED
 (2) FOR EXAMPLE: BOTTLE BROKEN, BOTTLE MISSING, BOTTLE CONTAMINATED, TEMPERATURE CRITERIA NOT MET
 (3) FOR EXAMPLE: ICE MELTED, NOT PACKING

7. SAMPLE CUSTODY

This section provides information concerning laboratory notification of sample schedule; EPA requirements for holding times, storage conditions and disposal; Clean Harbors's system for sample receipt and tracking, and for monitoring refrigerator temperatures where samples are stored.

7.1 NOTIFICATION OF LABORATORY

ICF will provide a printout of the sample shipment schedule for each upcoming 2-week period. ICF will also maintain a sample tracking system into which Clean Harbors will enter data concerning sample receipt.

7.2 HOLDING TIME, STORAGE AND DISPOSAL REQUIREMENTS

The maximum extraction holding time for field samples is 14 days from sample collection. Analysis on primary and confirmatory columns must be completed within 14 days after extraction. The maximum holding time for GC/MS extracts may be extended by the Technical Monitor to 28 days. Data from samples extracted or analyzed outside the holding times shall not be submitted to the EPA, nor shall compensation be received by the laboratory.

Extraction and analysis holding times for time storage samples will differ from holding times required for field samples. Table 7.1 depicts holding time requirements for time storage samples and extracts.

All samples and extracts will be stored in the dark at 4 degrees Centigrade. Refrigerator temperatures must be verified and recorded on each working day.

Water samples will be disposed of after the 14-day holding time has been exceeded. Sample extracts will be maintained until disposal is approved by the TSD or OPP Laboratory Coordinator. All sample containers and boxes will be returned collect to the EPA or ICF.

7.3 CUSTODY PROCEDURES AT THE CLEAN HARBORS LABORATORY

Clean Harbors, Inc. maintains a Sample Log-in area to implement custody procedures and to provide proper storage for all samples collected by, and/or submitted to Clean Harbors. The log-in area is located in the laboratory and is staffed by the Sample Log-in Coordinator who reports to the Program Manager. The Sample Log-in Coordinator accepts custody of all samples received by Clean Harbors.

Upon receipt at Clean Harbors, each sample shipment is inspected to assess the condition of the shipping container and the individual samples. The enclosed custody records are cross-referenced with all the samples and sample tags in the shipment; the custody records are signed by the Sample Log-in Coordinator and placed in the project file. The Sample Log-in

TABLE 7.1 HOLDING TIMES FOR TIME STORAGE SAMPLES



Sample I.D.	Spiking DATE (A)	Extraction Date (B)	Analysis Date (C)	Re-analysis Date (D) (HTE)
TS ₀ (DTS) Time Storage t=0 days	Day 0 to 13	Day A to Day A + 4	Day B to Day B+4	Day B+10 to Day B+18
TS ₀ (DTS) (Time Storage Dup; t = 0 days)	Day 0 to 13	Day A to Day A + 4	Day B to Day B + 4	Day B +10 to Day B + 18
TS ₁ (HTS) (Time Storage; t = 14 days)	Day 0 to 13	Day A+10 to Day A + 18	Day B to Day B + 4	No re-analysis
TS ₂ (HTS) (Time Storage Dup; t = 14 days)	Day 0 to 13	Day A+10 to Day A + 18	Day B to Day B + 4	No re-analysis

Note: Above dates assume collection is on Day -1 and receipt at the laboratory on Day 0.

Coordinator continues the custody by assigning a Clean Harbors Control Number to each sample on receipt; this number identifies the sample through all further handling.

The physical appearance of the individual sample containers upon arrival at Clean Harbors is noted by the Coordinator. A sample is labeled in "good" condition when the following criteria are met:

- Sample identification tags and seals are securely attached and legible, and agree with other custody records; and
- Samples are iced.

Each sample is then recorded in the bound Master Sample Log under its Clean Harbors Control Number. Each page of the handwritten Master Log has the following format:

- Clean Harbors Control Number;
- Sample Description;
- Sample Condition;
- Signature of person completing sample record; and
- Date of Sample Receipt.

Each analyst working with the sample, records in the Master Sample Log their initials thereby enabling the tracking of the samples throughout the lab. Figure 7-1 shows the organic sample prep record, which is used to track initial sample volume, final extract volume, sample holding times and other pertinent sample information as listed on the form. When samples are sent to the client or to another laboratory for analysis, the External Transfer of Custody Form (Figure 7-2) is used, and the recipient of the samples is requested to return a copy of the signed form for the Sample files.

Clean Harbors, Inc. maintains large, locked, refrigerated, and nonrefrigerated storage areas with provision for hazardous material storage. After logging and necessary preservation or subdivision, the Sample Coordinator stores each sample in the appropriate area under its Clean Harbors Control Number.

8. CALIBRATION PROCEDURES AND FREQUENCY

8.1 PREPARATION OF SURROGATE AND INTERNAL STANDARDS

EPA will provide neat reference materials for 4,4'-Dichlorobiphenyl (DCB) for use as a surrogate standard and Pentachloronitrobenzene (PCNB) for use as an internal standard. Spiking solutions will be prepared by accurately (+ 0.01 mg) weighing approximately 0.0050 grams of DCB and 0.001 grams of PCNP into two 10.0 ml volumetric flasks and diluting to volume then serially diluting 1:5 with MTBE. Acetone will be used as solvent for DCB and MTBE for PCNB. Aqueous samples will be spiked with 5.0 ul of the DCB solution, prior to extraction. All standards and blank and sample extracts will be spiked to contain 0.1 ug/mL of PCNB (5.0 ul added to 1 mL of sample). All stock solutions will be entered into the Pesticide Stock Solution Logbook and assigned a unique identification number traceable to the date of preparation, analyst, lot number of the stock used and volume taken for dilution.

8.2 PREPARATION OF INSTRUMENT QC STANDARD

EPA will provide ampuls of reference material diluted in MTBE for QC standard preparation. The instrument QC standard will be prepared by diluting the four stocks to the following concentrations:

- Heptachlor epoxide -- 0.0040 ug/mL
- DCPA -- 0.050 ug/mL
- Chlorothalonil -- 0.050 ug/mL
- HCH-delta -- 0.040 ug/mL

All stock solutions will be entered into the Pesticide Stock Solution Logbook and assigned a unique identification number traceable to the date of preparation, analyst, date of receipt of the stock used and volume taken for dilution.

An instrument QC standard will be analyzed daily, or with each sample set, whichever is more frequent.

8.3 PREPARATION OF CALIBRATION STANDARDS AND LCS/TIME STORAGE SPIKING SOLUTIONS

Calibration standards will be prepared from stock solutions provided by EPA in sealed ampuls. Two intermediate stock solutions will be prepared containing approximately 15 analytes in MTBE which do not co-elute on the primary GC column. Five dilutions will then be prepared from these independent stocks. The lowest dilution must be prepared at the minimum reporting level (MRL), as determined in Section 3.

LCS spiking solutions will also be prepared from stock solutions provided by EPA. The solution will be prepared in acetone at a concentration which will generate component concentrations at 10x

the MRL when 0.5 to 1.0 ml is added to 1 liter of reagent water. This solution will also be used to spike time storage samples at 10x the MRL.

All stock solutions will be entered into the GC Standard Stock Solution Logbook and assigned a unique identification number traceable to the date of preparation, analyst, date of receipt of the stock used and volume taken for dilution.

8.4 INSTRUMENT CALIBRATION

8.4.1 GC/ECD Analysis

Analysis will be performed on a Hewlett-Packard 5890 gas chromatograph, equipped with dual electron capture detectors and a 7673 automatic liquid sampler, capable of simultaneous injection onto primary and confirmatory columns.

A primary and confirmatory calibration curve will be generated at a minimum of three (suggested five) concentration levels, including the MRL, for each analyte. Qualitative analyses will be performed for the following compounds, Endosulfan I, Endosulfan II, Delta-BHC and Chlorobenzilate. The relative response of each analyte (RRa) to the internal standard will be tabulated using the equation:

$$RRa = A/Ais,$$

where: A = the peak area of the analyte, and

Ais = the peak area of the internal standard.

The calibration curve will then be generated by plotting the analyte relative response, RRa, versus analyte concentration in the sample in ug/L.

The working calibration curve will be verified at alternating concentrations every 24 hours during analysis of NPS samples; occasionally, that concentration will be the MRL. The response for any analyte must agree with the predicted response within 25%, or a new calibration curve will be prepared. Each time new calibration standard dilutions are prepared, they must be compared to the existing calibration curve, and the observed concentration must agree within 25% of the expected concentration.

9. ANALYTICAL PROCEDURES

Samples submitted to Clean Harbors by U.S. EPA from the National Pesticide Survey will be prepared and analyzed in accordance with the October 27, 1987 version of Method 2 (Appendix A). No deviations from this procedure will be made with respect to the following: reagents (Section 7) apparatus and equipment (Section 6), procedure (Sections 11.2 and 12.3) and data reduction (Section 12). One deviation occurs in glassware cleaning (Section 4.1.1) with the replacement of heating glassware at 400°C by a terminal acetone rinse. This procedure has been demonstrated to provide glassware of a suitable quality at the Clean Harbors laboratory. Further precautions include the segregation of glassware for the NPS analysis. The maximum number of samples (including QC) that will be extracted and analyzed as a set is fifteen (15).

All samples submitted to Clean Harbors under this program for analysis via this method, as well as method blanks, matrix spikes and laboratory control samples, will be preserved with mercuric chloride, surrogate-spiked with 4,4'-Dichlorobiphenyl (DCB), buffered to pH 7, mixed with 100 g NaCl and extracted in a 2-liter separatory funnel with methylene chloride. The methylene chloride extracts from each of three extractions will be combined, dried over anhydrous sodium sulfate and concentrated via Kuderna-Danish apparatus to approximately 2 mL. The extract will then be solvent exchanged into methyl-t-butyl ether (MTBE) for gas chromatographic analysis.

The analysis for the compounds listed in Table 9-1 will be performed using a Hewlett-Packard 5890 gas chromatograph, equipped with dual Ni63 electron capture detectors and dual automatic liquid samplers. This GC will be interfaced to a Hewlett-Packard 3359 data acquisition system. As stated in Method 2, separation will be performed using an SPB-5 capillary column for primary analysis and a DB-1701 for confirmatory analysis. Table 9.2 provides chromatographic conditions for this analysis.

Prior to the injection of program samples, each gas chromatograph will be calibrated at three to five concentration levels with the components of interest. Calibration solutions will also contain the internal standard, PCNB. Calibration curves will be generated plotting the analyte concentration versus relative response to the internal standard. Each sample extract will also be spiked with internal standard solution prior to gas chromatographic analysis. Concentrations of analytes in the samples will be determined from the relative response to the internal standard via the calibration curve. The analyst will monitor internal standard (IS) area count responses for all sample injections. A deviation in a sample of greater than 30 percent of the average IS response of the calibration standards indicates the possibility from method or matrix interferences with internal standard measurement.

Appendix A, Section 10.6.2 addresses analysis of QC check standards. This is not required by the NPS protocol and therefore not done. Section 10.7.1, referring to spiking of the target analytes into ten percent of the samples was met by the NPS survey design with the LSS samples.

The automated data entry system was implemented on November 16, 1989. Its application began with set 126 and continued until the final set.

TABLE 9-1

ANALYTES INCLUDED IN GROUND WATER ANALYSIS METHOD 2,
MIX A AND MIX B WITH MRL AND MDL DATA

A. Mix A	MRL	MDL
Chlorneb	1.4	0.276
Propachlor	1.3	0.261
Alpha-BHC	0.12	0.012
Gamma-BHC	0.085	0.107
Chlorthalonil	0.12	0.017
Aldrin	0.12	0.021
Heptachlor epoxide	0.12	0.022
* Endosulfan I	0.12	0.019
Dieldrin	0.12	0.025
Endrin	0.25	0.033
* Endosulfan II	0.25	0.029
Endrin Aldehyde	0.25	0.033
p,p'-DDT	0.3	0.06
Cis-permethrin	1.8	0.36
 B. Mix B	 MRL	 MDL
Ethridiazole	0.25	0.002
Trifluralin	0.25	0.005
Hexachlorobenzene	0.12	0.005
Beta-BHC	0.12	0.009
* Delta-BHC	0.12	0.005
Heptachlor	0.12	0.01
DCPA	0.12	0.016
Gamma-Chlordane	0.12	0.007
Alpha-Chlordane	0.12	0.008
p,p'-DDE	0.12	0.007
* Chlorbenzilate	0.68	0.136
p,p'-DDD	0.25	0.015
Endosulfan Sulfate	0.25	0.013
Methoxychlor	0.6	0.111
Trans-Permethrin	3.9	0.779

* Qualitative analysis only.

TABLE 9-2

INSTRUMENT CONDITIONS FOR ANALYSIS OF GROUND WATER BY METHOD 2

Primary Conditions

Column:	30 m x 0.25 mm I.D. SPB-5 bonded fused silica column, 0.25 m 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
Oven temp:	Program from 60°C to 300°C at 4°C/min

Confirmation Conditions

Column:	30 m x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 m 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
Oven temp:	Program from 60°C to 300°C at 4°C/min

10. DATA REDUCTION, VALIDATION AND REPORTING

Proper collection and organization of accurate information followed by clear and concise reporting of the data is a primary goal in all projects. This section describes the procedures routinely followed at Clean Harbors for data reduction, validation and reporting. All hard copy data of chromatograms, prep records, etc. will be stored together in the project file.

10.1 DATA REDUCTION

Analytical results will be reduced to concentration units specified in Method 2, using the equations given therein. Actual blank values will be reported; blank corrections will not be applied.

10.2 DATA VALIDATION

Data validation is the process of filtering data and accepting or rejecting it on the basis of sound criteria. Analytical supervisory and QC personnel will use validation methods and criteria appropriate to the type of data and the purpose of the measurement. Records of all data will be maintained, even that judged to be an "outlying" or spurious value. The persons validating the data will have sufficient knowledge of the technical work to identify questionable values. All chromatograms will be reviewed by Clean Harbors's GC Section Head to ensure proper compound identification and as a general quantitation check. Furthermore, approximately 25 percent of calculations and data transfer will be checked during validation. If any errors are found, all calculations or data transfer of that type will be checked.

Analytical data will be validated by the laboratory QC coordinator or supervisory personnel using criteria specified and in this QA Plan. Clean Harbors routinely uses results from laboratory reagent blanks, replicate samples and internal QC samples to validate analytical results. Generic criteria used to evaluate analytical data are listed below:

- Use of approved analytical procedures;
- Use of properly operating and calibrated instrumentation;
- Acceptable results from analyses of Lab Control samples; and
- Precision and accuracy meeting QA objectives as stated in the methods and this QA Plan.

10.3 FAST TRACK REPORTING

Since normal reporting requirements allow sample data to be provided 2 months after sample collection, a mechanism for fast track reporting is necessary. Reports to the Technical Monitor will be expedited when the following situations arise:

- Confirmed positives for a list of analytes to be specified by EPA.

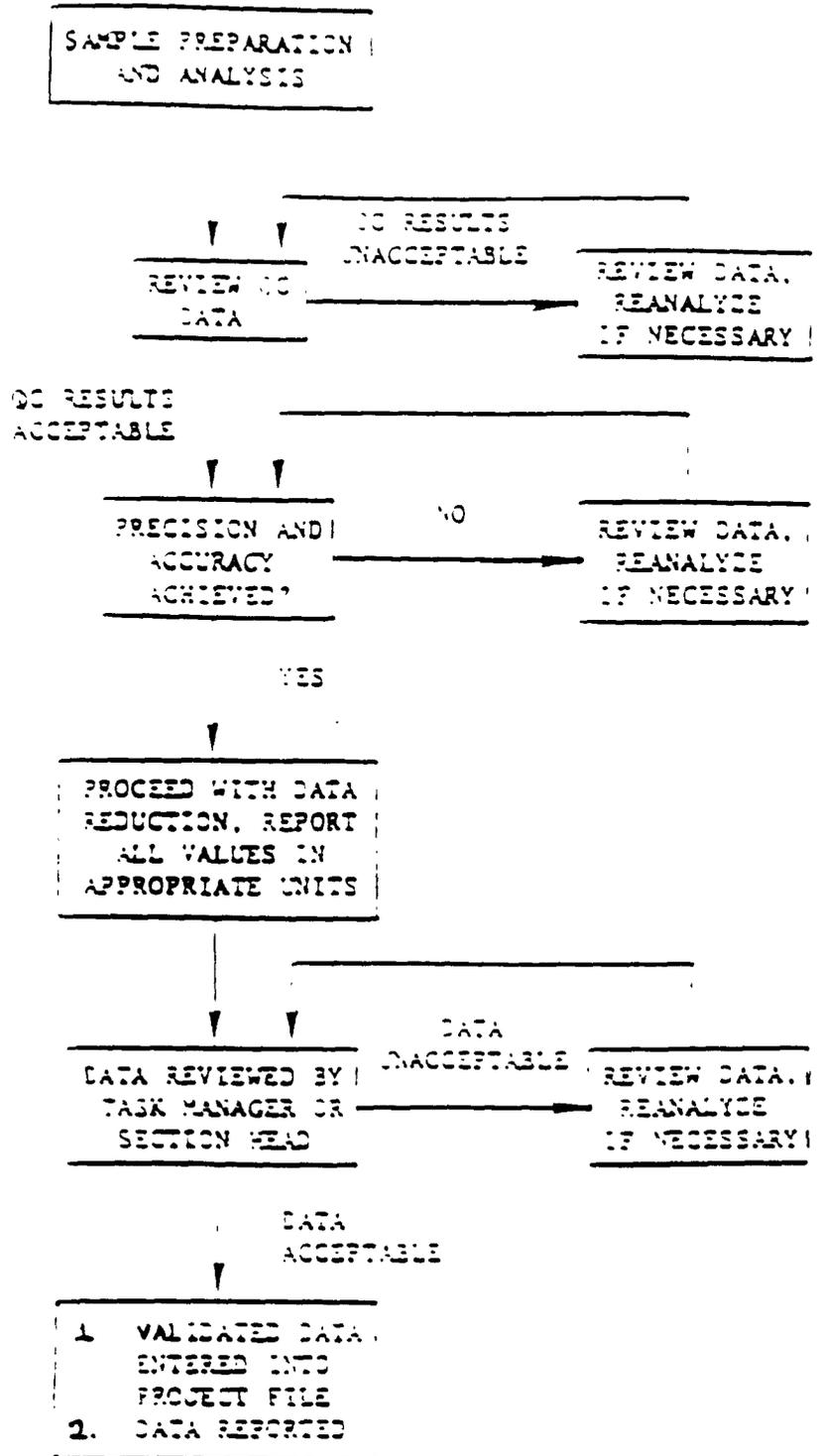
- Lack of agreement of + 25 percent between results from primary and confirmatory analysis by GC/ECD.
- Frequent occurrence of a peak or peaks which are not NPS analytes (excluding phthalates), or which are at levels between the EDL and MRL (no quantitation or confirmation is performed).
- Refer to Rapid Reporting Memo of June 9, 1989 - Appendix J

10.4 DATA REPORTING

A flow chart depicting the analytical data validation and reporting scheme, routinely used at Clean Harbors, is shown in Figure 10-1. Validation occurs at a minimum of two levels. For this program, the Technical Coordinator, John Verban, will review all QC data as soon as possible. He will initiate sample re-extraction if project QC criteria are not met. A second review by the Project Manager will take place prior to final reporting of the data.

All data for a set of samples, including QC and confirmatory data, will be reported by the laboratory as a complete set. Data must be provided within 2 months of sample collection. Data are to be provided as an ASCII file in the format specified by EPA on floppy disk. Hard copies of all data will be kept with the project file by set number.

FIGURE 10-1
CLEAN HARBORS ANALYTICAL DATA VALIDATION AND REPORTING SCHEME



11. INTERNAL QUALITY CONTROL CHECKS

Quality control checks will be performed to ensure the generation of valid analytical results on these samples. These checks as listed in Table 11.1 will be performed by appropriate personnel throughout the program under the guidance of the QA Director and the Laboratory QC Coordinator. A brief description of each of these elements is provided below.

11.1 METHOD BLANKS

Method blanks will be preserved with mercuric chloride and contain all the reagents used in the preparation and analysis of samples. Method blanks are processed through the entire analytical scheme to assess spurious contamination arising from reagents, glassware and other materials used in the analysis. A method blank is processed with each set of samples extracted. If the method blank exhibits a peak for any analyte (on both columns) which is greater than or equal to one-half the MRL, the source of contamination must be determined and the sample set re-extracted.

11.2 CALIBRATION CHECK SAMPLES

A working calibration standard at alternating concentrations (occasionally at MRL) which is repeated every 24 hours to verify the working calibration curve. If the response for any analyte varies from the predicted response by more than 25%, a new calibration curve must be prepared for that analyte.

11.3 REPLICATE AND SPIKED SAMPLES

Additional samples will be collected at 10% of the sample sites for spiking at the laboratory. These samples are to be spiked at analyte concentrations equal to 2x, 5x, or 10x the MRL (level specified on sample label). Samples for replicate analysis will also be submitted at the required frequency.

11.4 LABORATORY CONTROL SAMPLES

A laboratory control sample must be prepared with preservative and analyzed with each set of samples extracted. For Method 2, this will consist of two reagent water samples, each spiked with one of the two calibration mixes, independently prepared in acetone. The concentration of these samples will be 10x the MRL.

An "out of control" situation exists if more than 15 percent of the LCS analyte recoveries are outside the control limit (3 standard deviations), or if the same analyte is outside the control limit twice in a row. All analytical work must be stopped until control is re-established. Re-extraction of that set/batch of samples is required.

TABLE 11.1
INTERNAL QC CHECKLIST

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

Is the instrument control standard's peak symmetry, resolution and geometry factors within the limit set by the method?

Is the date from sampling to receipt within the limits set by the survey requirements?

Is the date from sampling to extract within the limits set by the survey requirements?

Is the date from extract to analysis within the limits set by the survey requirements?

Is the percent recovery of the surrogate in the LCS within the Control Chart limits?

Is the concentration of a blank above half of the MRL?

Is the concentration of a field sample above 1/2 the minimum reporting limit?

A. If so, is there a confirmation analysis for the analyte?

B. Is the concentration of the confirmatory column within the limits set by survey requirements?

Is the percent recovery of each analyte in the lab control standard within the upper and lower control limits?

Is the percent recovery of each analyte in the lab spike sample within the upper and lower control limits?

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

Is the internal standard area within + 30% from the average IS response of the calibration standards?

Does the calibration check standard compare within 25% of the Initial calibration curve?

11.5 SURROGATE SPIKES

All samples, blanks and laboratory control standards will be fortified with DCB before extraction. A surrogate standard determination must be performed on all samples (including matrix spikes) and blanks. The acceptance criteria for surrogate standard recoveries are ± 3 sigma for the lab control samples and $\pm 30\%$ from the mean as determined from the current control chart for all other sample types. Control charts for surrogate recoveries in the LCS will be prepared and updated as detailed in Section 3.3. When the surrogate recovery for a sample is outside control limits, the laboratory must establish that the deviation is not due to laboratory problems. The laboratory shall document deviations by taking the following actions:

- (1) Checking calculations to make sure there are no errors.
- (2) Checking internal standard and surrogate standard spiking solutions for degradation, contamination, or other obvious abnormalities.
- (3) Checking instrument performance.

Recalculation or reanalysis of the sample or extract will be performed 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 the sample data from the analysis with surrogate spike recoveries within the required limits will be submitted. If reanalysis of the sample extract fails to solve the problem, then both sets of data for that sample will be reported.

If the surrogate recovery for an LCS is outside the control limits, then the analyst must evaluate the sample set for blank surrogate recovery and LCS analyte recovery. The sample set/batch must be re-analyzed only if the blank surrogate recovery or the LCS analyte recoveries do not meet acceptance criteria.

If the surrogate recovery for a method blank is outside the control limits, then the analyst must check the sample set/batch for a sample free from analyte positives (i.e. a blank). If the surrogate recovery from that sample meets criteria, then analysis of the set can proceed.

11.6 INTERNAL STANDARD CHECKS

Internal standard areas will be evaluated for acceptance by determining whether the measured peak area or height in any sample deviates by more than 30% from the average for the internal standard in the calibration standards. Corrective action for internal standard area count deviations is detailed in Appendix A, Section 10.5.3.

11.7 INSTRUMENT QUALITY CONTROL STANDARDS

Instrument QC standards will be evaluated according to Table 10 in Appendix A for detection, peak symmetry, resolution and peak Gaussian factor using the calculations provided with the table. Analysis will not be performed if criteria are not met.

12. PERFORMANCE, SYSTEM AND DATA AUDITS

12.1 DATA AUDITS

Ongoing data audits will be provided by the project coordinator, project manager or Laboratory QC Coordinator. These audits will consist of a verification of 25% of the calculations generated under this program and of all positive identifications.

12.2 SYSTEMS AUDITS

A system audit is a qualitative review to ensure that the quality measures and the analytical procedures outlined in the QA Project Plan are in place and being followed. Clean Harbors's QA Director selects projects representing different types of measurement activities for audit by the QA staff. System audits of analytical work on this program will be scheduled in accordance with the volume and diversity of the samples received, and the severity and number of problems uncovered in early system audits but at a minimum will be held quarterly. Written summary reports for each audit will be submitted as noted in Section 14.0.

12.3 EXTERNAL AUDITS

Clean Harbors will cooperate fully in any performance or system audits conducted or arranged by EPA. The Project Manager, QA Director and QC Coordinator are available to aid in scheduling such audits.

13. PREVENTIVE MAINTENANCE

Clean Harbors follows an orderly program of positive actions to prevent the failure of equipment of instruments during use. In the analytical laboratories, preventive maintenance includes attention to glassware, water supply, reagents and analytical balances as well as more complex instrumentation. Table 13-1 summarizes the preventive maintenance procedures for the instruments to be used in this project. Also listed in the table are the spare parts normally kept in inventory to minimize instrument down time.

**TABLE 13-1
MAINTENANCE PROCEDURES AND SCHEDULE FOR MAJOR INSTRUMENTATION**

Instrument	Maintenance Procedure/Schedule	Spare Parts
Gas Chromatograph (HP5890)	<ol style="list-style-type: none"> 1. Change septa daily. 2. Check syringe for burrs daily. 3. Change gas line dryers quarterly. 4. Leak check when installing new analytical column. 5. Periodically check inlet system for residue build-up. 	<ol style="list-style-type: none"> 1. Syringes 2. Septa 3. Columns
Gas Chromatographs/ Mass Spectrometers (Hewlett Packard 5970)	<ol style="list-style-type: none"> 1. Replace pump oil annually. 2. Change septa daily. 3. Change gas line dryers quarterly. 4. Replace Electron Multiplier as needed. 	<ol style="list-style-type: none"> 1. Syringes 2. Septa 3. Column

14. SPECIFIC PROCEDURES FOR ASSESSING MEASUREMENT SYSTEM DATA

Compare the percent recovery (R_i) for each analyte with established QC acceptance criteria. QC criteria are established by initially analyzing twenty (20) laboratory control standards and calculating the average percent recovery (R) and the standard deviation of the percent recovery (SD) using the following equations:

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

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

The QC acceptance criteria is calculated as follows:

$$\text{Upper Control Limit (UCL)} = R + 3SD$$

$$\text{Lower Control Limit (LCL)} = R - 3SD$$

$$\text{Upper Warning Limit (UWL)} = R + 2SD$$

$$\text{Lower Warning Limit (LWL)} = R - 2SD$$

The data generated during the initial demonstration of capability (3.3) will be used to set the initial upper and lower control and warning limits.

The performance criteria will be updated on a continuous basis. After each five new recovery measurements, R and RSD will be recalculated using all the data, and new control charts reconstructed, deleting the five earliest values. Dixon's Test (Appendix C) will be applied where appropriate. Spiked samples will be corrected for concentrations of analytes native to that sample if the analyte is present at $> 1/2$ the MRL.

The instrument QC standard will be assessed using the calculations provided in Table 10 (Appendix A). Accuracy will be estimated from the analysis of laboratory control samples, and will be expressed as percent recovery. The formula used to calculate percent recovery is as follows:

$$\text{Percent Recovery} = 100 \times \frac{\text{measured value}}{\text{true value}}$$

15. CORRECTIVE ACTION

The acceptance limits for the analyses to be conducted in this program will be generated as stated in Section 3. The corrective actions are likely to be immediate in nature and most often will be implemented by the analyst or technical coordinator. The corrective action will usually involve recalculation, or reanalyses. Clean Harbors' ongoing corrective action policy is described here.

15.1 IMMEDIATE CORRECTIVE ACTION

Specific QC procedures are designed to help analysts detect the need for corrective action. Often the person's experience will be more valuable in alerting the analyst to suspicious data or malfunctioning equipment. Instrument and equipment malfunctions are amenable to immediate corrective action. The actions taken should be noted in laboratory notebooks, but no other formal documentation is required, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system. An example of bench level corrective action is provided in Figure 13-1. This reextraction request will usually be initiated by the Technical Coordinator. Additional corrective actions will be noted in instrument maintenance log books and analysts' notebooks. These data will be filed in the project file to facilitate monthly reports about bench-level problems to the EPA Technical Monitor that include the date, problem, action taken, verification that the problem was solved, and identification of the sample sets analyzed just prior to and immediately following the corrective action.

If a corrective action can be taken at this point, as part of normal operating procedures, the collection of poor quality data can be avoided. If a problem is not solved in this way, more formalized long-term corrective action may be necessary.

15.2 LONG-TERM CORRECTIVE ACTION

The need for this action may be identified by standard QC procedures, control charts, performance or system audits. Any quality problem which cannot be solved by immediate corrective action falls into the long-term category. Appropriate corrective actions may be similar in nature to immediate corrective action; i.e., collecting a new set of samples or reanalyzing samples, but the correction may proceed more slowly. Clean Harbors uses a system to ensure that the condition is reported to a person responsible for correcting it who is part of the closed-loop action and follow-up plan. The essential steps in the closed-loop corrective action system are:

- Identify and define the problem.
- Assign responsibility for investigating the problem.
- Investigate and determine the cause of the problem.
- Determine a corrective action to eliminate the problem.

- Assign and accept responsibility for implementing the corrective action.
- Establish effectiveness of the corrective action and implement it.
- Verify that the corrective action has eliminated the problem.

Documentation of the problem is important to the system. A Corrective Action Request Form (shown in Figure 15-2) is filled out by the person finding the quality problem. This form identifies the problem, possible causes and the person responsible for action on the problem. The responsible person may be an analyst, field team leader, QC Coordinator or the QA Director. If no person is identified as responsible for action, the QA Director investigates the situation and determines who is responsible in each case.

The Corrective Action Request Form includes a description of the corrective action planned and the date it was taken, and space for follow-up. The QA Director checks to be sure that initial action has been taken and appears effective and, at an appropriate later date, checks again to see if the problem has been fully solved. The QA Director receives a copy of all Corrective Action Forms and then enters them in the Corrective Action Log. This permanent record aids the QA Director in follow-up and makes any quality problems visible to management; the log may also prove valuable in listing a similar problem and its solution.

16. QA REPORTS

16.1 INTERNAL REPORTS

The QC Coordinator will prepare written monthly reports on QC activities for the Laboratory Manager and the QA Director. These reports detail the results of quality control procedures, problems encountered, and any corrective action which may have been required. As these reports pertain to this project, they will be made available to the Program Manager and QA Officer.

All Corrective Action Forms are submitted to the QA Officer for initial approval of the corrective action planned and a copy is provided to the Program Manager. All system audit reports are provided to the Program Manager and may be presented to the Clean Harbors President.

16.2 EXTERNAL REPORTS

Six copies of the monthly report will be provided within 15 (calendar) days after the end of the period being reported. The copies will be sent to the appropriate EPA Technical Monitor.

A copy of the cover letter which transmits the monthly report will be forwarded to Mona S. Snyder, Contract Specialist for the NPS, EPA-CMD, Cincinnati, OH 45268.

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

- Summary of progress
 - samples received, analyzed, 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 action
- Identification of problems about any phase of the project
- Copies of representative and, if applicable, unusual chromatograms.
- Information requested by the Technical Monitor because of specific methodology or problems encountered
- Changes in personnel
- Any other comments.

17. ARCHIVAL OF RAW DATA

NPS ARCHIVAL PROCESS

1. The NPS data sets will be stored at the Clean Harbors of Bedford facility at 213 Burlington Road, Bedford, MA 01730 for a period of one year from the closeout audit date of August 30, 1990. After one year the data will be transferred to Clean Harbors' warehouse at 10 Mercer Road, Natick, MA 01760. The data will remain at this site for a period of seven years from the closeout audit date of August 30, 1990. Laurian Carroll, Documents Manager for Clean Harbors, is responsible for all data stored in the warehouse. After the seven year period, the data will be disposed of unless otherwise requested by the EPA.

2. Each data set consists of the following:
 - 2.1 Copy of the formattable
 - 2.2 Copy of the ICDS
 - 2.3 Copy of Clean Harbors' Chain of Custody
 - 2.4 Copy of GC injection log run sheet
 - 2.5 Copy of extraction log sheet
 - 2.6 Copy of drying and concentrating log sheet
 - 2.7 Internal Standard summary
 - 2.8 Continuing Calibration
 - 2.9 Standard curve data including retention time window data
 - 2.10 Raw areas, concentrations, and percent recoveries for samples
 - 2.11 Flag data for determining outliers
 - 2.12 Internal Quality Control Check
 - 2.13 GC chromatograms for standards and samples
 - 2.14 Hand calculations and notes on set

3. The following information is archived in labeled boxes and will follow the same storage procedures as the data sets.
 - 3.1 Initial demonstration of capability
 - 3.2 Index for EPA well ID number versus Clean Harbors' set number
 - 3.3 Data sets 1 through 153
 - 3.4 Copies of standard logbook pages
 - 3.5 Copies of refrigerator logbook pages
 - 3.6 Sample tracking forms
 - 3.7 In-house audits
 - 3.8 Corrective action forms
 - 3.9 Monthly reports
 - 3.10 Copies of instrument maintenance logbook pages
 - 3.11 Standard Operating Procedure for NPS
 - 3.12 Control Charts for Quality Control Limit
 - 3.13 Statement of Qualification and copies of resume's for employees involved in NPS
 - 3.14 Correspondence
 - 3.15 Standard comparisons
 - 3.16 NPS check lists for each set
 - 3.17 NPS sample analysis tracking logbook
 - 3.18 QA Plan for NPS

4. To access data by EPA well number, the Clean Harbors identification number and data set that the number is grouped in must be determined. The index found in first data set box can be used to determine the set number for any corresponding EPA well number. The appropriate set should be obtained and the necessary information for the sample can be acquired.

APPENDIX A

METHOD 2. DETERMINATION OF CHLORINATED PESTICIDES 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 pesticides in ground water. Analytes that can be determined by this method are listed in Table 1.
- 1.2 This method has been validated in a single laboratory. Estimated detection limits (EDL's) 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.

2. SUMMARY OF METHOD

- 2.1 A measured volume of sample of approximately 1L 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 tertbutyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by GC with an electron capture detector (ECD).
- 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 student's 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 is higher.

- 3.4 Instrument quality control (QC) standard -- a MBTE 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 standard compound that is not a sample component.
- 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 -- 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 interference 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.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 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 PCB's 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 Interference by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatograms 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 solvent-wetted surfaces are handled. Interference 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}

4.3 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 MBTE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MBTE should be made to ensure that accurate values are obtained for the next sample.

4.4 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 must 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 5-7 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 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-570050-1025 or K-570050-2525 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 – three 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- 6.2.6 Snyder column, K-D – three ball micro (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 then 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 four to six tumbler bottles and tumbling them end-over-end at 30 turns/min. (Associated Design and Mfg. Co., Alexandria, VA.).
- 6.5 Boiling stones – carborandum, #12 granules (Arthur H. Thomas Co. #1590-033). Heat at 400°C for 30 min prior to use. Cool and store in a 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 – 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, 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, 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 Pentachloronitrobenzene (PCNB) -- >98% purity, for use as internal standard.
- 7.6 4,4'-Dichlorobiphenyl (DCB) -- 96% purity, for use as surrogate standard (available from Chemicals Procurement, Inc.).
- 7.7 Reagent Water -- Reagent water is defined as water in which an interferant 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.
- 7.8 STOCK STANDARD SOLUTIONS (1.00 ug/uL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standards materials using the following procedure
 - 7.8.1 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 volume in a 10-mL volumetric flask. 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.
 - 7.8.2 Transfer the stock standard solutions....
 - 7.8.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.
- 7.9 INTERNAL STANDARD SPIKING SOLUTION -- Prepare an internal standard spiking solution by accurately weighing approximately 0.0010 g of pure PCNB. Dissolve the PCNB 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 5 uL of the internal spiking solution to 5 mL of sample extract results in a final internal standard concentration of 0.1 ug/mL. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

- 7.10 **SURROGATE STANDARD SPIKING SOLUTION** -- Prepare a surrogate standard spiking solution by accurately weighing approximately 0.0050 g of pure DCB. Dissolve the DCB 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 μ L of the surrogate standard spiking solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 25 μ g/L and, assuming quantitative recovery of TDBP, a surrogate standard concentration in the final extract of 5.0 μ g/mL. Solution should be replaced when ongoing QC (Section 10) indicates a problem.
- 7.11 **INSTRUMENT QC STANDARD** -- Prepare instrument QC standard stock solutions by accurately weighing 0.0010 g each of chlorothalonil, heptachlor epoxide, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10-mL volumetric flasks. Combine 2 μ L of the heptachlor epoxide stock solution, 50 μ L of the DCPA stock solution, 50 μ L of the chlorothalonil stock solution, and 40 μ L of the HCH-delta stock solution to a 100-mL volumetric flask and dilute to volume with MTBE. Transfer the instrument QC standard solution to a TFE-fluorocarbon-sealed screw cap 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 should be followed; however, the bottle must not be prerinsed with sample before collection.
- 8.2 **SAMPLE PRESERVATION**
- 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 10 mg/mL solution 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 adding the sample to the bottle containing preservative, seal the sample bottle and shake vigorously for one minute.
- 8.2.3 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results presented in Table 11 indicate that most of the target analytes present in the 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 Sample extracts should be stored at 4°C away from the light. 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 CALIBRATING 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. PCNB 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 standard, 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 μ L of each calibration standard and tabulate the relative response for each analyte (RRa) to the internal standard using the equation: $RRa = Aa/Ais$ where: Aa = the peak area of the analyte, and Ais = the peak area of the internal standard. Generate a calibration curve of analyte relative response, RRa, versus analyte concentration in the sample in μ g/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 25%, 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 4 1-L aliquots of reagent water. A representative groundwater 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 percent recovery (RSD), for the results. Ground water background corrections must be made before R and RSD 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 $R + 30\%$ 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 of the mean from the control charts.
- 10.4.3 When the surrogate recovery for a laboratory method blank is less than 70 or greater than 130 percent of the mean from the control charts, 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 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 from the mean, 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 recover is 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 that internal standard in any sample deviates by more than 30 percent from 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 samples 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 insure 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. Remove an another aliquot of the sample extract and re-spike internal standard solution. Repeat sample analysis.
- 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 25 percent 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) spike a fresh sample aliquot with the internal standard solution for those 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 $(100 \times A) \% / T$, 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 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 (SR) using the following equations:

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

and $SR =$

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

Calculate QC acceptance criteria as follows:

$$\begin{aligned} \text{Upper Control Limit (UCL)} &= R + 3SR \\ \text{Lower Control Limit (LCL)} &= R - 3SR \end{aligned}$$

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_i s), recalculate R and SR 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 Sr using only the most recent 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 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 (Ri) as $100(A-B)/T$, where T is the known true concentration of the spike.
- 10.7.1.3 Compare the percent recovery (Ri) for each analyte with QC acceptance criteria established from the analyses of laboratory control standards. Monitor all data from closed 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 the 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 re-evaluation of the GC-ECD system. A GC-ECD chromatogram generated from the analysis of the instrument QC standard is shown in Figure 3. The sensitivity requirements are set based on the EDL's published in this method. If the laboratory EDL's differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDL's. 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 separatory funnel shaker.
- 11.1.1 Add preservative to any 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 sample with 50 μ L 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 seconds to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 seconds, 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 and thorough mixing of the organic and aqueous phases should be observed at least 2 minutes 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 minutes. If the emulsion interface between labels layers is more than one third the volume of the solvent layer, the analysts 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 minutes.

- 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 any 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 μ L of the surrogate standard spiking solution. Pour the sample the entire sample into a 2-L separatory funnel.
- 11.2.2 Adjust 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 seconds to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the 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.
- 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 minutes.
- 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 a 500-mL evaporative flask. Decant methylene chloride extract into K-D concentrator. Rinse remaining sodium sulfate with two 25-mL portions of methylene chloride and decant 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. Preset 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 minutes. At the proper rate of

distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

- 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 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 the 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 and a boiling stone to the micro K-D and reconcentrate to 2mL. 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 Transfer extract to an appropriately sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-ECD.

11.4 GAS CHROMATOGRAPHY

- 11.4.1 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 1 and 2. Other GC columns, Chromatographic conditions, or detectors may be used if the requirements of Section 10.3 are met.
- 11.4.2 Calibrate the system daily as described in Section 9. The standards and extracts must be in MTBE.
- 11.4.3 Inject 2 μ L of the sample extract. Record the resulting peak sizes in area units.
- 11.4.4 The width of the retention time window use to make identifications should be based upon measurements of the actual retention time variations of standards over the course of the 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.
- 11.4.5 If the response for a 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 (RRa) 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 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 EDL's and demonstrate method range. Analytes were divided into two spiking groups (A and B) for recovery studies. 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. Analytes were divided into two spiking groups (A and B) 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. Results were used to predict expected analyte stability in ground water samples. Analytes were divided into two spiking groups (A and B) for recovery studies. Analyte recoveries from the preserved, spiked ground water samples are given in Table 11.

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TABLE 1. METHOD ANALYTES

Analyte	Chemical Abstracts Service Registry Number	Ident. Code (a)
Aldrin	309-00-2	A7
Chlordane-alpha	5103-71-9	B9
Chlordane-gamma	5103-74-2	B8
Chlornep	2675-77-6	A1
Chlorobenzilate	501-15-6	B11
Chlorothalonil	2921-88-2	A6
OCPA	1897-45-6	B7
4,4'-DDD	72-54-8	B12
4,4'-DDE	72-55-9	B10
4,4'-DDT	50-29-3	A16
Dieldrin	50-57-1	A11
Endosulfan I	959-98-8	A10
Endosulfan II	33213-65-9	A14
Endosulfan sulfate	1031-07-8	B13
Endrin	72-20-8	A12
Endrin aldehyde	7421-93-4	A15
Etridiazole	2593-15-9	B1
HCH-alpha	319-84-6	A3
HCH-beta	319-85-7	B4
HCH-delta	319-86-8	B5
HCH-gamma	58-89-9	A5
Heptachlor	76-44-8	B6
Heptachlor epoxide	1024-57-3	A9
Hexachlorobenzene	118-74-1	B3
Methoxychlor	72-43-5	B14
cis-Permethrin	52645-53-1	A17
trans-Permethrin	52645-53-1	B15
Propachlor	1918-16-7	A2
Trifluralin	1582-09-8	B2

(a) Code used for identification of peaks in method figures:
 Letter indicates which spiking mix (A or B) contains the
 analyte; IS = internal standard; SUR = surrogate standard.

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

Analyte	Spiking level, $\mu\text{g/L}$	Amt. in Blank, $\mu\text{g/L}$	n (b)	R (c)	S (d)	RSD (e)	EDL (f)
Aldrin (h)	0.075	ND (g)	7	66	0.00456	9	0.0
Chlordane-alpha	0.015	ND	7	117	0.00132	8	0.0
Chlordane-gamma	0.015	ND	7	109	0.000515	3	0.0
Chlorobenzilate (h)	5.0	ND	8	99	0.7076	5	5.0
Chlorthalonil	0.025	ND	7	119	0.00354	12	0.0
CCPA	0.025	ND	7	112	0.00102	4	0.0
4,4'-DDD	0.025	ND	7	115	0.00140	5	0.0
4,4'-DDE	0.010	ND	7	127	0.000797	6	0.0
4,4'-DDT	0.060	ND	7	87	0.0123	23	0.0
Dieldrin	0.020	ND	7	77	0.0034	22	0.0
Endosulfan I	0.015	ND	7	78	0.00292	25	0.0
Endosulfan sulfate	0.015	ND	7	129	0.000779	4	0.0
Endrin	0.015	ND	7	72	0.00198	18	0.0
Endrin aldehyde	0.025	ND	7	95	0.00355	15	0.0
Endosulfan II	0.015	ND	7	148	0.00778	35	0.0
Ethionazole	0.025	ND	7	96	0.00416	17	0.0
HCH-alpha (h)	0.025	ND	8	94	0.00177	8	0.0
HCH-beta	0.010	ND	7	95	0.00113	12	0.0
HCH-delta	0.010	0.0036	7	84	0.000622	7	0.0
HCH-gamma	0.015	ND	7	80	0.00190	16	0.0
Heptachlor	0.010	ND	7	67	0.000484	7	0.0
Heptachlor epoxide	0.015	ND	7	71	0.00189	18	0.0
Hexachlorobenzene	0.0050	ND	7	115	0.00246	43	0.0
Methoxychlor	0.050	ND	7	120	0.00685	11	0.0
cis-Permethrin	0.50	ND	7	64	0.0782	24	0.5
trans-Permethrin	0.50	ND	7	122	0.0581	9	0.5
Propachlor	0.50	ND	7	90	0.0798	18	0.5
Trifluralin	0.025	ND	7	108	0.000816	3	0.0

(a) Data corrected for amount found in blank.

(b) n = number of 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 $\mu\text{g/L}$; calculated by multiplying standard deviation (S) times the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, or level of compound in 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) Data from spiking level 2.

TABLE 3. PRIMARY AND CONFIRMATION CHROMATOGRAPHIC CONDITIONS

Analyte	Relative Retention Time for Given Conditions (a)	
	Primary (b)	Confirmation (c)
Aldrin	1.18	1.12
Chlordane-alpha	1.31	1.31
Chlordane-gamma	1.28	1.29
Chlorob	0.75	0.77
Chlorobenzilate	1.41	1.42
Chlorothalonil	1.04	1.17
DDE	1.21	1.21
4,4'-DDD	1.42	1.38
4,4'-DDE	1.35	1.32
4,4'-DDT	1.48	1.48
Dieldrin	1.35	1.35
Endosulfan I	1.30	1.28
Endosulfan II	1.40	1.45
Endosulfan sulfate	1.47	(d)
Endrin	1.38	1.38
Endrin aldehyde	1.43	1.52
Etridiazole	0.69	0.67
HCH-alpha	0.93	0.97
HCH-beta	0.98	1.18
HCH-delta	1.03	1.22
HCH-gamma	0.99	1.04
Heptachlor	1.11	1.08
Heptachlor epoxide	1.24	1.24
Hexachlorobenzene	0.94	(d)
Methoxychlor	1.57	1.58
cis-Permethrin	1.72	(d)
trans-Permethrin	1.73	(d)
Propachlor	0.85	0.91
Trifluralin	0.93	(d)

(a) Retention time relative to PCNB internal standard which elutes at approximately 34 min.

(b) Primary conditions:

Column: 30 m long x 0.25 mm i.d. DB-5 bonded fused silica column, 0.25 µm film thickness (J&W)
Injection volume: 2 µL 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

c) Confirmation conditions:

Column: 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica
column, 0.25 μ m film thickness (0.3 μ m)
Injection volume: 0.1 μ L 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) Data not available

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

Analyte	Spiking Level, $\mu\text{g/L}$	Amt in Blank $\mu\text{g/L}$	n(b)	R(c)	S(d)	RSD(e)
Aldrin	0.075	ND (f)	7	66	0.00456	9
Chlordane-alpha	0.075	ND	8	93	0.0110	6
Chlordane-gamma	0.075	ND	8	92	0.0103	5
Chlornes	2.5	ND	8	95	0.203	9
Chlorobenzilate	5.0	ND	8	99	0.708	5
Chlorthalonil	0.13	ND	8	100	0.00916	7
DCCA	0.13	ND	8	93	0.0190	6
4,4'-DDD	0.13	ND	8	94	0.0163	3
4,4'-DDE	0.050	ND	7	96	0.00213	4
4,4'-DDT	0.30	0.101	6	96	0.0445	16
Dieldrin	0.10	ND	8	96	0.00841	9
Endosulfan I	0.075	ND	8	93	0.00593	3
Endosulfan sulfate	0.075	ND	8	96	0.00945	3
Endrin	0.075	ND	8	96	0.00618	9
Endrin aldehyde	0.13	ND	8	99	0.0103	8
Endosulfan II	0.075	ND	8	99	0.00658	9
Etridiazole	0.13	ND	7	92	0.0104	9
HCH-alpha	0.025	ND	8	94	0.00177	8
HCH-beta	0.050	ND	8	84	0.00709	8
HCH-delta	0.050	ND	8	100	0.00698	4
HCH-gamma	0.075	ND	8	93	0.00564	8
Heptachlor	0.050	ND	8	80	0.00716	7
Heptachlor epoxide	0.075	ND	8	97	0.00616	9
Hexachlorobenzene +	0.025	ND	8	138	0.00885	20
Methoxychlor	0.25	ND	8	97	0.0344	4
cis-Permethrin	2.5	ND	8	98	0.212	9
trans-Permethrin	2.5	ND	8	112	0.0985	4
Propachlor	2.5	0.534	7	103	0.223	9
Trifluralin	0.13	ND	7	87	0.0138	12

(a) Data corrected for amount found in blank.

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

Analyte	Spiking Level, $\mu\text{g/L}$	Amt in Blank $\mu\text{g/L}$	n(b)	R(c)	S(d)	RSD(e)
Aldrin	0.15	ND (f)	8	86	0.0142	11
Chlordane-alpha	0.15	ND	8	99	0.0183	12
Chlordane-gamma	0.15	ND	8	99	0.0181	12
Chlorneb	5.0	ND	6	97	0.601	12
Chlorobenzilate	10	ND	7	108	0.535	5
Chlorthalonil	0.25	ND	8	91	0.0210	9
OCPA	0.25	ND	8	103	0.0307	12
4,4'-DDD	0.25	ND	7	107	0.0157	6
4,4'-DDE	0.10	ND	8	99	0.0118	12
4,4'-DDT	0.60	ND	7	112	0.0984	15
Dieldrin	0.20	ND	8	87	0.0173	10
Endosulfan I	0.15	ND	8	87	0.0131	10
Endosulfan sulfate	0.15	ND	6	102	0.0221	15
Endrin	0.15	ND	8	88	0.0133	10
Endrin aldehyde	0.25	ND	8	88	0.0191	9
Endosulfan II	0.15	ND	8	92	0.0148	11
Etridiazole	0.25	ND	6	103	0.0166	6
HCH-alpha	0.050	ND	8	92	0.00490	11
HCH-beta	0.10	ND	7	95	0.00661	7
HCH-delta	0.10	ND	7	102	0.0115	11
HCH-gamma	0.15	ND	8	89	0.0150	11
Heptachlor	0.10	ND	7	98	0.0117	12
Heptachlor epoxide	0.15	ND	8	87	0.0134	10
Hexachlorobenzene \rightarrow	0.050	ND	5	99	0.0110	22
Methoxychlor	0.50	ND	8	105	0.0655	13
cis-Permethrin	5.0	ND	8	91	0.473	10
trans-Permethrin	5.0	ND	6	111	0.306	6
Propachlor	5.0	ND	7	103	0.440	9
Trifluralin	0.25	ND	7	103	0.0121	5

- (a) Data corrected for amount found in blank.
 (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 5. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 4) (a)

Analyte	Spiking Level, $\mu\text{g/L}$	Amt in Blank $\mu\text{g/L}$	n (b)	R (c)	s (d)	RSD (e)
Aldrin	0.38	ND (f)	8	95	0.0356	10
Chlordane-alpha	0.38	ND	6	89	0.0109	3
Chlordane-gamma	0.38	ND	6	88	0.00920	3
Chlornes	13	ND	7	90	0.834	7
Chlorobenzilate	25	ND	6	89	0.892	4
Chlorthalonil	0.63	ND	8	94	0.0540	9
DCCA	0.63	ND	6	89	0.0140	3
4,4'-DDD	0.63	ND	6	92	0.0248	4
4,4'-DDE	0.25	ND	6	93	0.00856	4
4,4'-DDT	1.5	ND	7	99	0.135	9
Dieldrin	0.50	ND	8	100	0.0505	10
Endosulfan I	0.38	ND	8	101	0.0391	10
Endosulfan sulfate	0.38	ND	6	93	0.0184	5
Endrin	0.38	ND	6	100	0.0295	8
Endrin aldehyde	0.63	ND	7	98	0.0547	9
Endosulfan II	0.38	ND	8	101	0.0399	10
Etridiazole	0.63	ND	6	84	0.0245	5
HCH-alpha	0.13	ND	7	91	0.00865	7
HCH-beta	0.25	ND	6	96	0.00820	3
HCH-delta	0.25	ND	6	84	0.0285	14
HCH-gamma	0.38	ND	8	93	0.0335	9
Heptachlor	0.25	ND	6	97	0.00667	3
Heptachlor epoxide	0.38	ND	8	88	0.0318	10
Hexachlorobenzene	0.13	ND	6	85	0.00335	3
Methoxychlor	1.3	ND	6	96	0.0614	5
cis-Permethrin	13	ND	7	101	0.986	8
trans-Permethrin	13	ND	6	94	0.511	4
Propachlor	13	0.526	7	88	0.925	8
Trifluralin	0.63	ND	7	90	0.0337	6

- (a) Data corrected for amount found in blank.
 (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 7. RECOVERY OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 5) (a)

Analyte	Spiking Level, $\mu\text{g/L}$	Amt in Blank $\mu\text{g/L}$	n(b)	R(c)	S(d)	RSD(e)
Aldrin	1.5	ND (f)	8	95	0.0516	4
Chlordane-alpha	1.5	ND	8	90	0.0904	7
Chlordane-gamma	1.5	ND	8	90	0.0855	7
Chlorneb	50	ND	8	97	1.75	4
Chlorobenzilate	100	ND	8	93	8.30	10
Chlorthalonil	2.5	ND	8	97	0.0966	4
OCPA	2.5	ND	8	93	0.176	8
4,4'-DDD	2.5	ND	8	91	0.189	10
4,4'-DDE	1.0	ND	8	89	0.0877	10
4,4'-DDT	6.0	0.122	8	93	0.362	6
Dieldrin	2.0	ND	8	95	0.0875	5
Endosulfan I	1.5	ND	8	95	0.0618	4
Endosulfan sulfate	1.5	ND	8	91	0.111	9
Endrin	1.5	ND	8	96	0.0691	5
Endrin aldehyde	2.5	ND	8	95	0.163	7
Endosulfan II	1.5	ND	8	94	0.0829	6
Etridiazole	2.5	ND	8	89	0.117	5
HCH-alpha	0.50	ND	8	95	0.0170	4
HCH-beta	1.0	ND	8	91	0.0673	8
HCH-delta	1.0	ND	8	91	0.0669	7
HCH-gamma	1.5	ND	8	96	0.0512	4
Heptachlor	1.0	ND	8	86	0.0474	6
Heptachlor epoxide	1.5	ND	8	96	0.0596	4
Hexachlorobenzene	0.50	ND	8	77	0.0241	6
Methoxychlor	5.0	ND	8	91	0.398	9
cis-Permethrin	50	ND	8	93	3.80	8
trans-Permethrin	50	ND	8	91	4.72	10
Propachlor	50	ND	8	98	1.78	4
Trifluralin	2.5	ND	8	88	0.149	7

(a) Data corrected for amount found in blank.

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

Analyte	Amt in Sample. µg/L	Amt in Blank. µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldrin	0.15	ND (f)	7	100	0.0163	11
Chlordane-alpha	0.15	ND	7	96	0.0189	13
Chlordane-gamma	0.15	ND	7	96	0.0180	13
Chlorneb	5.0	ND	7	95	0.339	7
Chlorobenzilate	10	ND	6	98	1.03	11
Chlorthalonil	0.25	ND	7	103	0.0252	10
DCCA	0.25	ND	7	100	0.0317	13
4,4'-DDD	0.25	ND	6	96	0.0221	9
4,4'-DDE	0.10	ND	7	96	0.0125	13
4,4'-DDT	0.15	ND	7	98	0.0169	12
Dieldrin	0.050	ND	7	103	0.00451	9
Endosulfan I	0.15	ND	7	102	0.0124	8
Endosulfan II	0.15	ND	6	94	0.0170	12
Endosulfan sulfate	0.15	ND	6	98	0.0141	10
Endrin	0.15	ND	7	103	0.0166	11
Endrin aldehyde	0.25	ND	7	98	0.0265	11
Etridiazole	15	ND	6	91	0.992	7
HCH-alpha	0.050	ND	7	106	0.00347	7
HCH-beta	0.050	ND	6	92	0.00282	6
HCH-delta	0.10	ND	7	99	0.0124	12
HCH-gamma	0.15	ND	6	115	0.0104	6
Heptachlor	0.10	ND	7	85	0.0108	13
Heptachlor epoxide	0.050	ND	7	103	0.00382	7
Hexachlorobenzene	0.050	ND	6	82	0.00511	12
Methoxychlor	0.50	ND	6	101	0.0502	10
cis-Permethrin	5.0	ND	7	96	0.594	12
trans-Permethrin	5.0	ND	6	97	0.487	10
Propachlor	5.0	ND	6	116	0.206	4
Trifluralin	0.25	ND	6	86	0.0257	12

- (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	Amt in Sample, ug/L	Amt in Blank, ug/L	n(b)	R(c)	S(d)	RSD(e)
Aldrin	0.15	ND (f)	7	69	0.0134	13
Chlordane-alpha	0.15	ND	7	99	0.0113	8
Chlordane-gamma	0.15	ND	7	99	0.0101	7
Chlorneb	5.0	ND	7	75	0.402	11
Chlorobenzilate	10	ND	7	102	0.889	9
Chlorthalonil	0.25	ND	7	71	0.0225	13
OCPA	0.25	ND	7	101	0.0153	6
4,4'-DDD	0.25	ND	6	101	0.0186	7
4,4'-DDE	0.10	ND	7	99	0.00706	7
4,4'-DDT	0.15	ND	7	84	0.0128	10
Dieldrin	0.050	ND	7	82	0.00387	9
Endosulfan I	0.15	ND	7	84	0.0132	10
Endosulfan II	0.15	ND	6	72	0.0187	17
Endosulfan sulfate	0.15	ND	6	104	0.0138	9
Endrin	0.15	ND	7	84	0.0132	11
Endrin aldehyde	0.25	ND	7	76	0.0168	9
Etridiazole	15	ND	7	98	0.624	4
HCH-alpha	0.050	ND	7	86	0.00388	9
HCH-beta	0.050	ND	7	100	0.00283	6
HCH-delta	0.10	ND	7	103	0.00594	6
HCH-gamma	0.15	ND	7	85	0.0118	9
Heptachlor	0.10	ND	7	85	0.00742	9
Heptachlor epoxide	0.050	ND	7	82	0.00478	12
Hexachlorobenzene	0.050	ND	7	68	0.00233	7
Methoxychlor	0.50	ND	7	104	0.0291	6
cis-Permethrin	5.0	ND	7	86	0.461	11
trans-Permethrin	5.0	ND	7	102	0.336	7
Propachlor	5.0	ND	7	95	0.375	8
Trifluralin	0.25	ND	7	87	0.0243	11

(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 QUALITY CONTROL STANDARD

Test	Analyte	Conc., µg/l	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection of analyte; S/N > 3
Chromatographic performance	DCPA	0.0500	PSF between 0.80 and 1.15 (a) PGF between 0.80 and 1.15 (a)
Column performance	Chlorothalonil HCN-delta	0.0500 0.0400	Resolution > 0.50 (b)

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

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

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 4).

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 4).

(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.

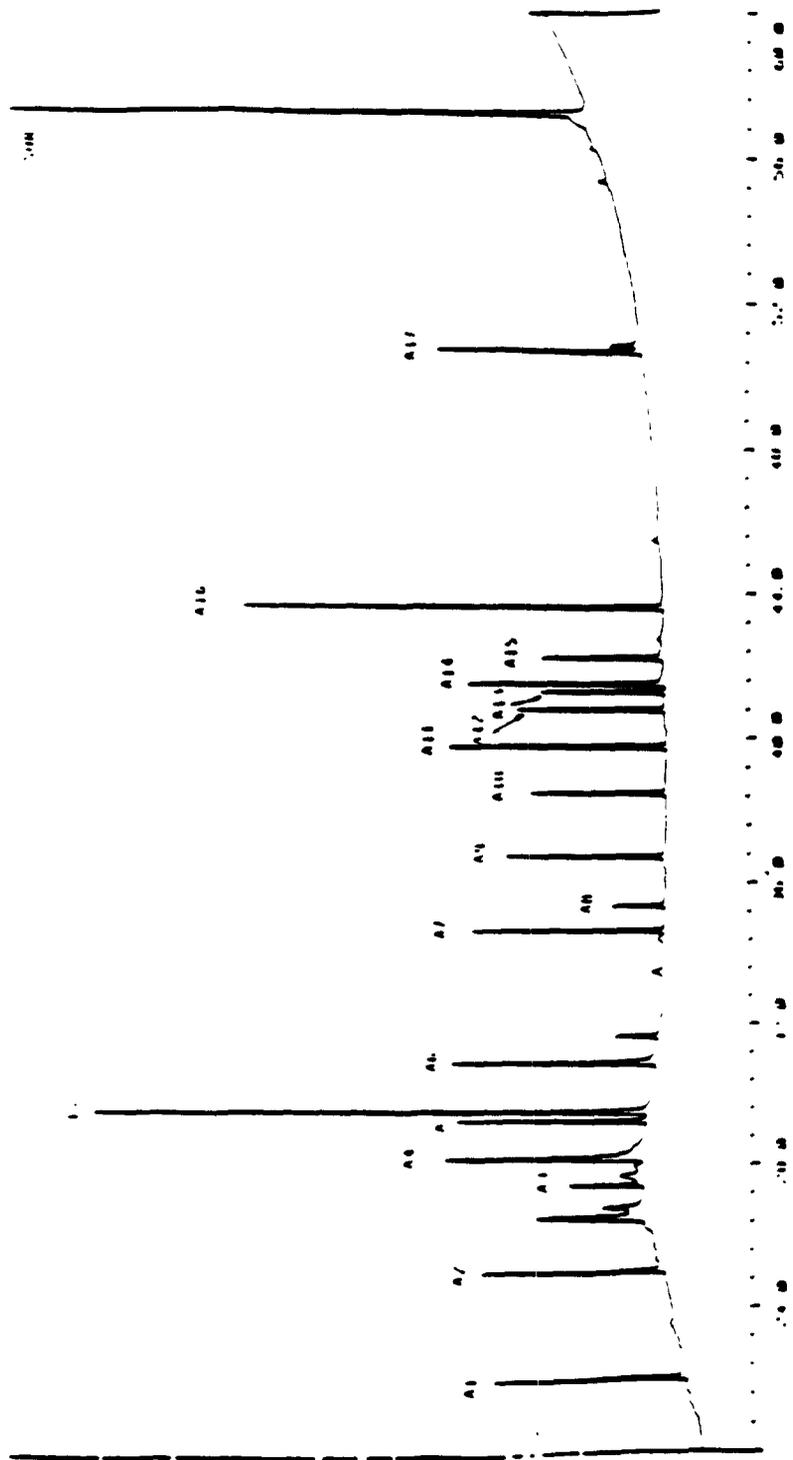
TABLE II. PRESERVATION STUDY RESULTS

Analyte	Soaking Level, $\mu\text{g/L}$	Day 0		Day 14		Day 28	
		R(a)	PSD(b)	R	RSD	R	RSD
Aldrin	0.15	75	4	94	9	57	24
Chlordane-alpha	0.15	78	10	102	12	99	12
Chlordane-gamma	0.15	78	10	101	14	98	13
Chlorned	5.0	89	2	90	6	82	9
Chlorobenzilate	10	103	9	108	16	103	14
Chlorthalonil	0.25	90	2	(c)	-	91	7
CCPA	0.25	95	10	103	11	101	12
4,4'-DDD	0.25	80	5	109	15	84	9
4,4'-DDE	0.10	83	10	98	14	91	14
4,4'-DDT	0.15	87	7	88	5	68	11
Dieldrin	0.050	88	3	84	5	77	10
Endosulfan I	0.15	89	3	40	20	72	34
Endosulfan II	0.15	85	4	85	5	76	7
Endosulfan sulfate	0.15	97	9	112	16	103	15
Endrin	0.15	91	4	89	7	79	9
Endrin aldehyde	0.25	85	5	85	3	70	2
Etridiazole	15	75	10	67	7	100	11
HCH-alpha	0.050	87	2	96	28	79	9
HCH-beta	0.050	88	8	(c)	-	102	14
HCH-delta	0.10	94	9	101	5	107	11
HCH-gamma	0.15	90	1	102	19	96	9
Heptachlor	0.10	62	11	74	8	71	10
Heptachlor epoxide	0.050	89	3	94	4	78	11
Hexachlorobenzene	0.050	67	11	80	9	89	13
Methoxychlor	0.50	103	9	115	17	103	17
cis-Permethrin	5.0	88	5	78	8	31	25
trans-Permethrin	5.0	111	9	109	21	86	13
Propacilor	5.0	87	3	105	3	94	12
Trifluralin	0.25	68	10	90	4	100	15

(a) R = average percent recovery from triplicate analyses.

(b) RSD = percent relative standard deviation

(c) Data not available; interferences present.



Retention Time, min.

FIGURE 1 GC-ICD CHROMATOGRAM OF SPIKING A (SPIKING LEVEL 11/1000) TO SAMPLE 1

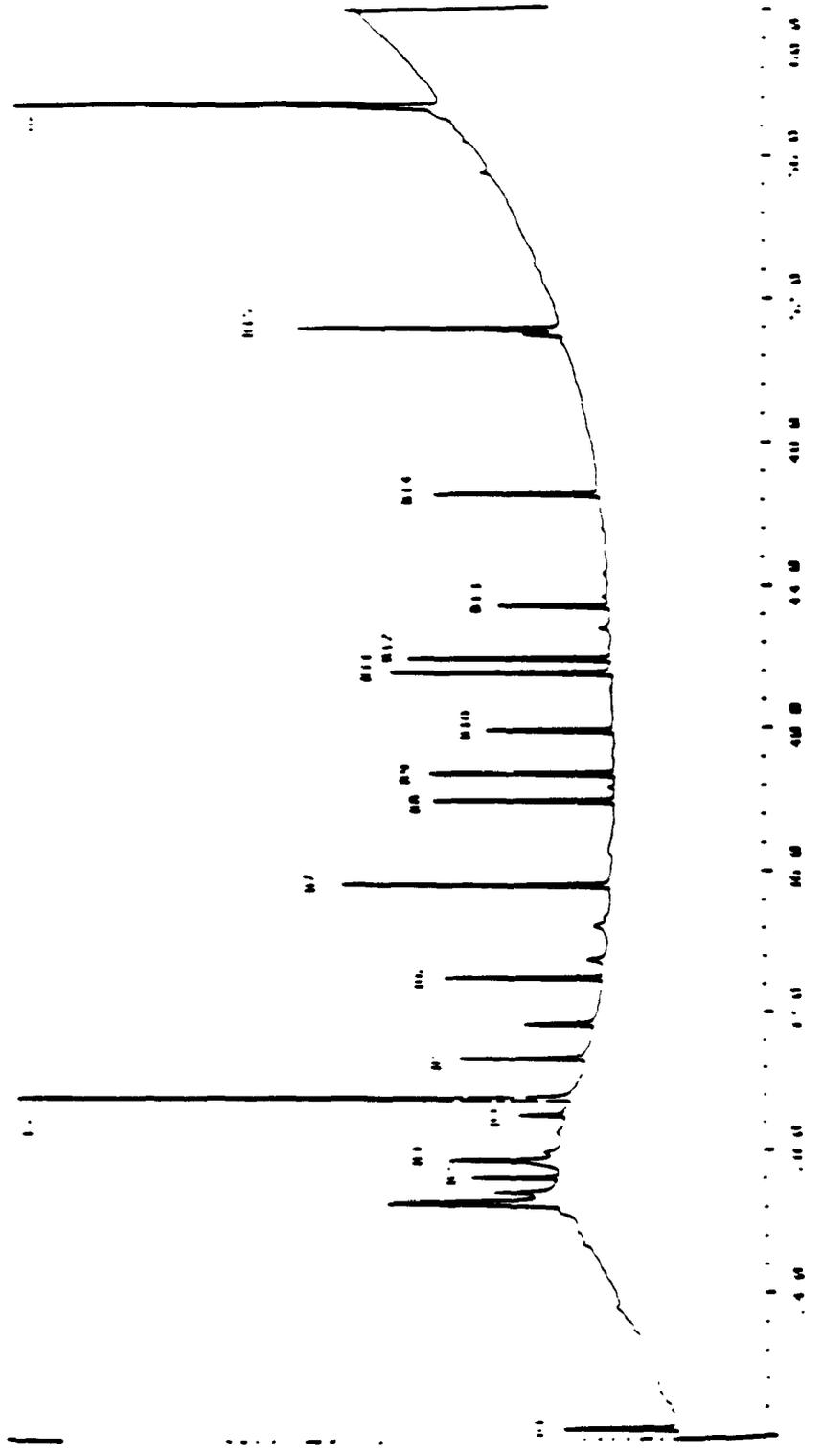
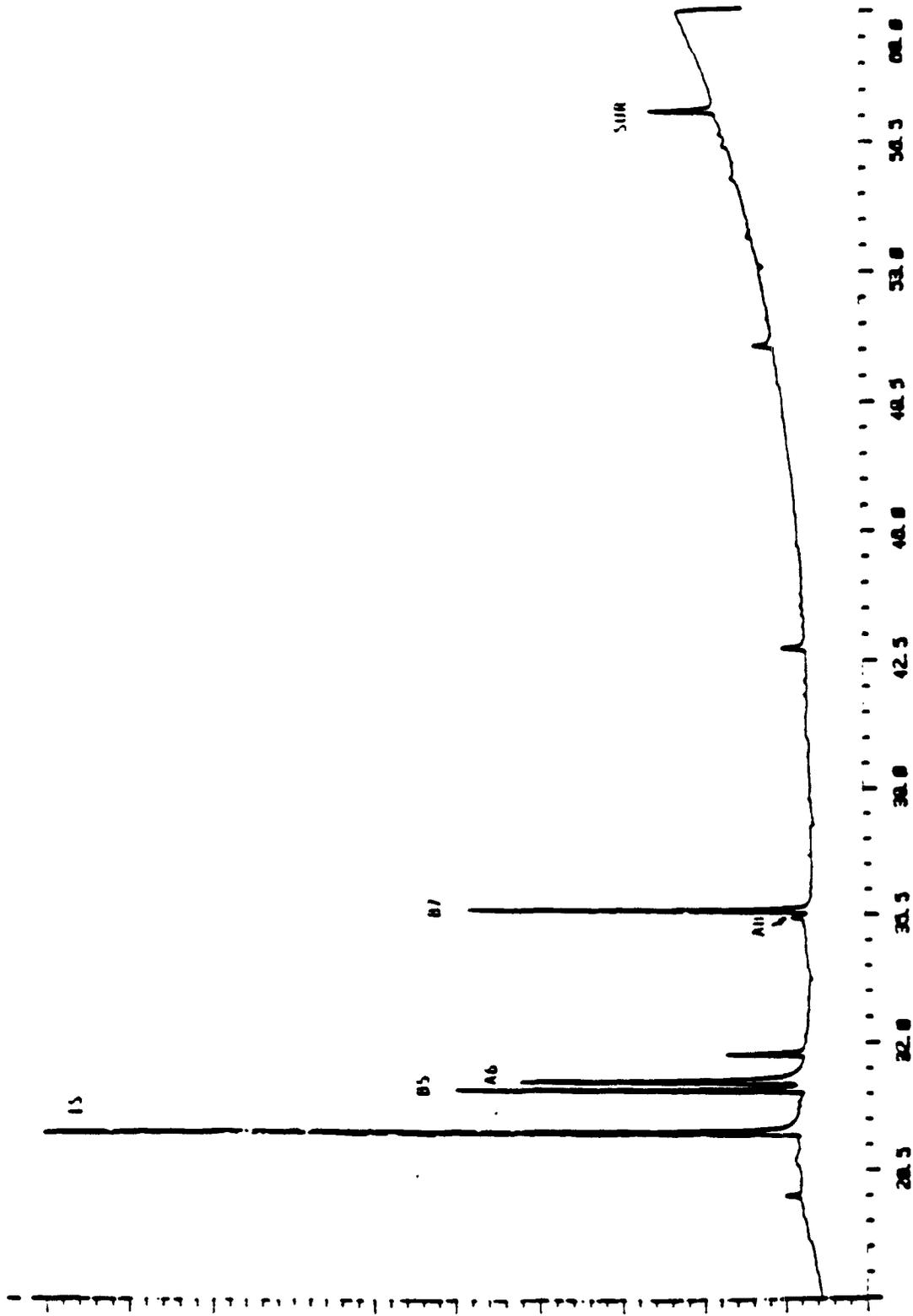


FIGURE 2 GC-ECD CHROMATOGRAM OF SPIKING MIX B (SPIKING LEVEL 3)(See Table 1 for peak identifications)



Retention Time, min.

FIGURE 3. GC-ECD CHROMATOGRAM OF METHOD 2 INSTRUMENT QC STANDARD
 IS = Internal Standard; SUR = Surrogate Standard; B5 = ICH-delta;
 AB = Chlorothalonil; B7 = DCPA; AB = Chlorpyrifos

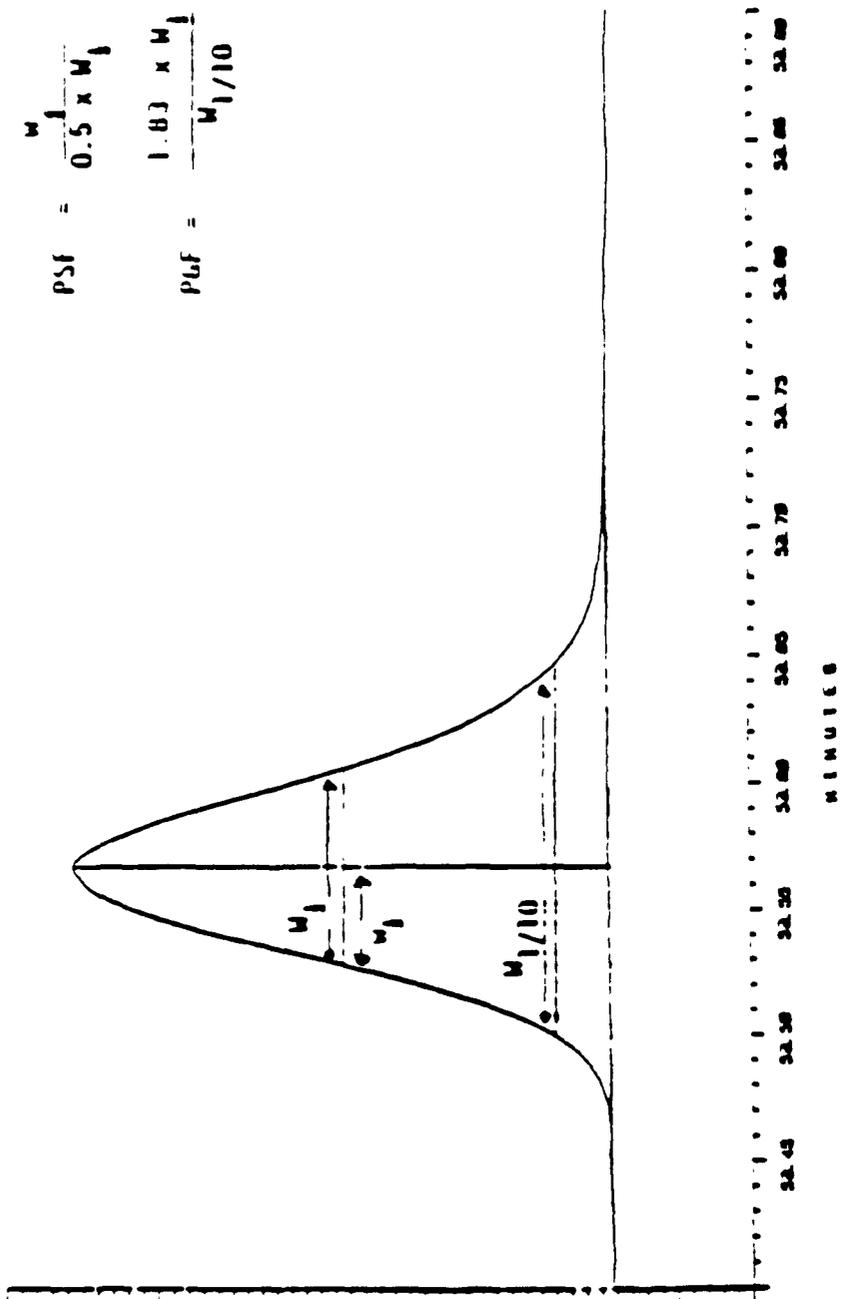


FIGURE 4. EQUATIONS USED TO CALCULATE PEAK SYMMETRY FACTOR (PSF) AND PEAK GAUSSIAN FACTOR (PGF)

APPENDIX B
GC/MS SPECTRAL INFORMATION

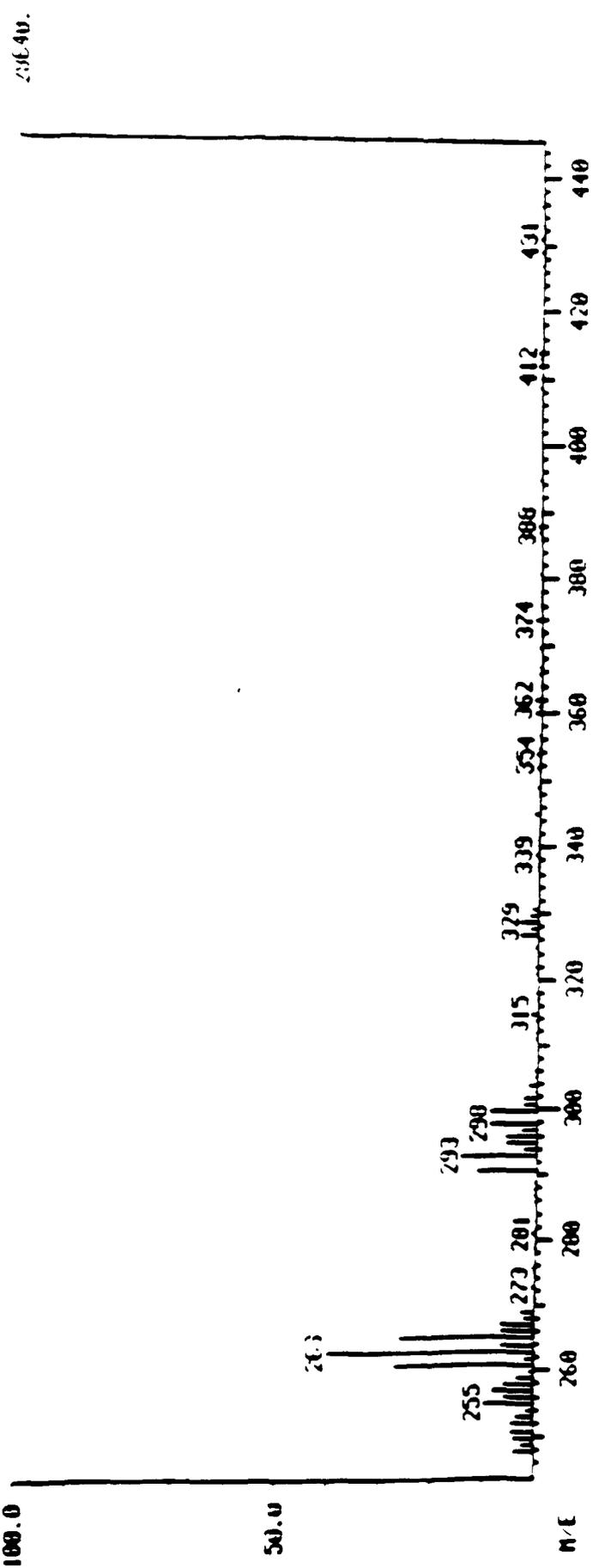
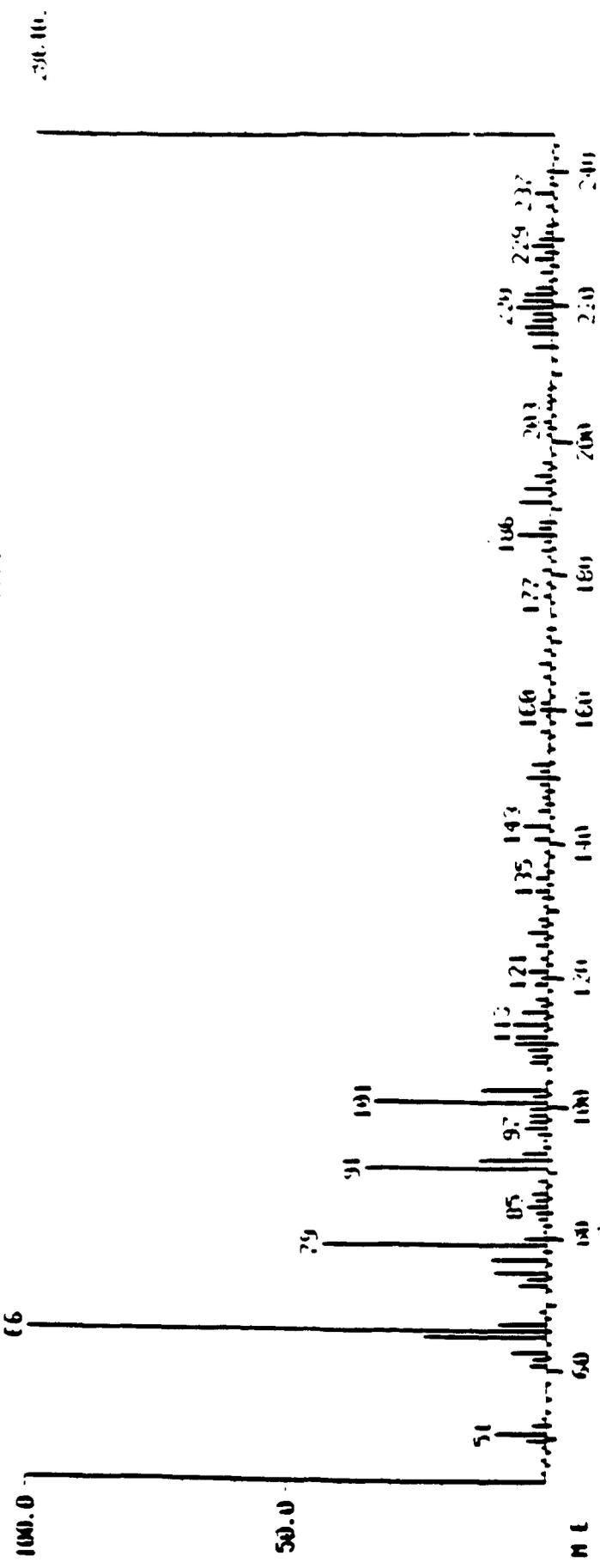
TABLE 1 (cont. Inmed)

ANALYTE	METHOD NUMBER	AMOUNT (INJECT.)	MS SCAN	EI CHARACTERISTIC IONS, m/z			EI CHARACTERISTIC IONS, m/z			SPECTRUM NUMBER	
				PRIMARY	2ND	3RD	PRIMARY	2ND	3RD		
PROPRAZINE	1	10	230 0	1508	214	229	231	210	232	194	B19
RONNELL	1	40	321 5	1024	205	207	125	323	321	111	B01
SECURMEIUM	1	40	225 3	1605	196	225	169	226	196	254	B58
SIMAZINE	1	20	201 7	1554	202	203	186	202	204	166	B18
SINLETYN	1	20	213 3	1010	213	155	198	214	168	242	B42
STERFOS	1	10	366 0	2130	(C)	-	-	127	367	365	B107
SULPROVUS	1	20	322 5	2363	156	322	140	323	141	169	B26
TEBUTHIUMON (A)	1	80	220 3	-	-	-	-	-	-	-	-
TEMBACIL (A)	1	20	216 7	-	-	-	-	-	-	-	-
TERBOPUS (A)	1	-	-	-	-	-	-	-	-	-	-
TERBUTHYLAZINE	1	20	229 0	1623	214	229	216	210	232	194	B17
TERBUTYLM	1	20	241 6	1073	105	241	226	242	196	186	B17
THIOMACIL	1	20	240 2	1311	97	240	107	249	97	277	B16
THIUMIUM	1	60	346 0	-	313	309	311	345	347	163	B108
THIAPROPIUM	1	60	293 0	1944	57	208	05	294	296	168	B48
THIETHIMARIS	1	10	312 6	1966	109	297	299	313	315	177	B20
THIETAZAN	1	60	109 7	2101	109	162	135	190	165	218	B64
THIEMATO	1	10	203 3	1048	120	203	06	204	120	232	B4
ALDRIN	2	20	364 9	1075	66	263	265	329	331	293	B76
A BHC	2	60	290 0	1461	219	217	101	219	217	255	B08
B BHC	2	60	290 0	1557	219	217	101	219	217	147	B72
D BHC	2	60	290 0	1651	219	217	101	219	217	147	B73
C BHC	2	60	290 0	1565	219	217	101	219	217	255	B90
A CHLORDANE	2	40	409 0	2109	373	365	272	101	373	375	B96
G CHLORDANE	2	20	409 0	2067	373	375	272	101	373	375	B79
CHLOROMERILLATE	2	10	325 2	2206	251	253	139	307	325	309	B64
CHLOROPROPYATE (A)	2	-	-	-	-	-	-	-	-	-	-
CHLOROPROPYATE (B)	2	20	207 1	1154	206	208	191	207	209	192	B68

TABLE I (continued)

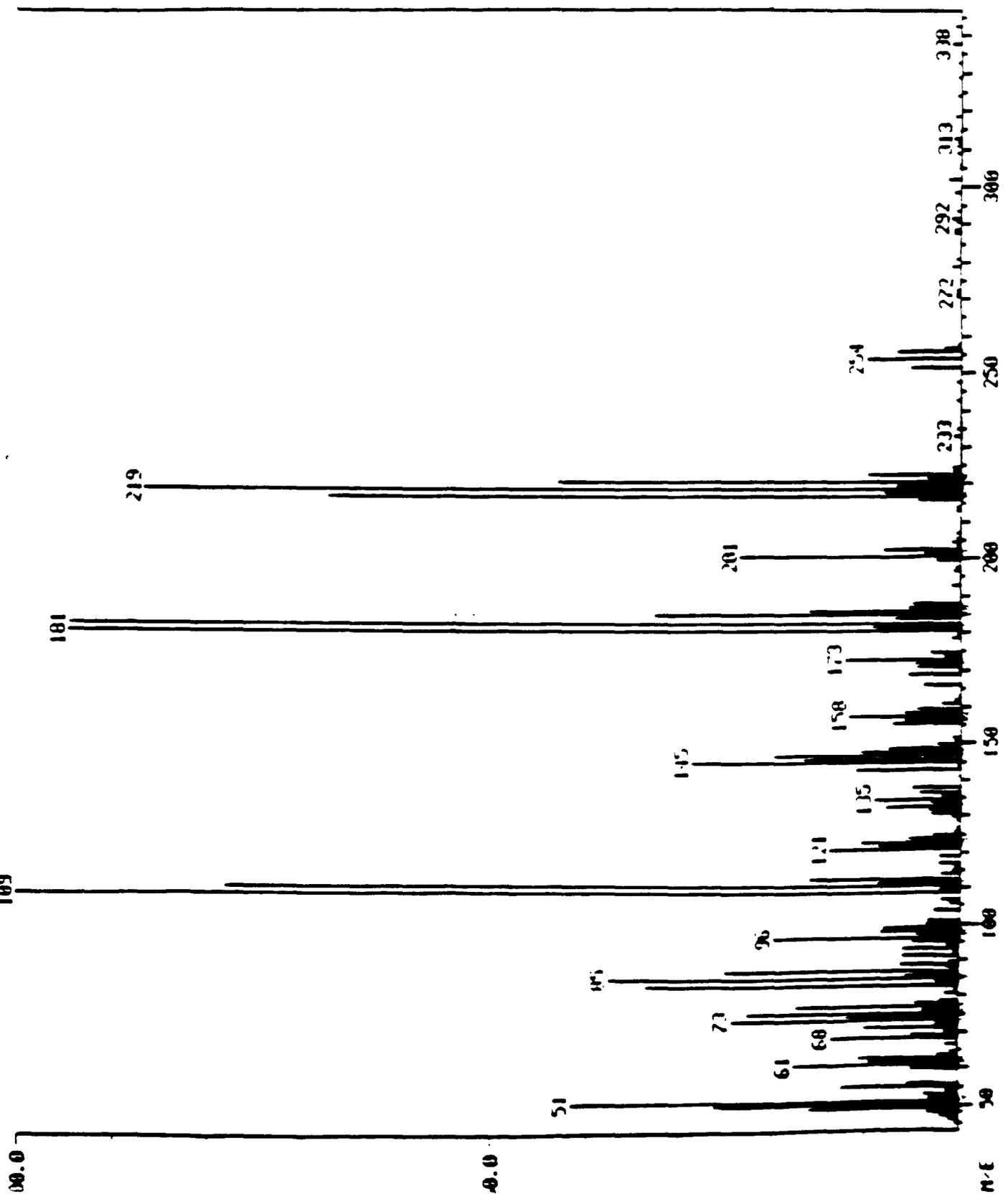
ANALYTE	MULTIPLY NUMBER	AMOUNT IN DTG, MG.	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z				CI CHARACTERISTIC IONS, m/z				LITHIUM NUMBER
					PRIMARY	2ND	3RD	SPECTRUM NUMBER	PRIMARY	2ND	3RD	LITHIUM NUMBER	
CHLORALHYDRATE	2	40	147.5	1666	266	264	231	A18	267	265	211	B74	
DCPA	2	10	112.0	1936	301	312	330	A19	333	311	299	B95	
4,4'-DDE	2	20	170.0	2209	235	237	165	A25	207	283	285	B81	
4,4'-DDD	2	20	178	2188	246	318	316	A10	319	317	283	B65	
4,4'-DDT	2	40	354.5	2404	235	237	165	A28	263	319	317	B84	
DICHLORAN (A)	2												
DIELDRIN	2	40	380.9	2171	79	108	263	A61	365	367	309	B97	
ENDOSULFAN I	2	80	406.9	2100	195	339	361	A24	407	409	371	B80	
ENDOSULFAN II	2	40	406.9	2263	195	339	361	A26	277	407	409	B82	
ENDOSULFAN SULFATE (A)	2												
EMURIN	2	40	380.9	2227	81	263	265	A62	365	367	381	B98	
EMURIN ALDHYDE	2	40	381.9	2315	67	365	367	A27	365	381	383	B83	
ETRIDIAZOLE	2	10	267.5		231	248	213	A68	211	247	249	B70	
HEPTACHLOR	2	20	373.3	1778	100	272	276	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	116	A29	239	365	367	B85	
PROPACHLOR	2	10	211.7	1331	120	211	176	A102	212	214	178	B53	
TRANS-FLUMETHLIN	2	2	391.3	2841	183	163		A30	183	213		B86	
TRIFLAN	2	40	335.3	1475	306	264	290	A15	336	316	232	B71	
ACIFLUORFEN	3	80	374.6	2590	75	375	223	A50	366	376	244	B100	
BENTAZON	3	60	254.3	2072	212	254	105	A68	255	213	241	B104	
CHLORAMBEN (A)	3												
2,4-D METHYL. ESTER	3	40	235.0	1174	199	234	236	A14	235	237	175	B69	
DALAPIN (D)	3	80	157.0										
2,4-D	3	20	261.1	1932	101	162	59	A67	101	263	211	B103	
DCPA DIACID METABOLITE	3	10	332.0	1936	301	332	330	A19	333	331	299	B95	
DCPA MONOACID METABOLITE	3	10	332.0	1936	301	332	330	A19	333	331	299	B95	
DICAMBRA	3	40	235.0	1165	203	234	205	A31	203	235	205	B87	

01871 TO 01873 STANDARD - 01865 TO 01867
 01882 TO 01884 01.01

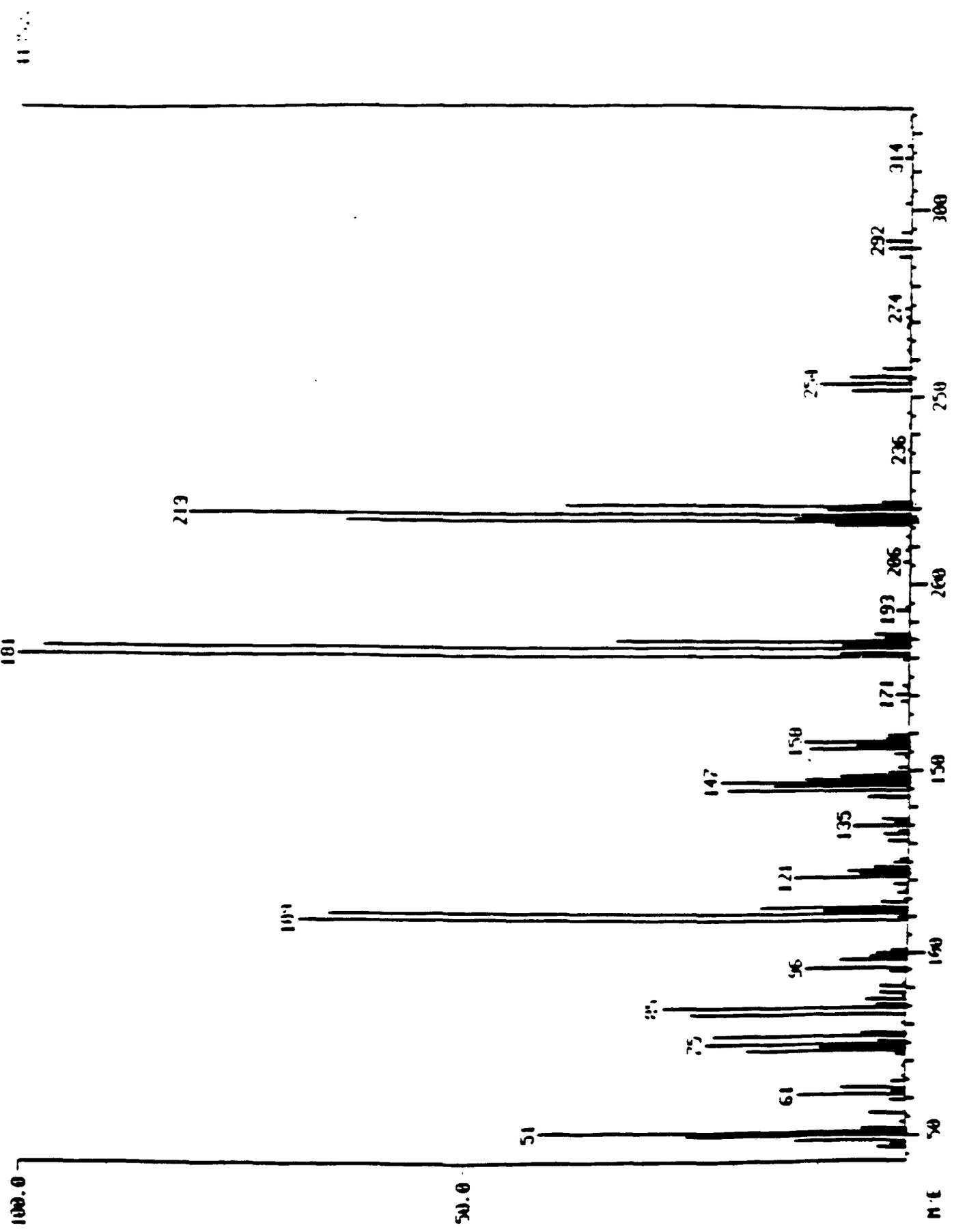


01:55 TO 01:50 SURMID - 01542 TO 01546 - 01562 TO 01567 .1.01

2904.4



0155.0 TO 0159.0 APPROX 0155.0 TO 0157.0
0155.0 TO 0159.0 APPROX 0155.0 TO 0157.0



491 1180 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500 3600 3700 3800 3900 4000 4100 4200 4300 4400 4500 4600 4700 4800 4900 5000 5100 5200 5300 5400 5500

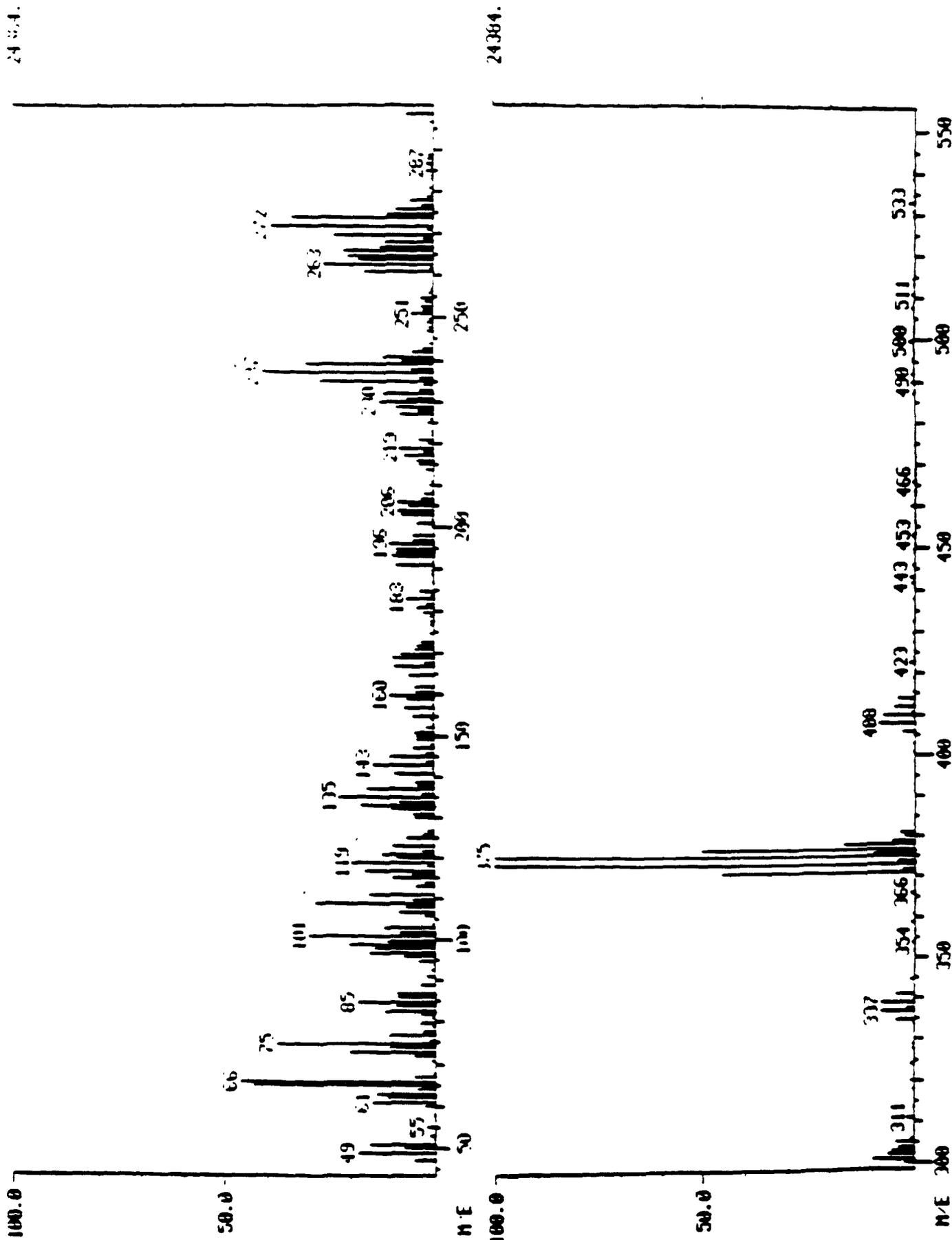


FIGURE A40. 11 MASS SPECTRUM OF A-CHEMINE.

MASS SPECTRUM
 01/07/06 14:50:00 + 38:02
 SAMPLE: 41160-02-2 MIX 03 2.044 SPLITLESS 10-7 e 18000 EU
 CURDS.: EI,GC/MS 30MX.25MM SPUS CH4(50) 1(300) 60(1)-30(0e4(4)
 #2278 TO #2287 SUMMED - #2250 TO #2301 - #2266 TO #2275 X1.00
 DATA: 553417 #2282
 CALL: 553510(RT 45.04)
 BASE M/Z: 251
 PIC: 128E40.

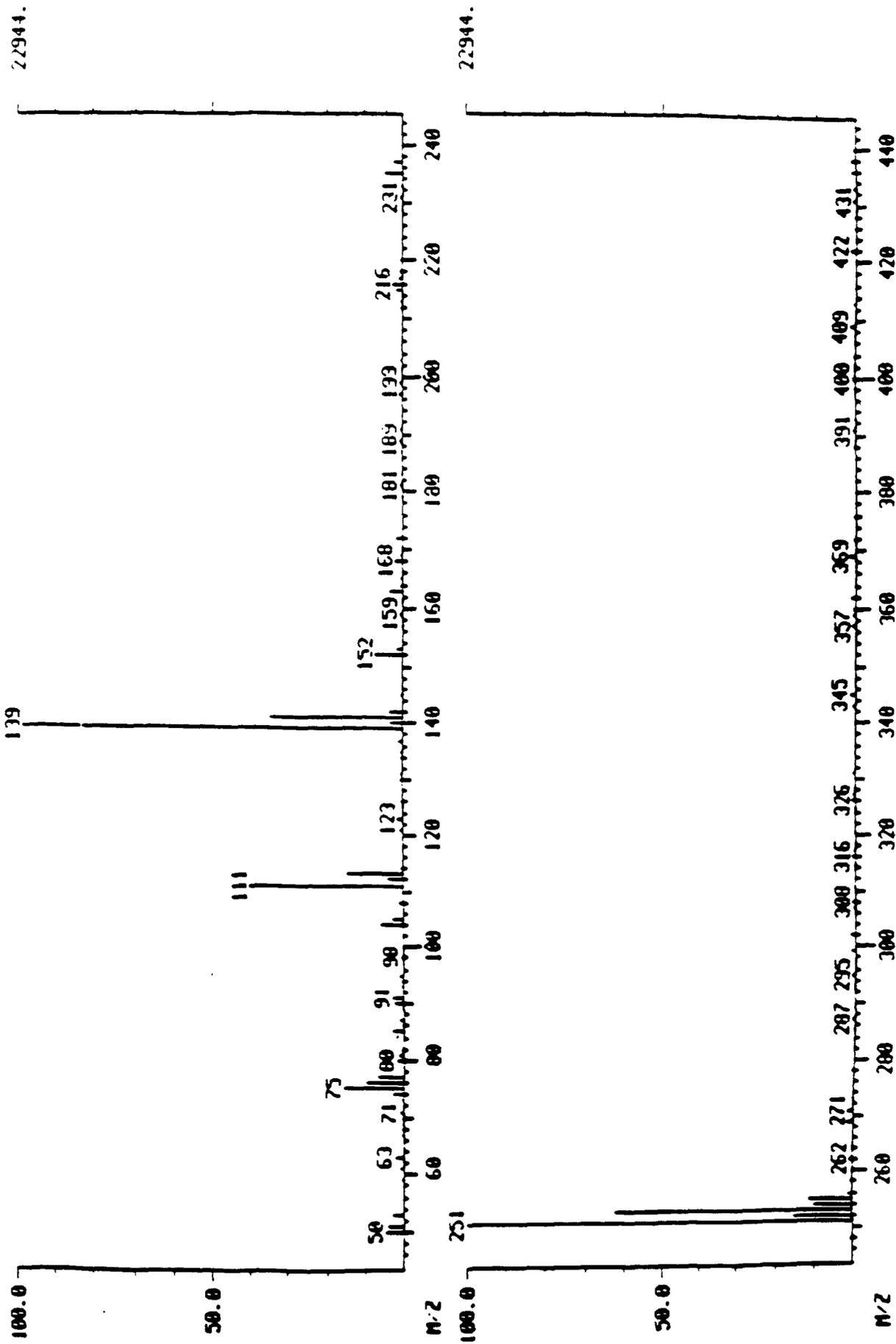
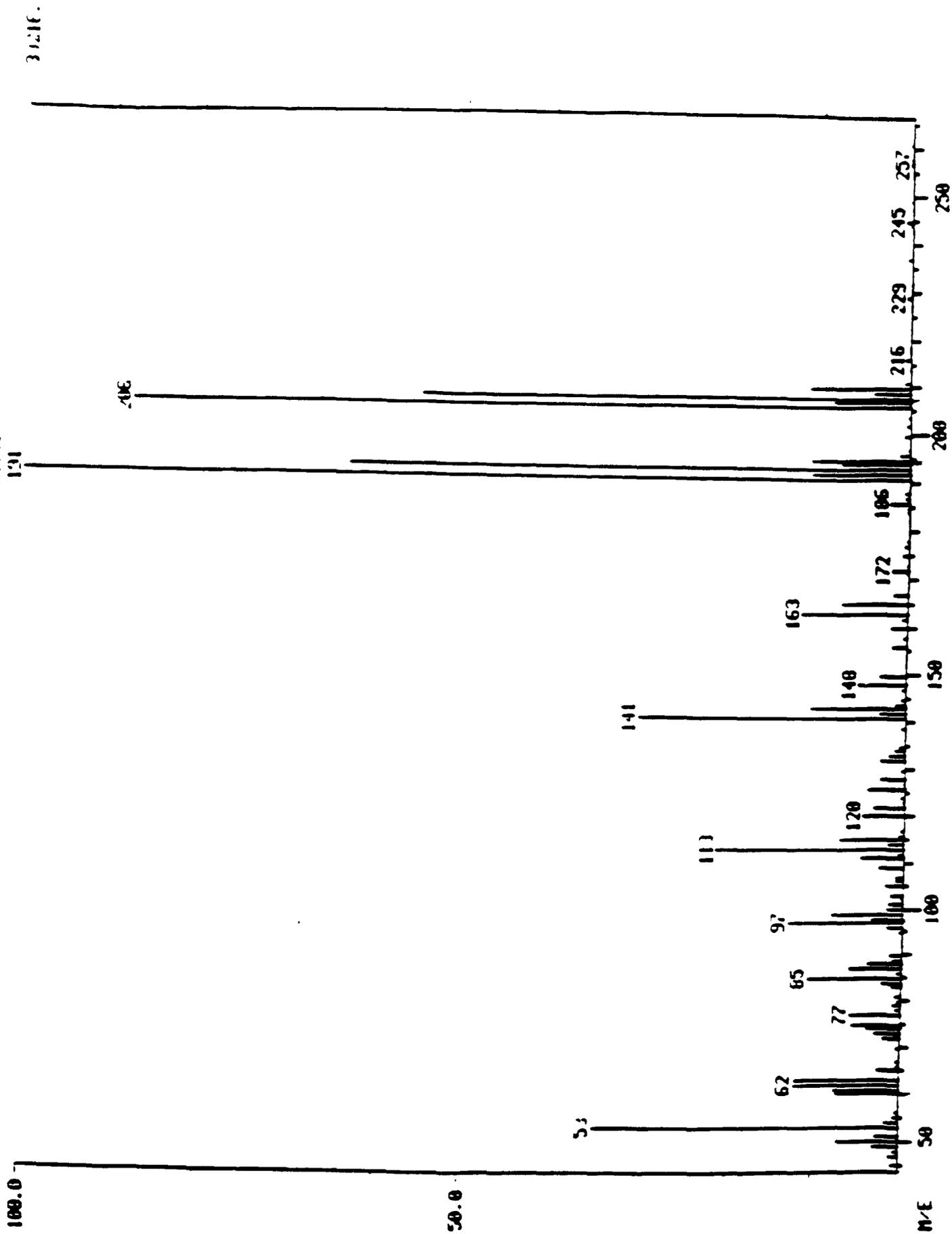


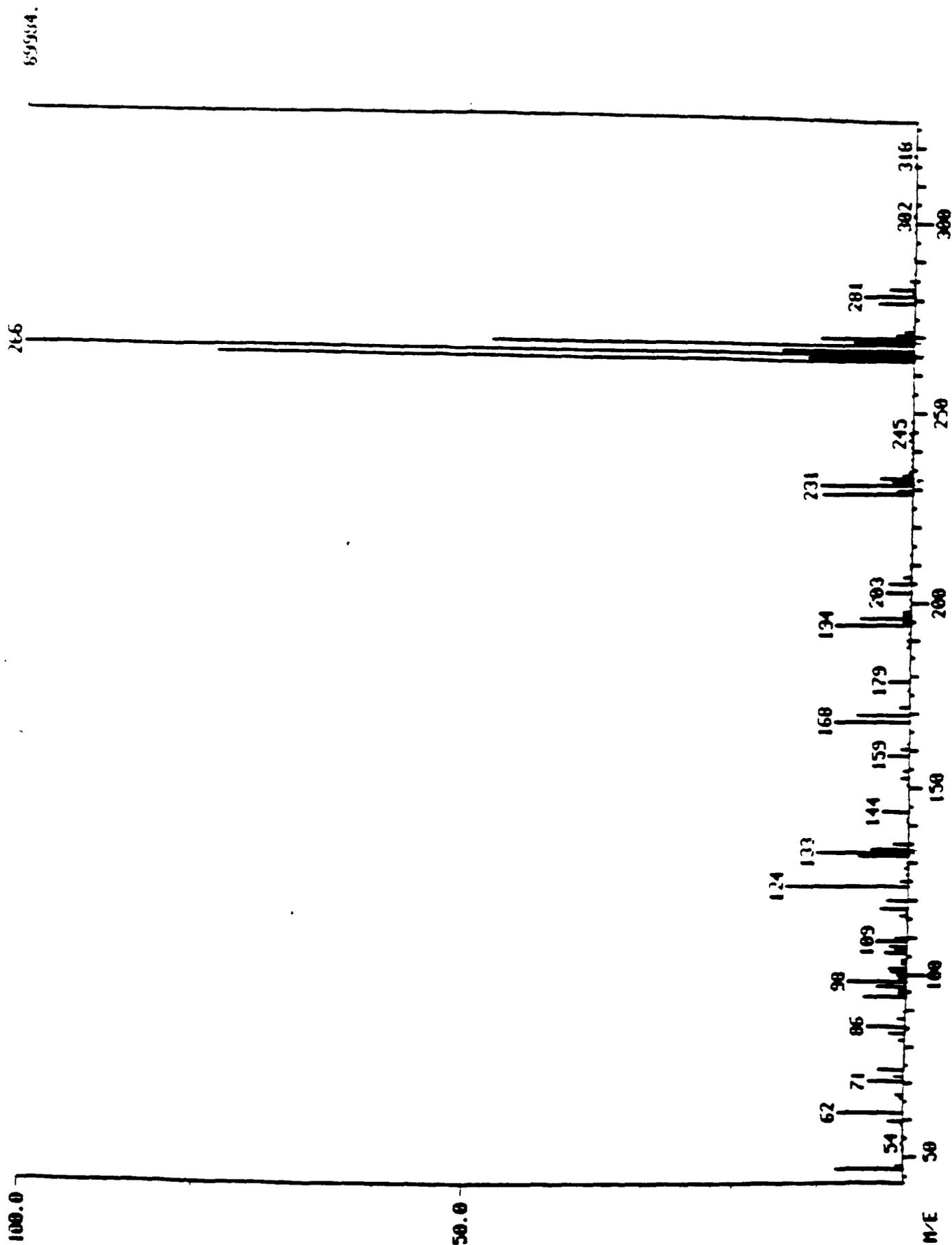
FIGURE A11. 11 MASS SPECTRUM OF CHLOROBENZENE

Sample No. 130 - 41.70 - 41.70 - 41.70 - 41.70 - 41.70
Date to start 2000 - 0142 to 0153 - 0166 to 0170 21.91



1. 4

Sample: 0130001, m/z 44, 2.004, 20111133, 10.7 e 1800.10
01660 10 01607 SAMPLED - 01650 10 01654 - 01670 10 01674 31.01



3448 411 13.700 111 111 111 111 111 111
 0.200 10 0.211 50000 - 0.198 10 0.203 - 0.212 10 0.219 10.01

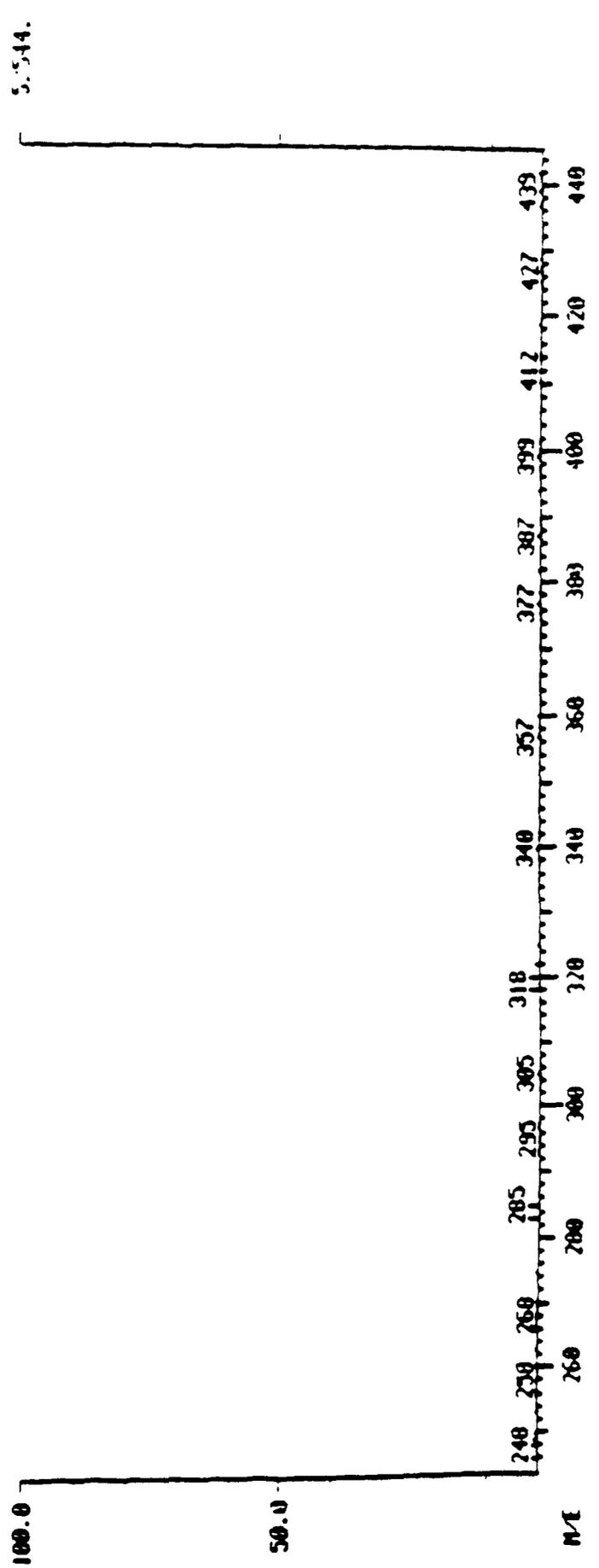
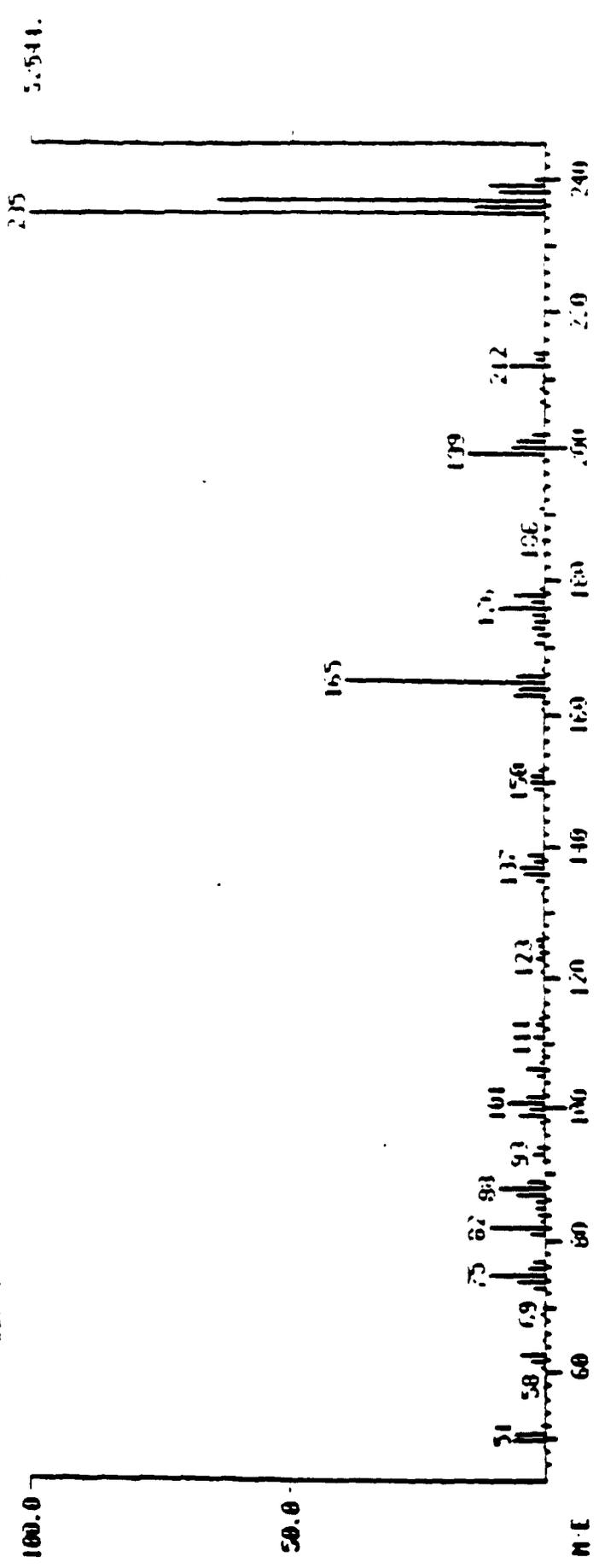
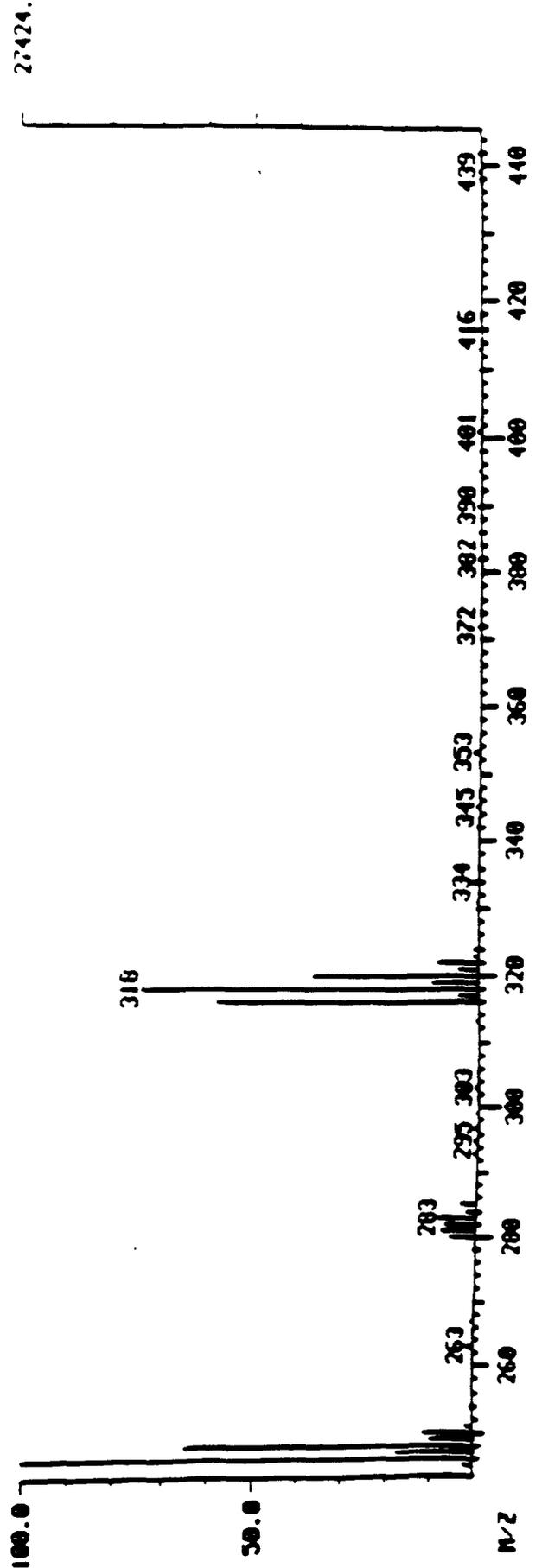
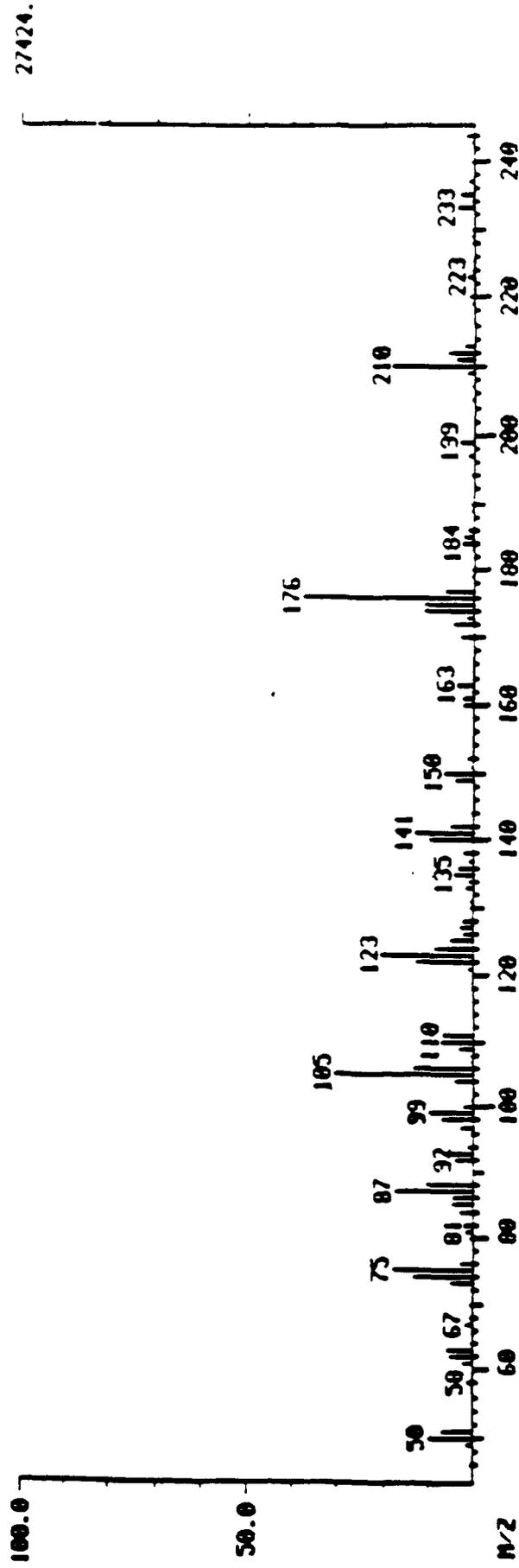


FIGURE A25 - 11 MASS SPECTRUM OF A ...

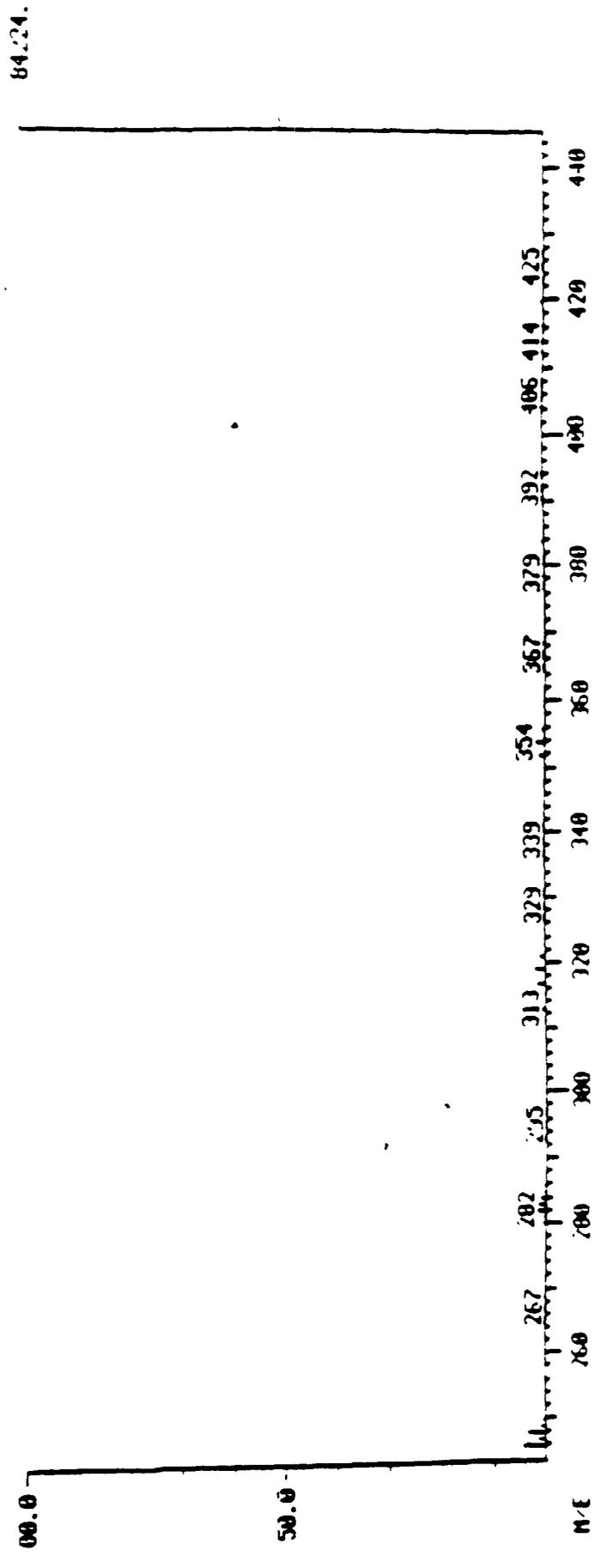
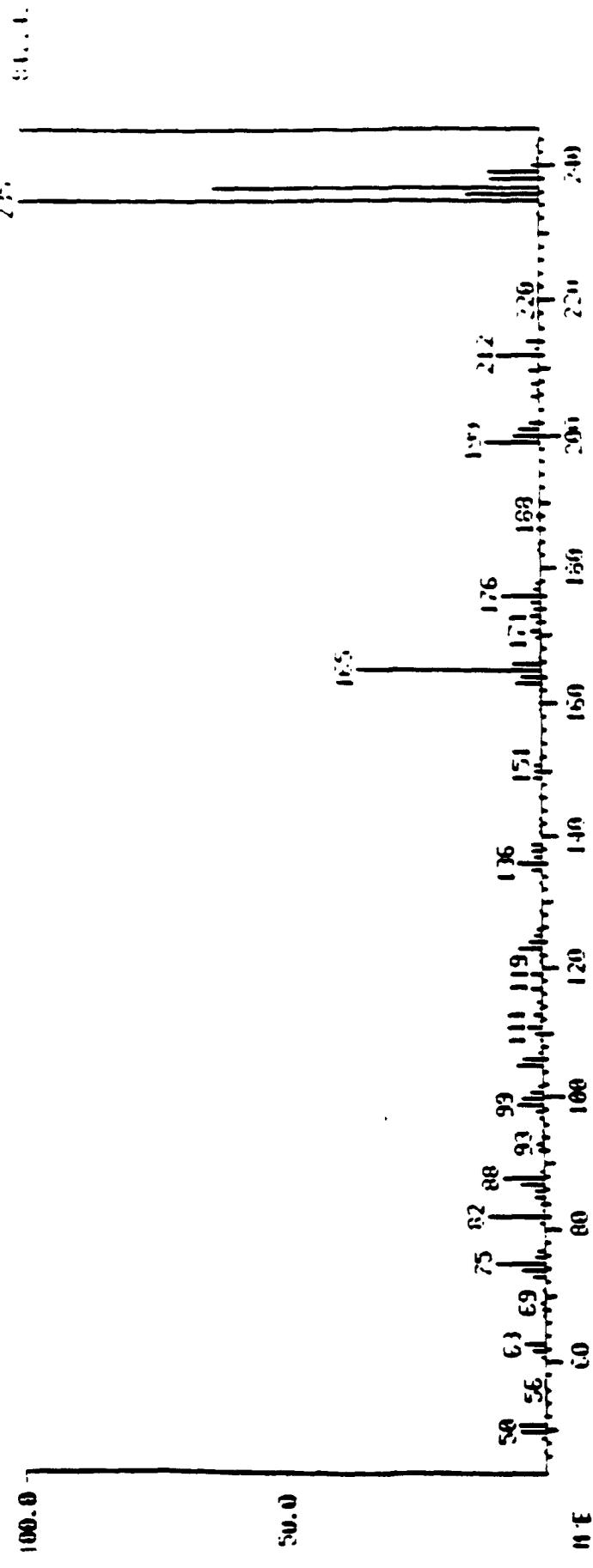
MASS SPECTRUM
 01/07/06 14:50:00 + 36:27
 SAMPLE: 41100-02-2 MIX 03 2.0ML SPLITLESS 10-7 @ 1800 EV
 COND.: EI.GC/MS 300X.25MM SP85 C14(50) I(300) 60(1)-30004(4)
 02103 10 02191 SUMMED - 02173 10 02179 - 02199 TO 02205 XI.00

DATA: 553417 02187
 CALI: 553510CAL45 04

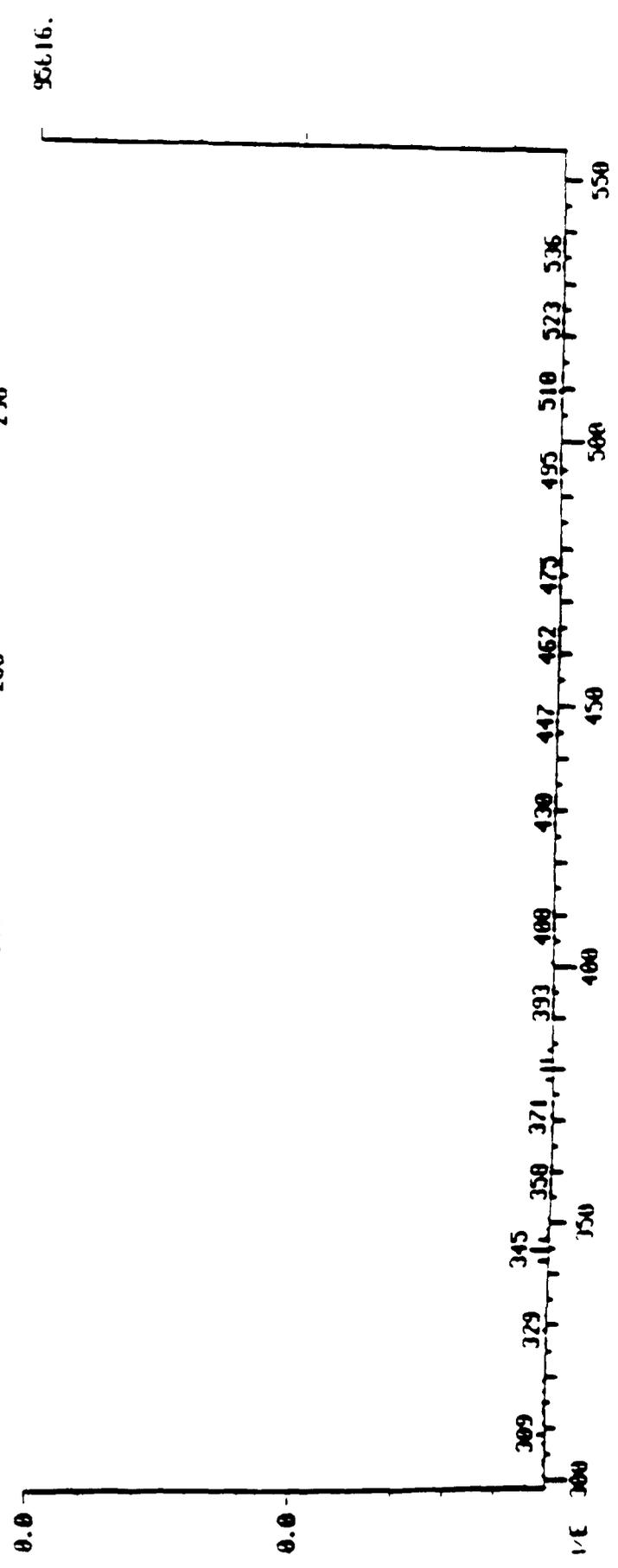
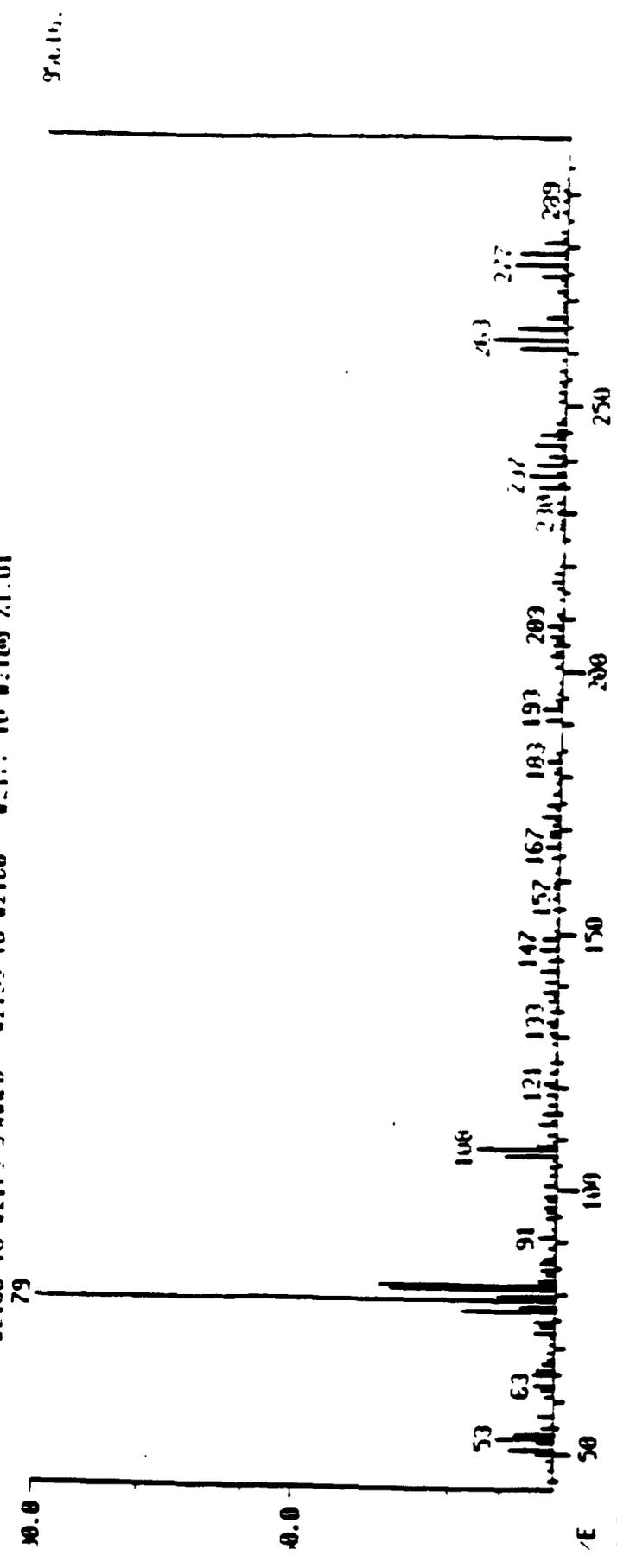
BASE M/Z: 246
 RIC: 257260.



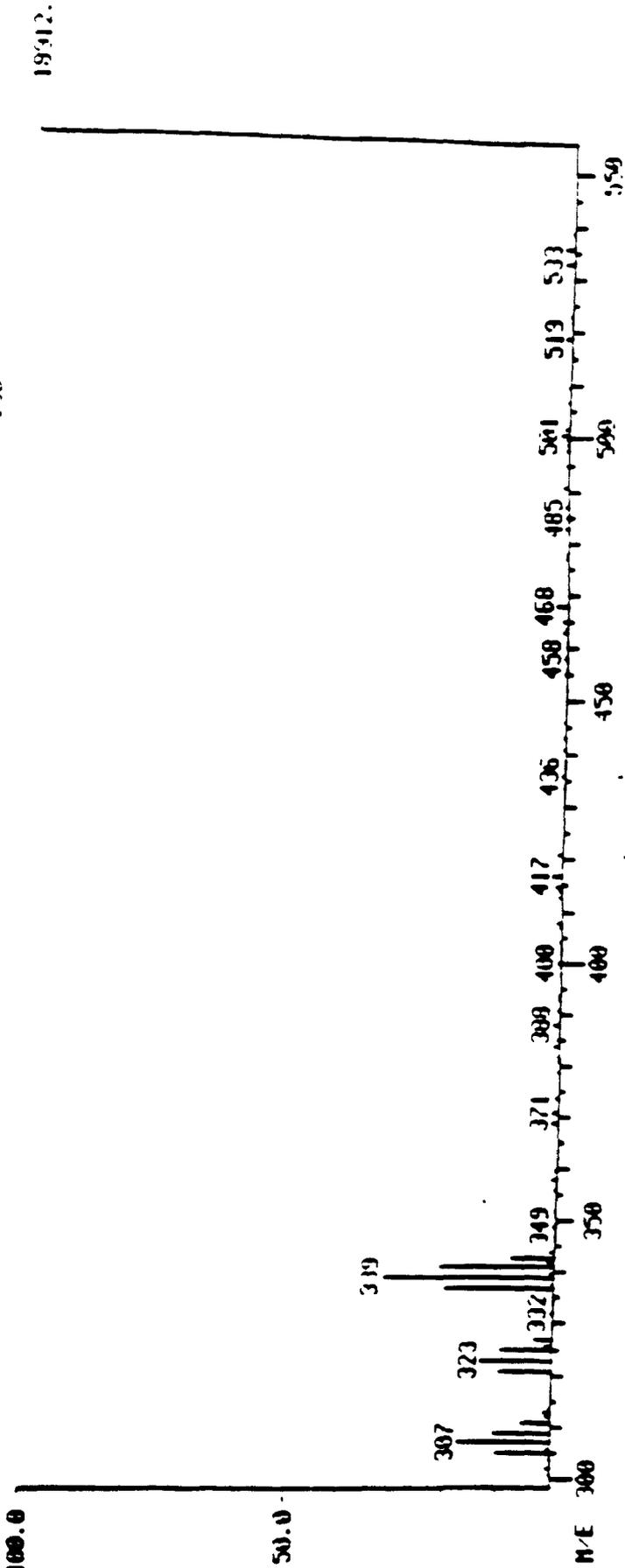
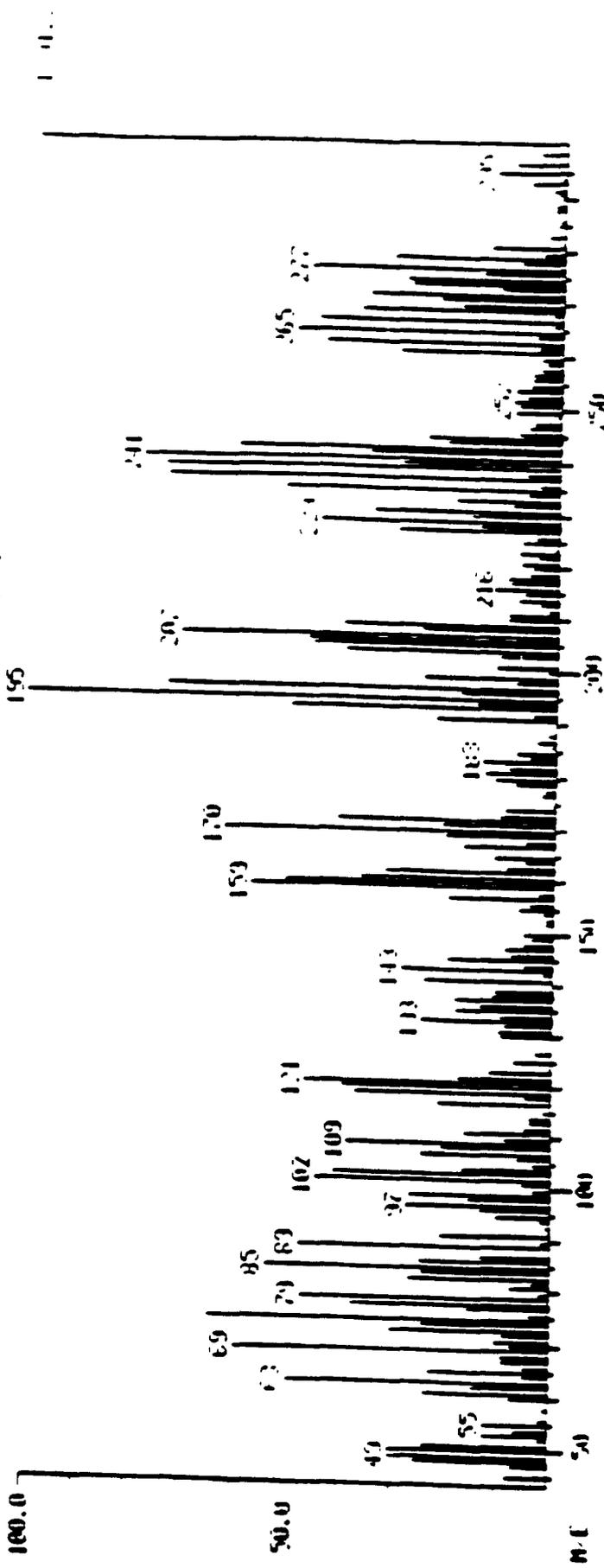
0.114 194 2.00 1.25 41 2.00 4
 0.259 10 0.200 0.0000 - 0.258 10 0.2000 - 0.300 10 0.415 0.101



WTE 198 2.0 5.0 50.0 55.0 10
02166 TO 02173 SUNDAY - 02166 TO 02173 TO 02189 21.01

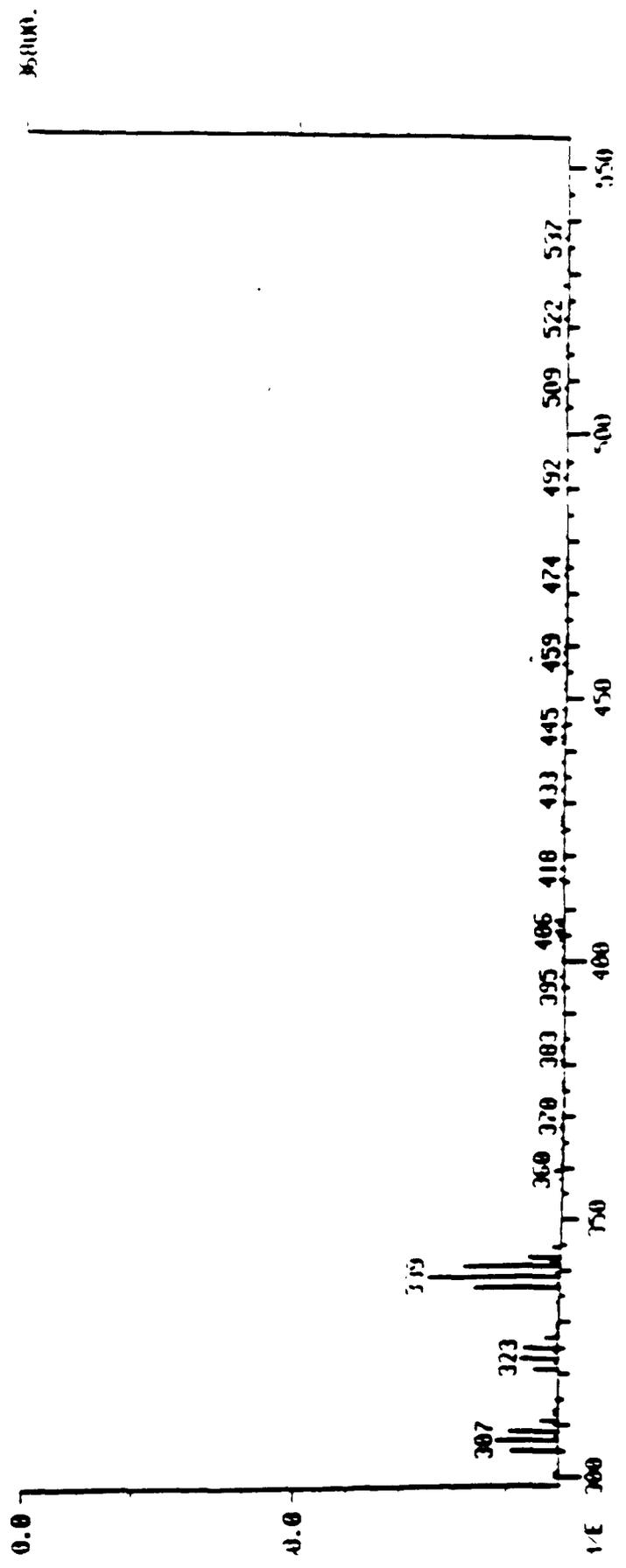
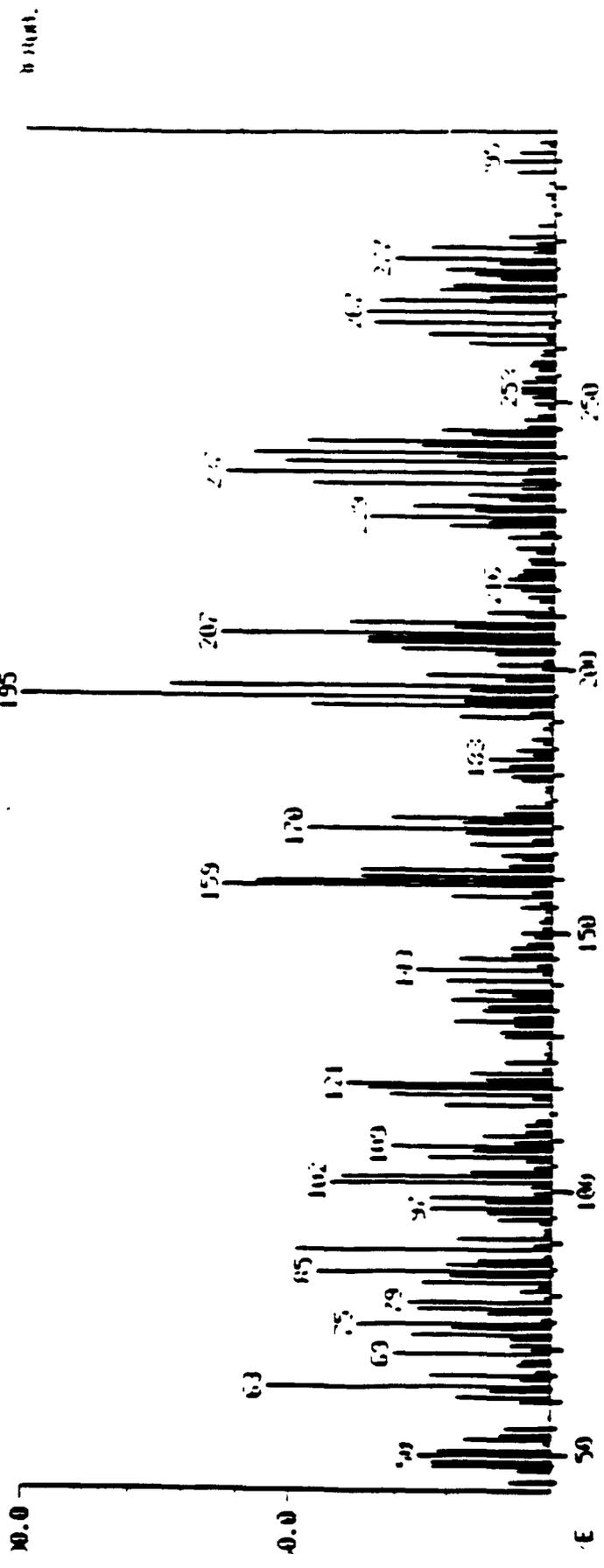


01 01 340 15
 Sample: 0185 B3 2.004 30111 10.2 100.0
 0209 10 02105 50000 0.001 10 0207 0.100 10 02100 1.001



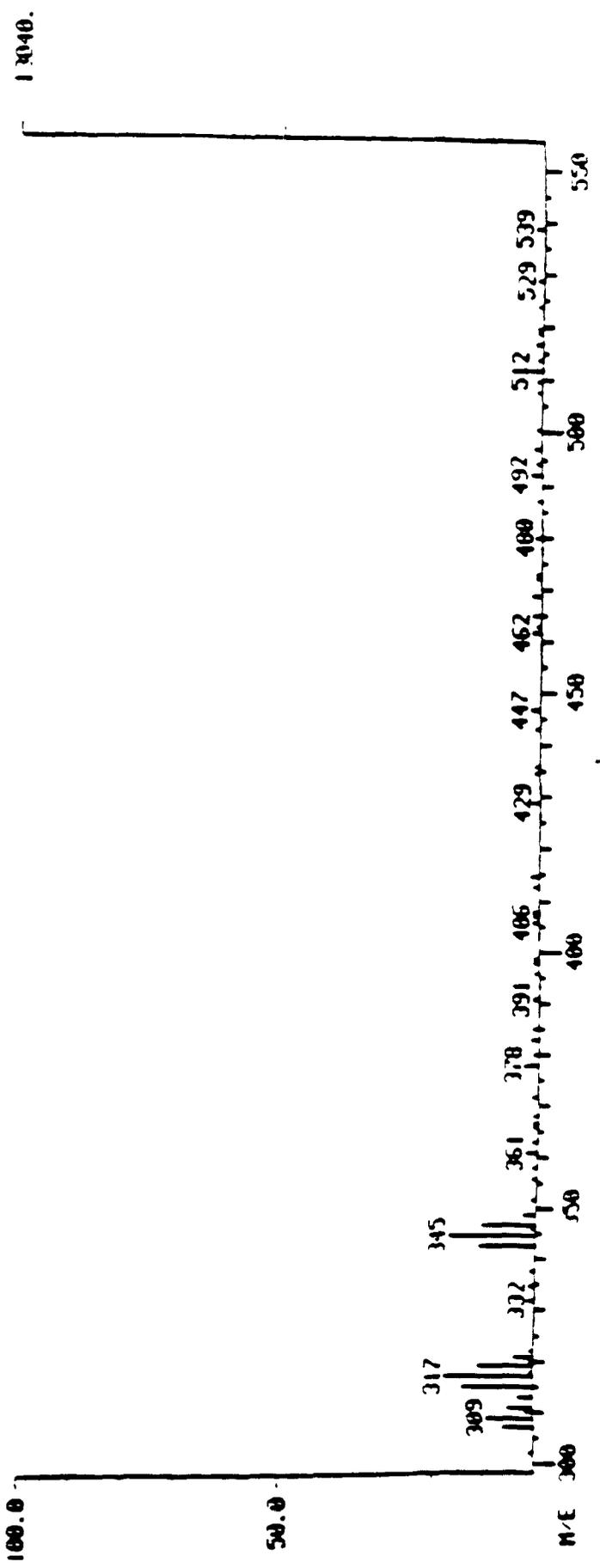
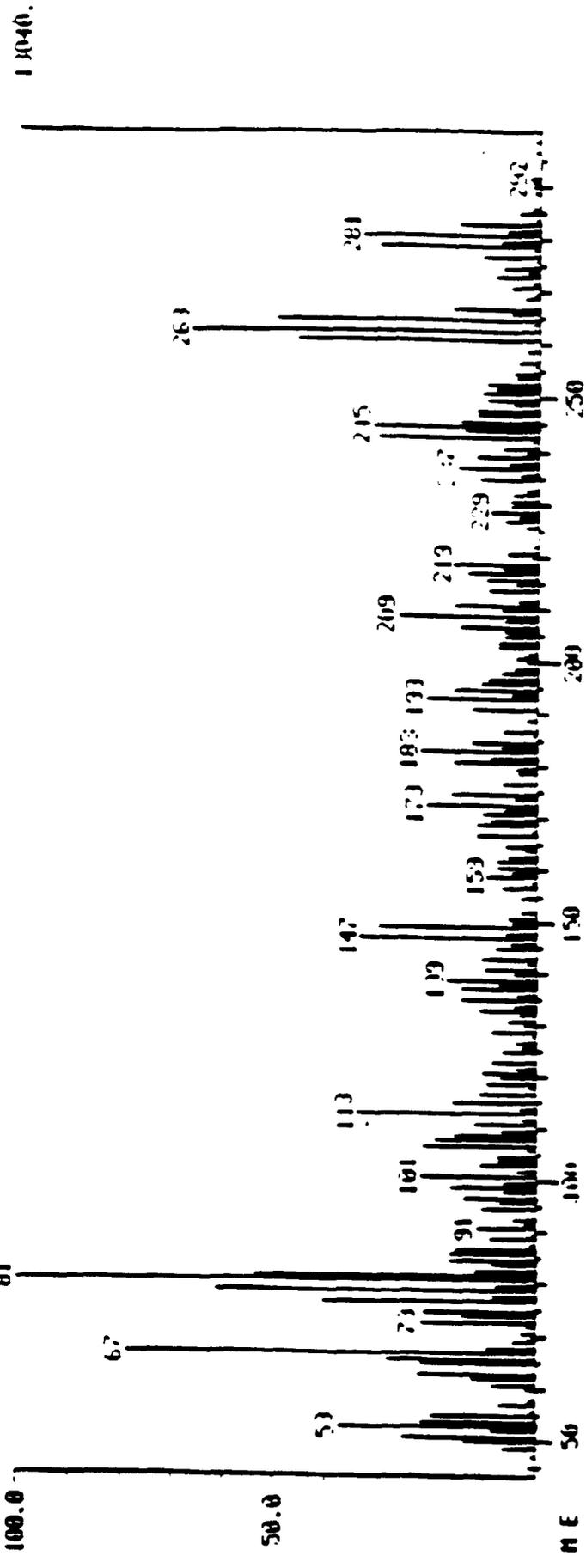
18912.

MFC 1100 21 14 54 135 76 311
 02254 10 02266 SUMMED - 02211 10 02248 - 02269 10 02275 01.01

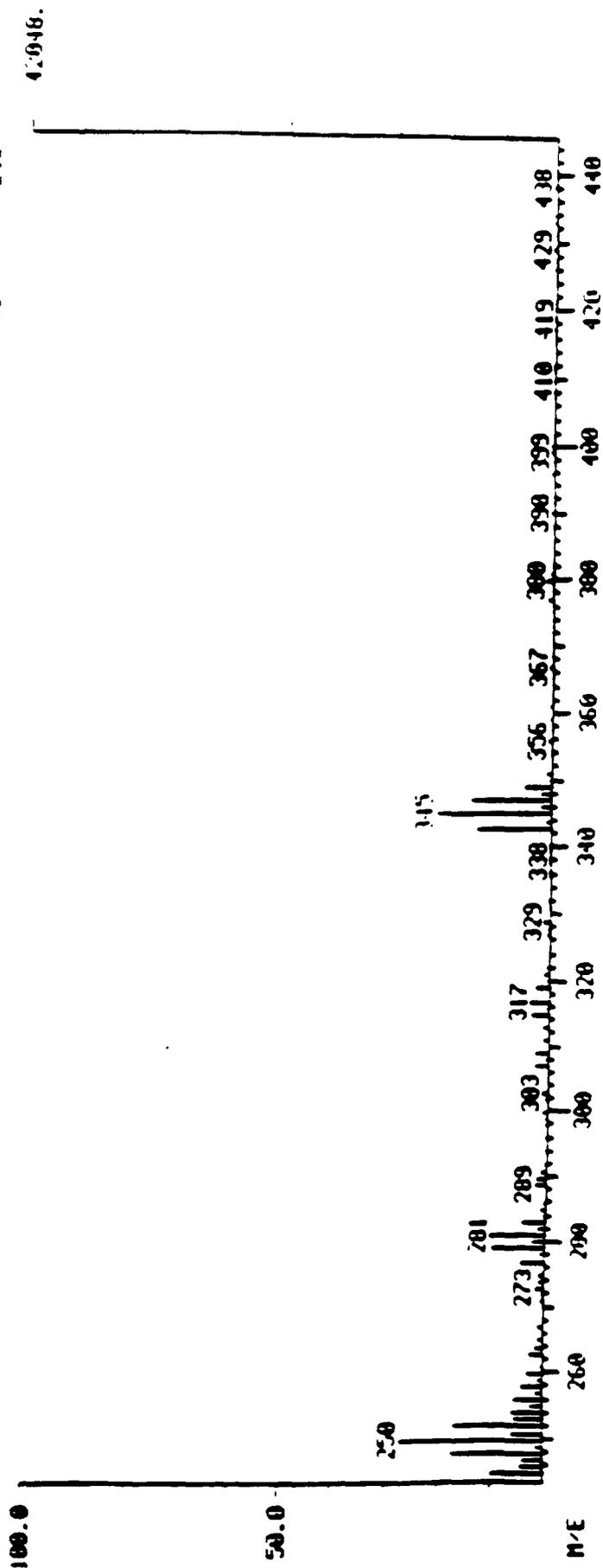
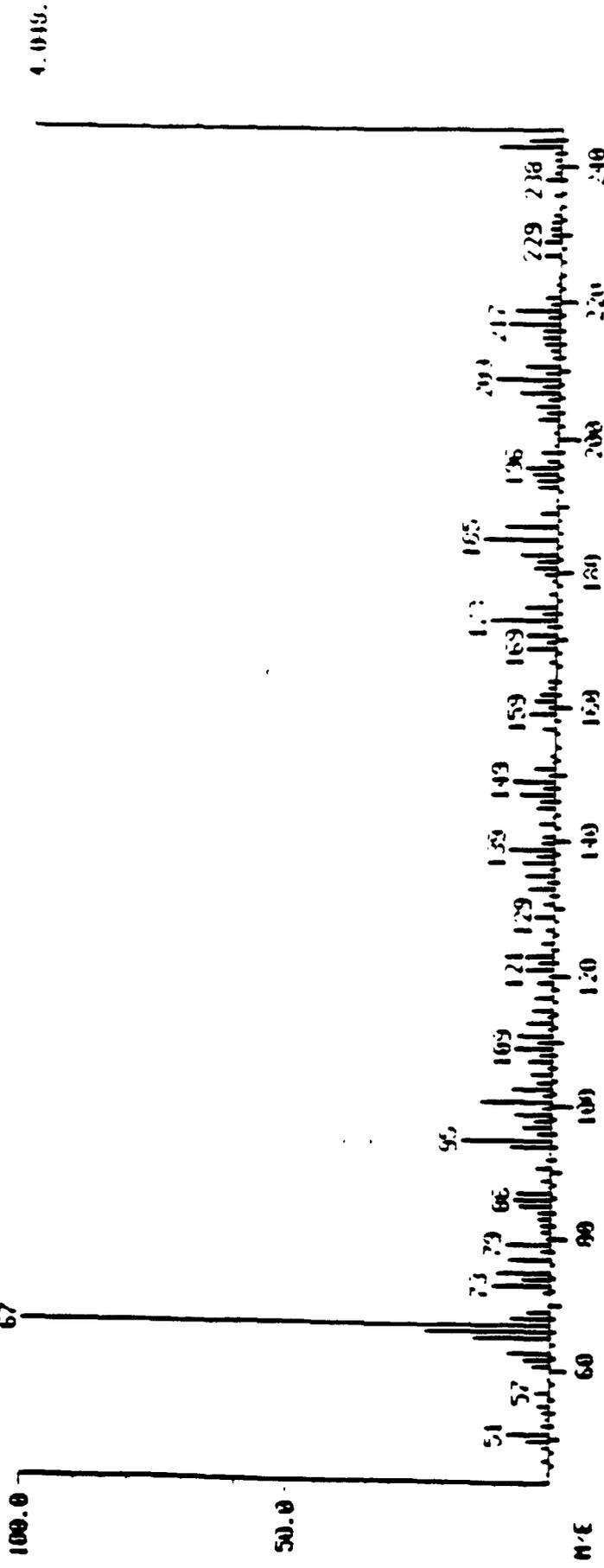


46
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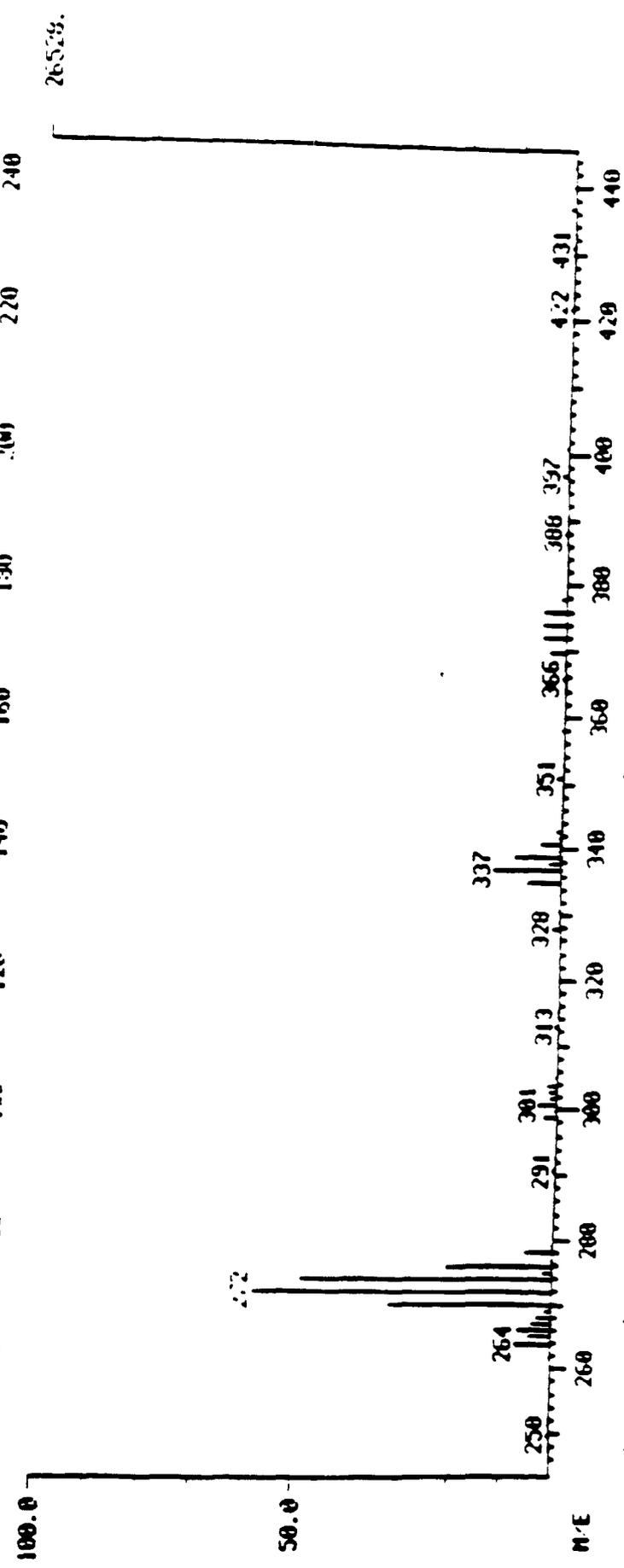
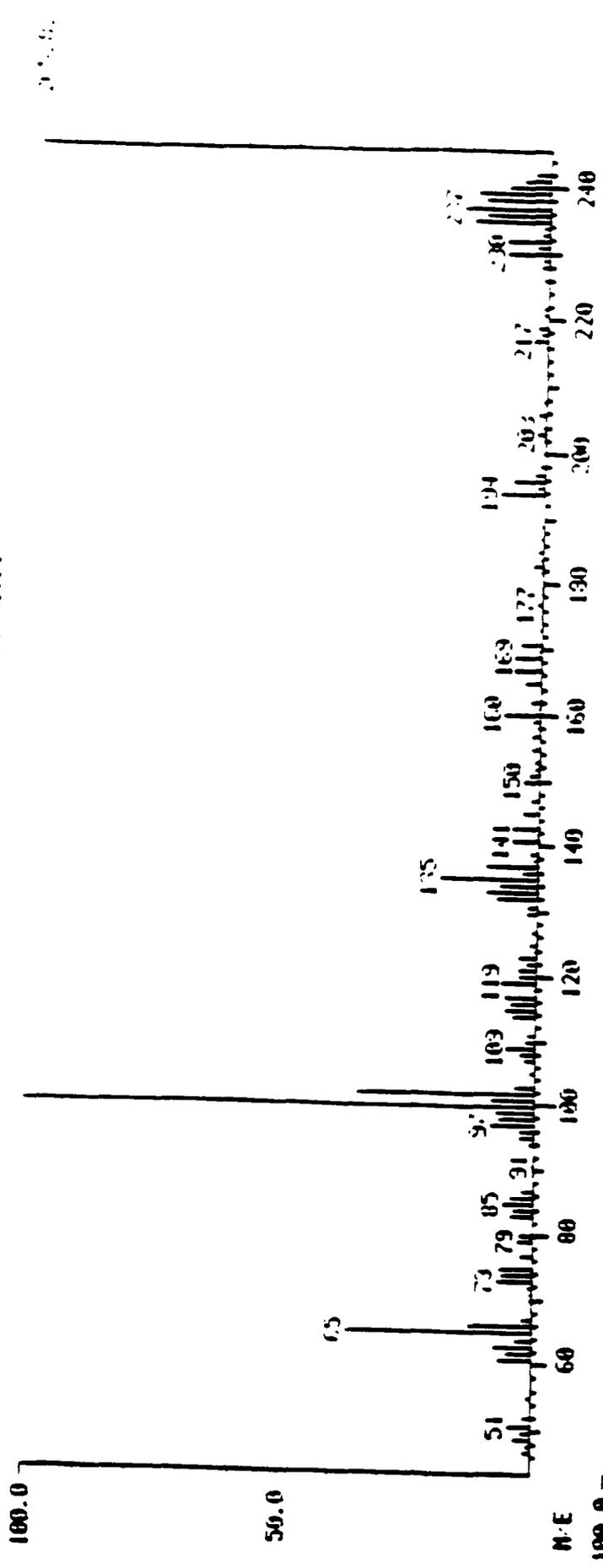
Sample: 41105 64 P.H.E. 05.0000 51111155 10 7 e 10000 EU
 02222 10 02229 500000 - 02316 10 02220 - 02332 10 02226 X1.01



Sid# 411... 02310 TO 02318 SAMPLED - 02300 TO 02306 - 02321 TO 02327 21.61
 67



411
01772 TO 01781 SUMMED = 01772 TO 01772 = 01772 TO 01781
01772 TO 01781 SUMMED = 01772 TO 01772 = 01772 TO 01781



50000 - 41000 2.000 01 011 000 011. 01. 0000 000
 01500 01 0.0002 500000 - 01505 10 01399 - 02005 10 02005 X1.01

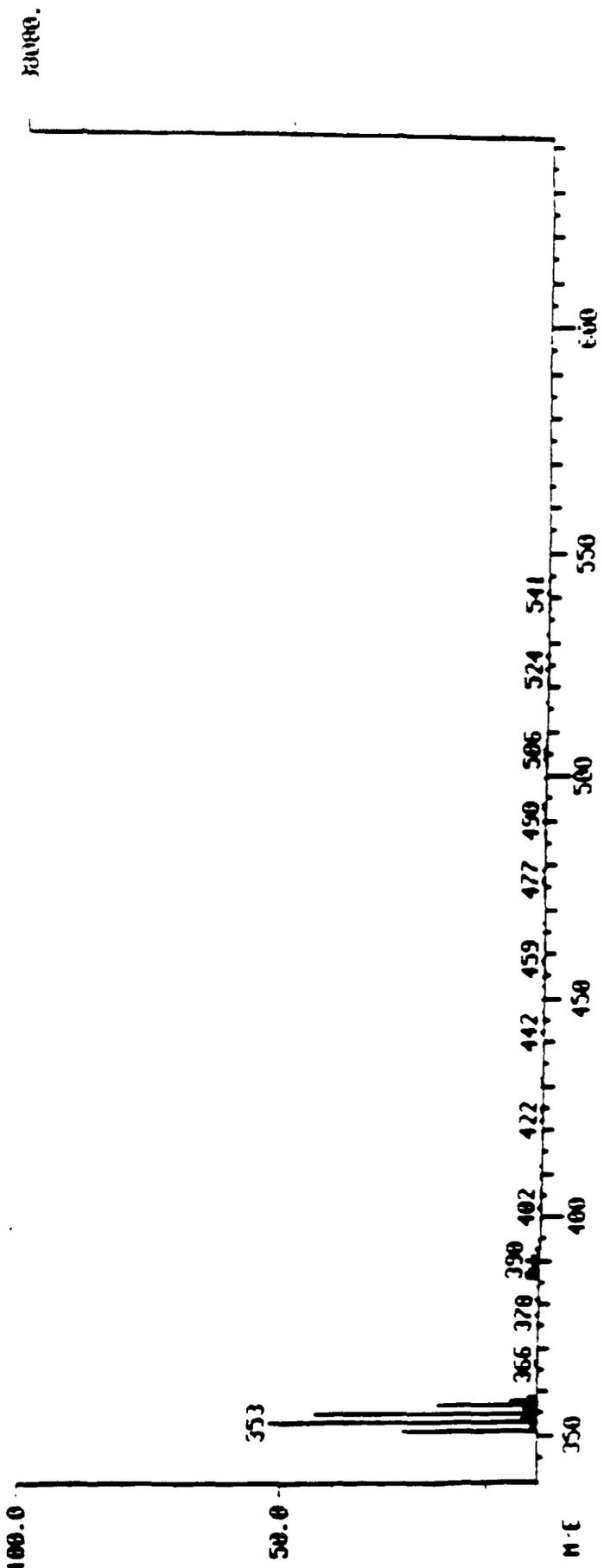
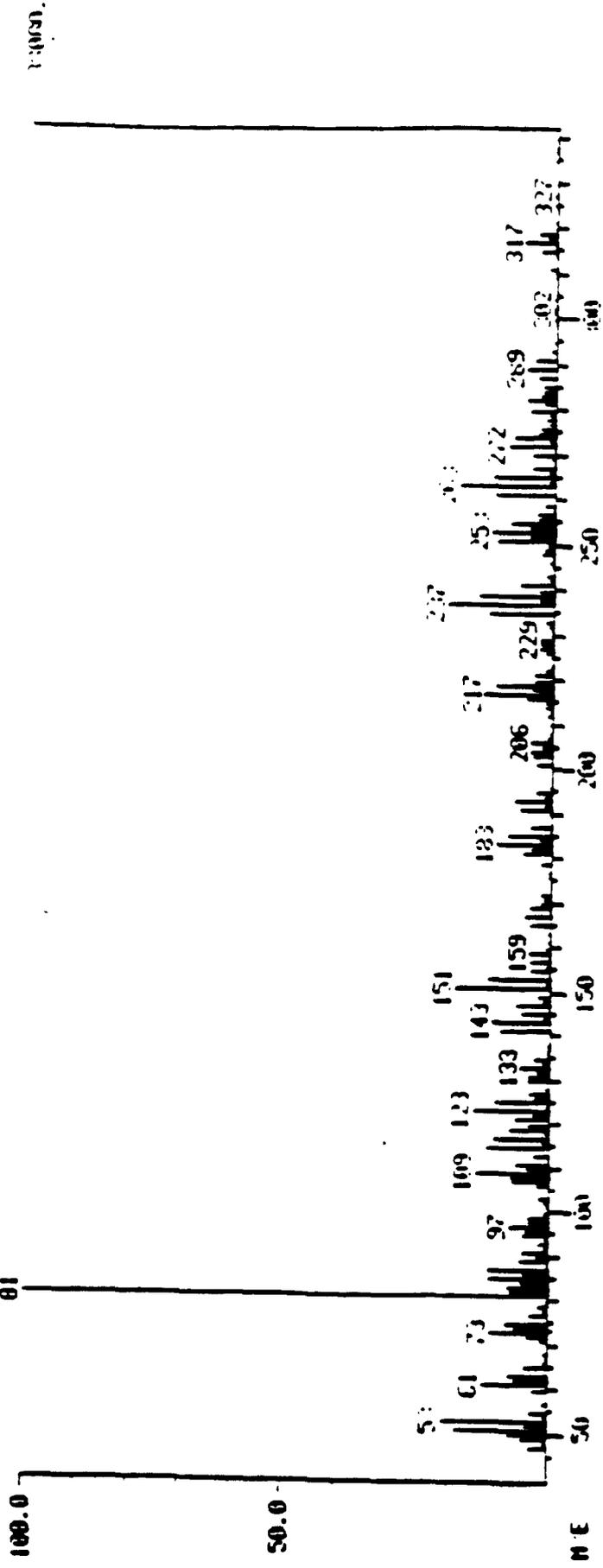


FIGURE A2.2. 11 MASS SPECTRUM OF HEPTACHLOR EPOXIDE

MASS SPECTRUM
 01/07/86 14:50:00 + 22:09
 SAMPLE: 41100-02-2 MIX 03 2.0ML SPLITLESS 10-7 @ 1000 EU
 CONDS.: EI,GC/MS 30MX.25MM SPB5 CH4(50) I(300) 60(1)-30004(4)
 01325 10 01334 SUMMED - 01339 10 01350 X1.00

DATA: 553417 01329
 CALI: 553510CAL45 04
 BASE M/Z: 120
 PIC: 127744.

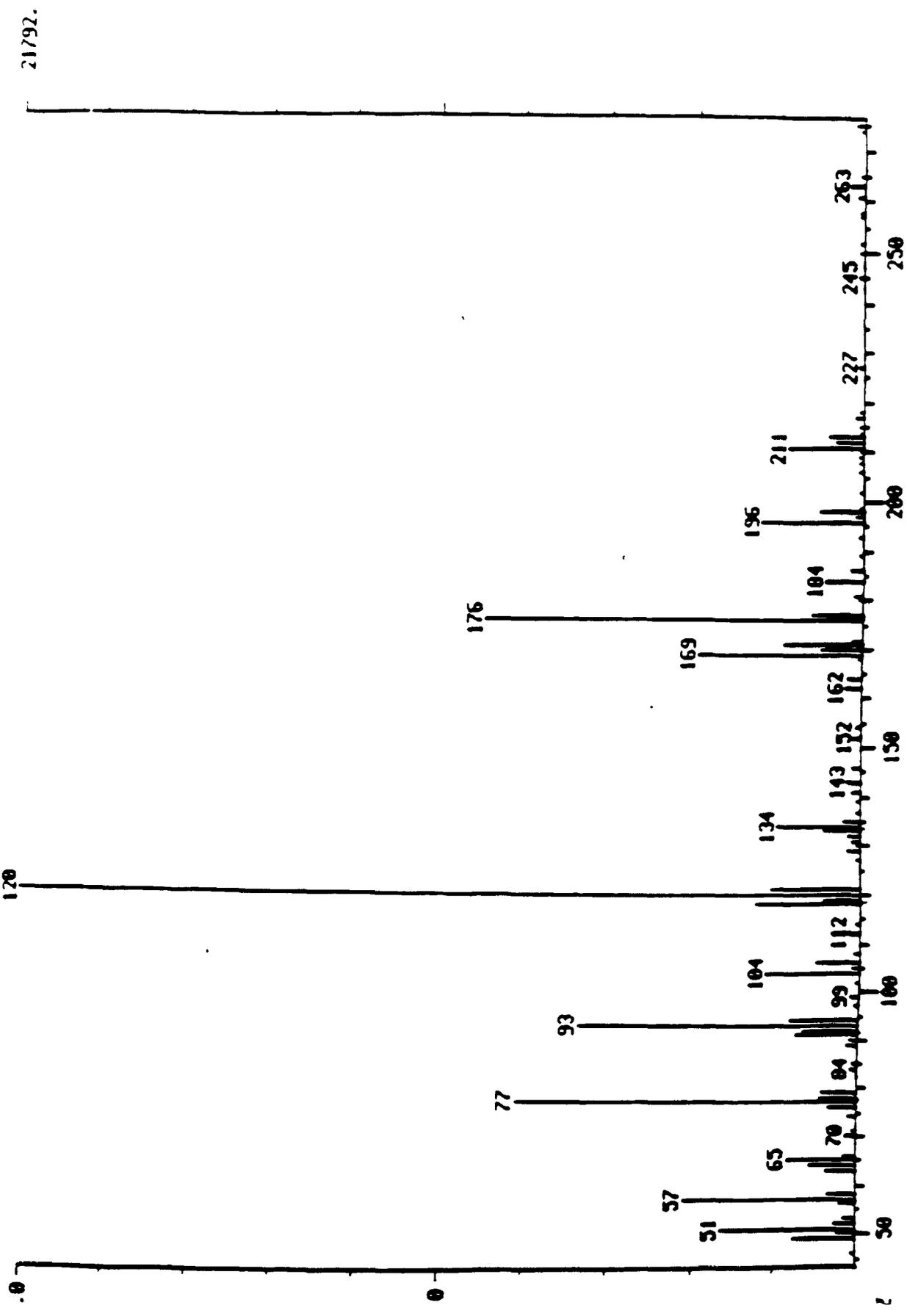


FIGURE A102. EI MASS SPECTRUM OF PROPACHLOR

411 102 01 14 112 17 (M)
 0.026 10 2044 SURFED - 02823 10 2834 - 02848 10 2853 21.91
 103

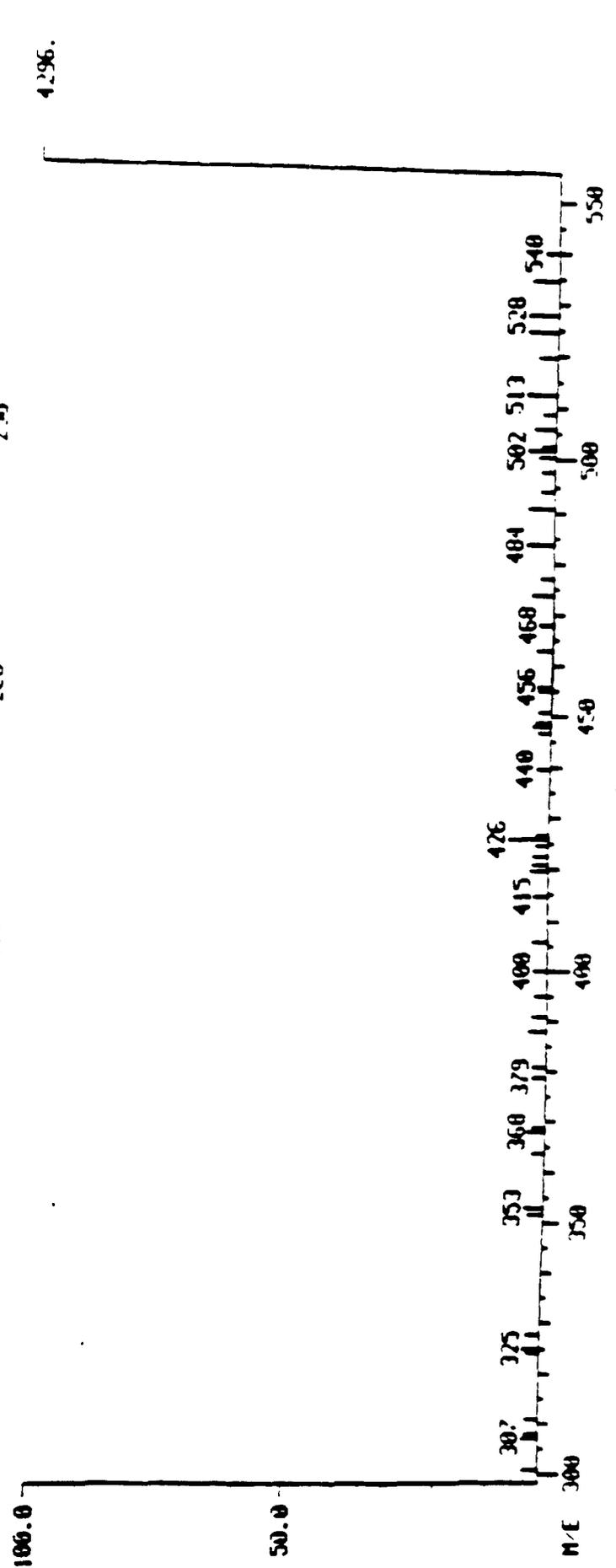
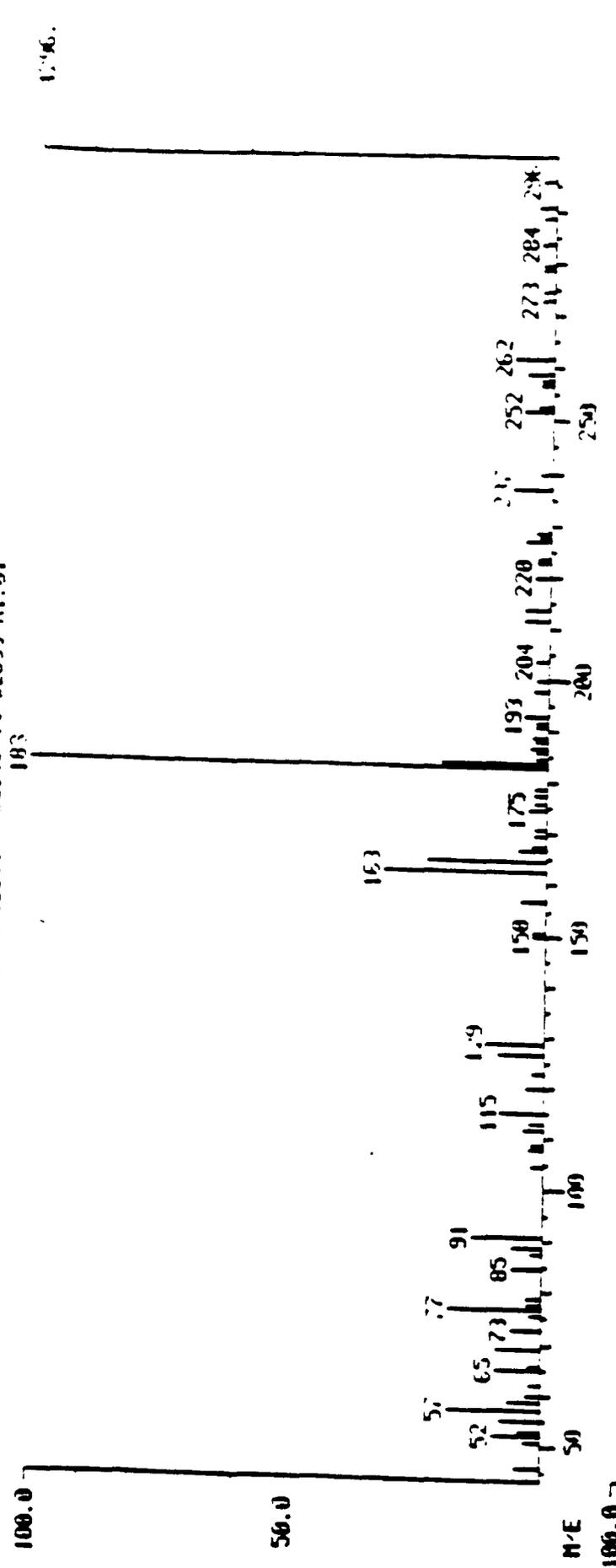
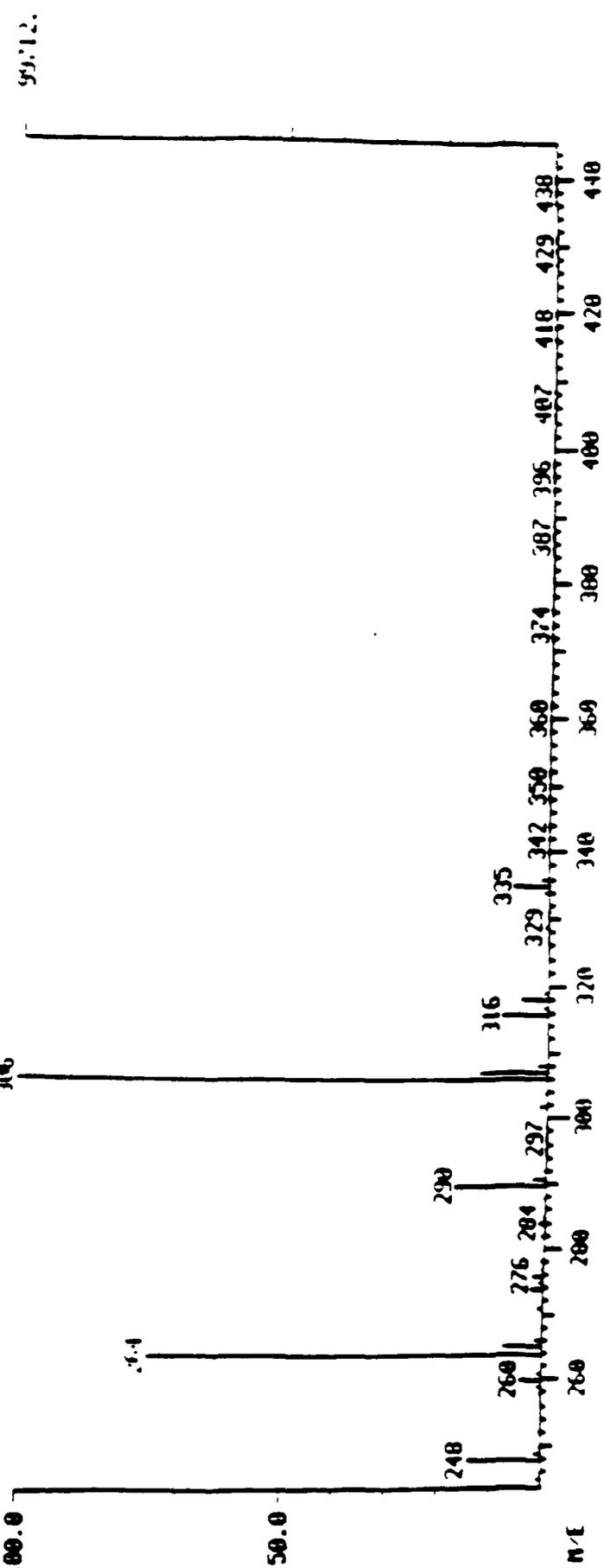
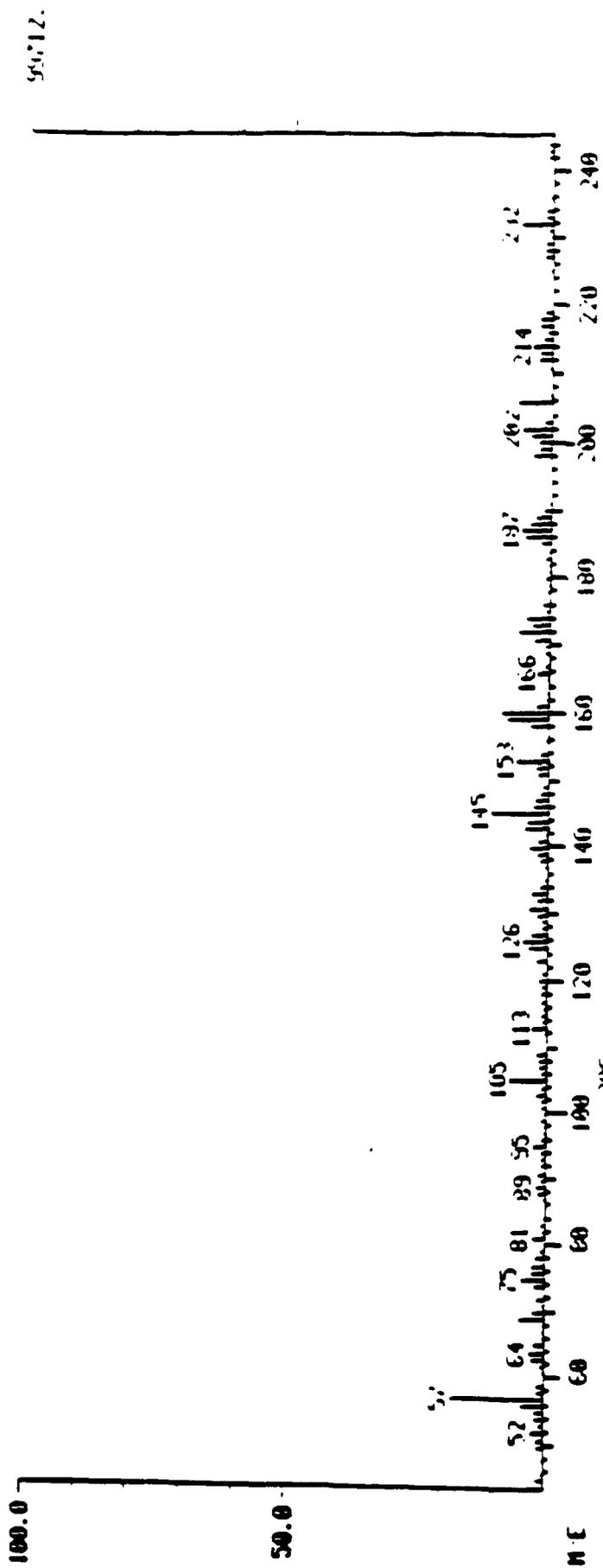


FIGURE A10. FT-MASS SPECTRUM OF ...

01468 TO 01477 SUMMED - 01463 TO 01466 - 01478 TO 01482 01.01
 01468 TO 01477 SUMMED - 01463 TO 01466 - 01478 TO 01482 01.01



APPENDIX C
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:

$$X_1 < X_2 < X_3 < \dots < X_{n-1} < X_n$$

- 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 tabulated risk. For this 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

<u>Ratio</u>	<u>n</u>	Risk of False Rejection			
		<u>0.5%</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>
r_{10}	3	0.994	0.988	0.941	0.806
	4	0.926	0.889	0.765	0.679
	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
r_{11}	8	0.725	0.683	0.554	0.479
	9	0.677	0.635	0.512	0.441
	10	0.639	0.597	0.477	0.409
r_{21}	11	0.713	0.679	0.576	0.517
	12	0.675	0.642	0.546	0.490
	13	0.649	0.615	0.521	0.467
r_{22}	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
	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.

APPENDIX D

STANDARD OPERATING PROCEDURE FOR MANUAL DATA ENTRY

Summary Of NPS Data Package

The information generated by NPS samples is combined into data sets. A set is defined as a group of samples which have been extracted on the same day. These samples are spiked with a surrogate (DCB) and an internal standard. The data from these samples is entered into five separate spreadsheets in the 2020 software package and analyzed according to the following plan.

A) Calibration Curve

A three point calibration curve is obtained for each individual set by analyzing three different concentrations of a group "A" pesticide stock solution and three different concentrations of a group "B" pesticide stock solution. [The reason for having two stock solutions is that some of the pesticides would co-elute if analyzed together. There are fourteen individual pesticides in the group "A" mix and fifteen in the group "B".

The information generated by these chromatograms (date, time, retention of compounds, peak areas, etc...) is entered into a spreadsheet in the 2020 software [pg 3] named CRVXX-X where XX-X is the month and day the curve was run. From this information, the 2020 software calculates a calibration curve for each compound along with other statistical data which includes the correlation coefficient. The correlation coefficient must be > 0.995 according to the QA plan. Otherwise, a new calibration curve must be prepared (see project manager).

B) Instrument Quality Control Check (IQCC)

The IQCC is a standard pesticide solution which monitors column performance, chromatography performance and sensitivity. The IQCC must be run prior to the analysis of each set and every 24 hours during the analysis of a set. The IQCC contains four pesticides that are used to monitor the above QC parameters. These pesticides are Heptachlor Epoxide, DCPA, Chlorothalonil and delta-BHC. The data from the IQCC chromatogram is entered into a spreadsheet [see pgs 11-12] named IQXX(month)-X(day).

Heptachlor Epoxide evaluates the sensitivity and must have a signal to noise ratio greater than 3. DCPA evaluates the peak symmetry factor (PSF) and peak gaussian factor (PGF). The PSF and PGF must both be > 0.8 and < 1.15 to satisfy QC requirements. Chlorothalonil and delta-BHC evaluate the peak resolution and must be > 0.50 . All of the above criteria must be satisfied. Otherwise, the analysis must be stopped and the problem rectified (see project manager).

C) Continuing Calibration (CC)

The CC is one of the standard pesticide solutions used to make the calibration curve. A CC must be run every 12 hours to verify the calibration curve. If the response for any analyte varies from the predicted response more than 20%, a new calibration curve must be prepared.

The information from the chromatogram is entered into the 2020 spreadsheet [see pgs 13-14] named CCXX-X.

D) Internal Standard Summary Table

In order for a sample, IQCC, CC, etc., to meet QC requirements, the Internal Standard (I.S.) area, for that run, must be within 20% of the average area of the standards used to make the calibration curve for that set. data from the chromatogram is entered into the 2020 spreadsheet [see pgs 15-16] named ISXX-X.

E) Warning and Control Limit Flag Table

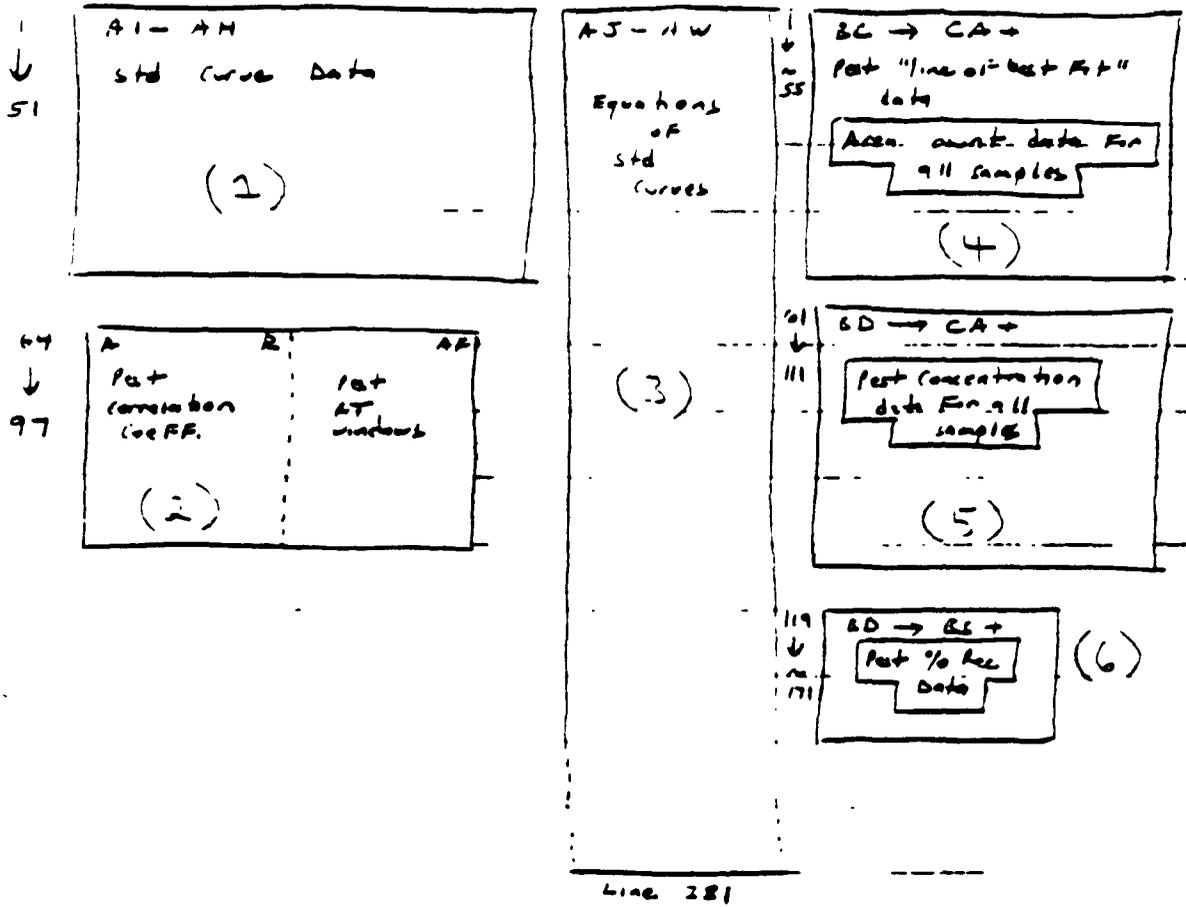
For every spiked sample, the percent recovery of each analyte must be calculated to see if the recovery is between the allowable control limits (Control limits are generated by using data from previous sets and the Dixon's Test). In order to meet QC requirements, each sample may have more than 15% of the analytes outside the control limits.

The 2020 spreadsheet [see pgs 17-18] used to calculate these recoveries is named FLAXX-X. The data entered into this spreadsheet is ~~extracted~~ extracted from the percent recovery portion of the CRVXX-X spreadsheet. *EXTRACTED*

GENERAL LAYOUT OF CURVE SPREADSHEET

- 1) **STANDARD CURVE DATA**
REFER TO DIAGRAMS LABELED (1) ON PAGES 4 AND 5.
IN THIS SECTION OF THE SPREADSHEET, DATA FROM THE CHROMATOGRAMS USED TO GENERATE THE CALIBRATION CURVE IS ENTERED.
SEE PAGE 9 FOR INSTRUCTIONS ON ENTERING DATA INTO THIS SECTION.
- 2) **CORRELATION COEFFICIENTS & RETENTION TIME WINDOWS**
REFER TO DIAGRAM LABELED (2) ON PAGE 4.
THIS SECTION OF THE SPREADSHEET AUTOMATICALLY CALCULATES STATISTICAL DATA SUCH AS CORRELATION COEFFICIENT, RETENTION TIME WINDOWS AND SLOPE.
- 3) **EQUATIONS OF STANDARD CALIBRATION CURVES**
REFER TO DIAGRAM LABELED (3) ON PAGE 4.
IN THIS SECTION, THE DATA THAT WAS ENTERED INTO THE STANDARD CURVE FROM STEP 1 IS USED TO GENERATE THE STANDARD CALIBRATION CURVES FOR EACH ANALYTE. NO DATA IS ENTERED IN THIS SECTION BY THE USER.
- 4) **SAMPLE PEAK AREAS**
REFER TO DIAGRAMS LABELED (4) ON PAGES 4 AND 6.
THIS PART OF THE SPREADSHEET IS USED TO ENTER THE PEAK AREAS OF THE PESTICIDES THAT ARE PRESENT IN EACH SAMPLE.
SEE PAGE 9 FOR INSTRUCTIONS ON ENTERING DATA INTO THIS SECTION.
- 5) **CONCENTRATION SECTION**
REFER TO DIAGRAMS LABELED (5) ON PAGES 4 AND 7.
IN THIS SECTION OF THE SPREADSHEET, THE CONCENTRATION OF EACH PESTICIDE THAT WAS ENTERED IN STEP 4 IS CALCULATED AUTOMATICALLY BY THE SOFTWARE.
SEE PAGE 9 FOR INSTRUCTIONS ON ENTERING DATA INTO THIS SECTION.
- 6) **PERCENT RECOVERY SECTION**
REFER TO DIAGRAMS LABELED (6) ON PAGES 4 AND 8.
THIS PORTION OF THE SPREADSHEET TAKES THE CONCENTRATIONS (FROM STEP 4) OF SPIKED SAMPLES ONLY AND DIVIDES THEM BY THE THEORETICAL CONCENTRATION TO YIELD A PERCENT RECOVERY OF EACH ANALYTE.
SEE PAGE 9 FOR INSTRUCTIONS ON ENTERING DATA INTO THIS SECTION.

General CPU x-xx structure



METHOD
 CONF: J08
 Config No: 1 729 001
 Set 13

Drinking Water Pesticide Analysis

Column SRS

Analysis Date: 0 30 9 31 00

Analyst: E/ESP

HP5890 Lymphab prep 65

pg 1

NO	Compounds	-1-			-2-			-3-			-4-			-5-		
		RT	Area (x10 ³)	ng/ml conc.	RT	Area (x10 ³)	ng/ml conc.	RT	Area (x10 ³)	ng/ml conc.	RT	Area (x10 ³)	ng/ml conc.	RT	Area (x10 ³)	ng/ml conc.
	Chlorpyrifos	35.08	67616	100	35.1	46002	100	35.08	40223	100	35.11	39446	100	35.09	42001	100
	Propachlor	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Chlorfenthion	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Alar	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Imazalil	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Endosulfan I	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Endosulfan II	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Endrin aldehyde	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	PEP Permethrin	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	DDA (aux)	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	PCOM (1.5.1) ..	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Ethionazole	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Tiludinalin	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Permethrin	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Deltamethrin	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	DDA	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Gamma-Chlordane	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Alpha-Chlordane	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	P'-DDD	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Chlorobenzilate	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	P,p'-DDD	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Endosulfan Sulfate	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	Permethrin	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	DDA (aux)	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300
	PCOM (1.5.1) ..	35.08	5169	5000	35.1	5590	1500	35.08	791.5	300	35.11	1976	300	35.09	1976	300

21 49 23 01

02:46 04 00

19:20/20:34

05:18 06 29

00:17-01-12

5

(2)

(4)

Contract No: 3-729-001
SET 12
Analysis Date: 9/2-9/6/88

CRV8-30B

Drinking Water

Pesticide Analysis
HP5890 Logbook page:

AREAS X10⁻³

Analyst: EF/EDP

Column: SPB5

NO.	Compounds	Cort Coeff	Int	Y	Slope	SAMPLE		PC3693		PC3694		NA06993A		NA06994		NA07
						OC3692 (M/B)	(LCS A)	(LCS B)	(F/S)	(SPIKE A)	(F/S)	(SPIKE A)				
1	Chlormep	0.998	0.0185	0.000045	0	0	7189.2	10.637	0	18.723	0	3784.1	0	0	0	14
2	Propachlor	0.999	0.0179	0.000874	34.656	0	6247.5	38.247	0	0	0	3040.8	0	0	0	14
3	alpha-BHC	0.999	0.0138	0.000776	0	0	5908	0	0	0	0	1919.8	0	0	0	14
4	gamma-BHC	1.000	0.0061	0.000644	0	0	4116.3	0	0	0	0	1428.7	0	0	0	14
5	Chlorthalonil	1.000	0.0096	0.000701	0	0	2357.3	0	0	0	0	1015.9	0	0	0	72
6	Aldrin	1.000	0.0014	0.000465	0	0	3784.5	0	0	26.032	0	1406.3	0	0	0	72
7	Hepta. epoxide	1.000	0.0037	0.000451	0	0	3055.1	0	0	0	0	1270.1	0	0	0	72
8	Endosulfan I	0.999	0.0034	0.000368	0	0	2529.8	0	0	0	0	1018.1	0	0	0	72
9	Diieldrin	1.000	0.0075	0.000386	0	0	4758.3	0	0	0	0	1873.5	0	0	0	72
10	Endrin	1.000	0.0074	0.000386	0	0	4614.2	0	0	0	0	1873.5	0	0	0	72
11	Endosulfan II	1.000	0.0020	0.000294	0	0	3824.4	0	0	0	0	1595.6	0	0	0	72
12	Endrin aldehyde	1.000	0.0020	0.000294	0	0	3824.4	0	0	0	0	1595.6	0	0	0	72
13	p,p'-DDE	0.999	0.0107	0.000307	0	0	3343.7	0	0	0	0	1213.3	0	0	0	14
14	cis-Permethrin	1.000	0.0013	0.000021	0	0	2181.3	0	0	0	0	766.38	0	0	0	14
15	DCB (sur)	0.992	0.0025	0.000112	1282.1	0	1306.2	1385	0	1212.6	0	1251.4	0	0	0	14
PCNB (I.S.) **																
16	Ethridiazole	1.000	0.0046	0.000485	15.84	0	20.27	10516	16.715	0	36.505	0	0	0	0	3
17	Trifluralin	1.000	0.0062	0.000281	0	0	0	6694.3	0	0	0	1919.8	0	0	0	24
18	Hexachlorobenz	0.999	0.0291	0.000808	233.54	0	264.69	5382.8	244.54	0	255.12	0	0	0	0	24
19	beta-BHC	1.000	0.0039	0.000366	0	0	0	3094.5	0	0	0	0	0	0	0	24
20	delta-BHC	0.999	0.0037	0.000658	0	0	0	3142.2	0	0	0	0	0	0	0	24
21	Heptachlor	1.000	0.0161	0.000731	0	0	0	6434.4	0	0	0	0	0	0	0	24
22	DCPA	1.000	0.0024	0.000441	0	0	0	4239.2	0	0	0	0	0	0	0	24
23	gamma-Chlordane	1.000	0.0017	0.000501	0	0	0	4235.2	0	0	0	0	0	0	0	24
24	alpha-Chlordane	1.000	0.0042	0.000494	0	0	0	4211.1	0	0	0	0	0	0	0	24
25	P,p'-DDE	0.998	0.0096	0.000248	0	0	0	4981.6	0	0	0	0	0	0	0	24
26	Chlorbenzilate	0.999	0.0089	0.000246	0	0	28.67	2752	0	0	12.729	0	0	0	0	24
27	P,p'-DDD	0.999	0.0089	0.000246	0	0	0	2752	0	0	0	0	0	0	0	24
28	Endo. sulfate	1.000	0.0032	0.000285	0	0	0	4033.4	0	0	0	0	0	0	0	24
29	Methoxychlor	1.000	0.0001	0.000194	0	0	0	3905.2	0	0	0	0	0	0	0	24
30	trans-Permethrin	1.000	0.0001	0.000022	0	0	0	4707.8	0	0	0	0	0	0	0	24
31	DCB (sur)	0.998	0.0002	0.000117	1282.1	0	1306.2	1385	0	1212.6	0	1251.4	0	0	0	149
PCNB (I.S.) **																
		NA	NA	NA	NA	NA	37369	40124	37687	37774	38908	37				

LD

LD

6

Contract No: 3-729-001
 set 12
 Analysis Date: 9/2-9/6/88

Drinking Water Pesticide Analysis
 CRV8-308 Analyst: EF/EDP
 HP5890 Logbook page: 66
 CONCENTRATIONS UG/L Column: SPB5

NO.	Compounds	SAMPLE OC3692 (M/B)	OC3693 (LCS A)	OC3694 (LCS B)	NA06993A (F/S)	NA06994 (SPIKE AI)	NA0701 (F/
1	Chlorob	-2.05	17.83	-2.05	-2.05	8.74	-1.0
2	Propachlor	-1.15	16.67	-1.12	-1.10	7.79	-1.0
3	alpha-BHC	0.11	0.94	0.11	0.10	0.38	0.0
4	gamma-BHC	0.09	0.75	0.09	0.09	0.33	0.0
5	Chlorthalonil	0.05	0.56	0.05	0.05	0.29	0.0
6	Aldrin	0.07	0.73	0.07	0.07	0.38	0.0
7	Hepta. epoxide	0.01	0.92	0.01	0.02	0.40	0.0
8	Endosulfan I	0.04	0.85	0.04	0.04	0.33	0.0
9	Endosulfan II	0.04	0.74	0.04	0.04	0.33	0.0
10	Dieldrin	0.10	1.67	0.10	0.10	0.76	0.0
11	Endosulfan II	0.10	1.63	0.10	0.10	0.84	0.0
12	Endrin aldehyde	0.03	1.65	0.03	0.03	1.13	0.0
13	P,p'-DDT	0.17	2.18	0.17	0.17	0.96	0.0
14	Cis-permethrin	0.31	12.53	0.31	0.31	4.28	0.0
15	DCB (surt)	1.42	1.34	1.53	1.32	1.32	1.0
REC	DCBTRUE VAL-	1.7					
16	Ethridiazole	0.05	0.05	2.93	0.05	0.06	0.0
17	Trifluralin	-0.11	-0.11	3.05	-0.11	-0.11	0.0
18	Hexachlorobenz	-0.14	-0.14	0.70	-0.14	-0.14	0.0
19	beta-BHC	0.05	0.05	1.18	0.05	0.05	0.0
20	delta-BHC	0.12	0.12	0.76	0.12	0.12	0.0
21	Heptachlor	0.03	0.03	1.19	0.03	0.03	0.0
22	DCPA	0.03	0.03	1.30	0.03	0.03	0.0
23	gamma-Chlordane	0.02	0.02	1.14	0.02	0.02	0.0
24	alpha-Chlordane	0.02	0.02	0.88	0.02	0.02	0.0
25	P,p'-DDE	0.06	0.06	0.65	0.06	0.06	0.0
26	Chlordanzilate	-1.73	-1.73	1.56	-1.73	-1.73	0.0
27	P,p'-DDD	0.18	0.20	1.94	0.18	0.19	0.0
28	Endo. sulfate	0.06	0.06	1.98	0.06	0.06	0.0
29	Methoxychlor	0.00	0.00	4.98	0.00	0.00	0.0
30	trans-permethrin	0.00	0.00	28.60	0.00	0.00	0.0
31	DCB (surt)	-0.01	-0.01		-0.01	-0.01	0.0

\$- P193-1 OR P194-1 USED. *- P193-2 OR P194-2 USED. #- P193-3 OR P194-3 USED

SET 12
Analysis Date: 9/2-9/6/88

PERCENT RECOVERY

21/10/11 L 1 (6)

NO.	Compounds	LCS SPIKE		OC3694 (LCS A)		NA06994 (SPIKE A1)		NA07015 (SPIKE A0)		NA07022 (T/S 0)		NA07023 (T/S 0 D)	
		A2	B2	(LCS B)	(LCS B)	(T/S 0)	(B2)	(VIAL)	(VIAL)	(T/S 0)	(B2)	(T/S 0)	(A2)
1	Chlorobp	1.4		127.33		124.02		113.37		91.14		91.07	
2	Propachlor	1.3		128.23		119.82		124.23		108.34		107.23	
3	alpha-BHC	1.3		78.12		76.12		97.19		99.15		98.23	
4	gamma-BHC	0.85		88.30		86.68		119.19		112.87		111.89	
5	Chlorthalonil	1.1		46.67		46.33		67.06		63.33		63.33	
6	Aldrin	1.1		60.99		63.33		74.30		93.49		92.92	
7	Hepta. epoxide	1.1		76.87		74.41		91.16		95.64		93.92	
8	Endosulfan I	1.1		70.78		64.62		101.11		92.15		91.92	
9	Endosulfan II	1.1		61.42		60.57		88.54		92.49		91.92	
10	Endrin	1.1		66.12		60.39		84.63		95.20		92.44	
11	Endrin aldehyde	2.2		66.12		58.39		84.63		97.44		92.44	
12	p,p'-DDT	1.1		72.67		71.58		78.69		85.93		85.93	
13	cis-Permethrin	1.1		69.61		67.72		100.24		136.48		136.48	
14	DCB (surf)	1.7		78.74		77.72		105.56		102.09		101.37	
15													
16	Ethridiazole	3.6		81.26		68.04		2.2		16.30		15.10	
17	Trifluralin	4.4		76.12		63.76		2.4		15.65		15.65	
18	Hexachlorobenz	0.9		78.12		69.49		0.5		12.52		11.18	
19	beta-BHC	1.1		69.13		66.89		0.6		11.18		11.18	
20	delta-BHC	1.1		63.12		66.22		0.6		11.18		11.18	
21	Heptachlor	1.1		65.31		64.78		1.1		12.43		12.43	
22	DCPA	1.1		65.18		57.10		0.9		12.51		12.51	
23	gamma-Chlordane	1.8		63.28		55.67		0.9		11.46		11.46	
24	alpha-Chlordane	1.1		60.53		47.37		0.8		11.63		11.63	
25	P,p'-DDE	1.1		51.90		47.37		0.8		11.63		11.63	
26	P,p'-DDD	1.1		38.29		33.88		1.7		11.69		11.69	
27	Chlorbenzilate	2.2		47.55		43.24		2.2		10.64		10.64	
28	Endo. sulfate	3.3		53.80		47.08		4.1		10.43		10.43	
29	Methoxychlor	9.5		50.82		43.98		6.6		9.72		9.72	
30	trans-Permethrin	5.5		52.82		47.08		4.1		9.72		9.72	
31	DCB (surf)	1.7		89.75		90.88		1.7		92.30		92.30	

OC 3694 AND NA07017 LAST SAMPLES SPIKED WITH PS70 VIAL WHICH HAD EXCESSIVE HEADSPACE. NA07018 FIRST SAMPLE SPIKED WITH NEWLY-DILUTED PS70 SEE DOCUMENTATION ACCOMPANYING PACKAGE

Curve Spreadsheet - Std Crv, Areas, Conc, Percent recoveries
All data is to be obtained from chromatograms

1) Standard Curve

- a) Bring cursor to A0 position by hitting "HOME" key. Bring cursor A-1 and replace test with set number being worked on.
- b) Bring cursor to C3 - replace XX with set number being worked on.
- c) Analysis date: enter range of dates for the standard curve.
- d) Enter the raw areas and retention times for the corresponding concentrations at top of each section. Only the A spike conc ID number is at the top of the columns. The B spikes are as follows

<u>A</u>	<u>B</u>
A028	A032
A029	A033
A030	A034

- e) Hit space bar to calc

2) Sample Peak Areas

- a) Move cursor to "HOME" then move to right until at block BC5. Edit and enter set # being worked on.
- b) Analysis date: Enter range of dates for samples in set being worked on.
- c) In block BG4 - enter curve # ie crv-set # being worked on.
- d) Analyst: Hit edit, end and enter JV/EDP
- e) Page: XX- replace XX with logbook page number for set being worked on.
- f) Go to block BD13, hit /,W,T,V this freezes the compounds so you can tell where you are entering areas.
- g) Go to BI9. Enter sample blank. All lines across for each sample number gets entered for M/B, LCSA & B this is QC ###, for all other samples it will be NAOXXX. IQ's and CC's are not entered here.
- h) Cell BI10 is for the sample type code. Refer to IS summary section for these codes.
- i) Enter heading info for all samples
- j) Enter raw areas for each sample

3) Concentration

- a) Go to BD65 - update set #, date, CRV, page #.
- b) Go to BI9, hit /, C, everything, . and highlight all the headings ie BI9-11 BJ9-11... Target range will be BI69 enter
- c) Go to BI69, hit space bar. The concentrations will be calculated

4) Percent Recovery

- a) The percent recoveries are only calcd for spike samples. Any file samples are going to be ignored. Go to BI69. Hit /, copy, everything, highlight BI69..BI71. Target range BJ123. enter
- b) Go to BK69 and repeat above step

- c) Next go down the line. Copy headings for A spikes next to the CSA and B spikes down the line from LCSB
- d) Once headings are copied - go up to conc section for each spike sample - write the column letter the values are in ie LCSA - BJ, LCSA - BK NAO3714 - BM
- e) Go down to percent recovery BJ127, hit /, C, everything, range BJ127..BJ141 Target range BK127.. to last sample. Make sure:
1) the column letter corresponds with the sample #, if not edit to correct 2) The formula for DCB should be (column letter 87/SBI141)*100 across for each DCB (A and B)
- f) Repeat above steps for B spikes including 1 & 2. Hit space bar to calc
- g) Hit /, S, W, crv-set #, enter

Instrument Quality Control Check - (IQ)

All of the followed data is obtained from the chromatograms

- a.) For each IQCC, 6 measurements must be taken on the chromatogram:
 - 1.) Distance from start - d BHC peak (mm)
 - 2.) base width d BHC (mm)
 - 3.) Distance from start - chlorthal (mm)
 - 4.) base width - chlorthal (mm)
 - 5.) Width at 1/2 height - 1/2 width DCPA (mm)
 - 6.) Width at 1/10 height - 1/10 width DCPA (mm)
- b.) Hit "Home" key to get cursor located in cell A0. Key in set # the IQ was run with by hitting the edit key and typing set # in place of the X's. If there is more than one per set letter then A,B,C etc.
- c.) Analysis date:
hit "Edit" then "end" and enter the date the IQ was run on
- d.) Time:
repeat above step and enter time as appears on the chromatogram
- e.) Move cursor down to "W(1/2)=" line and over to 0.5. Enter 1/2 of the 1/2 peak width of DCPA (should always be 0.5)
- f.) Move cursor down. Enter 1/2 peak width of DCPA should be 1.0
- g.) Move cursor down. Enter 1/10 peak width of DCPA
- h.) Move cursor down. Enter start - chlorthal value
- i.) Move cursor down. Enter start - dBHC value
- j.) Move cursor down. Enter base width chlorthal value
- k.) Move cursor down. Enter base width dBHC value
- l.) Hit space bar to calculate
- m.) Move cursor to "RESULTS" column. Compare the results to the requirements. If any fall outside the set limits, make a note of IQ-set#, date, time, and report to project manager
- n.) Hit /, S, W
- o.) Entr IQ-set # & letter if needed
DU2:(EPA_workarea.users)IQ-set# & letter
hit enter

SAMPLE

INSTRUMENT QUALITY CONTROL CHECK

ANALYSIS DATE: 9/2/88

TIME: 14:29

TEST	ANALYTE	CONC. (UG/ML)	RESULTS	REQUIREMENTS
SENSITIVITY	HEPTACHLOR EPOXIDE	0.004	D	SAD3
CHROMATO. PERFORMANCE	DCEA	0.05	1.00	RSF > 0.8 AND < 1.15
			1.08	RF > 0.8 AND < 1.15
COLUMN PERFORMANCE	CHLOROTHALONIL	0.05	0.64	RESOLUTION > 0.50
	HCB-delta	0.04		

D- COMPOUND DETECTED

Lm

Continuing Calibration (CC)

All of the following data is obtained from the chromatograms

- a.) Hit "Home" key to get the cursor located in cell A0. Key in set # CC was run by hitting the edit key and typing in the set number. If there are more than one CC per set, label then as above with A, B, C, etc. to differentiate.
- b.) Contract No: 3-729-001 should be left alone
- c.) Calibration date: Find the appropriate concentration in the std curve data (ie same as the CC you are working on) Enter the month day and year by moving the cursor to the beginning of this cell and striking the "edit" key. Move th cursor to the right by hitting the "end" key and type in date.
- d.) Cont. cal date:
Enter month, day, and year as above
- e.) Laboratory: Clean Harbors
Leave as is
- f.) Time: (calibration)
In the first time cell from the top of the spreadsheet, enter the time as it appears on the chromatogram for the std curve conc.
- g.) Time:
Enter as above
- h.) Move cursor to line "MIX A & B-X" Hit "edit", "end" and replace "X" with code for concentration (i.e. 1b,3, 4b, L,M,H...) for both initial and daily columns
- i.) Calc the mean I.S. value for the A and B spike compounds from the std curve for the given concentration. Then enter the raw areas for each compound. Use the calc'd mean value for DCB.
- j.) repeat above step for daily cont. cal
- k.) hit space bar to calculate % difference
- l.) move cursor to percent difference column if any are over 20%, note sample #, compound and percent difference. Inform project manager
- m.) hit /,S,W
- n.) enter cc - (set # & letter if any) at end of
DU2:[EPA_workarea.users]cc-
the cc-# entered should be the same as cell A0

METHOD 2 - CONTINUING CALIBRATION CHECK

SAMPLE

Contract No: 3-729-001 SET 12

Laboratory: Clean Harbors

Calibration Date: 8/31/88

Time: 02:46/04:00

Cont. Cal. Date: 9-2-88

Time: 16:08/17:35

Method 2 Compound List	Initial	I.S.	Daily Conti	I.S.	Percent
	Calibration	Area*10 ⁻³	Calibration	Area*10 ⁻³	Difference
	Mix A & B-2	42950	Mix A & B-2	40248	
	AREA*10 ⁻³	RR*	AREA*10 ⁻³	RR*	%
1.) Chlorthal	3601.7	0.083857	3332.50	0.082799	1.3%
2.) Propachlor	2869.8	0.066817	2638.80	0.065563	1.9%
3.) alpha-BHC	2342.2	0.054533	2008.60	0.049905	8.5%
4.) gamma-BHC	2286.6	0.053238	1924.40	0.047813	10.2%
5.) Chlorothalonil	2413.5	0.056193	2129.00	0.052897	5.9%
6.) Aldrin	2278.1	0.053040	1859.90	0.046210	12.9%
7.) Heptachlor Epoxide	1875.8	0.043674	1516.30	0.037673	13.7%
8.) Endosulfan I	1770.8	0.041229	1397.90	0.034732	15.8%
9.) Dieldrin	1520.2	0.035394	1190.30	0.029574	16.4%
10.) Endrin	2660.4	0.061941	2036.80	0.050606	18.3%
11.) Endosulfan II	2811.9	0.065469	2147.90	0.053366	18.5%
12.) Endrin Aldehyde	2458.1	0.057231	1947.90	0.048397	15.4%
13.) p,p'-DDE	1758.9	0.038235	1297.40	0.032123	16.0% #
14.) cis-Permethrin	560.55	0.013051	454.68	0.011296	13.4%
15.) DDB	7314.8	0.170309	6888.60	0.171153	0.5%
16.) Ethion	3898	0.090756	4107.50	0.102054	12.4%
17.) Trifluralin	2988.5	0.069115	3043.90	0.075628	9.4%
18.) Heptachlorobenzene	9260.2	0.215604	9401.40	0.233586	8.3%
19.) beta-BHC	1213.4	0.028251	1140.70	0.028341	0.3%
20.) delta-BHC	1337.2	0.031133	1223.80	0.030406	2.3%
21.) Heptachlor	2778.7	0.064696	2725.90	0.067727	4.7%
22.) DDBA	1644.2	0.038281	1567.40	0.038943	1.7%
23.) gamma-Chlordan	1926.6	0.044856	1733.60	0.043072	4.0%
24.) alpha-Chlordan	1892	0.044051	1686.30	0.041897	4.9%
25.) p,p'-DDE	1018.2	0.023706	900.35	0.022370	5.6%
26.) Chlordanz-Late	1939.4	0.045154	1668.20	0.041448	8.2%
27.) p,p'-DDD	1216.3	0.028318	1044.40	0.025949	8.4%
28.) Endosulfan sulfate	2027.7	0.047210	1725.00	0.042859	9.2%
29.) p,p'-Methoxychlor	4336.5	0.100966	3532.00	0.087755	13.1%
30.) trans-Permethrin	478.89	0.011149	369.38	0.009177	17.7%

= Used individual I.S. area instead of average. (Initial: 46002, Continuing: 40388)

Am

Internal Standard Summary - IS

All of the following data is obtained from the chromatogram

- a.) Hit "Home" key to get cursor located in cell A0. Key in set # b worked on by hitting "Edit" key, "Home" key and replace X's with
- b.) Laboratory & Contract # stay the same
- c.) Enter "set number" by hitting "Edit" "End" and enter set # being on
- d.) The "I.S. X area * 10³" is obtained from the standard curve in lower right corner. Enter this number in block F9.
- e.) Enter date or date range of the set being worked on
- f.) "Alliance Sample #"
Enter numbers from the log sheet (either QC, P or A, NAO #)
The order should be IQCC, blank, LCSA, LCSB, samples including CC's and IQCC's.
For each sample # the sample type in parenthesis must be entered
These are: DTS A or B = TS day 0 1st analysis
HTE A or B = TS day 0 2nd analysis
HTS A or B = TS day 14 analysis
LSSA 0,1, or 2 = Lab spike A with conc level
LSSB 0,1, or 2 = Lab spike B with conc level
FLS = Field Sample
LCSA = Lab control Spike A
LCSB = Lab control Spike B
- g.) Enter the raw areas for the I.S. for each of the samples in the set
- h.) Enter the dates each sample was run
- i.) "EPA sample #"
For each NAO # there is a corresponding EPA number. These are found in John Verban's office for each set. Enter each EPA number. For cont calibrations enter "cont. cal." For IQ enter "Inst. check", method blank = "Meth. Blank" LCSA = "LCSA" and LCSB = "LCSB"
- j.) hit space bar to calculate
- k.) If any % difference is over 20, note sample number, and a difference Report to project manager
- l.) hit /, S, W
- m.) enter IS - set # in place of ISX-XX
DU2[EPA_workarea.user]IS-set#

I.S. SUMMARY TABLE

Sample

LABORATORY: Clean Harbors

Contract# 3-729-001
Set Number 12

I.S. \bar{X} AREA * 10⁻³ 44209

DATE: 9/2-9/6/88

EPA SAMPLE #	ALLIANCE SAMPLE #	AREA X10 ⁻³	DATE ANALYZED	% DIFFERENCE	% OF CRV.
INST. CHECK	P179-1	47066	9/02/88	6.46%	106%
CONT. CAL.	P193-2	40388	9/02/88	8.64%	91%
CONT. CAL.	P194-2	40107	9/02/88	9.28%	91%
METHOD BLANK	QC3692	37369	9/02/88	15.47%	85%
LCS A2	QC3693	40124	9/02/88	9.24%	91%
LCS B2	QC3694	37687	9/02/88	14.75%	85%
PC-2497-2-2-01	NA06993 (F/S)	37774	9/02/88	14.56%	85%
PC-2497-2-2-04	NA06994 (LSSA1)	38908	9/02/88	11.99%	88%
CONT. CAL.	P193-4	40815	9/03/88	7.68%	92%
CONT. CAL.	P194-4	44716	9/03/88	1.15%	101%
PC-2002-2-2-01	NA07013 (F/S)	37063	9/03/88	16.16%	84%
PC-2242-2-2-01	NA07014 (F/S)	41022	9/03/88	7.21%	93%
PC-2242-2-2-06	NA07015 (LSSA0)	40858	9/03/88	7.58%	92%
PC-2164-2-2-01	NA07016 (F/S)	39348	9/03/88	11.00%	89%
INST. CHECK	P179-1	44682	9/06/88	1.07%	101%
CONT. CAL.	P193-3	47777	9/06/88	8.07%	108%
CONT. CAL.	P194-3	47625	9/06/88	7.73%	108%
PC-2164-2-2-08	NA07017 (DTSB)	45984	9/06/88	4.02%	104%
PC-2164-2-2-13	NA07018 (DTSB)	42888	9/06/88	2.99%	97%
PC-2584-2-2-01	NA07021 (F/S)	42044	9/06/88	4.90%	95%
PC-2584-2-2-05	NA07022 (DTSA)	39904	9/06/88	9.74%	90%
PC-2584-2-2-13	NA07023 (DTSA)	40152	9/06/88	9.18%	91%

LD<20%

Flag program = Fla

Data is obtained from the curve program.

- a) Bring up the curve program for the set being worked on. Move to the percent recovery section.
- b) The Flag program can evaluate 3 A spike samples and 3 B spike samples per program. Therefore, when extracting information, keep in sets three or less. To file extract hit /, S, C enter name (NAME A1), supersede enter range- you should be highlighting LCSA and next two spikes - the headings and values. Once range is entered, you will back to ready. (It may be helpful to write down your file names. They will be needed.)
- c) Continue until all A spikes have a cut file
- d) Repeat above step for B spikes but extract 1st the labels then the values separately. Name these files Name B1, Name B2 ect.
- e) Bring up flag program. Bring cursor to A0. "Edit" and replace X's with set #. If there are more than one, name set # A, B, etc.
- f) Enter set # being worked on.
- g) Enter analysis date for set being worked on
- h) Enter same as in A0
- i) Enter "From CRV" enter curve # for set
- j) Position cursor in H10 sample
- k) Hit /, S, L
- l) Enter consolidate, then enter 1st A file ie Name A1
- m) Enter "Replace"
- n) "Input Range" - hit enter
- o) "Target Range" - hit enter
The headings & values from the LCSA & 2 A spikes should be in the flag program
- p) Repeat above steps for 1st 3 B spikes but position cursor in H30 for B values H47 for B labels
- q) Hit the space bar to recalc
- r) Hit /, S, W - replace FLAX-XX with Fla - set #
DU2: [EPA_Workarea.Users] Fla-set# & letter
- s) Repeat above steps for each set of 3 A & 3 B spikes or less than 3

APPENDIX E

STANDARD OPERATING PROCEDURE FOR AUTOMATED DATA ENTRY



Standard Operating Procedure for Transferring
NPS Data from the Hewlett-Packard Laboratory Automation
System to a 20/20 worksheet on the DEC MicroVax

1.0 SCOPE AND APPLICATION

This is a process whereby retention times and area counts from standard runs are put in a file and transferred from the Laboratory Automation System (LAS) to an IBM PC and then into a 20/20 worksheet on the DEC MicroVax. The IBM PC is physically linked to both the LAS and the DEC MicroVax.

2.0 SUMMARY OF PROCEDURES

The LAS command RF (Report to File) is used to put compound names, retention times, and area counts from the six standard result files into a file called CALNPS.RPT. A command file called FROMLAS.COM is then invoked from the IBM PC. This command file transfers the CALNPS.RPT file from the LAS to the hard disk on the IBM PC via NFS (a common file transfer protocol). A command file called TO20.COM is then invoked on the IBM PC. This command file transfers the CALNPS.RPT file into a temporary 20/20 file called TEMP and from this file extracts the area counts and retention times and places them on the final worksheet.

3.0 STEP BY STEP PROCEDURES

- 3.1 Once the six standard result files exist, go to the directory command line in LAS and type RF (Report to File). This will bring up the Report to File screen.
- 3.2 Hit F1 to create a report based on file names/masks. This will bring up the File Names Masks screen. Enter the name of the first A standard result file and press the tab key to move the cursor to the next line. Enter INIT CAL in the Rep.Format line and press the tab key to move to the next line. Enter CALNPS in the Rep.File line and press the tab key to move the cursor to the Overwrite option. Type YES and then hit return. Wait until the File Names/Masks screen re-appears. Then type in the name of the High B standard result file. Then tab to the Overwrite option and type in NO. Tab to the Append option and type in YES. Hit return. Wait until the File Names/Masks screen re-appears. Now enter the name of the MED B standard result file and hit return. Repeat this step until all six of the result files have been entered. **NOTE: It is VERY important that the result**



get entered in the correct order. The correct order is: High B; MED A; MED B; LOW A; LOW B. After all the results have been entered and the File Names/Masks screen re-appears, hit the End Function softkey (f8).

- 3.3 Go to the IBM PC in the LABSAM computer room. If it says "USE THIS TERMINAL", hit the ALT and S keys together. This stops the automatic report generator program. If the terminal looks busy, you will have to wait until it says "DO NOT USE THIS TERMINAL". After hitting ALT-S you will get a green command line at the bottom of the screen in which the cursor will be blinking. Type INVOKE FROMLAS.CMD and hit enter. The PC will then make a few beeps, transfer the CALNPS.RPT file to the terminal and then log off. Wait until it is finished doing this (should only be about 30 seconds). Instructions on what to do next will appear on the screen as a reminder. When this happens, it is finished with this step.
- 3.4 Hit f10, then hit f8 twice. A "C>" prompt will appear on the terminal screen. Flip the switchbox to position B and type R3V and hit enter. This will stop the IBM from emulating an HP terminal and start the DEC terminal emulation.
- 3.5 The Basic Configuration menu will appear on the screen. Hit f8 to accept the default configuration.
- 3.6 Hit the ALT and Y keys together. This will make the green command line appear at the bottom of the screen. Type INVOKE TO2020.CMD and hit enter.
- 3.7 Enter the name of the 20/20 template worksheet and hit enter. **NOTE: You DO NOT have to enter the file prefix DU2:[EPA_WORKAREA.USERS]; but you must spell the rest of the file name correctly or the program will bomb.**
- 3.8 Enter the name you want to save the 20/20 worksheet under and hit enter. Again, you DO NOT have to enter the file prefix; you must enter a file name that doesn't already exist or the program will bomb.
- 3.9 The program will then copy the CALNPS.RPT file from the PC to the DEC MicroVax, import that file into a temporary 20/20 file, import the information from the temporary 20/20 file into a blank template file and save it under the name you specified. This will take about three minutes. When the program is finished, instructions on what to do next will appear on the terminal screen as a reminder.
- 3.10 Hit f8 twice to stop the DEC terminal emulation. Turn the switchbox back to the A position. At the "C>" prompt, type



and hit enter. When the screen turns blank, hit enter to
"Login Name?" prompt. Login as user LABSAM with password
At the "Module Selection:" prompt hit the ALT and Y keys
together. This will give you the green command line as be
Type INVOKE AREPT.CMD and hit enter. This will re-start the
automatic report generator program that was running before

- 3.11 Go back to your DEC MicroVax terminal and call up the new
created worksheet. You will have to CALC the worksheet and
analysis times, etc. The above process only enters retention
times and area counts for the six standard runs.

APPENDIX F

NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES DATED 4/5/88

MEMORANDUM

4/5/88

TO: JOANNA HALL, ALLIANCE TECHNOLOGIES, INC.

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 and their condition. Please find enclosed the following items: 1) A users memo containing all operating instructions, and 2) A copy of Carbon Copy software 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 which 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 ICF staff member during your session.

It is important that you test the communications link between the NPSIS 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 card.

For testing purposes, your sample kit identification numbers and FedEx airbill numbers (respectively) are: PD-0000-241 and 1111111111, and PD-0000-242 and 2222222222. Use these sample kit identification numbers when trying out the NPSIS Sample Receipts Program.

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 day 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 NPS. 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 modem 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 you 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 Copy software onto your PC. The directions are provided in the Carbon Copy manual. 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 Carbon Copy Parameters' Screen. The information you must enter consists of the following:

- Name: NPS
- Telephone Number: 703-961-0629 ⁶⁷¹
- 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 ICF. To do this:

Type: C:> CCHKLP 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 will see on the screen exactly what is on the screen of the NPSIS computer. This 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 you 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 few 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 be 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 data entry, simply press "Esc" to exit the Sample Searching screen and be 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 the 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 any 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 unusable 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 information reporting damaged kits or samples. Therefore, not all of the screens depicted 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:

NPS Sample Receipt Searching Screen

** Enter the following items to access kit information **

To find the Kit information in NPSIS in the most complete and accurate fashion, please enter the Kit number and the FedEx airbill number.

Enter kit number:

----> PD-0001-151

Enter FedEx airbill #:

----> 1111111111

Enter your last name:

----> CHIANG

* Press ESC to exit the searching *

If the kit number you have entered is incorrect, or if the kit number and FedEx airbill number combination is incorrect, NPSIS will prompt you to try and enter these numbers 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 airbill number which was entered into the NPSIS system. This could happen if the field team loses or damages the airbill.

Once you have correctly identified the sample kit, NPSIS will ask you if there is any damage to the kit as a whole:

Kit No.: PD-0001-151

Was there any damage to the sample kit? (Y/N) Y

PgDn (Next page), PgUp (Previous page), Esc (Exit)

Next, NPSIS will ask you to survey the contents of the kit and check the 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:

Kit No.: PD-0001-151

Please compare the following bottle numbers
with those in the sample kit.

Bottle No:	PD-0001-1-1-01
Bottle No:	PD-0001-1-1-03
Bottle No:	PD-0001-1-3-01
Bottle No:	PD-0001-1-3-03
Bottle No:	PD-0001-1-9-01
Bottle No:	PD-0001-1-9-03

Did you receive exactly these bottles in the sample kit? (Y/N)

PgDn (Next page), PgUp (Previous page), Esc (Exit)

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)

Next, NPSIS prompts you to indicate if any of the individual bottles have been damaged and rendered unusable for analysis:

Kit No.: PD-0001-151

Was there any damage to the sample Bottles? (Y/N) Y

PgDn (Next page), PgUp (Previous page), Esc (Exit)

If you press "Y", NPSIS will then prompt you for the apparent cause of damage:

Kit No.: PD-0001-151

Was there any damage to the sample kit? (Y/N) Y

Please indicate the cause for damage:

Kit is broken (Y/N) Y

Ice is melted (Y/N)

Other Reason (Y/N)

Please enter any comments about the sample kit.

Comments: Broken upon arrival.

Comments:

PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ← to select field.

There may already be comments regarding the kit in the comment field shown in the above screen. In this case, please enter your comments after an which already appear. This insures that no information is destroyed.

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 place you back at the beginning of your entry.

You have completed all of the data entry screens for this Kit.

You may save your entry by pressing 'Enter'.

You may cancel your entry by pressing 'N' and 'Enter'.

You may verify or edit this entry by pressing 'R' and 'Enter'.

* * * Accept entries? * * *

* Press ← to Save *

* Press N and ← to Cancel *

* Press R and ← to Verify or Edit * Y

By pressing "Enter" , you have saved all of the information necessary for 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 mail 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 software 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.

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.

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.

--- C A U S E ---

Bottle No:	Damaged (Y/N)	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.

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 menu. Highlight read, then press <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 highlight moves to "TO".
3. Select the recipient(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 bar twice to "de-select" recipients. The small mark will disappear.
 - d. Press <ESC> to cancel the entire list.
4. Select the initials of those who will receive copies:
 - a. Press the down arrow to move to "CC".
 - b. Select recipients as instructed 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 G

NPS RAPID REPORTING SYSTEM DATED 4/12/88



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI OHIO 45268

MEMORANDUM

DATE: April 12, 1988

SUBJECT: NPS Rapid Reporting System

FROM: David J. Munch, Chemist *DJM*
Drinking Water Quality Assessment Branch

TO: NPS Technical Monitors

Jerry Kotas has requested that any confirmed results of health significance be reported as quickly as possible. Therefore, if an analyte listed in the attached tables is observed in the primary analyses, at or above the rapid reporting limit, the following actions should be instituted. For any listed analyte where the rapid reporting level is less than or equal to 1/2 the minimum reporting level (MRL), any occurrence at or above 1/2 the MRL should also be processed as below. (Note: The procedures for determining the occurrence of NPS analytes that may occur below the MRL, and are not listed on the attached tables, have not yet been finalized.)

1. The appropriate confirmational analyses (GC/MS for methods 1-3, 6-7, second column for Method 5) should be performed as soon as practical.
2. The laboratory should telephone their Technical Monitor, the same day the confirmation is completed.
3. The laboratory should immediately document the observed result in a letter to their Technical Monitor.
4. As quickly as possible on the day the above telephone call is received from the laboratory, the Technical Monitor should inform their Laboratory Analytical Coordinator of the finding. The Technical Monitor should forward on to the Laboratory Analytical Coordinator the above documentation, with any comments he/she may have concerning the validity of the result.
5. The Laboratory Analytical Coordinator should inform Jerry Kotas and the second Analytical Coordinator of the finding by telephone the same day if possible, and in writing after the documentation is received from the Technical Monitor.
6. The Analytical Coordinators are to request, through the appropriate Technical Monitors, that all analyses for this sampling site be conducted, and reported in writing, as soon as practical.

METHOD #2

<u>ANALYTE</u>	<u>RAPID REPORTING LEVEL</u>
alpha-Chlordane	0.5 ug/L
gamma-Chlordane	0.5 ug/L
Chlorothalonil	150 ug/L
Dacthal (DCPA)	5,000 ug/L
Dieldrin	0.5 ug/L
Propachlor	130 ug/L
Trifluralin	25 ug/L

APPENDIX H
DATA REPORTING FORMAT CHANGES DATED 4/18/88

MEMORANDUM

DATE: April 18, 1988

SUBJECT: Data Reporting Format Changes

FROM: David J. Munch, Chemist
Drinking Water Quality Assessment Branch

TO: WPS Technical Monitors (See below)

The purpose of this memorandum is to consolidate the changes to the NPS data reporting format, which have occurred since it was originally constructed. You have previously been supplied with most of these changes, but please check to be sure that they have all been relayed to your contract and referee laboratories.

1. Line 2, columns 1-6 are to be used to record the pH measured in the field. This data will be found on the field sample tracking sheet.
2. Line 2, columns 67-70 are to be used to record the pH measured upon sample receipt at the laboratory. This only applies to methods 5 and 9.
3. Line 8, columns 1-13, Sample Identification Number, have been expanded to columns 1-14.
4. The data entered on line 10, columns 52-60, concerning the internal standard, it should be entered not as the peak area but as the "percent recovery" as compared to the mean observed for the calibration curve.

In order to simplify the "Sample Type" code (line 11, columns 1-5), the following codes should be used to designate the various types of spiked samples.

LCS@ = Laboratory Control Sample
LSS@ = Laboratory Spiked Sample
DTS@ = Day 0 Time Storage Sample
ETS@ = Extract Time Storage Sample
STS@ = Sample Time Storage Sample

In addition, two clarifications have been made to the codes for analyte concentration entries.

-999 = Not Detected (< 1/2 Minimum Reporting Limit)
-111 = Below Minimum Reporting Limit but greater than or equal to 1/2 the Minimum Reporting Limit.

APPENDIX I

NPS ANALYTE REPORTING BELOW MRL AND IDENTIFYING UNKNOWN PEAKS DATED 6/1/88



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY LABORATORY, NASA/NSTL
BUILDING 1105, NSTL, MISSISSIPPI 39233

June 1, 1988

MEMORANDUM

SUBJECT: NPS Analyte Reporting Below MRL and Identifying Unknown Peaks

FROM: Bob Maxey, Analytical Coordinator
Environmental Chemistry Laboratory

Bob Maxey

TO: Dave Munch, Analytical Coordinator
TSD-Cincinnati

Aubry E. Dupuy, Jr., Technical Monitor
Environmental Chemistry Laboratory

Attached are the procedures that NPS analytical contractors and referee laboratories must adhere to in complying with the OPP request to report the presence of analytes below the Minimal Reporting Limits and to attempt identification of unknown peaks. Please see that your contractors and Technical Monitors get this information and that applicable parts are incorporated into their respective QAPPs.

If you have any questions, give me a call.

Determining and Reporting the Presence of NPS Analytes Below The
Minimal Reporting Levels and Identifying Unknown Peaks

Background Information

The Office of Pesticide Programs (OPP) has requested that the NPS analytical contractors and referee laboratories make an effort to report the presence of NPS analytes below the Minimal Reporting Levels (MRL). We have also been requested to attempt to identify unknown peaks or responses. To assure that spurious or ambiguous data is not reported and that a uniform system or analytical routine is used at all laboratories to accomplish these requests, criteria have been developed for handling both situations.

Procedure for Determining and Reporting the Presence of NPS Analytes Below the MRL

1. For methods 1-7, only peaks with responses of between one-half the established MRL and the MRL ^{A/} on the primary column will be investigated. A response on the "secondary" GC column, indicating the presence of the analyte, is all required for additional work.
- 2.a The first occurrence of a peak meeting the requirements of (1) is noted and reported to the Technical Monitor, but no action is taken ^{B/}. Upon a second occurrence of the same suspect analyte, additional work is required as follows. After five successive failures to "confirm" on the secondary column the response on the primary column, discussions with OPP personnel will take place before continuing low-level analytical work on the analyte(s).
- b With methods 1,2,3, 6 and 7, for responses meeting the requirements of (1), and (2), the laboratory will attempt LR GC/MS ^{C/} confirmation if the GC/MS analyst feels it is within the capability of his instrument. If the confirmation is not within the capability of the laboratory, such extracts are sent weekly, under iced conditions by next-day air, to the appropriate referee laboratory having HR GC/MS ^{C/} capabilities. Copies of chromatograms and all pertinent sample information must be sent along with the extracts including extracts of the related Method Blank. (NPS will absorb the cost of these shipments.) 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.

A/ = NPS method 1 MRL = 4 x EDL	NPS method 5 MRL = 3 x EDL
NPS method 2 MRL = 5 x EDL	NPS method 6 MRL = 3 x EDL
NPS method 3 MRL = 5 x EDL	NPS method 7 MRL = 3 x EDL
NPS method 4 MRL = 5 x EDL	

B/ = Method 6 has an MRL > the Health Advisory Level. All suspect ETU responses of 1/2 MRL - MRL require additional work for this method.

C/ = LR = GC/MS = Low Resolution mass spectrometry.
HR GC/MS = High Resolution mass spectrometry.

- c. For Methods 4 and 5, HPLC Methods, there is no provision for GC/MS confirmation. Suspect analytes between 1/2 MRL - MRL will be subject -- (1) and (2a) above.

Provisions of (2b) also apply except references to GC/MS requirements.

3. Whether the identification of the analyte is attempted at the contractor laboratory or at 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 analytical 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 from the various methods. The contractor or referee laboratories will be required to attempt identification of peaks or responses on the primary column exhibiting the minimal criteria below.

1. For Methods 1, 2, 3, 6, and 7, 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 x MRL (Minimal Reporting Level), an attempt must be made to identify that known 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 contractor and/or referee laboratories on the first occurrence of such a peak and the results of attempt reported to the Technical Monitor for the Method. If the analytical contractor feels his system or instrument is not capable of the confirmatory work, he must send both that extract and that of the related Method Blank to the appropriate referee lab 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 must be marked on the outside of the vial or ampule. (NPS will absorb costs of these shipments.)

Specific sample and analytical information must accompany each such extract.

- o Sample i.d. number, weight of sample matrix contained in the ampule, copies of chromatograms from the primary GC column, identification of the retention 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 the Contractor Laboratory or at the referee laboratory, only the compounds 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 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 continuing with identification work on that particular compound.

THE QUALITY ASSURANCE PROJECT PLANS FOR BOTH THE ANALYTICAL CONTRACTORS AND REFEREE LABORATORIES FOR METHODS 1, 2, 3, 6, AND 7 MUST REFLECT THEIR COMMITMENTS TO THESE TWO REQUIREMENTS.

THE QUALITY ASSURANCE PROJECT PLANS FOR BOTH THE ANALYTICAL CONTRACTORS AND REFEREE LABORATORIES FOR METHODS 4 AND 5 MUST REFLECT THEIR COMMITMENTS TO THE REQUIREMENT FOR DETERMINING AND REPORTING NPS ANALYTES BELOW THE MRL.

APPENDIX J

REVISIONS TO NPS RAPID REPORTING SYSTEM DATED 6/9/89



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI OHIO 45268

MEMORANDUM

DATE: June 9, 1989

SUBJECT: Revisions to NPS Rapid Reporting System

FROM: David J. Munch, TSD Project Manager
National Pesticide Survey

Handwritten signature of David J. Munch in black ink.

TO: NPS Technical Monitors

Recently the health advisory documents for priority NPS analytes were finalized (at least as finalized as they ever get). In many cases, the health effect value used to determine the concentration of each analyte that "triggered" the rapid reporting system, has changed. The purpose of this memorandum is to transmit to you the final rapid reporting concentrations, and to remind everyone of the provisions of the rapid reporting system.

As you remember, if an analyte listed in the attached tables is observed in the primary analyses, at or above the rapid reporting limit, the following actions should be instituted. For any listed analyte where the rapid reporting level is less than or equal to 1/2 the minimum reporting level (MRL), any occurrence at or above 1/2 the MRL should also be processed as below.

1. The appropriate confirmational analyses (GC/MS for methods 1-3, 6-7, second column for method 5) should be performed as soon as practical.
2. The laboratory should telephone their Technical Monitor, the same day the confirmation is completed.
3. The laboratory should immediately document the observed result in a letter to their Technical Monitor.
4. As quickly as possible on the day the above telephone call is received from the laboratory, the Technical Monitor should inform their Laboratory Analytical Coordinator of the finding. The Technical Monitor should forward on to the Laboratory Analytical Coordinator the above documentation, with any comments he/she may have concerning the validity of the result.
5. The Laboratory Analytical Coordinator should inform the Survey Director and the second Analytical Coordinator of the finding by telephone the same day if possible, and in writing after the documentation is received from the Technical Monitor.

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590

METHOD #2

<u>ANALYTE</u>	<u>RAPID REPORTING LEVEL</u>
alpha-Chlordane	0.5 ug/L
gamma-Chlordane	0.5 ug/L
Chlorothalonil	150 ug/L
Dacthal (DCPA)	5,000 ug/L
Dieldrin	0.5 ug/L
Propachlor	130 ug/L
Trifluralin	25 ug/L

6. The Analytical Coordinators are to request, through the appropriate Technical Monitors, that all analyses for this sample site be conducted, and reported in writing, as soon as practical.

If you have any questions concerning these procedures, please let Bob Maxey or me know. Also, please pass on this information to your contract and referee laboratories.

Attachment

Addressees:

- M. Bolyard
- A. Dupuy
- C. Madding
- R. Maxey
- R. Sorrell
- M. Zuiker

cc:

- J. Boland
- H. Brass
- L. Johnson
- A. Kroner
- C. Lester
- L. Van Den Berg