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QUALITY ASSURANCE PROJECT PLAN
FOR THE
NATIONAL PESTICIDE SURVEY OF DRINKING WATER WELLS
ANALYTICAL METHOD 3

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NATIONAL PESTICIDE SURVEY
QUALITY ASSURANCE PROJECT PLAN FOR
ANALYTICAL METHOD 3

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* In this QAPjP Rev. 4, an asterisk in the left hand margin of the text indicates an addition or revision to the ECS NPS QAPjP Rev. 3 of June 15, 1988. The edited text will be followed by an effective date in parenthesis and, when applicable, a reference to the addendum in Appendix L which addressed the change.

2. LIST OF FIGURES

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3. PROJECT DESCRIPTION

The National Pesticide Survey (NPS) of drinking water wells is a joint project between the EPA Office of Pesticide Programs (OPP) and Office of Drinking Water (ODW). Expectations for the full Survey are that well-water samples will be analyzed for over 100 pesticides or degradation products from approximately 1500 domestic and community water system wells. Seventeen of these analytes are included in NPS Method 3 with which phenoxy and phenol compounds will be determined.

There is a referee laboratory for each method; the OPP Environmental Chemistry Laboratory at Bay St. Louis, MS will serve this function for NPS Method 3. The roles of the referee laboratory in this Survey are:

- to analyze duplicates of samples sent to the analytical contractor (primary lab.) limited to 20% or a maximum of 5 samples per week from those taken the first 6 months;
- to perform High Resolution GC/MS Confirmation of low concentration suspected residues not amenable to analysis by Low Resolution GC/MS;
- to provide a Technical Monitor and/or EPA Project Officer to oversee analytical and/or contractual aspects of work done by the analytical contractor;
- to evaluate any QC activities required of the analytical contractors, including conducting and participating in NPS audits;
- to provide verification analyses of blind samples;
- and to verify prior to use all analytical standards prepared for use with this method by EPA/Technical Support Division - Cincinnati or their contractor.

The phenoxy - phenol pesticides and/or degradation products included as analytes for this method are:

Acifluorfen
Bentazon
1/ Chloramben (Amiben)
2,4-D
Dalapon
2,4-DB
DCPA acid metabolites
Dicamba
3,5-Dichlorobenzoic acid
Dichlorprop (2,4-DP)
Dinoseb
1/ 5-Hydroxy dicamba
1/ 4-Nitrophenol
PCP
Picloram
2,4,5-T
2,4,5-TP (Silvex)

1/ Qualitative Analyte

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

Referee laboratory responsibilities for NPS Method 3 will be carried out by OPP's Environmental Chemistry Lab. (ECS) which is managed by Dr. Aubry E. Dupuy, Jr., Section Chief. Mr. Robert Maxey, chemist at ECS, will serve as both EPA Technical Monitor and Project Officer for the Method. Mr. Maxey, as ECS Project Leader, will also be responsible for day-to-day management of NPS analytical activities. Mr. Danny McDaniel, Acting ECS-QAO, will provide QA oversight (effective 050189; see Appendix L; Addendum of 050189). The Sample Custodian for ECS and for the NPS Project is Gerald Gardner.

Mr. Stanley Mecomber and Ms. Elizabeth Flynt will handle sample preparation. Analytical work will be handled by Ms. Jan Watkins backed up by Ms. Elizabeth Flynt. Data review has been assigned to Mr. William Mitchell and Mr. Joe Ferrario. Data handling and reporting will be handled by Ms. Watkins backed up by Ms. Flynt. Mr. Joe Ferrario will provide Low Resolution GC/MS confirmation while Mr. Danny McDaniel will handle High Resolution GC/MS work (effective 050189; see Appendix L; Addendum of 050189). Refer to the Method 3 Organization Chart, Figure 4-1, at the end of this Section.

Federal Express shipments of samples and of extracts for GC/MS analysis to ECS-Bay St. Louis, MS should be addressed to ECL's Sample Custodian:

* U.S. EPA
Environmental Chemistry Section
NASA/SSC Bldg. 1105
STENNIS SPACE CENTER, MS 39529-6000
ATTN: Gerald Gardner
(601) 688-3170 (or 3217)

* The Assistant Sample Custodians for NPS are:

Mr. John Cuevas
(601) 688-3170 (or 3217)

Mr. Stanley Mecomber
(601) 688-3170 (or 3217)
(effective 081288; see Appendix L; Addendum of 081288)

The telephone number for the EPA Technical Monitor and Project Officer for NPS Method 3 is:

Mr. Robert Maxey
(601) 688-1225 (or 3217)

In Mr. Maxey's absence, Dr. Aubry Dupuy will serve as the appropriate EPA contact for Technical Monitor and Project Officer responsibilities for Method 3.

Dr. Aubry E. Dupuy
(601) 688-3212

FIGURE 4-1

ECS ANALYTICAL TEAM - METHOD 3

5. QA OBJECTIVES FOR MEASUREMENT DATA

5.1 Initial Determination Of Capabilities; Determination Of EDLs; Determination Of Reporting Levels

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

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

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

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

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

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

7. These eight EDL extracts will also be analyzed using the confirmation column. EDLs determined on the confirmational column must equal those determined on the primary column; if not, the higher of the two EDLs will prevail to assure that there is a minimal response on both columns. Again, EDLs exceeding this requirement will be approved on a case-by-case basis, by the Technical Monitors.

* 8. The laboratories will be required to perform up to six analyses per analyte mix by GC/MS, for the appropriate Methods. These analyses will be performed by MID, using the three ions specified by EPA. The purpose of these analyses are to determine the concentration at which a 5/1 signal to noise ratio, for the least intense of the three ions, is obtained. See Appendix K for a Table of the three ions for each analyte (effective 06/15/88; see Appendix L; Addendum 0f 07/12/88).

9. The Minimum Reportable Level (MRL) for Method 3 is 5 X EDL.

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

5.2 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, the following procedures will be used.

5.2.1 Procedure for Determinining and Reporting the Presence of NPS Analytes Below the Minimal Reporting Level

1. For Method 3, only peaks with responses of between one-half the established MRL and the MRL [A]/ on the primary column will be investigated. The first time such a response is noted on the primary column, no further analytical work is underdertaken; the second time such a response is noted, analysis on the confirmatory GC column is required.

2.(a) For Method 3, if the response on the second column is positive, further analytical work under (3) below is required.

(b) For Method 3, if the response on the second column is negative, that fact is noted. After five attempts at second column confirmation have failed for the same analyte, the ECL Project Leader is informed, and discussions with OPP personnel will take place before continuation of analytical work on that analyte.

3. For responses meeting the requirements of (1) and 2(a), the laboratory will attempt LR GC/MS [B]/ 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 LR GC/MS, the extracts will be run on HR GC/MS. Copies of chromatograms the related Method Blank, and all pertinent sample information must accompany the extracts. Correct volume level should be clearly marked on the outside of the extract tube.

A/ = NPS Method 3 MRL = 5 X EDL

B/ = LR GC/MS = Low resolution mass spectrometry
HR GC/MS = High resolution mass spectrometry

Only analytes positively confirmed by GC/MS will be reported beyond the ECL Project Leader for Method 3 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 ECL Project Leader.

5. Following either the successful GC/MS confirmation of two such responses for the same analyte or two successive failures to confirm the analyte 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 particular analyte.

6. As a referee laboratory, ECL will also be receiving sample extracts from the contractor when HR GC/MS work is required. These extract shipments will be received and logged in by the ECL Sample Custodian or his Representative, and the ECL Project Leader will be notified.

5.2.2 Procedure for Determining The Identity of and Reporting the Presence of NonNPS 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 referee laboratories will be required to attempt identification of peaks or responses exhibiting the minimal criteria below.

1. For Method 3, if the response of an extraneous peak upon initial injection and exclusive of the Method Blank, on the primary column is equal to or greater than the response of the nearest NPS analyte on that column at 10X MRL (Minimal Reporting Level), an attempt must be made to identify that peak by GC/MS. Full scan spectra and subsequent library search is expected and must be followed by comparison of the spectra of the unknown compound with that of an authentic standard of the suspected compound.

2. The work in (1) must be attempted on the first occurrence of such a peak and the results of the attempt at confirmation reported to the ECL Project Leader for Method 3. If the LR GC/MS analyst feels his instrument is not capable of the confirmatory work, the extract is submitted to the HR GC/MS analyst. Volume level of extract should be marked on the outside of the extract vial.

   Specific sample and analytical information must accompany each such extract.

   - Sample i.d. number, weight of sample matrix contained in the vial, copies of chromatograms from the primary GC column, identification of the retention window for the unknown peaks as defined by the last NPS analyte to elute before the unknown peak and the first NPS analyte to elute following the unknown peak. The related Method Blank extract must also be included.

3. Only those compounds positively confirmed by GC/MS will be reported beyond the ECL Project Leader for Method 3 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 ECL Project Leader.

4. Following either the successful confirmation of two such extraneous peaks proving to be the same compound or two failures to identify the same unknown peak, discussions with OPP personnel will take place before continuation with identification work on that particular compound.

5.3 Laboratory QC Requirements For Primary Analyses

1. Laboratory control standard mixes, which together contain all method analytes and the surrogate, will be analyzed with each set of samples.

2. A set of samples is defined as all samples, blanks, spiked samples, etc., on which similar analytical operations are performed at the same time and which are analyzed in a single run.

3. The internal standard area checks detailed in Method 3, will be used but may not deviate by more than $\pm$ 20% of the average peak height or area of the internal standard in the calibration standards. The control limits will be reassessed following completion of the initial demonstration of capabilities.

* 4. The calibration curves, as defined in Section 8.12, are not used for quantitation, but for a check of linearity. For quantitation, procedural standards (calibration standards prepared by methylation of weighed acids or phenols) containing the method analytes and the surrogate will be prepared for each set of samples. The concentration of each analyte in each procedural mix will be 10xMRL. These will be used as the "single point quantitation" standards for the LCS's which have been spiked at 10xMRL. Positives, analyte amounts at 1/2 MRL or above, are analyzed by use of these procedural standards that are within +/- 20% of the response of the suspect residue. The column check must be quantitated

against the weighed ester standard at 10xMRL. Refer to Section 8.20 for detailed procedure (effective 06/88).

5. The measurement system is to be evaluated whenever any analyte is observed in a Method Blank, at a concentration greater than or equal to 1/2 the Minimum Reportable Level. Method Blanks are to be analyzed with each set of samples.

   A sample set in which the surrogate compound recovery of the Method Blank has failed to meet the ± 30% criteria can be validated by use instead of a Field Sample, from that same sample set, which meets all of the quality control requirements for a Method Blank.

   Note: This is not a procedure to validate the surrogate or the Method Blank; rather, it is a procedure to validate the sample set by use of a Field Sample as a Method Blank.

6. The criteria for monitoring instrument control standards will be utilized as stated in the method.

* 7. The requirement for surrogate recoveries from Field Samples and Method Blanks is the Mean Recovery, R, on the applicable Control Chart ± 30 percentage points (i.e. R ± 30%). It is not R ± .30 R. (effective 081888).

8. The requirements for monitoring calibration standard responses will be followed as written in the method.

9. Samples failing any QC criteria must be reanalyzed.

* 10. Only qualitative analysis will be required for chloramben, 4-nitrophenol, 5-OH dicamba and acifluorfen. While these analytes are to be analyzed in at least one of the concentration levels of the calibration standards, they are not subject to any of the QC requirements.

11. Each time that a new calibration standard dilution is prepared, it must be compared to the existing calibration curve, and the observed concentration must agree within +/- 20% of the expected concentration.

12. Any deviation from the analytical procedures or QC requirements, must be approved by the appropriate ECS-NPS Project Leader and documented in writing.

5.4 Laboratory QC Requirements For Second Column Analyses

1. Quantitate by comparison to a calibration standard, which is within +/- 20% of the concentration of the analyte(s) determined using the primary column.

* 2. The concentration(s) for the analyte(s) on the secondary column should quantitate within +/- 25% of the result determined on the primary column (effective 03/20/89).

* 3. If the concentration determined on the secondary column does not agree within the limits stated above, the analyst must confer with the ECS-NPS Project Leader concerning resolution of the discrepancy prior to submitting the extract for GC/MS analysis (effective 06/88).

* 4. If the concentration determined on the secondary GC column meets the criteria in 2 above and GCMS is positive, report the concentration of the analyte found on the primary column (effective 06/88).

5.5 Laboratory QC And Extract Handling Related To GC/MS Confirmation

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

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

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

4. If low concentrations of the analyte(s) preclude confirmation using Low Resolution GC/MS, High Resolution GC/MS Confirmation must be attempted. HRGC/MS may also be required if the analyte concentration is greater than or equal to 1/2 the lowest adverse health effect for that analyte or if requested by the ECS-NPS Project Leader.

5.6 Sample Management

* 1. Samples must arrive at the laboratory with ice still remaining in the shipping box. If a sample box arrives at the laboratory without any ice remaining, the Sample Custodian should adhere to the following instructions (effective 11/06/89).

* a. Analyze the affected samples - you will receive payment for samples that arrive with melted ice.

* b. Take the temperature of the standing water in the bottom of the sample kit, record the temperature in degrees Centigrade on the sample tracking form and input the value into NPSIS. DO NOT TAKE THE TEMPERATURE OF THE SAMPLE IN THE BOTTLE.

* c. Record any subjective observations you have about the samples and/or sample kit (i.e. the bottle was warm to the touch).

* d. Contact the ECS-NPS Project Leader if you have any further questions.

2. Strict adherence to sample and extract maximum holding times (14 days) is required for both primary and secondary column analyses. All analyses should be completed as soon as possible, but under extenuating circumstances, the maximum extract holding time may be extended to 28 days for GC/MS analyses only, if approved by the ECS-NPS Project Leader.

3. Water samples are to be disposed of after the 14 day sample holding time has been exceeded. Sample extracts must be maintained until disposal is approved by the ECS-NPS Project Leader.

6. SAMPLING PROCEDURES

6.1 Sample Requirements

For this method, ECL will be provided one 1-Liter sample preserved with mercuric chloride at 10 mg/liter. This sample is to be shipped iced along with those needed for Methods 1 and 6, by overnight air and is to arrive iced at ECL. This sample is for duplicate analysis of the field sample sent to the primary analytical contractor. No "backup" or reserve sample will be shipped.

ECL, as a referee laboratory, is envisioned to receive no more than 10% of the total 1500 samples now expected to be taken in the Survey. Table 6-1, found at the end of Section 6.0, summarizes these sample requirements.

6.2 Labelling Of Sample Bottles

The Implementation Contractor, ICF, will supply information on the labels, sample numbering system, and explanations for field coding or decoding at the laboratory. This label is shown in Figure 6-1.

6.3 Field Sample Tracking Form

ICF will supply a copy of this form along with explanations for field coding or decoding at the laboratory. This form is shown in Figure 6-2.

TABLE 6-1

ENVIRONMENTAL CHEMISTRY LABORATORY SAMPLE REQUIREMENTS

LAB NAME			
KIT TYPE Sample Types	BSL Referee		
BOTTLE TYPE	1000mL	1000mL	60mL
ANAL. METHOD	1	3	6
Primary			
Referee	1	1	1
Shipping Blank			
Backup Sample			
Lab Spikes			
Time/Storage			
..			
Totals	1	1	1
No. of Sites	150	150	150
TOTAL REQ'D	150	150	150

Total Bottles:

1000mL = 300
250mL = N.A.
60mL = 150

FIGURE 6-1

LABEL OF SAMPLE BOTTLES

SAMPLE #: PD-0000-6-1-01

BSL - METHOD# 1 KIT: 611
FIELD SAMPLE
PRESERVATIVE: HgCl2

DATE	TIME	SAMPLER

NATIONAL PESTICIDE SURVEY

SAMPLE #: PD-0000-6-3-01

BSL - METHOD# 3 KIT: 611
FIELD SAMPLE
PRESERVATIVE: HgCl2

DATE	TIME	SAMPLER

NATIONAL PESTICIDE SURVEY

SAMPLE #: PD-0000-6-6-01

BSL - METHOD# 6 KIT: 611
FIELD SAMPLE
PRESERVATIVE: HgCl2

DATE	TIME	SAMPLER

NATIONAL PESTICIDE SURVEY

SAMPLE #: PD-0000-6-1-03

BSL - METHOD# 1 KIT: 611
BACKUP SAMPLE
PRESERVATIVE: HgCl2

DATE	TIME	SAMPLER

FIGURE 6-2

FIELD SAMPLE TRACKING FORM

WELL I.D. NO.: 0000

FRDS I.D. No. (CWS WELL ONLY):

LAB: BSL
SCENARIO: 1

SAMPLE COLLECTION DATE: ___/___/___

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

TRACKING FORM COMPLETED BY: _____

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-e-01	60	FIELD SAMPLE		:		: N	
PD-0000-6-1-03	1000	BACKUP SAMPLE		:		: N	

CHLORINE TEST: _____ mg/L

SHIPPED BY:		RECEIVED AT LAB BY:
_____		_____
DATE _____ TIME _____		DATE _____ TIME __
SENT TO:	LAB ADDRESS:	CONDITION (3)
_____	BAY St. LOUIS EPA/ENVIRONMENTAL	_____
_____	CHEMISTRY LAB, BLDG. 1105	_____
_____	_____	_____
_____	NSTL, MS 39529	_____

(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, BOX LEAKING
(Lab comments should concur with NPSIS SAMPLE RECEIPT)

7. SAMPLE CUSTODY

7.1 Tracking And Notification Of Sample Shipments

The proposed EPA system for notification of the laboratory of sample shipments and for notification of the Implementation Contractor (ICF) of receipt of the samples is delineated on the flow chart and diagram, Labelled Figure 7-1, "SAMPLE RECEIPT SCREENS FOR NPS LABORATORIES" at the end of Section 7.0. This system will be computerized.

7.2 Sample Requirements Following Receipt At Laboratory

Tracking of all samples arriving at the laboratory will begin upon receipt of any sample and will continue through each phase of the analysis.

- Upon receipt of samples, each is identified according to its "Field Sample Number", logged in and stored at 4°C. This information is documented on a "NPS LOGGING FORM".
- The Sample Custodian or his/her Representative will compile "sets" of samples for Method 3 comprised of 8 samples and appropriate controls as covered in Section 9.4 of this QAPjP. The composition of each set is documented on a "NPS SET COMPOSITION FORM".
- Transfer of samples into and out of storage will be documented on an internal chain-of-custody record. Only those samples in the "set" on which analytical work will be done will be removed. This information is documented on a "SAMPLE CONTROL RECORD FORM". The analyst will sign and date this Record when removing or returning samples to storage.
- After removal from storage, samples are tracked through extraction and G.C. Analysis via an "ECL/NPS SAMPLE TRACKING FORM".
- Following extraction, sample extracts are stored in a refrigerator at 4°C until analyses are complete. Following analysis, they are transferred to screw-cap tubes (teflon liners), the extract level marked, and stored by set in a freezer at 0' to -20'C.
- An "EXTRACT STORAGE DATA SHEET" records chain-of-custody of extracts from GC Analysis to GC/MS Confirmation, if required, and to disposal.
- Copies of all the above mentioned Forms and Records can be found in Appendix A.

7.2.1 Storage Conditions

Upon receipt at the laboratory, samples will be stored under refrigeration at 4°C and protected from light.

7.2.2 Holding Times

Samples have a maximum holding time of 14 days from time of collection until the start of extraction.

Extracts have a maximum holding time of 14 days from date of extraction to GC Analysis and GC/MS Confirmation, if required. The holding time for GC/MS Analysis may be extended an additional 14 days upon approval of the ECL Project Leader.

7.2.3 Disposal

Samples held longer than 14 days without being extracted are to be disposed of after approval is given by the ECL Project Leader.

The samples arrive with a 10 mg/liter concentration of mercuric chloride which is added as a preservative. Disposal of these samples will be to an EPA-approved water treatment system capable of handling these concentrations of mercuric chloride and which is connected to the ECL facility.

7.3 Return Of Sample Kits To EPA Contractor (ICF)

ICF is to provide information on this.

* 7.4 Receipt and Tracking of Extracts from Analytical Contractors for GC/MS Confirmations at ECS (effective 06/05/89)

To carry out its responsibilities as a referee lab. (see Section 3), ECS will be receiving from Analytical Contractors sample extracts meeting the requirements of Section 5.2. For all such extracts arriving at ECS, tracking will begin upon receipt and continue through final disposition according to the following procedure.

- Upon receipt at ECS, the Sample Custodian or his representative will check extracts against the NPS EXTRACT SHIPMENT form, filling in the Date Received at ECS, Conditions of Shipment, Number of Refrigerator where strored, the Container Number and signing where appropriate. (A copy of this form is attached at the end of this Section and is labelled Figure 7-2.) He should then place the extracts in containers labelled by date and store in a refrigerator at 4°C.

- The Sample Custodian will make necessary copies of paperwork received with the extract shipment, giving all the original paperwork to the NPS Technical Monitor for the Analytical Contractor and a copy of the original paperwork to the GCMS analyst. The Sample Custodian should keep on file, in the receiving room, a copy of the NPS EXTRACT SHIPMENT form.

- The GCMS analyst should remove extracts from the designated refrigerator, analyze the extracts by GCMS, then complete the remainder of the NPS Extract Shipment form and the GCMS Data Sheets. The analyst should give all completed forms and GCMS spectra to the NPS Technical Monitor.

- The Technical Monitor will use the information from the NPS EXTRACT SHIPMENT form to complete an overall tracking form, the NPS GCMS EXTRACT TRACKING FORM. He will send a copy of the GCMS Data Sheet to the NPS Data Manager and to the Analytical Contractor. He will also send the Analytical Contractor a copy of the GCMS spectra. ECS will maintain the original paperwork on file.

- GC/MS results will be reported as in Sections 10.5 and/or 10.63.

- The Technical Monitor for the appropriate Method will receive all results and reports of GC/MS confirmation analyses and a monthly report from the ECS Sample Custodian on the total number of extracts received for each Method.

- The Technical Monitor will inform the Analytical Contractor, in writing, of the results of each GC/MS confirmation attempt.

- Disposal of extracts will be according to Section 7.23 and will be authorized by the Technical Monitor.

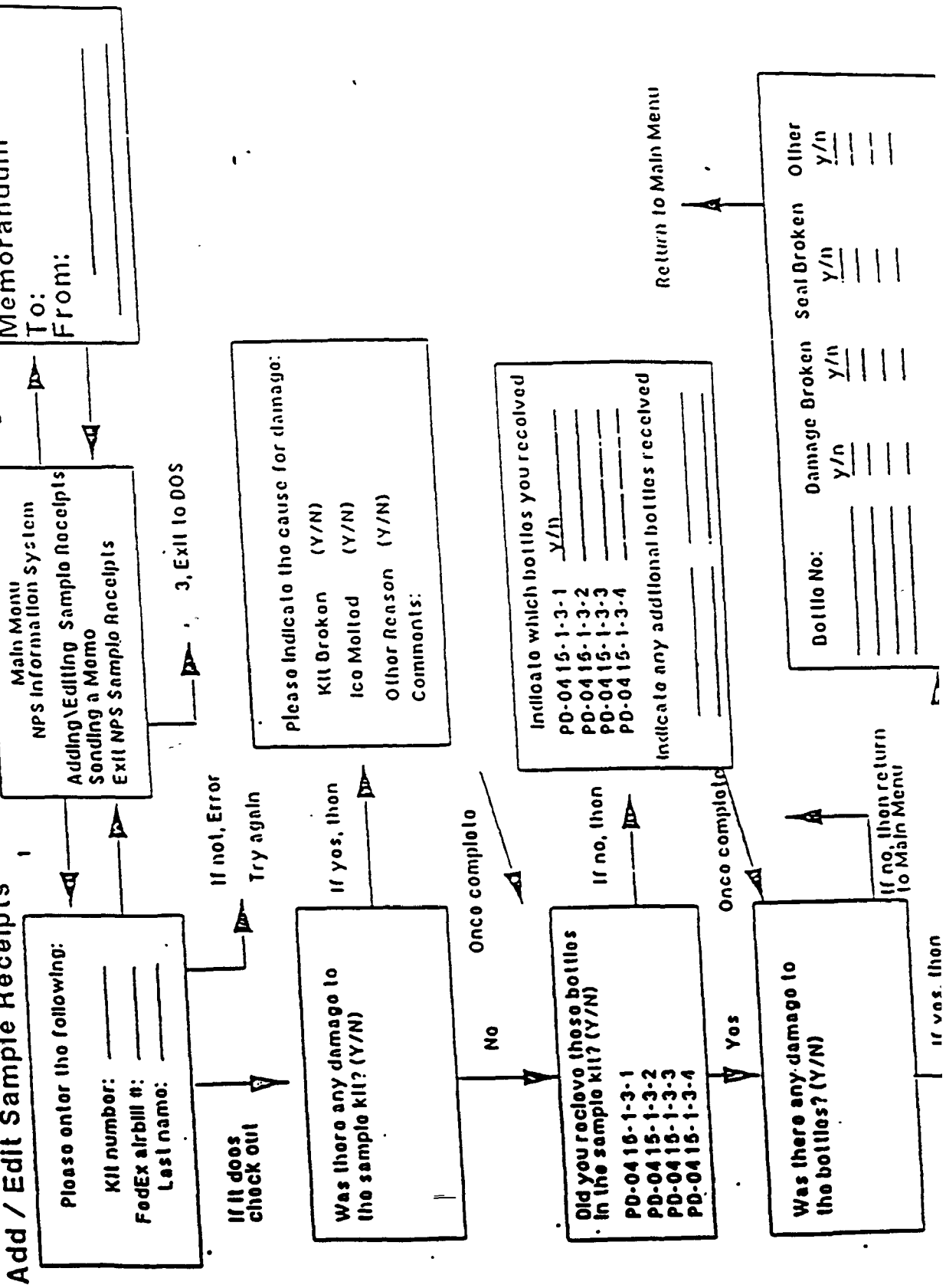
7.5 Internal Practices Concerning Sample Storage

The temperatures of coolers, refrigerators, and freezers where samples and/or extracts are stored are monitored each working day and this activity and the temperature are recorded in a log book maintained for this purpose. A copy of this record is included as Figure 7-3 at the end of this Section.

The ECS Sample Custodian, Gerald Gardner, or the Assistant Sample Custodians are responsible for monitoring these storage areas (effective 081288; see Appendix L; Addendum of 081288). ECS has an agreement with the facility contractor to provide weekly preventive maintenance and emergency repair services on large coolers where samples will be stored.

FIGURE 7-1

SAMPLE RECEIPT SCREENS FOR NPS LABORATORIES



NPS EXTRACT SHIPMENT

Date Shipped:
Approved:

Date Received at ECS:
Received By:
Condition of Shipment:

Sample No.	JMM Set No.	Dates			GC Results			GC/MS Results		GC/MS Data Sheets Completed (Date)
		Sampled	Extracted	28-Day H/T Expire	Analyte	Prim (ppb)	Conf (ppb)	Date Analyzed by GC/MS	Results (Pos/Neg)	

Extract Stored in Refrigerator No._____
Container No. _____
Stored By _____

Instructions For ECS:
- o Original and Related Forms to Technical Monitor
- o Copy to GC/MS Section

FIGURE 7-2
NPS EXTRACT SHIPMENT

FIGURE 7-3

TEMPERATURE MONITOR CHART EPA/ECL

# WALK-IN COOLERS/BLDG. 1105			# WALK-IN/UPRIGHT FREEZERS/BLDG. 2204/1105			REMARKS
DATE	TEMP.	PERSON CHECKING	DATE	TEMP	PERSON CHECKING	

8. CALIBRATION PROCEDURES AND FREQUENCY

8.1 Method 3 Standards

8.1.1 Calibration Solutions

Calibration solutions will be provided and sent to both the referee lab (ECL) and primary analytical contractor by EPA/TSD-Cincinnati through their contractor Bionetics. The solutions are to be in flamesealed glass ampules. These solutions will be sent iced by next-day air to ECL and will be accompanied by a "STANDARD SOLUTION DATA FORM". The ECL Sample Custodian or other Designated Representative will receive these standards shipments, note whether or not they were iced and date of receipt, and relinquish custody of the standards to a member of the Method 3 analytical team. A sample copy of this form is attached at the end of this Section and is labeled Figure 8-1.

A "CALIBRATION SOLUTION RECEIVING FORM" will be initiated to record the date solutions are received, number of sets, condition, and place of storage at ECL. These forms will be kept in a designated folder. A copy is found at the end of this Section and labeled Figure 8-2.

8.1.2 Standards Prepared at ECL

ECL will prepare and maintain separately weighed stock standards of each analyte. These stock standard materials should be from the same lot numbers as those used to prepare the EPA/Bionetics-supplied calibration solutions. These ECL-prepared standards will be used to verify the concentrations of the calibration solutions and resolve problems or questions that may arise concerning any of the standards.

A standards log book is maintained to record name of person weighing the standard, chemical identifier of standard, date of preparation, purity lot no., source, balance calibration data, and standard weighing data.

8.1.3 QA for Diluting and Checking the Standards

Prior to dilution, calibration solutions and/or EPA/ECL stock standards are removed from freezer storage and allowed to reach room temperature.

Calibration solutions and all subsequent dilutions are labeled with the standard identifier, Batch No, solvent, preparer, date and concentration. The Batch Nos. provide a means of tracking them to origin.

The EPA/ECL prepared standards are labeled with standard identifier, date standard was weighed, solvent, preparer, and concentration. These standards can be tracked to origin by the date the standard was weighed which will lead to a specific entry in the ECL standards log book as covered in 8.12.

A "STANDARD DILUTION FORM" (Figure 8-3) at the end of this Section is used to record all information on dilutions and to facilitate the tracking of standards.

8.1.4 Calibration Solutions and ECL Standards Verification

Calibration solutions will be the stock material for all standards used in the NPS at both the referee and analytical contractor laboratories. To verify their concentrations, they must by analyzed against the ECL prepared standards before use. The calibration solutions and ECL prepared standards must differ by no more than $\pm$ 15%. Following the comparison, all values must be reported to the ECS Project Leader. Standards with differences $>\pm$ 15% require resolution at this point before work with the standard can proceed.

8.1.5 Frequency of Calibration Standards Checks

Calibration standards must be checked against ECS prepared standards each time a new calibration standard is prepared from a calibration solution. Criteria in 8.14 apply.

Concentrations of calibration solutions must be verified at ECS each time new Batch Nos. are prepared at EPA/TSD-Cincinnati or Bionetics and before shipment to the analytical contractor. Criteria in 8.14 apply.

8.1.6 Association of Calibration Standards to Survey Sample Analyses

Each calibration (bench) standard used in analytical determinations must be able to be traced to its origin and every field sample or control sample analyzed must be associated with the specific calibration standard(s) used.

To facilitate these requirements, each standard mix with different components or different concentrations of these components must have a uniquely different name and a date of preparation. This standard identifier and date must appear on each chromatogram of the standard. It may also appear on the computerized data printout.

* 8.2 Instrument Calibration and Quantitation (effective 06/88)

A Hewlett-Packard 5890 A dual capillary GC with electron-capture detectors is used to analyze Method 3 samples. The internal standard (ISTD) selected for use with Method 3 is 4,4-dibromooctafluorobiphenyl (DBOB) and is compatible with the GC columns and chromatographic conditions for this Method.

Weighed methyl ester standards are used for the calibration/ linearity check of the gas chromatograph. A minimum of three standards will be diluted from an ECS-prepared standards mix, and the lowest concentration of each must be at the Minimum Reporting Level (MRL). The higher concentrations will span the range of concentrations expected in the sample extracts and in the Laboratory Control Spikes (LCS). Thus, the standards for instrument calibration should range from MRL to 10xMRL.

Following injection of the ECS-prepared standards, the relative response (RRa) of each analyte to the ISTD is calculated with the following equation:

$RR_a = A_a / A_{IS}$, where

A_a = Area of the analyte

A_{IS} = Area of the internal standard

The calibration curve is generated by plotting RR_a versus analyte concentration in ug/liter.

Although a calibration curve is drawn for each analyte, it is not used for quantitation but only for QC purposes. The working calibration curve must be verified previous to sample analysis and every eight hours during an analysis sequence. If the response for any analyte varies from the predicted response by more than +/- 20%, the GC injection should be repeated and/or a new calibration curve prepared for that analyte. If the predicted response for an analyte continues to vary by more than +/- 20%, a new calibration standard mix should be prepared. If a new calibration standard is prepared, the ECS Project Leader must be informed.

Initially, the current requirements of the Instrument Quality Control Standard must be met.

Procedural Standards are prepared at 10xMRL by methylating weighed acids or phenols. The surrogate must be incorporated into one of the mixes. These analyte mixes are used as "single point quantitation" standards. (See Section 5.3.)

Following injection of a standard, the relative response (RRstd) of each analyte to the internal standard is calculated with the following equation:

RRstd = (Aa/Ais) /C, where

Aa = Area of the analyte

Ais = Area of the internal standard

C = Concentration of analyte at 10xMRL.

In a similar manner, a response factor (RRsamp) of each analyte to the internal standard of each sample is calculated with the following equation:

RRsamp = (Aa/Ais), where

Aa = Area of the analyte

Ais = Area of the internal standard

The ratio of the RRsamp to the RRstd of a given analyte in a sample will result in the determination of the concentration of the analyte.

If a new calibration curve must be prepared, the ECS Project Leader must be informed.

8.2.1 Calibration of HR GC/MS

Scanning Mode - The instrument is calibrated by the MCAL and CALIB routines in the MAT 312 operations manual

MID Mode - The instrument must be further calibrated by using the ESCAN and ECAL routines in the manual

The instrument will be tuned for proper relative ion intensities by using DFTPP[1/] (if possible) when library searches are indicated.

* **8.2.2 Calibration of Low Resolution GC/MS (effective 06/88)**

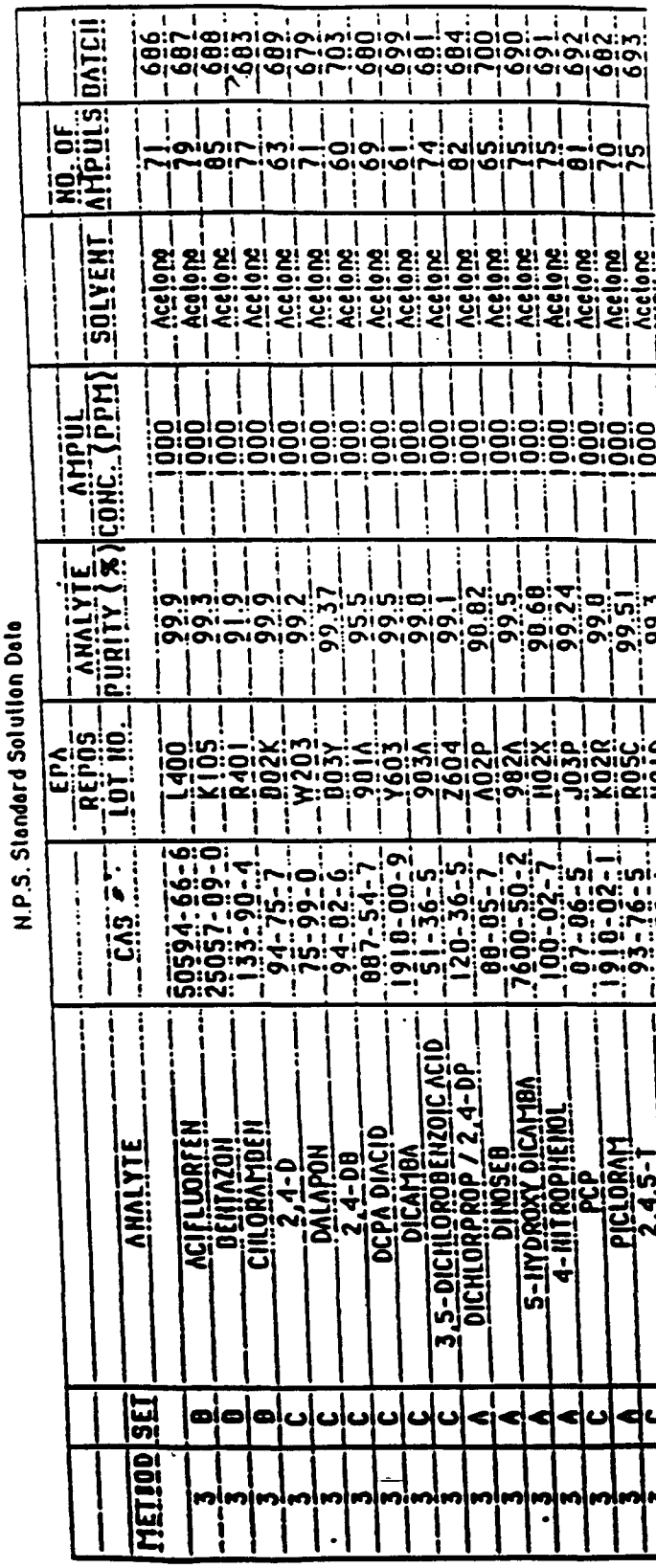
The instrument is calibrated according to the manufacturer's recommendations using the CALIBRATION (CAL) routines specified in the manual.

The mass spectrometer will be tuned to EPA's specifications using DFTPP (effective 06/88).

[1/] Eichelburger, J.W.; Harris, L.E.; Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography - Mass Spectrometry Systems" Anal. Chem. 1975, 47(7), 995-1000.

FIGURE 8-1

STANDARD SOLUTION DATA FORM



N.P.S. Standard Solution Data

METHOD	SET	ANALYTE	CAS #	EPA REPOS LOT NO.	ANALYTE PURITY (%)	AMPUL CONC. (PPM)	SOLVENT	NO. OF AMPULS	DATE
3	B	ACIFLUORFEN	50594-66-6	L400	99.9	1000	Acetone	71	686
3	D	DEMTAZON	25057-09-0	K105	99.3	1000	Acetone	79	687
3	D	CHLORAMDEN	133-90-4	R401	91.9	1000	Acetone	85	688
3	D	2,4-D	94-75-7	D02K	99.9	1000	Acetone	77	7683
3	C	DALAPON	75-99-0	W203	99.2	1000	Acetone	63	689
3	C	2,4-DB	94-82-6	D03Y	99.37	1000	Acetone	71	679
3	C	DCPA DIACID	887-54-7	901A	95.5	1000	Acetone	60	703
3	C	DICAMBA	1918-00-9	Y603	99.5	1000	Acetone	69	680
3	C	3,5-DICHLOROBENZOIC ACID	51-36-5	903A	99.0	1000	Acetone	61	699
3	C	DICHLORPROP / 2,4-DP	120-36-5	Z604	99.1	1000	Acetone	74	681
3	A	DINOSEB	88-85-7	A02P	90.82	1000	Acetone	82	684
3	A	5-HYDROXY DICAMBA	7600-50-2	902A	99.5	1000	Acetone	65	700
3	A	4-NITROPHENOL	100-02-7	H02X	90.68	1000	Acetone	75	690
3	A	PCP	87-86-5	J03P	99.24	1000	Acetone	75	691
3	C	PICLORAM	1918-02-1	K02R	99.8	1000	Acetone	81	692
3	A	2,4,5-T	93-76-5	R05C	99.51	1000	Acetone	70	682
3	C	2,4,5-TP (SILVEX)	93-72-1	H01D	99.3	1000	Acetone	75	693

FIGURE 8-2

CALIBRATION SOLUTION RECEIVING FORM

Date Received:_____ Date Checked:_____

Person Receiving:_____ Person Checking:_____

Were Samples Iced?_____ Relinquished Custody:(Yes/No)_____

Method No: (1,3,or 6)_____
(circle one)

Comments:

Person Assuming Custody:_____ Date:_____

Number of Sets:_____

Date Calibration Solutions arrived at EPA/ECL written on individual standard cartons: (Yes/No)_____

Date Stored:_____ Freezer No:_____ Room No:_____

Comments on condition of Calibration Solutions:

STANDARD DILUTION FORM

Signature_____

Date_____

Source of Std: Type Standard:_____
(Single or Multicomponent and Name)

Calib. Sol. or EPA/ECL Prepared

(1) Compound Name	* (2) Batch No.	* (3) Date Rec.	** (4) Stock Std Date	(5) Starting Conc.	(6) Dilution	(7) Conc.	(8) Dilution	(9) Conc.	(10) Dilution	(11) Conc.

* Column 2 and 3 - Fill out for Calibration Solutions only.
** Column 4 - Fill out for EPA/ECL Prepared Standards only.

FIGURE 8-3
STANDARD DILUTION FORM

9. ANALYTICAL PROCEDURE

9.1 Summary Of Method

This Method is applicable to the determination in ground water of the phenoxy acid and phenol analytes listed in Section 3 and their salts and esters.

A measured volume of sample (approximately 1-Liter) is adjusted to pH 12 or greater with 6N sodium hydroxide and allowed to sit, with periodic shaking, for 1 hour to hydrolyze salts and esters of the phenoxy/phenol analytes. Extraneous organic material is removed by dichloromethane solvent washes. The sample is acidified, and the chlorinated acids are then extracted with diethyl ether by shaking in a separatory funnel. Using diazomethane as a derivatizing agent, the acids are converted to their methyl derivatives. Excess derivatizing reagent is removed, and the esters are determined by electroncapture gas-chromatography (ECD).

A Florisil® cleanup procedure is included to aid in the elimination of interferences that may be encountered.

Capillary gas-chromatography with ECDs is used for both primary and secondary analyses of the sample extracts.

For sample extracts with suspect-positive analytes, (i.e.-those with positive responses on both the primary and secondary GC columns), such extracts will be analyzed by either Low Resolution GC/MS (LRGC/MS) or High Resolution GC/MS (HRGC/MS) to confirm the presence or absence of the analyte.

9.2 Major Equipment/Instrumentation To Be Used With Method 3

- Hewlett-Packard 5890A dual capillary gas-chromatograph with dual ECD. Identical instrument for backup.
- Hewlett-Packard 7673A autosampler. Identical unit for backup.
- Hewlett-Packard 3359A Lab Automation System
- Finnigan MAT 312 High Resolution GC/MS
- Finnigan Mat 5100 Low Resolution GC/MS

9.3 Analytical Method

9.3.1 Method As Developed By Battelle

This Method is presented in Appendix B.

9.3.2 Differences From Battelle Method

* 3.5 Instrument Quality Control (QC) Standard - use isooctane instead of methyl tert-butyl ether (MTBE)

* 4.1.1 Glassware Cleaning and Preparation

1. All new glassware should be pre-soaked in Chromic-Sulfuric acid cleaning solution.
2. Wash glassware with 2-5% Chem-solv, Micro®, or similar cleaning solution. Pre-soak heavily soiled glassware.
3. Rinse will with tap water.
4. Rinse glassware with acetone, methylene chloride and hexane respectively. (Safety note: wear rubber gloves not permeable to or attacked by solvents and wear safety glasses.)
5. Bake glassware in oven overnight (approx. 12 hours) at 400'C. For this purpose, glassware is stacked on aluminum or stainless steel trays and loaded into the oven.
6. Upon cooling, rinse glassware with acetone, methylene chloride and hexane.

* 4.2 All clean baked glassware will be rinsed with acetone, methylene chloride, and hexane prior to use. No acid-rinsing of glassware.

* 6.2.7 Flask - flat bottom - 250 ml with 24/40 ground glass joint. Fisher (or equiv.) cat no. 10-101B

* 6.9 See Appendix No. C for Diazald Kit for diazomethane generator apparatus and procedure.

* 7.3 Acidified sodium sulfate - Acidify by slurrying 100g of sodium sulfate (heated at 400°C overnight and stored in a desiccator) with enough acetone to just cover the solid. Add 1 ml Ultrex concentrated sulfuric acid to slurry and mix thoroughly. Remove the acetone under vacuum using a rotary evaporator. Bake dried acidified sodium sulfate at 400'C overnight then store in desiccator until needed. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture with pH paper. The pH must be below pH 4.

* 7.1.6 Stock Standard Solutions are prepared in acetone.

* 7.1.7 Internal Standard Solutions are prepared in isooctane. Final internal standard concentration should read 0.25 ug/ml.

* 7.1.8 Surrogate Standard Spiking Solutions are prepared in acetone; concentration will differ.

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* Denotes reference to Battelle's Method and is not part of the ECL numbering system.

* 7.1.9 Instrument QC Standards are prepared in isooctane from known amounts of methyl derivatives, not acids; concentrations will differ.

* 10.6.1 The laboratory must, on an ongoing basis, analyze at least two laboratory controls (all analytes) per sample set.

* 10.6.1.1 The spiking concentrations in the laboratory control standard should be 10 times the MRL.

* 10.6.1.2 Add mercuric chloride to the laboratory control sample in amounts to produce a concentration of 10 mg/L. See 8.21 Sample Preservation.

* 10.7 Will not be done at Referee Laboratory.

* 10.8 Add mercuric chloride to the Method Blank in amounts to produce a concentration of 10 mg/L. See 8.21 Sample preservation. Change EDL to MRL.

* 10.10 Refer to Section 5.4 and 5.5.

* 11.1 Automated Hydrolysis, cleanup, and extraction Method is not used (11.2 Manual Method used)

* 11.2.1 Spiking volume of the Surrogate Standard Solution may vary, but will not exceed 200 ul.

* 11.2.3 Let the sample sit at room temperature for 1 hour, shaking the separatory funnel and contents periodically (every 15 min.).

* 11.2.7 Drain lower aqueous layer into a 2 Liter Erlenmeyer flask and combine ether extracts in a 250 ml Erlenmeyer flask over approximately 1 g of acidified sodium sulfate (avoid getting water into the ether extract).

* 11.2.8 Periodically (every 15 min.) vigorously shake the sample and drying agent.

* 11.2.9 Record weight of filled water sample bottle. Pour contents into a 2 Liter separatory funnel. Record weight of empty bottle and subtract difference to determine weight of sample.

* 11.3 Extract Concentration - Using a warm (35o-40o) water bath and a stream of dry filtered nitrogen, concentrate the ether extract to about 8 ml. Do not let ether approach dryness. Quantitatively, transfer contents to a centrifuge tube with ethyl ether and using a warm water bath (35o-40oC) and a stream of dry filtered nitrogen, further concentrate extract to 0.5 ml. Add 2ml of MTBE and reconcentrate to 2 ml. Add 250 ul of methanol and adjust volume to 4.5 ml with MTBE.

Note: Centrifuge tubes must be used instead of concentrator tubes. Avoid use of ground-glass joints with diazomethane. (See 11.51 - Preparation of diazomethane)

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* Denotes reference to Battelle's Method and is not part of the ECL numbering system.

* 11.4 The gaseous diazomethane method is not used.

* 11.5.1 and 11.5.2 Use Method, Appendix # C, for preparing diazomethane (alcoholfree ethereal solutions). Diazomethane solution should remain tightly capped, have a yellow color, and may be stored at 0'-5'C for a period of up to 6 months.

* 11.5.3 Add 1 ml of diazomethane solution to each centrifuge tube. Samples should turn yellow after addition of the diazomethane solution and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

* 11.5.5 Do not use silicic acid. Use dry filtered nitrogen, and warm water bath to remove any diazomethane that may remain. Adjust the volume to 5.0 ml with MTBE.

* 11.6 Preparation of Column Check - Prepare a Column Check by pipetting, onto a Florisil® column, 1 ml of a standard containing the methyl derivatives of the analytes of interest at 10 times the concentration of the bench or calibration standards. This control is carried through the normal Florisil® cleanup.

9.3.3 Requirement For Authorization To Deviate From Battelle's Method

Any differences from the Method in Section 9.31 must be discussed with and approved by the ECL Project Leader for this Survey. The ECL Project Leader may require that such requests be in writing and be supported by a rationale, facts, or laboratory data.

9.4 Sample Sets

Samples will be carried through the analytical work in discrete groups or "sets". A set is a collection of field samples and QC checks or controls sufficient to assess the quality and validity of any data generated from the set independently of any other set. Specific controls included in sets with this Method are a Florisil® Cleanup Control, Method Blank, and 2 Laboratory Control Spikes which together comprise all analytes. At a maximum, 8 Field Samples may be run in a set.

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* Denotes reference to Battelle's Method and is not part of the ECL numbering system.

10. DATA REDUCTION, VALIDATION, AND REPORTING

10.1 Data Reduction

ECL will use an H-P 3354 Data System to acquire, store, and analyze raw data from the instrument and to generate data reports associated with each analysis. Information generated are compound retention times, peak areas, relative response factors, and analyte concentrations. These values plus sample i.d. and instrument parameters will comprise a DATA REPORT. Concurrent with sample analyses, hardcopy chromatograms will be generated and along with the DATA REPORTS will form a HARDCOPY DATA FILE. (Refer to Figure 10-1 at the end of this Section.)

Each sample chromatogram will be labelled with the Field Sample Number, final volume of extract, ul injected, dilution information if applicable, mg-eq. of sample, date, and initials of analyst.

Each chromatogram of a standard must be labelled with the unique identifier of the bench or calibration standard, amount injected, date of preparation of the standard, date of analysis, and initials of the analyst.

10.2 Data Validation

Information from each DATA REPORT will be evaluated and verified by an analyst experienced in chromatography and with this Method. Evaluation will include all QC CHECKS against ACCEPTANCE CRITERIA as specified in Section 11.0 and the DATA MEASUREMENT requirements for analyses as specified in Section 5.0.

Additionally, the following sampling and tracking data will be evaluated:

- Is the date from sampling to receipt at ECL within the NPS requirements? (1 day)
- Is the date from sampling to extraction within the NPS requirements? (14 days)
- Is the date from extraction to analysis, including GC/MS confirmation, within NPS requirements? (14 days)

SAMPLE DATA REPORTS on all samples and controls within the set will be prepared along with QC SUMMARIES of all QC DATA from the set. For these sample extracts that must be referred to GC/MS confirmation, the GC analyst will prepare the "GC/MS CONFIRMATION SHEET" which conveys to the GC/MS operator information on the extract necessary for the confirmation work. See Figure 10.2 at the end of this Section.

All data generated under 10.1 and 10.2 will be PEER REVIEWED by an analyst under the direction of the ECL Quality Assurance Coordinator (QAC) or his Designated Representative. This review will include review of the HARDCOPY DATA FILE for the sample set and validation of all sample data and QC checks from which SAMPLE DATA REPORTS and QC SUMMARIES are derived. Discrepancies will be resolved by the ECL QAC, Project Leader, and the analyst. Upon completion of all reviews, the PEER REVIEWER will sign and date all forms and records indicating validation of the data.

10.3 Data Reporting

Analytical sample data and QC data from the Instrument Control Standard (see Section 11.1) will be reported via an ASCII text file on a floppy diskette. See Appendix C for instructions on the data format and specific data to be keyed into the ASCII files. The data in the SAMPLE DATA REPORTS and QC SUMMARIES will contain any data to be entered into the ASCII file.

A d-Base III program has been written to generate and manage these ASCII files.

Sampling data and tracking data will be entered into the files by the ECL Sample Custodian and/or analytical team members who are completing analytical work with time limits (i.e. sample or extract holding times).

The floppy diskettes containing these files will be sent each month to EPA/Cincinnati, Ohio to:

Christopher Frebis
EPA/Technical Support Division
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

Data for a set of samples are to be reported no later than 2 months from the earliest sample collection date within that set.

Where rounding of numbers or determination of significant digits is required, ECL will adhere to the procedures and criteria in Appendix E.

10.4 Storage of Lab. Data

The HARDCOPY DATA FILE (chromatograms of samples, controls, associated standards and the related DATA REPORTS or computerized printouts) will be maintained and filed by Method and set. The data file on a set will also contain all forms used in evaluating samples and and QC SUMMARIES. Sampling and tracking data will also be filed.

It is the responsibility of the analyst to assure that all elements of the HARDCOPY DATA FILE are in the file. It is the responsibility of the PEER REVIEWER to see that these same elements remain intact following review, and that they are stored by Method and Set in the RECORDS ROOM.

These files will be retained in storage until ECL is notified by NPS Management of further disposition.

Raw data is acquired and stored on hard-disk and can be retrieved if necessary. There is no provision for back-up magnetic tape storage. The HARDCOPY DATA FILE will contain all elements needed to support a sample analysis. The Procedure for storage of NPS files is attached as Appendix F.

10.5 Fast-Track Reporting

The NPS has determined that two situations will require "FastTrack Reporting" of data.

- Confirmed positive residues for certain analytes to be specified by EPA. This data will also be reported routinely with the appropriate set data.

- A situation when results from the secondary GC column do not agree with results from the primary column within criteria set forth in Section 5.4. This situation is to be discussed with the ECL Project Leader prior to reporting the data.

A protocol has been provided by NPS on reporting the "confirmed positives" mentioned above. See Appendix J for the NPS protocol and the list of analytes and their rapid reporting levels. The ECL Project Leader will assume the duties and responsibilities assigned to the Technical Monitor in the memo.

Also included in the Appendix are forms to be used at ECS in reporting analytes subject to rapid reporting requirements. Forms for all three Methods being run at ECS are included with this QAPjP since an action level in one Method triggers rapid reporting for all Methods.

It is the responsibility of the GC analyst for this Method to be aware of these rapid reporting levels, to assure that the ECS report forms are initiated upon determining that a particular residue associated with his/her Method is subject to rapid reporting, and to inform the ECS Project Leader immediately.

10.6 GC/MS

10.6.1 Data Reduction

All HR GC/MS data are acquired by a Digital PDP II/34 computer and stored on a CDC-CMD disc drive. The LR GC/MS data are acquired by a Finnigan 5100 data system based on SuperIncos software. Identification is based on selected ion monitoring of EPA-designated ions and the retention time of the analyte of interest. The GC/MS analyst will search for the analyte of interest at the proper retention time of the standard and also look for characteristic ions. The peak areas of the selected ions for the analyte of interest in the sample being confirmed are then compared to the same ions generated from a standard of the analyte of interest at about the same concentration level. If marked differences in relative abundance are observed, the analyst and Technical Monitor should account for the discrepancy before a positive identification is established (effective 06/88). Hard copies of data are made and kept on file. After all the results have been reviewed, the raw data is transferred to a magnetic tape.

10.6.2 Data Validation

The hard copies of the MS data are reviewed by the mass spectrometrist for accuracy and completeness. The data must also meet the other QA requirements in this QAPjP [See Section 5.1(8), 5.21, 5.22, 5.5, 5.6(2)], that apply. Then the Section Chief or the ECS Project Leader reviews the data, and a decision is made as to whether or not the presence of a compound can be confirmed.

10.6.3 Data Reporting

The results of the GC/MS confirmatory analyses will be reported to the ECS Project Leader if the sample(s) were extracted at ECS and to the appropriate Technical Monitor for the analytical contractor if the extractions were done by the contractor. (See Figure 10-2 at the end of this Section.) One set of hardcopy data supporting each confirmation should be attached to the form.

10.6.4 Filing and Storage of GC/MS Data

The NPS Project Officer will be responsible for the initial filing and storage of GC/MS results and data as described in Sections 10.4.

Raw data will be stored on magnetic tape by the GC/MS analyst as described in Section 10.61. Any GC/MS analysis or confirmation can be reconstructed from this raw data.

STORAGE OF NPS HARDCOPY DATA FILES AT ECL

The HARDCOPY DATA FILES and all related reports will be filed according to NPS Method No., and then by Sample Set.

ECL has a RECORDS ROOM available for this purpose. It is equipped with shelving for storage, a smoke alarm, and a sprinkler system. Activation of the smoke alarm is monitored 24 hours a day by the NSTL fire department which can respond within 2 minutes to an alarm. ECL will take precautions to protect from sprinkler syystem water damage all files stored in this room.

The RECORDS ROOM is also the office of the ECL QAC and is locked when the room is unoccupied. Access is limited to the ECL Laboratory Manager, the ECL QAC, and Project/Team Leaders.

The STORED RECORDS LOG is used to log files into the RECORDS ROOM and to record removal and subsequent return of these files.

FIGURE 10-1

FLOW CHART FOR DATA REDUCTION, VALIDATION, AND REPORTING

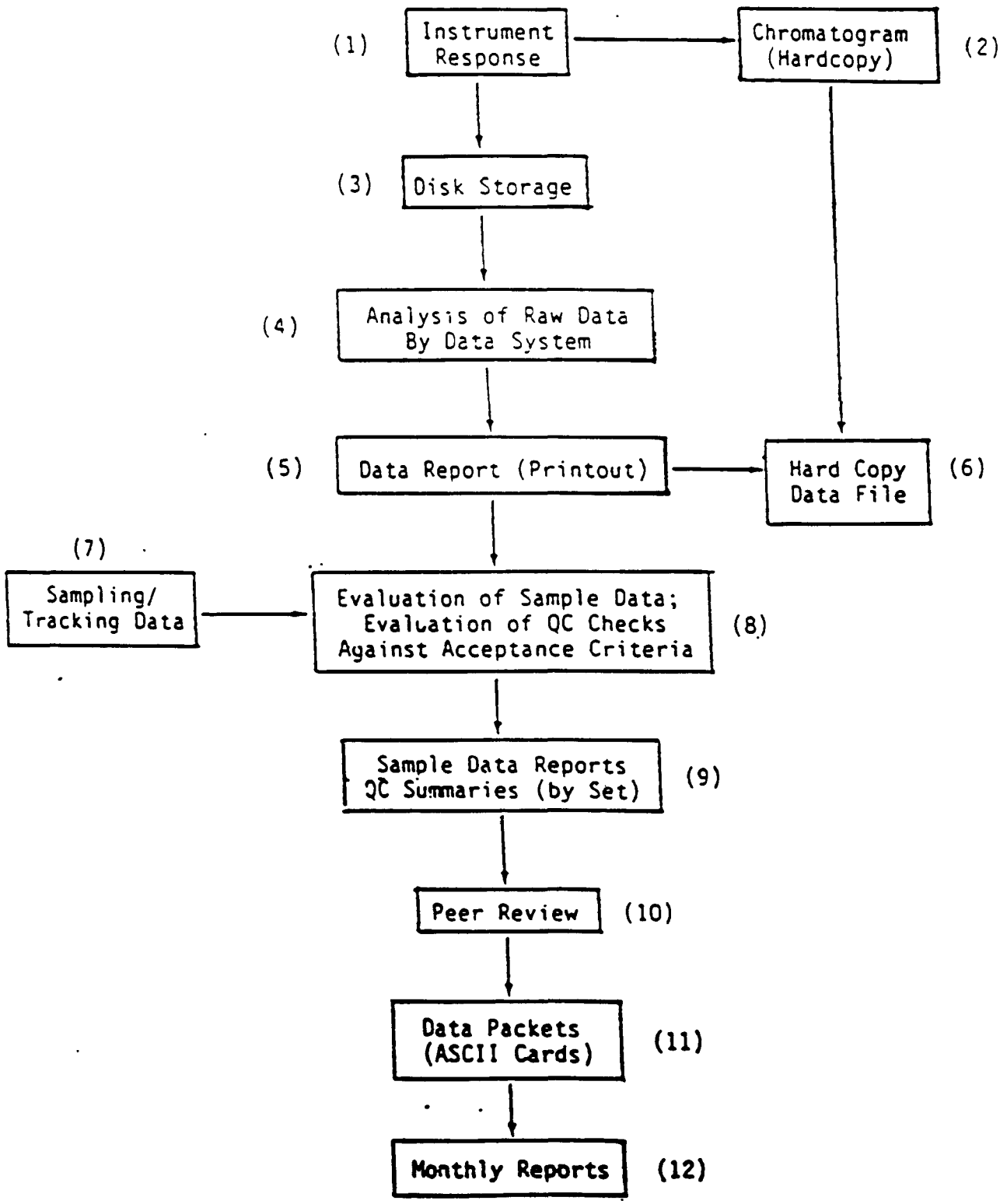


FIGURE 10-2

MASS SPEC CONFIRMATION SHEET

Major project name ______________ Sub-project name ______________
Person requesting Confirmation ______________ Person preforming Confirmation ______________
Date submitted ______________ Date completed ______________

Specific details of sample extracts

Sample No. ______________ Sample Conc g/ml ______________

	Compound	Conc Ng/ml	Mass Spec Number	Mass Spec Confirma-tion	Mass Spec est Conc.	Mass Spec Confirmation Code
1.						
2.						
3.						
4.						

Sample No. ______________ Sample Conc g/ml ______________

	Compound	Conc Ng/ml	Mass Spec Number	Mass Spec Confirma-tion	Mass Spec est. Conc	Mass Spec Confirmation Code
1.						
2.						
3.						
4.						

Sample No. ______________ Sample Conc g/ml ______________

	Compound	Conc Ng/ml	Mass Spec Number	Mass Spec Confirma-tion	Mass Spec est. Conc	Mass Spec Confirmation Code
1.						
2.						
3.						
4.						

Sample No. ______________ Sample Conc g/ml ______________

	Compound	Conc Ng/ml	Mass Spec Number	Mass Spec Confirma-tion	Mass Spec est. Conc	Mass Spec Confirmation Code
1.						
2.						
3.						
4.						

11. INTERNAL QUALITY CONTROL CHECKS

Summarized in this Section are all the QC checks and controls required for analysis of NPS samples. These QC checks are classified according to the analysis type (i.e.- primary column, secondary column, GC/MS Confirmation).

11.1 Primary Analyses

Type of QC Check	Frequency	Criteria for Acceptance	Corrective Action
• Instrument Control[1/] Standard PSF PGF Resolution Sensitivity	1 day (or 1 set if uninterrupted analysis of the set extends to 2 days)	 0 70 < PSF < 1 05 0 70 < PGF < 1 05 > 0 40 ≥ EDL for dinoseb	 Reevaluation of GC System Reevaluation of GC System Reevaluation of GC System Reevaluation of GC System
• Method Blank	1 set	No peaks within the retention window of any analyte ≥ ½ MRL for that analyte	Out-of-control situation, Method Blank must be brought in control before proceeding
• Lab Control Standard	1 std mix	Refer to Section 11 4 3	Out-of-control situation, work must be stopped until control is establihsed Refer to Section 11 4 3
• Calibration Standards	Min 1 day or each working shift	All analyte repsonses within ± 20% of that predicted by current calibration curve	1 Prepare a fresh calibration standard, or 2 Prepare a new calibration curve
• Field Samples	Maximum 5 set	See individual QC checks	See individual QC checks
- Internal Standard	Each sample	Response must be within ± 20% of average response of internal standard in calibration stds.	Refr to Appendix C, Section 10 5, in the written method
- Surrogate Spike	Each sample	Recovery must fall within window of R (recovery of surrogate from applicable control chart) ± 30 percentage points (effective 08/18/89)	1. Check calculations 2 Check internal and surrogate std spiking solutions 3 Reanalyze the sample extract 4 If reanalysis of extract results in surrogate being "in-control," submit only data from "in-control" analysis 5. If reanalysis fails to put surrogate in control, reevaluate analytical method and measurement system Reextract failed sample when system is again in control
• Performance Eval Samples	As needed	To be determined	Out-of-control situation, problem must be corrected and analytical system put back in control as evidneced by successfully analyzing a second P-E Sample
• Shipping Blank	NOT APPLICABLE TO ECL REFEREE RESPONSIBILITIES		
• Spiked Sample	NOT APPLICABLE TO ECL REFEREE RESPONSIBILITIES		
• Time Storage Samples	NOT APPLICABLE TO ECL REFEREE RESPONSIBILITIES		

1/ Refer to Section 14 1 and to Appendix C, Table 10 on page 35 of the written Method

11.2 Confirmational (Secondary-Column) GC Analyses

Type of QC Check	Frequency	Criteria for Acceptance	Corrective Action
• Calibration Standards	min 1 day or each working shift	All analyte responses within 20% of that predicted by current calibration curve	1 Prepare a fresh calibration standard, or 2. Establish a new calibration curve
• Instrument Control[1/] Standard Sensitivity	1 day	> EDL for dinoseb	Reevaluation of GC System
• Method Blank	1 set	No peak within retention window of any analyte ≥ ½ MRL for that analyte	Out-of-control situation; Method Blank must be brought back in control before proceeding
• Shipping Blank	NOT APPLICABLE TO ECL REFEREE RESPONSIBILITIES		
• Quantitation	As required by suspect positives from primary column		
- Calibration Std.		± 20% of conc. of the analyte determined on the primary column	Use proper std. conc.
- Analyte Concentration Value	Per analyte	± 25% of the conc. determined on the primary column	Confer with ECL Project Leader.

1/ Refer to Section 14.1 and to Appendix C, Table 10 on page 35 of the written Method.

11.3 GC/MS Confirmation

- GC/MS Confirmation will be required for all compounds confirmed by second column GC analysis.

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

* • If an analyte is confirmed by second column GC analysis but is not present when analyzed by GC/MS, the analyst must demonstrate that the analyte was not lost while concentrating the extract. A standard of the analyte should be prepared at the concentration determined by GC analysis, and then concentrated and analyzed in the same manner as the sample extract.

* • The Method Blank should be prepared and analyzed using the same procedures as those used for the sample.

* • Confirmation is accomplished by comparison to the mass spectra of the authentic standard and is based on characteristic EPA-designated ions and on the retention time.

* • In the event that interferences preclude the use of the designated EPA ions, other characteristic ions may be substituted on approval by the ECS-NPS Project Leader.

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

- Mass Spectral Confirmation Codes

  - MIS - Three individual ions are scanned
  - SPECTRA - All or a significant portion of the spectra is scanned

11.4 Control Charts

11.4.1 Establishing Control Charts

A. ECL, as a referee lab for Method 3, will be required to demonstrate control of the measurement system via use of control charts. Control must be demonstrated for each analyte for which quantitation is required and for the surrogate at a concentration equal to that spiked into samples.

B. To establish the control charts, following initial demonstration of capability, 5 reagent water samples will be spiked at 10 times the Minimal Reporting Level (MRL) for the method and carried through extraction and analysis. Only results of analyses on the primary column are used in establishing the control charts. An additional 15 samples will be spiked and analyzed, 5 on each of 3 days. The data from these 20 spiked samples will be used to construct control charts.

C. Criteria for Accuracy and Precision

1. The RSDs for any analyte must be $\leq$ 20%, except where data, generated by Battelle at the corresponding level, indicated poorer precision. The RSDs exceeding 20% will be evaluated on a case-by-case basis by Technical Monitors for each method.

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

   Example:

   For an analyte "A"

   - Battelle demonstrated recovery (x) of 80% for Analyte "A" with RSD of 5%. Acceptable recoveries will be 80% $\pm$ 3 (5%) = 80% $\pm$ 15% = 65% - 95%;

   - or, Battelle demonstrated recovery (x) of 80% with RSD of 15% for analyte "A". The acceptable recovery would be limited to 80% $\pm$ 30% = 50% - 110%.

3. Surrogate

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

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

An LCS in which the surrogate compound recovery has failed to meet the quality control limits can be validated if the following conditions are met.

a. The LCS meets all other quality control criteria; and

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

4. Warning Limits/Control Limits

The control charts will be drawn up so as to depict both warning limits ($\pm$ 2 σ) and control limits ($\pm$ 3 σ) about the mean.

11.4.2 Outliers

Dixon's test will be used to determine outliers. There can be no more than 3 outliers per analyte from the 20 spiked controls. The Dixon test for outliers can be found in Appendix G.

11.4.3 Plotting Data on Control Charts

Data (analyte recoveries in percent) from the LCS on the primary column will be plotted on the control chart for each analyte.

11.4.4 Out-of-Control Situations

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

   a. More than 15% of the analytes of a particular method are outside $\pm$ 3 σ

   b. The same analyte is outside $\pm$ 3 σ twice in a row, even though >85% of the total analytes are in control.

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

   a. Three or more consecutive points for an analyte are outside $\pm$ 2 σ but inside the $\pm$ 3 σ

   b. A run of 7 consecutive points for an analyte above or below the mean.

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

   The "alert" situation implies a trend toward an "out-ofcontrol" situation. The analyst is required to evaluate his analytical system before proceeding. If "alert" or "out-of-control" situations occur frequently, re-establishing control charts may be required by the ECL Project Leader before analytical work can proceed.

11.4.5 Up-dating Control Charts

Following establishment of the control chart, a spiked control(s) is part of each analytical or sample "set". When 5 such controls have been run, the recoveries of these analytes will be incorporated into the control chart by adding these 5 most recent recoveries to the 20 original points and then deleting the first 5 of the original points. Accuracy and precision are re-calculated and the

chart re-drawn. The newly drawn chart will then apply to all data in sample sets subsequent to the last one used to update the chart.

In the event there were 1-3 outliers when establishing the control chart, add the 5 most recent points and delete only the first 2-4 points so that a total of 20 points are used in the up-dated control chart.

11.5 Other QC Checks Performed at ECL

11.5.1 Diazomethane QC Check

See "DIAZOMETHANE QC CHECK FORM" and Instructions at the end of this Section, Figure 11-1.

11.5.2 Florisil® Elution Check

See the "ADSORBENT CHECK FORM" and Instructions at the end of this Section, Figure 11-2.

11.5.3 Quality Control Data Sheet

Information on all solvents, reagents, and solutions used during each NPS set extraction and cleanup, must be kept on a "QUALITY CONTROL DATA SHEET". This information sheet would also record storage conditions and disposal. See Appendix H.

11.5.4 NPS Groundwater Quality Assurance Data Form

Before any work begins on samples or controls, a "NPS GROUNDWATER QUALITY ASSURANCE DATA FORM", is initiated by the processing laboratory. After extraction, concentration, and cleanup, all pertinent set information is recorded on this form. This form and information for completing it are in Appendix H.

11.6 Exceptions to the QAPjP

11.6.1 Request for Approval

Occasionally, it may become necessary for personnel assigned to the NPS to request approval for exceptions or deviations from this QAPjP. This approval must come from the ECL Project Leader and may be initially requested either verbally or in writing, but in either case, the request must be supported by a clear rationale, laboratory data, and documentation. When approval is requested, the particular issue or exception will be assigned a reference number consisting of the laboratory name, NPS Method No., date, and a number to differentiate among the several discussions that may take place on that day.

EXAMPLE: ECL 3-040888-1 indicates that an exception to the QAPjP for Method 3 was requested on April 8, and it was the first one that day.

11.6.2 Documentation and Following Requirements

The ECL Project Leader will enter into a log book the reference number, the exception requested, and the information and documentation required to support approval of the exception to the QAPjP.

The person requesting the exception to the QAPjP must prepare a folder labelled with the reference number and his/her name, and within a time frame specified by the ECL Project Leader have in the folder documentation of the problem/exception and all supporting information and data. A form "EXCEPTIONS TO NPS QAPjP" is included at the end of this Section as Figure 11-3. A completed version must be included with each request for an exception to the QAPjP.

FIGURE 11-1

DIAZOMETHANE QC FORM

PREPARATION:

Date Prepared: _____ Analyst Preparing _____

Diazald Lot No. _____ Date: _____

KOH Lot No. _____ Date: _____

PROCESSING:

Date Methylated _____ Analyst Methylating _____

* Standard Used _____ Date: _____

1. Reagent Blank -
2. Spike A -
3. Spike B -
4. Spike C -

G.C. ANALYSIS:

Date Analyzed _____ Analyst _____

Diazomethane Satisfactory? Yes ___ No ___

G.C. Bench Standard _____ Date: _____

COMMENTS:

* Standard must have been prepared no longer than 30 days before Diazomethane check.

FIGURE 11-1 (continued)

DIAZOMETHANE QC FORM/INSTRUCTION

INSTRUCTIONS FOR HE DIAZOMETHANE QC CHECK

For each batch of diazomethane prepared for use with NPS Method 3, complete Part A of the "DIAZOMETHANE CHECK FORM".

To check the quality of the batch, prepare a BLANK (1 ml diazomethane w/no spike) and 3 replicate SPIKES at the Method 3 Control Spike Level. Bring final volumes to 10.0 ml in isooctane following derivatization procedure. Analyze the BLANK and 3 replicate SPIKES by GC. Mean recoveries of the analytes and the surrogate must be within the control limits (except for chloramben) as reflected by the control chart in current use with Method 3. There must also be no interfering peaks in the BLANK (for ANY Method 3 analytes) $\geq$ ½ MRL. If the diazomethane meets the above criteria, it can be used for NPS analytical work.

For any exceptions to the above criteria, check with the ECL Project Leader before using diazomethane.

FIGURE 11-2

ADSORBENT CHECK FORM

PROCESSING date: _____

Adsorbent checked: Silica-gel _____ Florisil _____

Bottle date _____ Jar letter _____

Lot No. _____ Lot No. _____

Cat. No. _____

* Adsorbent Batch # _____ Prepared by _____

** Standard Used _____ Date: _____

G.C. ANALYSIS date: _____

G.C. Analyst _____ G.C. Column _____

Adsorbent Satisfactory? Yes __ No __

Bench Standard _____ Date: _____

RESULTS/COMMENTS:

---

* Adsorbent Batch # - Silica-gel: The date deactivated.
Florisil: The date removed from oven and placed in desiccated

** Florisil/Intermediate Standard used must match Bench Standard.

FIGURE 11-2 (continued)

ADSORBENT CHECK FORM/INSTRUCTIONS

INSTRUCTIONS FOR THE ADSORBENT CHECK FORM

A Florisil® QC check must be run each time new batches of Florisil® have been activated (see Battelle Method, Section 7.1.5) and before use with NPS Method 3 work. A Florisil® QC check is also run with each sample set.

To check a newly activated batch of Florisil® prior to use, pipette 2 ml of a recent NPS3-7 procedural standard onto a column prepared according to Battelle Method 11.6, and elute as per instructions in 11.6.2 - 11.6.6. Final volume is 10 ml. Compare to the same procedural standard, and be aware that the concentration of the analytes in the Florisil® eluate are now at half-concentration of the procedural standard. (5 ml -> 10 ml final volume.)

Determine recoveries (%) and enter them on the "ADSORBENT CHECK FORM". Recoveries must be 80% - 120% for all analytes EXCEPT chloramben, and there must be no interfering peaks $\geq$ ½ MRL for any Method 3 analyte.

For any exception to the above criteria, check with the ECL Project Leader before using the Florisil®.

For the Florisil® QC check run with each set, the procedural standard from that set must be used.

FIGURE 11-3

EXCEPTIONS TO NPS QAPjP

Date _____ Method _____

Reference No. _____

Suggested Exception(s): _____

_____

_____

_____

_____

_____

_____

_____
Signature of Person Seeking Exception

Approved ____ Disapproved ____

Comments: _____

_____

_____

_____

_____

_____

_____

_____
Bob Maxey, Technical Monitor

12. AUDITS (Technical Systems/Data Quality/Performance Evaluation)

12.1 Requirements

Technical Systems and Data Quality Audits shall be conducted by the ECL QAC on NPS Method 1 analytical work to assess the adherence to the QA Project Plan and to assess the quality of data generated by the analytical systems. Performance Evaluation Audits will be initiated by ECL's QAC to evaluate the technical personnel and the analytical system.

12.2 Frequency

12.2.1 Technical Systems and Data Quality

These audits shall be conducted at the beginning of the survey after 30 samples have been analyzed and at least once every six months thereafter, exclusive of external audits.

12.2.2 Performance

At least one audit every six months.

12.3 Nature of Audits

12.3.1 Technical Systems Audits shall include the following:

- 12.3.1.1 Project Management System
  - 12.3.1.1.1 Personnel - Qualifications
  - 12.3.1.1.2 Documentation - QAPjP and SOPs
  - 12.3.1.1.3 Communications about changes in requirements
  - 12.3.1.1.4 Analyst feedback
- 12.3.1.2 Sample Tracking System - receipt through disposal or storage
- 12.3.1.3 Systems for Sample Preparations, e.g. extractions, clean up, etc.
- 12.3.1.4 Systems for Analytical Operations
  - 12.3.1.4.1 Standards
  - 12.3.1.4.2 Calibrations
  - 12.3.1.4.3 Documentation of Analytical Operations
  - 12.3.1.4.4 Corrective Action Loop
  - 12.3.1.4.5 Instrument Maintenance
- 12.3.1.5 Data Management Systems
  - 12.3.1.5.1 Collections
  - 12.3.1.5.2 Reduction
  - 12.3.1.5.3 Verification
  - 12.3.1.5.4 Internal Review
  - 12.3.1.5.5 Reporting
  - 12.3.1.5.6 Use of QC Data at Bench Level
  - 12.3.1.5.7 Data Storage and Retrieval

12.3.1.6 Laboratory Management Systems

12.3.1.6.1 Major Equipment Purchases

12.3.1.6.2 Services and Supplies (solvents, etc.)

12.3.1.6.3 Maintenance of Ancillary Equipment

12.3.1.6.4 General Physical Set Up - space, cross contamination. etc.

12.3.1.6.5 Cold Storage Facilities

12.3.2 Data Quality Audits

Shall include tracking 3 samples from Method 1 from log-in through preparation, primary and confirmatory analyses (including related set QC checks and other information), data handling and disposal.

12.3.3 Performance Evaluation Audits

Shall consist of providing a P-E sample every six months. The audit will consist of a P.E. solution to be spiked into a water matrix and analyzed as a routine NPS sample. The concentration of the analytes in the P.E. solution will be unknown to the analysts involved in the method.

12.4 Standard

ECL's Quality Assurance Project Plan for Method 1; Printed Analytical Procedure for Method 1 and ECL's Quality Assurance Facilities Plan.

12.5 Reporting and Use of Audit Results

Following any of the above audits, the ECL QAC shall report the results in writing to both the Lab Section Chief and NPS Project Leader. If deficiencies are found, each shall be specifically identified along with the cause, if known. The QAC will provide a written plan or suggestion for corrective action to the NPS Project Leader with a copy to ECL's Section Chief. The QAC shall also follow up with a limited audit to verify that deficiencies were resolved by the proposed corrective action.

13. PREVENTIVE MAINTENANCE

13.1 Gas Chromatographs

Two Hewlett Packard 5890A dual EC/capillary Gas chromatographs are used with Method 3 related analyses. An HP7673A autosampler is also used. Routine maintenance for these instruments is described below.

Maintenance Item	Schedule
• change injection port septa	• following 2 days analytical work or as required
• change compressed gas traps and filter dryers	• every 6 months or as required
• service or change injection port liner	• as required by instrument performance
• bake-out or replacement of GC column	• as required by instrument performance
• replacement of EC detector	• as required by lack of sensitivity or noise

Spare parts are maintained at ECL to accommodate the above maintenance requirements, and at least one spare GC column of each required type is on hand. ECL has a blanket purchase-order with Hewlett-Packard. Through it, parts and service can be accessed by telephone and usually are provided in 2-5 working days, if needed.

A log book will be maintained for each instrument. In it will be kept records of all daily or routine maintenance, problems and their resolution, and major repairs. It is the responsibility of the analyst to make the above entries, and sign and date them.

13.2 GC/MS

The following schedule of maintenance tasks and spare parts applies to the Varian Mat 312 and the Finnigan 5100.

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

Tasks	Frequency
Clean source	Monthly or as required by performance
Bake out magnetic and electric sectors	Monthly or as required by performance
Bake out GC column	Daily or as required
Change pump oil	Every 6 months or as required by use
Change GC column	As required by performance
Change injection port septa	Weekly or as required
Clean injection port liner	Monthly or as required by performance

Most maintenance is done inhouse. When a problem is encountered which cannot be resolved here, Finnigan MAT is contacted and service is arranged. Critical spare parts are also available to minimize downtime and the following list of replacement parts and consumable spares is maintained within the laboratory at all times.

1) Columns (at least one of each type used)
2) Ferrules for columns
3) Syringes

4) Filaments (at least two of each)

5) Gold gaskets

6) Injection port septa

7) Vacuum pump oil

14. SPECIFIC PROCEDURES FOR ASSESSING MEASUREMENT SYSTEM DATA

The formulas in this section are those used to calculate internal QC checks and statistics related to QC checks.

14.1 Formulas Related to Instrument Control Standards and Determination of Chromatographic and Column Performance

- Peak Symmetry Factor (PSF). See Figure 14-1 at the end of this section.

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

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

- Peak Gaussian Factor (PGF). See Figure 14-1 at the end of this section.

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

W(1/2) = peak width at half-height

W(1/10) = peak width at tenth-height.

- Resolution (R)

R = t/W , where

t = the difference in elution times between two peaks, and

W = the average peak width, at the baseline, of the two peaks.

14.2 Formulas For Calculating Statistics

- Standard Deviation(s)

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$,where

$x_1 \ldots x_n$ = individual sample values

$\bar{x}$ = sample mean

n = sample size or no. of sample values

- Coefficient of Variation (CV)

$$CV = \frac{s}{\bar{x}}$$

- Relative Standard Deviation (RSD)

  RSD = CV X 100

- Mean Recovery (R)

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

- Percent Recovery (%R)

$$\%R = \frac{\text{(net value of spike) X 100}}{\text{True value of spike}}$$,where

  (net value of spike) = (gross value) - (value attributed to background or Blank)

- Minimum Detection Limit (MDL)

  $MDL = s \times t(.99)_{(n-1)}$, where

  t(.99) = "Student's t-value appropriate for a one tailed test at 99% confidence level and a standard deviation estimate with (n-1) degrees of freedom.

14.3 Formulas Defining Control Limits

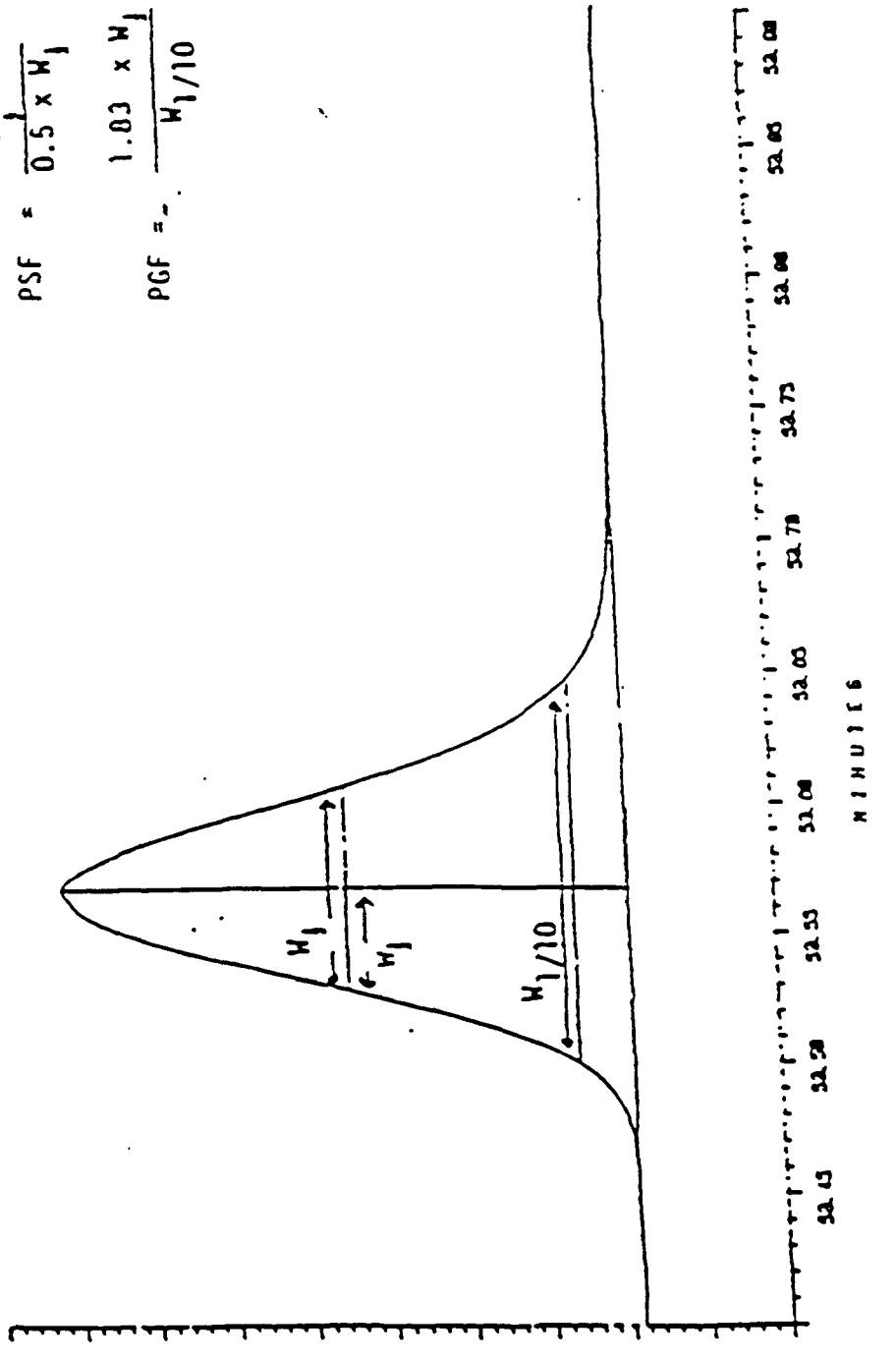
- Upper Control Limit (UCL) = R + 3s
- Upper Warning Limit (UWL) = R + 2s
- Lower Warning Limit (LWL) = R - 2s
- Lower Control Limit (LCL) = R - 3s ,where

  R = Mean Recovery

  S = Standard Deviation

FIGURE 14-1

EQUATION USED TO CALCULATE PEAK SYMMETRY FACTOR (PSF)
AND PEAK GAUSSIAN FACTOR (PGF)



15. CORRECTIVE ACTION

Corrective action is required when out-of-control situations develop regarding QC criteria, procedures, or specific Survey requirements. Sections 5 and 11 contain specific QC objectives and criteria for this Method, and Section 7 contains specific sampling and tracking requirements. All of these elements are evaluated as required by established NPS guidelines, and log books are maintained as documentation.

An analyst, team member, or Sample Custodian experienced with this Method and involved in day-to-day activities with it will be the first to be aware of a problem, inconsistency, or QC parameter outside acceptance limits. It is his/her responsibility to note the nature and significance of the problem and to bring it to the attention of the ECL Project Leader. Such problems shall be properly documented through use of the "SAMPLE RECEIPT SCREENS FOR NPS LABORATORIES" (refer to end of Section 7) and a related log book in Sample Receiving or by means of the "QUALITY ASSURANCE DATA FORM" (see Appendix H).

The following areas will be addressed:

- specific exception to the QC requirement
- when the problem was first noted and by whom
- who was notified
- corrective or remedial action required
- action taken
- verification that a QC exception or problem was resolved and the date
- sample "set" numbers and specific samples involved

If the ECL Project Leader cannot readily resolve the problem or provide guidance for corrective action, the ECL Quality Assurance Coordinator (ECL QAC) must be notified. The QAC will take a lead role in developing a strategy to resolve the problem. Verification that the problem has been resolved must also be provided before analytical work continues.

All QC exceptions, problems, corrective actions, and verification documentation must be reported monthly to the ECL Project Leader for this Method. For any problems requiring involvement of the ECL QAC, the ECL Project Leader must be immediately informed.

16. QA REPORTS TO MANAGEMENT

Internal Referee Laboratory QA Reporting System

The ECL NPS Project Leader will interact daily with the analyst performing the bench work and data generation for Method 3. The analyst will inform the Project Leader immediately when any QA problem or unusual situation develops. The analyst will follow the verbal notification with a written note explaining the problem. The ECL Project Leader will keep ECL's QA Coordinator informed and will discuss unresolved problems with him. The Project Leader will inform the ECL Section Chief of major problems.

The analyst for Method 3 will complete an "EPA Referee-Laboratories Progress QA Report". A copy of this form, Figure 16-1, is included in this section. Copies of this form will be submitted monthly to the Project Leader, who will in turn provide copies to the Section Chief and ECL QA Coordinator. The ECL QA Coordinator will submit on a quarterly basis copies of these forms to OPP's Quality Assurance Officer and to the NPS Quality Assurance Officer. Copies of the ECL internal audit reports (refer to Section 12.5) will be sent to OPP's Quality Assurance Officer.

Referee Laboratory Responsibilities for External Contract Monitoring - QA Monitoring - QA Reporting System

Six copies of the Primary Analytical Contractor Laboratory's report are to be provided monthly to the ECL Technical Monitor for Method 3. These reports are to be provided within 15 calendar days after the end of the month being reported. The format of this report is covered in the contractor's QAPjP for Method 3.

The Technical Monitor for Method 3 will provide the ECL Analytical Coordinator with a quarterly "Technical Monitor Progress - QA Report", Figure 16-2, a copy of which appears in this section. Copies of the "Monthly Contract Monitoring QA Report" for that quarter will be attached to the Technical Monitor Report. A copy of these reports will also be provided quarterly by the ECL Analytical Coordinator to ECL's Quality Assurance Coordinator, to OPP's QAO and to the NPS QAO.

The ECL Analytical Coordinator will submit an "Analytical Coordinator Status Report" through the ECL Section Chief to the Director of the NPS. Copies of the quarterly reports from the Technical Monitor will be attached to the Analytical Coordinator Status Report. A copy of the latter report, Figure 16-3, is included in this section.

FIGURE 16-1

EPA REFEREE LABORATORY PROGRESS - QA REPORT

Method # _____

Report Period _____

Analyst _____

Date _____

1. Progress:

   # samples received _____

   # samples analyzed _____

   # samples invalidated _____

   No. of data sets sent to EPA Data Manager _____

2. Standards: # stock standards diluted _____

   Results of check before using dilution _____

3. Bench Level Corrective Actions (s)

   Date _____

   Problem _____

   _____

   Action Taken _____

   _____

   Verification of Correction _____

   _____

   Sample set analyzed prior to problem _____
   (Use back of page and same format to report additional corrective actions.)

4. Problems (Project-Related):

5. Information requested by Technical Monitor - (control charts, etc.)

6. Changes in Personnel:

7. Comments:

FIGURE 16-2

TECHNICAL MONITOR PROGRESS - QA REPORT

Method # _____

Laboratory _____

Report Period _____

Date _____

1. Progress:

   # samples received _____

   # samples analyzed _____

   # samples invalidated _____

   No. for data sets sent to EPA Data Manager _____

2. Major Problems and Status

   a. Technical:

   b. Contractual:

3. Comments

FIGURE 16-3

ANALYTICAL COORDINATOR STATUS REPORT

Report period____

Prepared By _____

Date _____

Monthly - Financial States

- Contract Administrative Needs

Quarterly - Data Summary

- Copies of quarterly reports from Technical Monitors

APPENDIX A
SAMPLE CUSTODY

ENVIRONMENTAL CHEMISTRY LABORATORY
NPS SAMPLE LOGGING

METHOD _____ PREPARED BY: _____

(1,3,6) DATE: _____

LAB. I.D. (FIELD SAMPLE #)	DATE SAMPLED	DATE SHIPPED	DATE RECEIVED	TIME SAMPLED	CONDI

NPS SET COMPOSITION FORM
METHOD 3

APPROVED BY PROJECT OFFICER
SIGNATURE _____
DATE _____

Set No._____

SET CONTROLS

1. Florisil elution check
2. Method Blank
3. Lab Control Spike A
4. Lab Control Spike B

NPS FIELD SAMPLES

	Field Sample No.	Date Sampled	Date Arrived at ECL
5.	_____	_____	_____
6.	_____	_____	_____
7.	_____	_____	_____
8.	_____	_____	_____
9.	_____	_____	_____
10.	_____	_____	_____
11.	_____	_____	_____
12.	_____	_____	_____

SAMPLE CONTROL RECORD
EPA/ECL

LABORATORY SAMPLE NO.	REMOVED BY	DATE AND TIME REMOVED	REASON	DATE AND TIME RETURNED

ECL NPS SAMPLE TRACKING FORM

Set #____ Sample Number	METHOD 3					
	Date Sample Taken	Date Rec'd at ECL	Date Extracted	Date Analysis Completed	Date Removed for GC/MS Confirmation	GC/MS Confirmation Completed

NPS Method # 3 Extract Storage Data Sheet Set: _____

Extracts Relinquished By _____ Date: _____ Received By _____ Date: _____

ample Code #	Who Stored	Date Stored	Refrig. or Freezer No. Room No.	Removed By	Purpose	Date Removed	Returned by	Date Return

Date Disposed: _____ **Authorized by:** _____

APPENDIX B
BATTELLE'S VERSION

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

1. SCOPE AND APPLICATION

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

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

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

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

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

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is adjusted to pH 12 with 6 N sodium hydroxide and shaken for 1 hour to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed, and the esters are determined by GC using an electron capture detector (ECD).[1]

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

3. DEFINITIONS

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

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

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

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

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

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

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

3.8 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.

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

4. INTERFERENCES

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

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

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

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

4.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic

sample remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.[3,4]

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

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

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material 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.

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

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

5.2.2 Use a safety screen.

5.2.3 Use mechanical pipetting aides.

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

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

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

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

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

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

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed 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 stopcocks, ground glass or TFE-fluorocarbon stoppers.

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

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

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

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

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

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

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

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

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

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

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

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

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

6.8 Gaseous diazomethane generator -- Diazomethane generator assembly as shown in Figure 1 (available from Aldrich Chemical Co.).

6.9 Diazomethane solution generator -- Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. The diazomethane collector is cooled in an approximately 2-L thermos for ice bath or a cryogenically cooled vessel (Thermoelectrics Unlimited Model SK-12 or equivalent). The generation/collection assembly is shown in Figure 2.

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

6.11 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.

6.11.1 Primary column -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 µm 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.

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

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

7. REAGENTS AND CONSUMABLE MATERIALS

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

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

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

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

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

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

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

7.6 Potassium hydroxide (KOH), pellets -- ACS grade.

7.6.1 KOH, 37% (w/v) -- Dissolve 37 g KOH pellets in reagent water and dilute to 100 mL.

7.7 Carbitol (diethylene glycol monoethyl ether), ACS grade -- available from Aldrich Chemical Co.

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

7.9 Diazald solution -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber bottle with a Teflon-lined screw cap.

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

7.11 4,4'-Dibromooctafluorobiphenyl (DBOB) -- >99% purity, for use as surrogate standard (available from Aldrich Chemical Co).

7.12 2,4-Dichlorophenylacetic acid (DCAA) -- >99% purity, for use as surrogate standard (available from Aldrich Chemical Co).

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

7.14 Silicic acid, ACS grade

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

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

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

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

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

7.17 INTERNAL STANDARD SPIKING SOLUTION -- Prepare an internal standard spiking solution by accurately weighing approximately

0.0010 g of pure DBOB. Dissolve the DBOB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 25 µL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/L. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

7.18 SURROGATE STANDARD SPIKING SOLUTION -- Prepare a surrogate standard spiking solution by accurately weighing approximately 0.0010 g of pure DCAA. Dissolve the DCAA in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 µL of the surrogate standard spiking solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 5 µg/L and, assuming quantitative recovery of DCAA, a surrogate standard concentration in the final extract of 0.5 µg/mL. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

7.19 INSTRUMENT QC STANDARD -- Prepare a diluted dinoseb solution by adding 10 µL of the 1.0 µg/µL dinoseb stock solution to MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the instrument QC standard, add 40 µL of the diluted dinoseb solution, 16 µL of the 4-nitrophenol stock solution, 6 µL of the 3,5-dichlorobenzoic acid stock solution, 50 µL of the surrogate standard spiking solution, 25 µL of the internal standard spiking solution, and 250 µL of methanol to a 5-mL volumetric flask and diluting to volume with MTBE. Methylate sample as described in Section 11.4. Dilute the sample to 10 mL in MTBE. Transfer the instrument QC standard to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. 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[8] should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

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

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

8.2.3 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results given in Table 11 indicate that most analytes present in samples stored under these conditions are stable for at least 28 days after collection. However, analyte stability may be affected by the matrix; therefore, the analyst should verify that the preseraation technique is applicable to the samples under study.

8.3 EXTRACT STORAGE

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

9. CALIBRATION

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

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

9.2.1 Prepare calibration standards at a minimum of three (suggested five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and 250 µL methanol, and dilute to volume with MTBE. Esterify acids with diazomethane as described in Section 11.3. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

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

$RR_a = A_a/A_{is}$

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

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

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

10. QUALITY CONTROL

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

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

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

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

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

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

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

10.4 ASSESSING SURROGATE RECOVERY

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

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

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

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

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

(3) Check instrument performance.

Reinject the laboratory method blank extract. If the reanalysis fails the 70 to 130 percent recovery criteria, the analytical system must be considered "out

of control." The problem must be identified and corrected before continuing.

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

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

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

(3) Check instrument performance.

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

10.5 ASSESSING THE INTERNAL STANDARD

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

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

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

10.5.3.1 Single occurrence -- Reinject an aliquot of the extract to ensure proper sample injection. If the reinjected sample extract aliquot displays an internal standard peak area or height within specified limits, quantify and report results. If the reinjected sample extract aliquot displays an internal standard peak area or height outside the specified limits, but extract aliquots from other samples continue to give the proper area or

height for the internal standard, assume an error was made during addition of the internal standard to the failed sample extract. Repeat the analysis of that sample.

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

10.6 ASSESSING LABORATORY PERFORMANCE

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

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

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

10.6.1.3 Compare the percent recovery (R_i) for each analyte with established QC acceptance criteria. QC criteria are established by initially analyzing five laboratory control

standards and calculating the average percent recovery (P) and the standard deviation of the percent recovery (S_R) using the following equations:

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

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

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

Calculate QC acceptance criteria as follows:

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

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

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

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

If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the source of the problem must be immediately identified and resolved before continuing the analyses. The analyti-

cal result for that analyte in samples is suspect and must be so labeled. All results for that analyte in that sample set must also be labeled suspect.

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

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

10.7 ASSESSING ANALYTE RECOVERY

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

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

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

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

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

10.7.1.4 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is judged to be in control, the recovery problem encoun-

tered with the dosed sample is judged to be matrix-related, not system-related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

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

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

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

10.11 ADDITIONAL QC - It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples.

11. PROCEDURE

11.1 AUTOMATED HYDROLYSIS, CLEANUP, AND 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 µL of the surrogate standard spiking solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

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

11.1.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Shake sample for 1 hour using the appropriate mechanical mixing device.

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

11.1.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the organic phase. If the tumbler is used, return the aqueous phase to the tumbler bottle.

11.1.6 Add 17 mL of 12 N H_2SO_4 to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H_2SO_4.

11.1.7 Add 300 mL ethyl ether to the sample, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during

venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.1.8 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the aqueous phase. Collect the extract in a 500-mL round-bottom flask containing about 10 g of acidified anhydrous sodium sulfate. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

11.1.9 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 HYDROLYSIS, CLEANUP, AND 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. Pour the entire sample into a 2-L separatory funnel. Spike sample with 50 µL of the surrogate standard spiking solution.

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

11.2.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature for 1 hour, shaking the separatory funnel and contents periodically.

11.2.4 Add 60 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min.

If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

11.2.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

11.2.6 Add 17 mL of 12 N H_2SO_4 to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H_2SO_4.

11.2.7 Add 120 mL ethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ethyl ether phase in a 500-mL round-bottom flask containing approximately 10 g of acidified anhydrous sodium sulfate.

11.2.8 Return the aqueous phase to the separatory funnel, add a 60-mL volume of ethyl ether to the sample, and repeat the extraction procedure a second time, conbining the extracts in the 500-mL erlenmeyer flask. Perform a third extraction with 60 mL of ethyl ether in the same manner. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

11.2.9 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 concentrator tube to a 500-mL evaporative flask.

11.3.2 Pour the dried extract thrpugh a funnel plugged with acid washed glass wool, and collect the extract in the

K-D in concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom flask and funnel with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether. Add 2 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 250 µL of methanol. If the gaseous diazomethane procedure (Section 11.4) is used for esterification of pesticides, rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. If the pesticides will be esterified using the diazomethane solution (Section 11.5), rinse the walls of the concentrator tube while adjusting the volume to 4.5 mL with MTBE.

11.4 ESTERIFICATION OF ACIDS USING GASEOUS DIAZOMETHANE -- Validation results presented in this method were generated using the gaseous diazomethane derivatization procedure.

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

11.4.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.2 grams Diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 1 min. Remove first sample. Rinse the tip of the diazomethane

generator with ethyl ether after methylation of each sample. Bubble diazomethane through the second sample extract for 1 min. Diazomethane reaction mixture should be used to esterify only two samples; prepare new reaction mixture in Tube 2 to esterify each two additional samples. Samples should turn yellow after addition of diazomethane and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

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

[illegible] any unreacted diazomethane by adding 0.1 to [illegible] grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.5 ESTERIFICATION OF ACIDS USING DIAZOMETHANE SOLUTION -- Alternative procedure.

11.5.1 Assemble the diazomethane generator (Figure 2) in a hood. The collection vessel is a 10- or 15-mL vial, equipped with a Teflon-lined screw cap and maintained at 0-5°C.

11.5.2 Add a sufficient amount of ethyl ether to tube 1 to cover the first impinger. Add 5 mL of MTBE to the collection vial. Set the nitrogen flow at 5-10 mL/min. Add 2 mL Diazald solution (Section 7.9) and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the nitrogen flow to purge the diazomethane from the reaction vessel into the collection vial for 30 min. Cap the vial when collection is complete and maintain at 0-5°C. When stored at 0-5°C this diazomethane solution may be used over a period of 48 h.

11.5.3 To each concentrator tube containing sample or standard, add 0.5 mL diazomethane solution. Samples should turn yellow after addition of the diazomethane solution and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

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

11.5.5 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.6 FLORISIL CLEANUP

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

11.6.2 Apply 5 mL of 5 percent methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.

11.6.3 Apply 5 mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.

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

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

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

11.7 GAS CHROMATOGRAPHY

11.7.1 Table 3 summarizes the recommended operating conditions for the GC. Included in Table 3 are retention times observed using this method. Examples of the separations achieved using these conditions are shown in Figures 4 and 5. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.3 are met.

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

11.7.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.7.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of

the analyst should weigh heavily in the interpretation of chromatograms.

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

12. CALCULATIONS

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

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

13. PRECISION AND ACCURACY

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

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

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

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TABLE 1. METHOD ANALYTES

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

(a) CAS No. - Chemical Abstracts Service Registry Number.
(b) Code used for identification of peaks in figures; IS - 4,4'-dibromooctafluorobiphenyl internal standard; SUR - 2,4-dichlorophenylacetic acid surrogate standard.
(c) DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies.

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

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)	EDL(g)
[illegible]	[illegible]	ND(f)	7	88	0.00826	23	0.040
[illegible]	[illegible]	ND	7	92	0.0346	19	0.20
[illegible]	0.080	ND	7	118	0.0310	33	0.093
2,4-D (i)	0.20	ND	7	90	0.0248	14	0.20
Dalapon	1.0	ND	6	90	0.400	45	1.3
2,4-DB (h,j)	4.0	ND	6	87	0.518	15	4.0
DCPA diacid metabolite (j)	0.20	ND	6	74	0.0200	13	0.20
Dicamba (i)	0.080	ND	7	155	0.0269	22	0.081
2,4-Dichlorobenzoic acid	0.060	ND	6	69	0.0194	38	0.061
Dichlorprop (i)	0.40	ND	7	110	0.0689	16	0.40
Dinoseb (h,j)	0.40	ND	6	42	0.0971	34	0.40
5-Hydroxydicamba (i)	0.040	ND	7	49	0.00547	28	0.040
4-Nitrophenol (i)	0.20	ND	7	148	0.0450	15	0.20
PCP (k)	0.10	ND	6	82	0.00950	9	0.10
Picloram (i)	0.12	ND	7	166	0.0468	24	0.14
2,4,5-T (i)	0.080	ND	7	87	0.0144	21	0.080
2,4,5-TP (h,j)	0.20	ND	6	134	0.0631	23	0.20

(a) Data corrected for amount detected in blank.
(b) n - number of recovery data points.
(c) R - average percent recovery.
(d) S - standard deviation.
(e) RSD - percent relative standard deviation.
(f) ND - interference not detected in blank.
(g) EDL - the level calculated by multipyling the standard deviation of replicate measurements times the students' t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom or the level of the compound in a sample yielding a peak in a final extract with signal-to-noise ratio of approximately five, whichever value is greater.
(h) Results from confirmatory analysis conditions.
(i) Results from spiking level 2.
(j) Results from spiking level 3.
(k) Results from spiking level 4.

TABLE 3. PRIMARY AND CONFIRMATION CHROMATOGRAPHIC CONDITIONS

Analyte	Relative Retention Time for Given Conditions	
	Primary (a)(c)	Confirmation (b)(d)
[illegible]	[illegible]	1.55
[illegible]		1.27
Chloramben	1.08	1.19
2,4-D	0.927	1.02
Dalapon	0.126	0.171
2,4-DB	1.17	1.19
DCPA acid metabolites (c)	1.30	1.37
Dicamba	0.815	0.876
3,5-Dichlorobenzoic acid	0.662	0.705
Dichlorprop	0.923	0.971
Dinoseb	1.17	1.25
5-Hydroxydicamba	1.09	1.14
4-Nitrophenol	0.667	0.806
PCP	1.03	1.02
Picloram	1.25	1.36
2,4,5-T	1.10	1.15
2,4,5-TP	1.07	1.10
Surrogate	0.799	0.540

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

(b) Retention time relative to DBOB internal standard which elutes at approximately 27.6 min.

(c) 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

(d) Confirmation conditions:

Column: 30 m long x 0.25 mm I.D. DB-1701 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

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

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

(a) Data corrected for amount detected in blank.
(b) n = number of recovery data points.
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.
(g) Results from confirmatory analysis conditions.
(h) Analyte not detected at this spiking level.

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

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Acifluorfen	0.20	ND(f)	6	121	0.0318	13
Bentazon	1.0	ND	4	120	0.163	14
Chlor[illegible] (g)	0.40	ND	6	111	0.0615	13
2,4-D	1.0	ND	6	131	0.274	21
Dalapon	10	ND	6	100	2.24	20
2,4-DB (g)	4.0	ND	6	87	0.518	15
DCPA diacid metabolite	0.20	ND	6	74	0.0200	13
Dicamba	0.40	ND	6	135	0.129	24
3,5-Dichlorobenzoic acid	0.60	ND	6	102	0.098	16
Dichlorprop	2.0	ND	6	107	0.418	19
Dinoseb (g)	0.40	ND	6	42	0.0971	34
5-Hydroxydicamba	0.20	ND	6	103	0.0325	16
4-Nitrophenol	1.0	ND	6	131	0.234	18
PCP	0.040	ND	6	130	0.0242	47
Picloram	0.60	0.308	6	91	0.149	17
2,4,5-T	0.40	ND	6	117	0.0639	14
2,4,5-TP (g)	0.20	ND	6	134	0.0631	23

(a) Data corrected for amount detected in blank.
(b) n - number of recovery data points.
(c) R - average percent recovery.
(d) S - standard deviation.
(e) RSD - percent relative standard deviation.
(f) ND - interference not detected in blank.
(g) Results from confirmatory analysis conditions.

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

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

(a) Data corrected for amount detected in blank.
(b) n - number of recovery data points.
(c) R - average percent recovery.
(d) S - standard deviation.
(e) RSD - percent relative standard deviation.
(f) ND - interference not detected in blank.
(g) Results from confirmatory analysis conditions.

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

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

(a) Data corrected for amount detected in blank.
(b) n = number of recovery data points.
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.
(g) Results from confirmatory analysis conditions.

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

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

(a) Data corrected for amount detected in blank; hard artificial ground water used to generate these results was Absopure Natural Artesian spring Water obtained from the Absopure Water Company in Plymouth, Michigan.
(b) n = number of recovery data points.
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.
(g) Results from confirmatory analysis conditions.
(h) Analyte not recovered from hard artificial ground water.

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

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

(a) Data corrected for amount detected in blank; organic-contaminated artificial ground water used to generate these results was reagent water spiked with humic acid at the 1 mg/L concentration level. Humic acid (sodium salt) obtained from Aldrich (H1,675-2) was used.
(b) n = number of recovery data points.
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.
(g) Results from confirmatory analysis conditions.

TABLE 10. QUALITY CONTROL STANDARD

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	Dinoseb	0.004	Detection of analyte; S/N > 3
Chromatographic performance	4-Nitrophenol	1.6	0.70 <PSF<1.05 (a) 0.70 <PGF<1.05 (b)
Column performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 1.6	Resolution >0.40 (c)

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

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

where W(1/2) is the width of the front of the peak at half height assuming the peak is split at the highest point and W(1/2) is the peak width at half height (see Figure 6).

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

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

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height (see Figure 6).

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

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

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

TABLE 11. PRESERVATION STUDY RESULTS

Day Extracted / Day Analyzed		0 / 0		0 / 14		0 / 28		14 / 14		28 / 28	
Analyte	Spiking Level, µg/L	R(a)	RSD(b)	R	RSD	R	RSD	R	RSD	R	RSD
Acifluorfen	0.20	90	7	109	6	94	9	90	9	96	17
Bentazon	1.0	104	7	114	5	75	5	102	6	76	10
Chloramben(c)	0.40	111	7	100	6	117	1	95	22	110	8
2,4-D	1.0	122	14	110	12	130	20	112	9	111	14
Dalapon	10	70	33	60	26	90	23	04	11	123	7
2,4-DB(c)	4.0	52	30	50	32	31	31	57	6	45	40
DCPA diacid metabolite	0.20	80	0	91	15	56	13	112	27	56	10
Dicamba	0.40	106	7	106	4	121	5	107	6	117	11
3,5-Dichlorobenzoic acid	0.60	02	26	110	17	112	2	97	9	115	0
Dichlorprop	2.0	129	17	114	3	129	9	111	3	119	0
Dinoseb(c)	0.40	100	6	76	1	120	0	36	47	120	6
5-Hydroxydicamba	0.20	75	19	85	7	87	6	65	10	06	6
4-Nitrophenol	1.0	121	12	102	11	129	16	92	16	153	7
PCP	0.040	125	9	130	9	119	9	57	2	56	10
Picloram	0.60	121	6	134	4	83	0	135	5	75	16
2,4,5-T	0.40	120	13	115	3	103	11	103	2	09	7
2,4,5-TP(c)	0.20	103	4	90	3	99	11	60	1	95	4

(a) R = average percent recovery from triplicate analyses.
(b) RSD = percent relative standard deviation.
(c) Calculated using confirmatory analytical conditions.

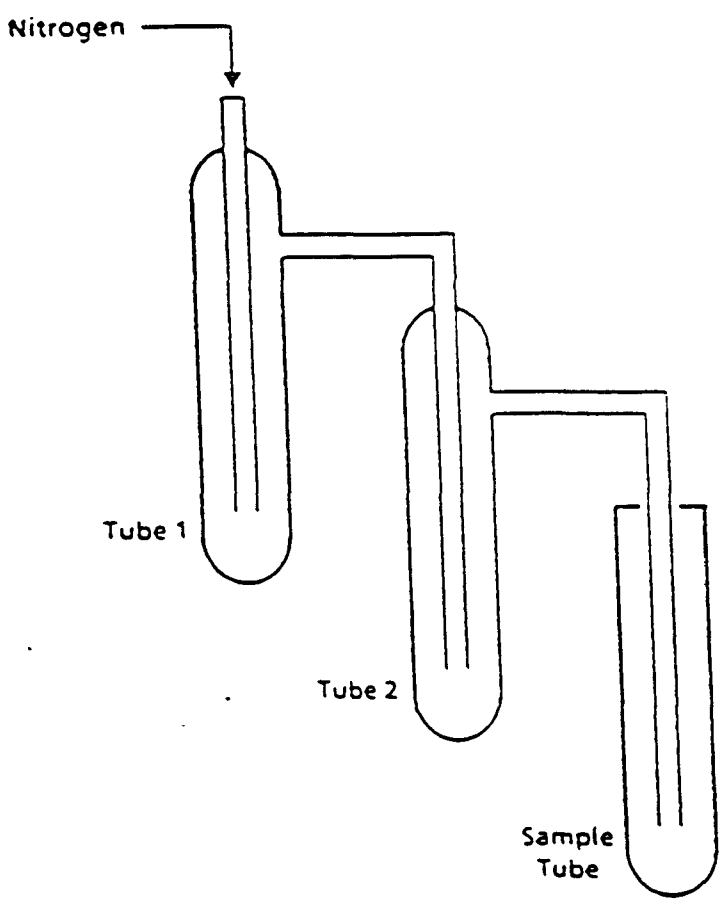
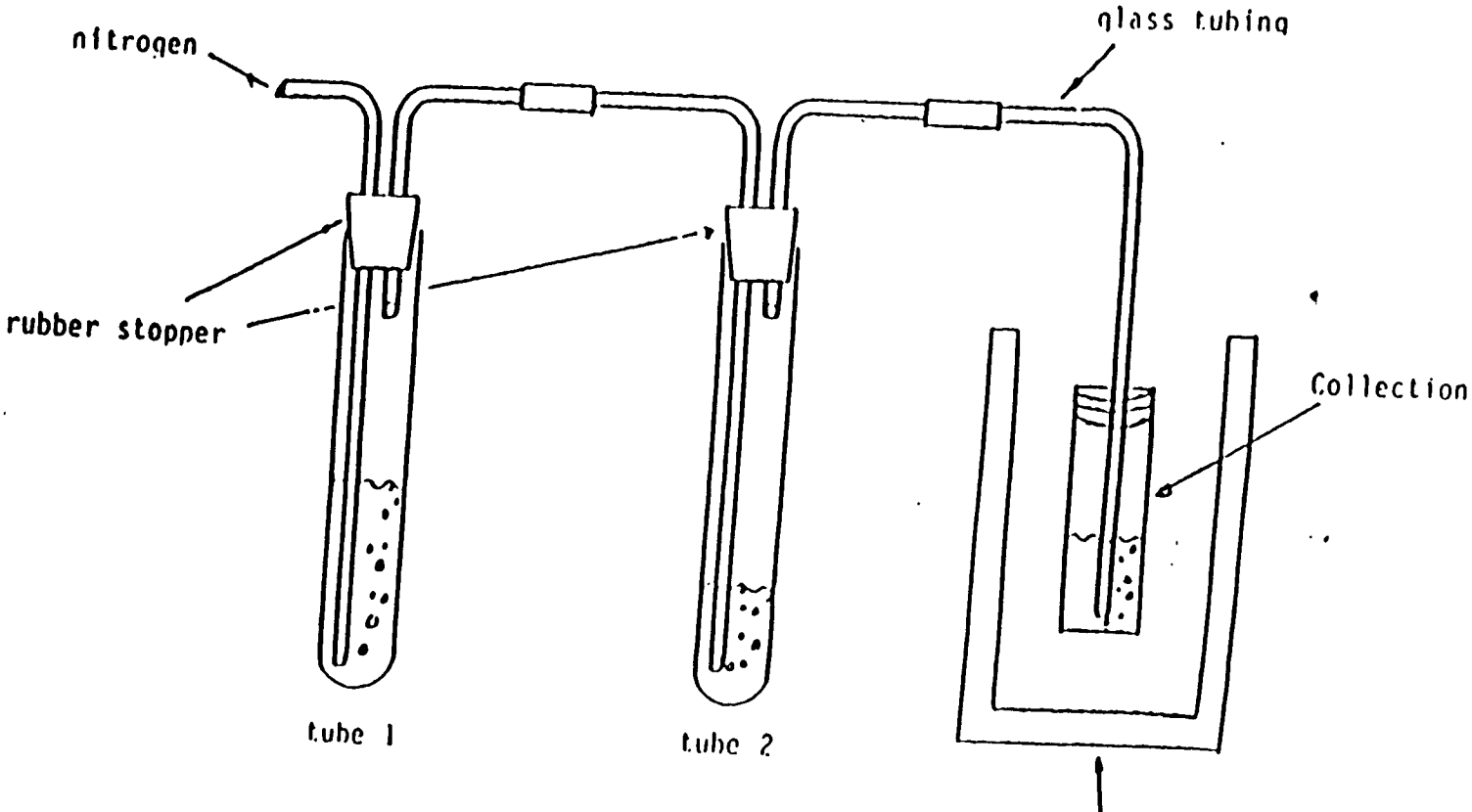


FIGURE 1. GASEOUS DIAZOMETHANE GENERATOR


nitrogen
glass tubing
rubber stopper
Collection
tube 1
tube 2

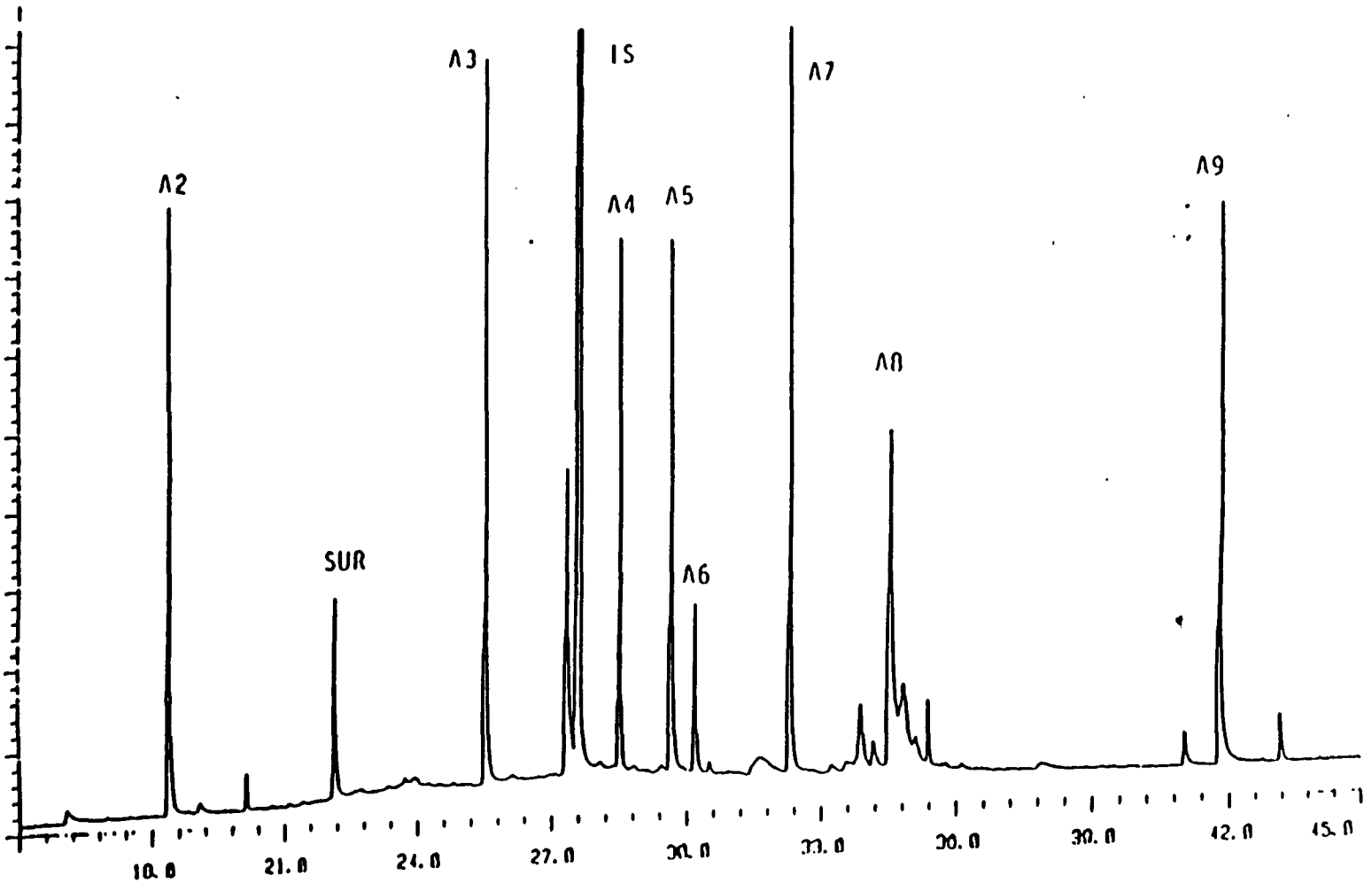


FIGURE 3. GC-ECD CHROMATOGRAM OF SPIKING MIX A (SPIKING LEVEL 5)
(Peak identification codes given in Table 1 of Appendix A)

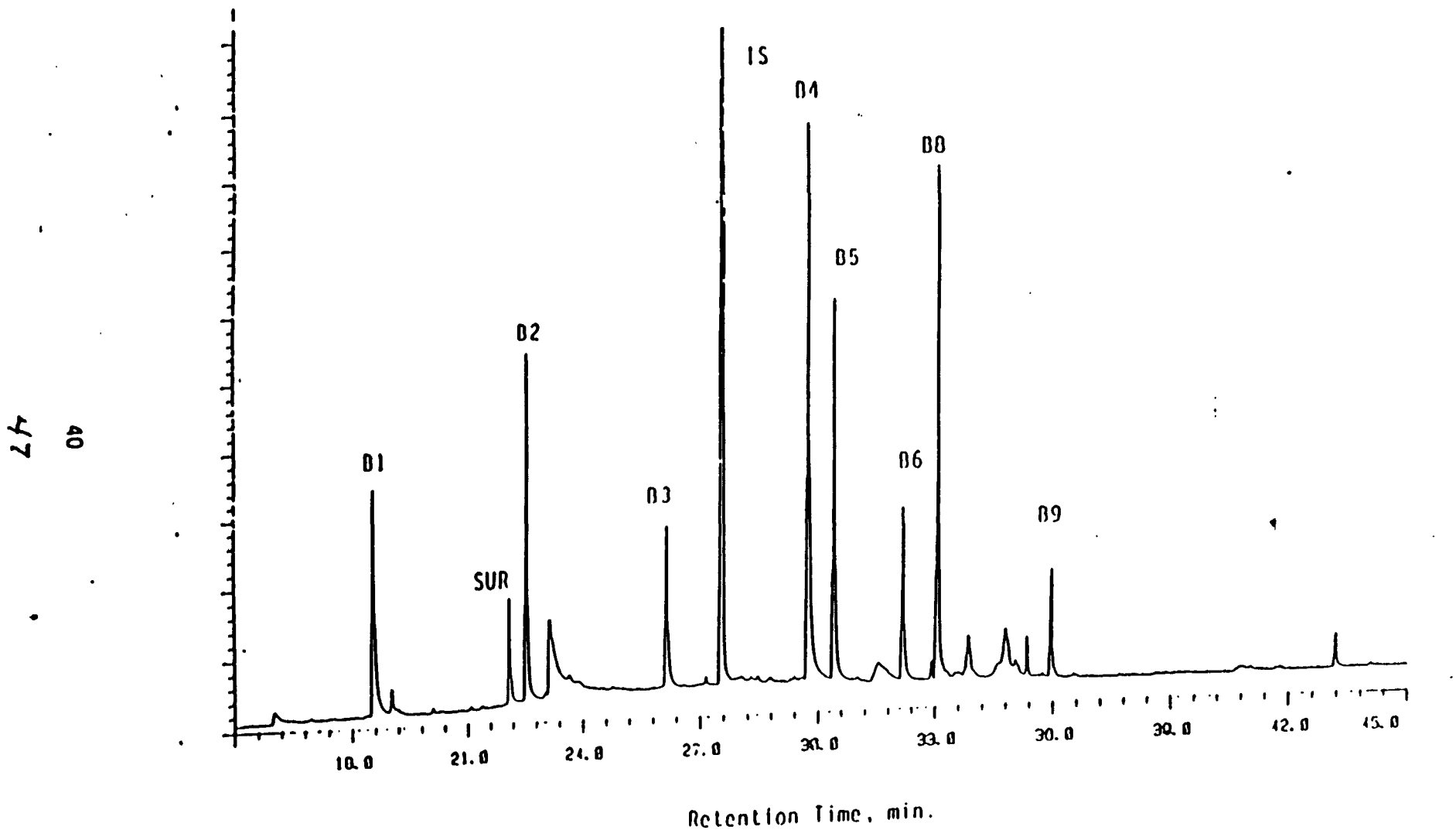


FIGURE 4. GC-ECD CHROMATOGRAM OF SPIKING MIX B (SPIKING LEVEL 5)
(Peak identification codes given i Table 1 of Appendix A)

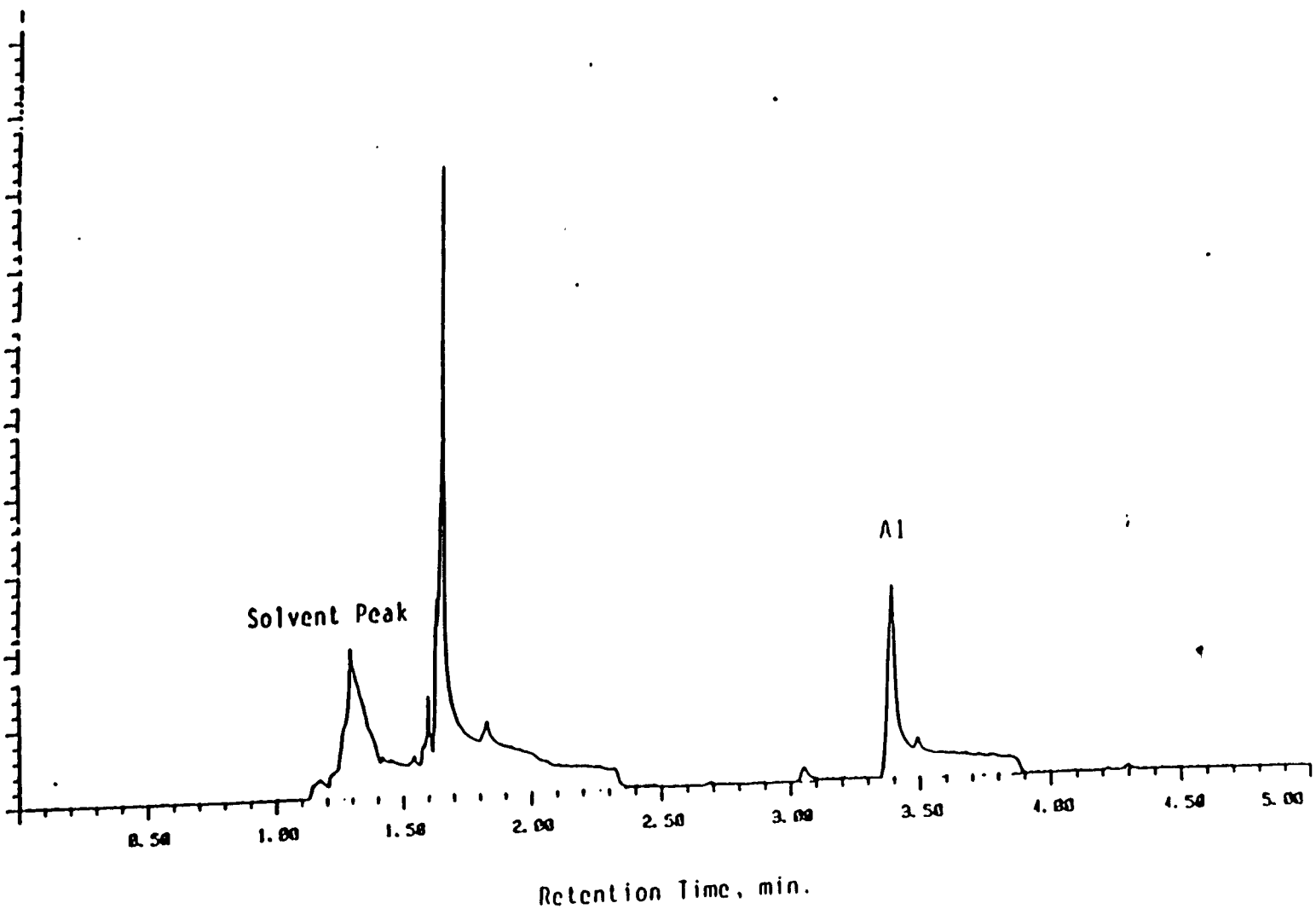


FIGURE 5. GC-ECD CHROMATOGRAM OF DALAPON (A1) FROM SPIKING MIX A (SPIKING LEVEL 3)

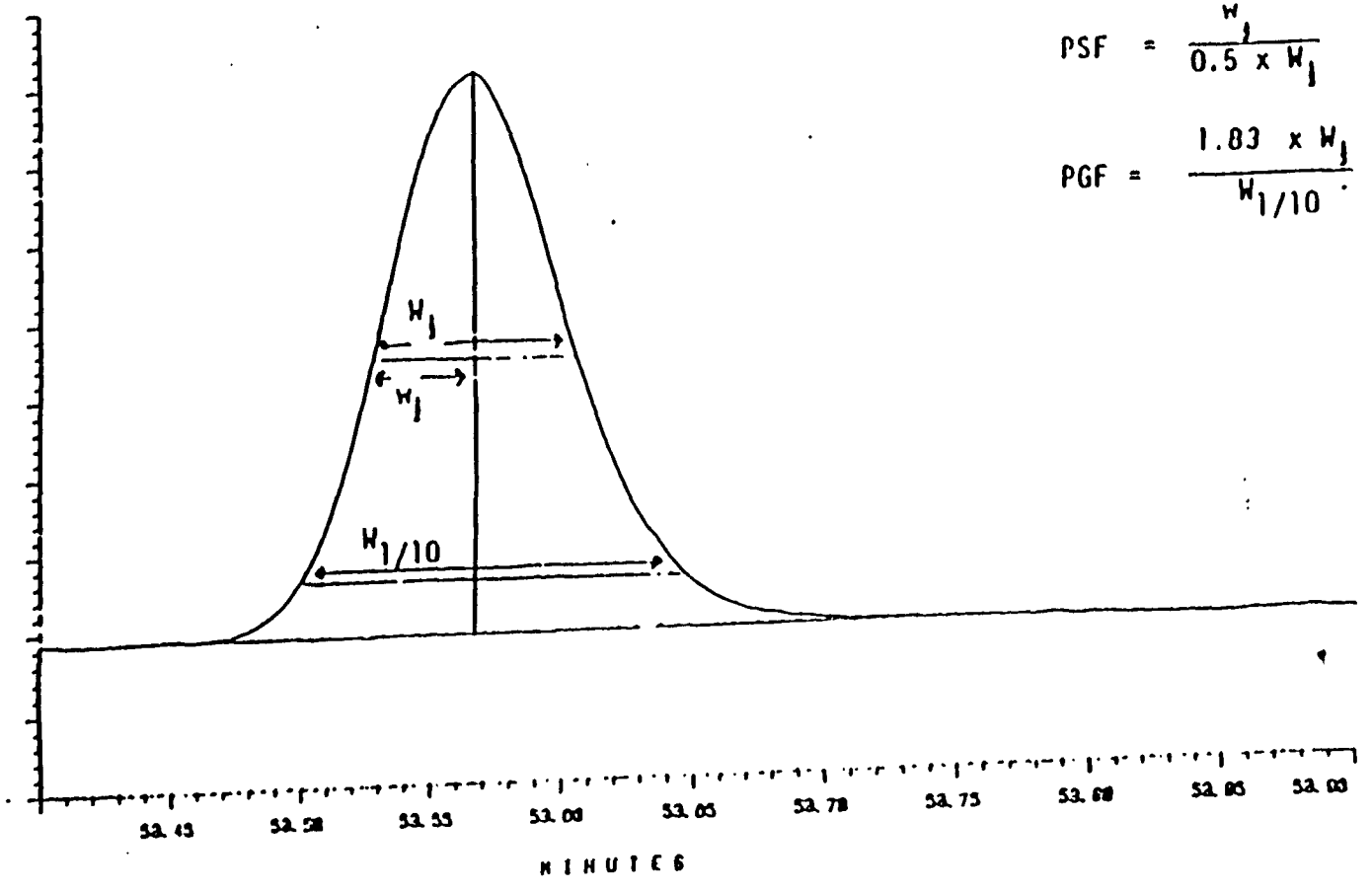


FIGURE 6. EQUATIONS USED TO CALCULATE PEAK SYMMETRY FACTOR (PSF) AND PEAK GAUSSIAN FACTOR (PGF)

APPENDIX C

DIAZOMETHANE PREPARATION AND SAFETY

Appendix: SAFETY:

All chemical compounds used in this method should be treated as potential hazards unless known to be otherwise. Analysts should become familiar with all the safety information provided here before attempting the analysis. Material Safety Data Sheets and other pertinent information have been supplied for the more hazardous substances used in this method (diazomethane, mercuric chloride, benzene, and ether). The individual laboratories are responsible for maintaining a file of Material Safety Data Sheets on all hazardous substances in use by that laboratory. All personnel should be made aware of the existence of the file and it should be readily available to them.

Precautions to be followed when handling or preparing diazomethane.

1. Use an efficient high draft hood - do not breath fumes.

2. Avoid use of ground-glass joints or any glassware which is chipped, cracked or has not been carefully firepolished. Failure to do so may result in an EXPLOSION. The DIAZALD kit supplies such glassware.

3. Use a sturdy explosion proof safety shield.

4. Use disposable PVC gloves.

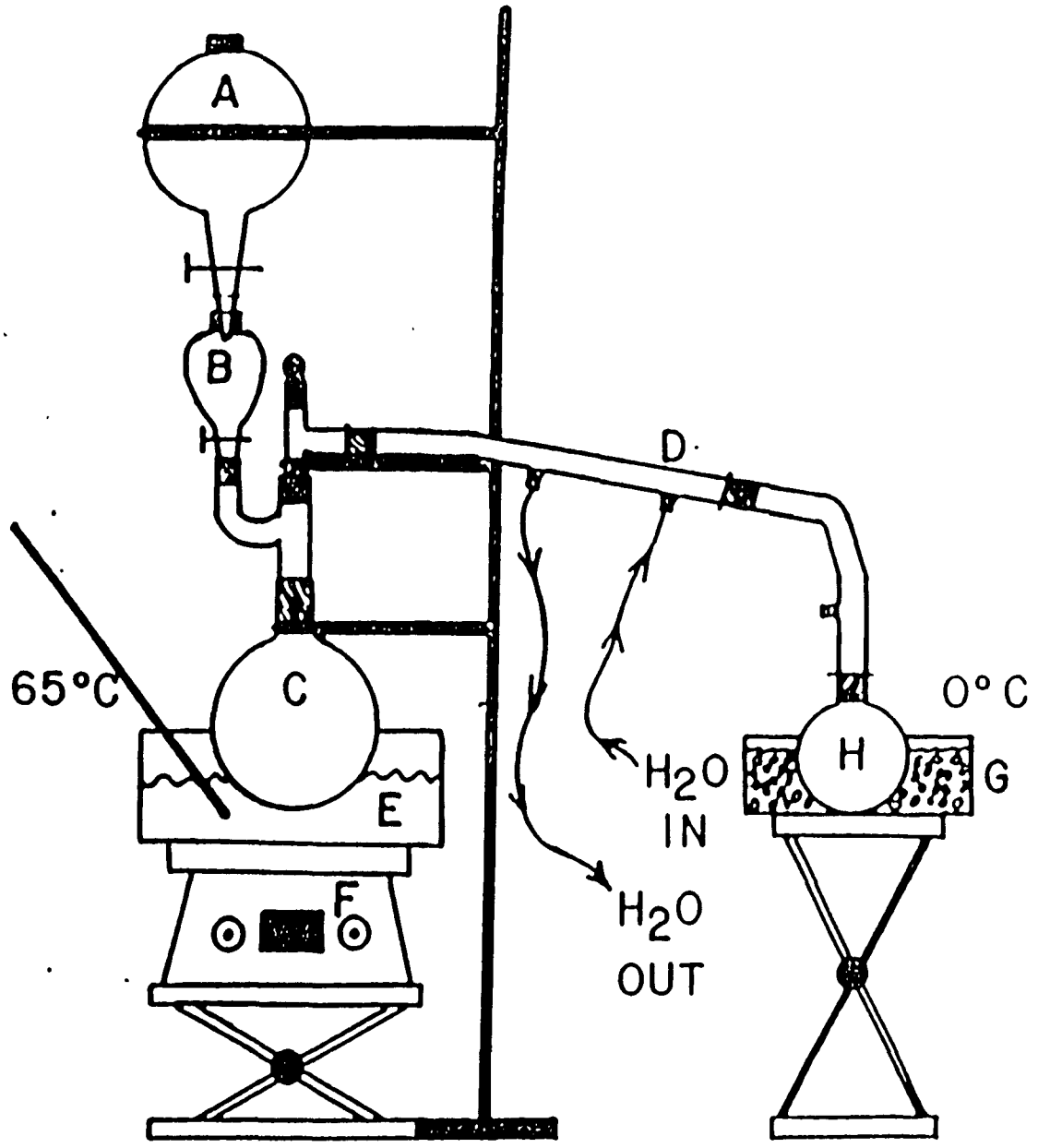
Preparation of diazomethane (alcohol - free ethereal solutions)

Add 2-(2-Ethoxyethoxy)-ethanol (35 ml) and ether (20 ml) to a solution of potassium hydroxide (6 g) in water (10 ml). This solution is placed in a 500 ml round bottom distilling flask fitted with dropping funnel and efficient condenser in a water bath at 65°C. As the distillation of the ether starts, a solution of 21.5 g of Diazald in about 200 ml of ether is added through the dropping funnel over 20 min. During the distillation, the solution is mixed continuously by a small magnetic stir bar. The rate of distillation should approximately equal the rate of addition. When the dropping funnel is empty, another 40 ml of ether is added slowly and the distillation is continued until the distilling ether is colorless. The combined ethereal distillate contains about 3 g of diazomethane. A diagram of the diazomethane apparatus has been provided.

Before attempting this procedure read all safety information concerning diazomethane preparation.

Storage:

Diazomethane solution should remain tightly capped, and may be stored at 0°-5°C for a period of up to 6 months. The intensity of the yellow color is an indicator of the strength of the diazomethane / ether solution.



A - 500 ml sep. funnel

B - 125 ml sep. funnel

C - 500 ml flask

D - condensor, H_2O cooled

E - water bath, 65°C

F - magnetic stirrer

G - ice bath, 0°C

H - 250 ml flask

DIAZOMETHANE APPARATUS

The Preparation and Reactions of Diazomethane

T. Howard Blac
Aldrich Chemical Company, Inc

In 1894, von Pechman established the structure CH_2N_2 for the yellow gas liberated from nitrosomethylurethane upon treatment with alkali.[1] During the subsequent 90 years, diazomethane (less commonly referred to as azimethylene or diazirane) has proven to be one of the most valuable and versatile reagents available to the synthetic chemist. It is easily the most common methylating reagent for carboxylic acids, and has found wide application in the methylation of phenols, alcohols, enols, and heteroatoms such as nitrogen and sulfur. Diazomethane effects the ring expansion (or chain homologation) of ketones or, under suitable conditions, forms epoxides from the same ketones in the manner of sulfur ylids. Acid chlorides are converted to α-diazoketones which are valuable synthetic intermediates in their own right. In addition, CH_2N_2 acts as a powerful dipole in many cycloaddition reactions with unsaturated systems, and often the resulting nitrogen-containing heterocyclic ring can be decomposed (either thermally or photochemically) to afford cyclopropane (or other) derivatives. Each of the above reaction categories will be treated separately in the REACTIONS section.

STRUCTURE

The structure of diazomethane can be represented by the valence tautomers 1 through 5 (Scheme I). Although the true electronic distribution over the the molecule can be represented as a weighted sum of the five structures shown, the majority of diazomethane reactions are best conceptualized and explained by structure 1. Recently the total electronic energies and energies of isomerization for the optimized geometries of the isomers of diazomethane were calculated.[2]

A gas at room temperature, diazomethane liquifies at -23 °C (density 1.45) and freezes at -145 °C. It can be protonated in fluorosulfonic acid at very low temperatures[3] and possesses an ionization potential of 9.03eV.[4]

The most recent comprehensive review of diazomethane chemistry appeared nine years ago;[5] the reader is directed to this work for references to earlier reviews. Recently, two reviews concerning diazoalkanes have appeared; one involves organometallic synthesis[6] and the other the synthesis of "unusual organic molecules".[7]

SAFETY CONSIDERATIONS

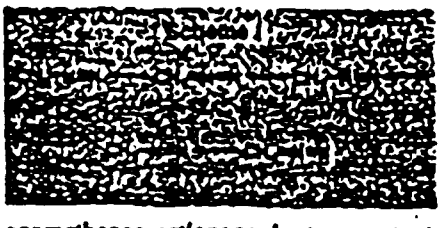
Although quite safe when handled as a dilute solution in an inert solvent, diazomethane presents several safety hazards of which all users of the reagent should be aware. It is both extremely toxic[8] and highly irritating,[9] causing pulmonary edema when inhaled in high concentrations. Long-term, low-level exposure may lead to sensitization, resulting in asthma-like symptoms.[10] Also, diazomethane and several of its chemical precursors have been cited as carcinogens.[11]

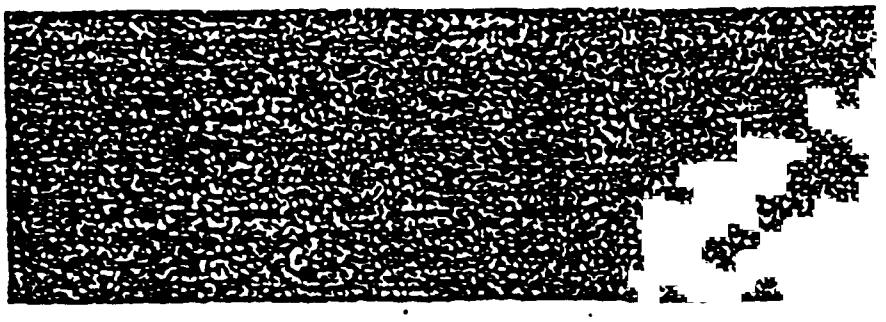
Diazomethane has been known to explode quite unaccountably, both as a gas and a liquid, although rough surfaces are proven initiators of detonations.[12] Thus, ground-glass joints and any glassware which have not been carefully firepolished must never be allowed to come in contact with diazomethane or its solutions. In addition contact with alkali metals or drying agen such as calcium sulfate can result in an e plosion. If moisture must be removed fro a solution containing diazomethane, the re ommended drying agent is potassium h droxide pellets. Finally, solutions should n be exposed to strong light, which has be reported[13] to initiate detonations.

Fortunately, if the reagent is generated ing the proper equipment and is handled c ly as a dilute solution at low temperature (0 °C), the risks cited above are minimiz Of course, all reactions involving dia methane should be carried out in an effici fume hood and behind a sturdy saf shield. Finally, it is recommended that sc tions of diazomethane be used *immedi* ly and not stored, even at low temperatu

PREPARATION

By far, the most common and conven method for generating diazomethane is the base-catalyzed decomposition of methyl-N-nitroso amines of the gen structure 6, where R represents a sulfo carbonyl, or similar electron-withdrav group. The mechanism of diazometh generation is outlined in Scheme II. For ity, a specific chemical presursor is ployed: *N*-methyl-*N'*-nitro-*N*-nitrosog idine (MNNG, 7). In the first step, a





aldrich chemical co.

P O Box 355 Milwaukee, Wisconsin 53201 USA • (414) 273 3850

ATTN: SAFETY DIRECTOR
EPA
ENVIRONMENTAL CHEMISTRY LAB
NASA/NSL
BLDG 1105
NSTL STATION MS 39529
ROBERT MAXEY

MATERIAL SAFETY DATA SHEET

DATE: 01/20/86 . CUST # 940048 P.C. # PAGE:

SECTION I PRODUCT IDENTIFICATION

D2800-0 DIAZALD, 99%
CAS # 80-11-5
MOLECULAR FORMULA: C8H10N2O3S

SECTION II TOXICITY HAZARDS

RTECS # XT5950000
P-TOLUENESULFONAMIDE, N-METHYL-N-NITROSO-

ORL-RAT LD50:2700 MG/KG NATWAY 48,165,61
IPR-MUS LD50:19 MG/KG CNREA8 30,11,70
REPORTED IN EPA TSCA INVENTORY, 1983
EPA GENETIC TOXICOLOGY PROGRAM, JANUARY 1984
MEETS CRITERIA FOR PROPOSED OSHA MEDICAL RECORDS RULE FEREAC 47,30420,
82

SECTION III PHYSICAL DATA

MELTING POINT: 61 C TO 62 C

SECTION IV FIRE AND EXPLOSION HAZARD DATA

EXTINGUISHING MEDIA:

WATER SPRAY.
CARBON DIOXIDE, DRY CHEMICAL POWDER, ALCOHOL OR POLYMER FOAM.

SPECIAL FIRE FIGHTING PROCEDURES:

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.

UNUSUAL FIRE AND EXPLOSION HAZARDS:

EMITS TOXIC FUMES UNDER FIRE CONDITIONS.

SECTION V HEALTH HAZARD DATA

MAY BE HARMFUL BY INHALATION, INGESTION, OR SKIN ABSORPTION.
CAUSES SEVERE IRRITATION.
MAY CAUSE ALLERGIC SKIN REACTION.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
FIRST AID:
IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED CLOTHING AND SHOES.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION, PREFERABLY MOUTH-TO-MOUTH. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
CALL A PHYSICIAN.

MATERIAL SAFETY DATA SHEET

DATE: 01/20/86 CATALOG # 02800-0 CUST # 940048 P.O. #

DISCARD CONTAMINATED CLOTHING AND SHOES.

SECTION VI REACTIVITY DATA

INCOMPATIBILITY:

STRONG ACIDS
STRONG BASES
STRONG OXIDIZING AGENTS
STRONG REDUCING AGENTS

HAZARDOUS DECOMPOSITION PRODUCTS:

TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE
NITROGEN OXIDES
SULFUR OXIDES

SECTION VII SPILL OR LEAK PROCEDURES

SPILLS OR LEAKS:

EVACUATE AREA.
WEAR RESPIRATOR, CHEMICAL SAFETY GOGGLES, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

WASTE DISPOSAL:

PLEASE CONTACT THE TECHNICAL SERVICES DEPARTMENT. BE SURE TO MENTION THE NAME, CATALOG NUMBER, AND THE QUANTITY OF THE MATERIAL.

OBSERVE ALL FEDERAL, STATE & LOCAL LAWS CONCERNING HEALTH & POLLUTION

SECTION VIII PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE

CHEMICAL SAFETY GOGGLES.
RUBBER GLOVES
OSHA/MSHA-APPROVED RESPIRATOR.
USE ONLY IN A CHEMICAL FUME HOOD.
DO NOT BREATHE DUST.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
WASH THOROUGHLY AFTER HANDLING.
SEVERE IRRITANT.
AVOID ALL CONTACT.
KEEP TIGHTLY CLOSED.
STORE IN A COOL DRY PLACE.

SECTION IX SPECIAL PRECAUTIONS AND COMMENTS

NOT APPLICABLE

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. ALDRICH SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKI SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE.

APPENDIX D

DATA FLOW (REDUCTION, VALIDATION, AND REPORTING)

CRUDE REPRESENTATION OF DATA FLOW

1. Samples are taken in the field.

2. Samples are iced and shipped to the laboratory.

3. [illegible] field samples along with QC samples.

4. Laboratory enters field and QC data on a computer in "sets" and it enters instrument control standard data in a seperate file.

5. Laboratory creates an ASCII file of the data using the specified formats on an IBM PC compatible floppy disk.

6. Laboratory sends the floppy disk to Christopher Frebis at the EPA in Cincinnati, Ohio.

   26 W. Martin Luther King Drive
   Cincinnati, OH 45268

NOTE: The maximum time from item 1 to item 6 is two (2) months.

7. Computer Sciences Corporation (CSC) personnel transfer the data from PC to IBM 3090 mainframe in North Carolina (or possibly to IBM Logical Mainframe in Cincinnati).

8. The data is edited on the mainframe and then checked for compliance with QC requirements using SAS, a statistical programming language.

9. A hard copy of the edited data, with "suspect" data highlighted, is sent to the technical monitor for their review.

10. The technical monitor returns the data to C. Frebis with comments, deletions, etc. — this is the <u>final</u> data.

11. The data is re-edited per the technical monitor's review and a SAS data set is created for the data.

12. The "approved" field samples are sent to ICF for their analyses.

13. All QC data is retained by C. Frebis to generate a QC report at the end of the survey and to write monthly reports to Dave Munch.

NOTES ON NPS DATA FORMATS

1. The format for any date is mm/dd/yy

   A missing date should be entered 01/01/60

2. The format for any time is hh:mm in military time

   A missing time should be entered 00:00

3. Any other data that is missing should be entered with a period (.)

4. The number of decimal places should be as follows:

Concentration	3	(significant digits)
Percent Recovery	1	
Internal Standard	0	
Instrument Controls	2	
pH	1	
Temperatures	0	
Volumes	0	

5. The codes for Column are as follows:

Primary	PRIM
Confirmatory	CONF
Third	GCMS

6. The codes for Lab are as follows:

TSD	TSD
OPP	OPP
WERL	WER
Radian	RAD
Battelle	BCD
James M. Montgomery	JMM
Alliance	ALL
Environmental Sciences and Engineering	ESE

7. The codes for Type are as follows:

Field Sample	SAMP
Shipping Blank	SBLK
Method Blank	MBLK
Lab Control Standard	LCS@
Lab Spike Sample	LSS@#
Time Storage for Extract	HTE@
Time Storage for Sample	HTS@

where @ is the mix letter: (A,B,C or D)
and # is the spiking level (1,2 or 3)

8. There should be at least one blank line between samples in the NPS data file.

9. The codes for Concentrations and Percent Recoveries are as follows:

Not Analyzed = missing	
Not Detected (< Minimum Reporting Level)	-999
Saturated	-777
Other	-333
Below Report Limit, but Distinct Peak	-111
Above Reporting Limit, but not Quantified	+888

10. If a reported value is greater than (>) some number in the NPS instrument control data, then use a minus sign (-) instead of >

REVISIONS TO FORMAT FOR NPS DATA FILES

- Format for National Pesticide Survey (NPS) Data

Line	Column	Revision
11	52-62	Revised "Enter Internal Standard" to "PERCENT RECOVERY OF INTERNAL STANDARD AS COMPARED AGAINST THE CALIBRATION STANDARD".

- Notes on NPS Format

4) Revised "Internal Standard 0 (area count)" to Internal Standard 1 (percent recovery)

9) - 999 - revised to denote "Not Detected (< 1/2 MRL)"

- 111 - revised to denote "> 1/2 MRL but < MRL"

TABLE 1: USES OF DATA CODES IN NPS

SAMPLE TYPE				
SAMP	MBLK	SBLK	LCS	LSS,DTS HTE,HTS
.(a)	.(a)	.(a)	.(b)	.(b)
-111(c)	-111(c)	-111(c)	****	****
-333(d)	-333(d)	-333(d)	****	-333(d)
-444(e)	****	-444(e)	****	-444(e)
-555(f)	-555(f)	-555(f)	****	****
-666(g)	****	-666(g)	****	****
-777(h)	-777(h)	-777(h)	-777(h)	-777(h)
888(i)	888(i)	888(i)	****	****
-999(j)	-999(j)	-999(j)	****	****
conc(k)	conc(k)	conc(k)	% rec(l)	% rec(l)

(a) Analyte dropped from survey (Demeton-S and Carboxin sulfoxide) or not analyzed on the second column or in GCMS analysis.

(b) Analyte not in mix.

(c) Analyte's concentration between MRL/2 and MRL. (If no confirmation is run, a comment as to why should be made.)

(d) A lab mishap, e.g. sample lost during extraction, or sample dropped, or a QC failure which causes the entire sample to be lost and no data reported. This is a unique situation. (A comment should give further explanation.)

(e) This analyte fails QC in this set (e.g. LCS out of control) and therefore cannot be reported; however, the analyte does not require a qualitative challenge. This code also applies to any spike sample in a set where the LCS is out of control.

(f) GCMS only: Sent to referee lab for GCMS analysis.

(g) This analyte fails QC in this set (e.g. positive method blank) and therefore cannot be reported; however, the analyte does require a qualitative challenge.

(h) Analyte was saturated. Should be diluted and re-done, if observed in a field sample. (Another sample with the exact same header information should appear, analytes not saturated in the original sample should be reported as ., and saturated analytes should be reported as their concentration.)

(i) Positive, can occur in two fashions: 1) any analyte in GCMS analysis; or 2) a qualitative only analyte on either of the first two columns.

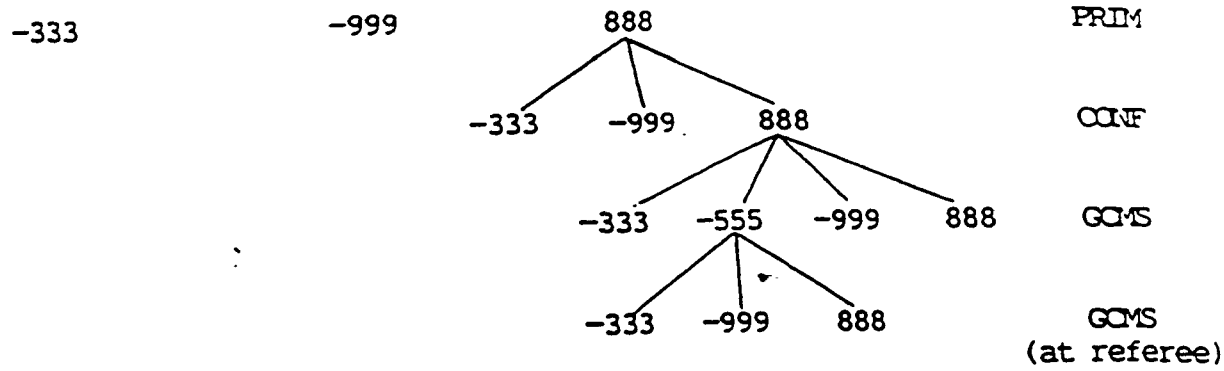
(j) Analyte's concentration below MRL/2.

(k) Concentration above MRL for quantitative analytes, reported to three significant figures.

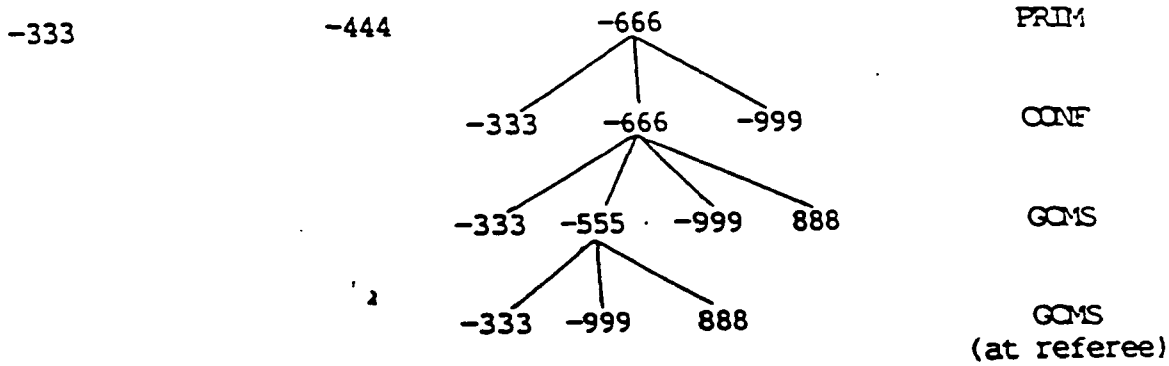
(l) Percent recovery, reported to one decimal place (even if recovery is 0.0%).

**** Code not applicable.

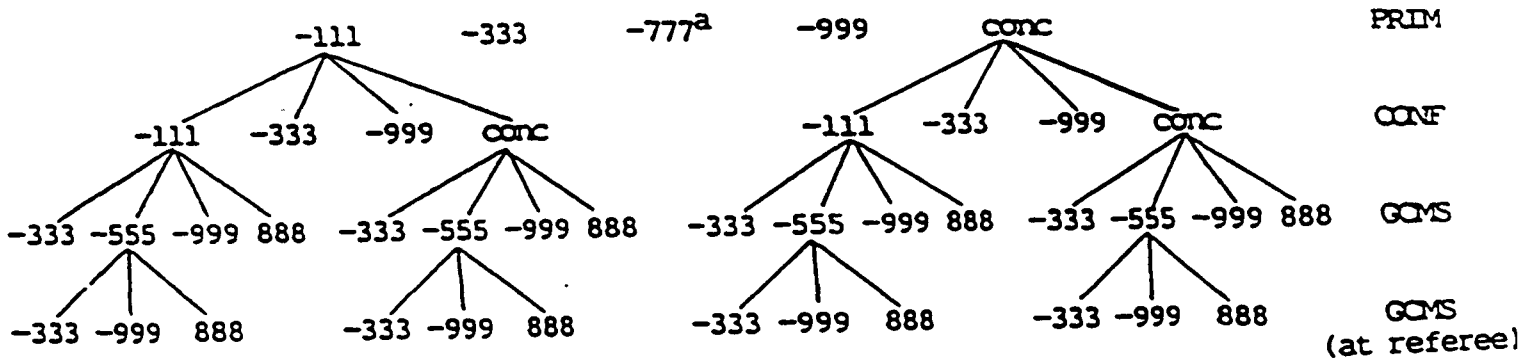
Sample (Qualitative only analyte)



Sample (Quantitative analyte with QC failure)



Sample (Quantitative analyte with no QC failure)



a = Dilute and reanalyze

DATA CHECKS PERFORMED ON NPS DATA BY CSC

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

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

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

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

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

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

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

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

9. Is the concentration of a blank above the reporting limit?

10. Is the concentration of a field sample above the 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?

---

11. Is the internal standard within the limits set by the method requirements?

12. Is the percent recovery of each analyte in the lab control standard within the limits set by the survey requirements?

13. Is the percent recovery of each analyte in the lab spike sample within the limits set by the survey requirements?

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) DATA

LINE	COLUMNS	DESCRIPTION
1	1-9	Well I.D.
	13-20	Date_Sam
	23-30	Date_Shp
	33-40	Date_Rec
	43-50	Time_Sam
	53-60	Time_Ice
	[FOR METHODS 5 AND 9 ONLY]	
	64-65	pH
2	1-10	enter WELL IDENTIFICATION NUMBER
	13-20	enter DATE SAMPLED
	23-30	enter DATE SHIPPED
	33-40	enter DATE RECEIVED
	43-50	enter TIME SAMPLED
	53-60	enter TIME ICED
	[FOR METHODS 5 AND 9 ONLY]	
	63-66	enter pH
3	BLANK	
4	1-8	Ini_Temp
	11-18	Stb_Temp
	21-29	Condition
5	1-8	enter INITIAL TEMPERATURE OF WATER
	11-18	enter STABILIZED TEMPERATURE OF WATER
	21-80	enter CONDITION OF SAMPLE UPON RECEIPT AT LABORATORY
6	BLANK	
7	1-6	Samp #
	9-11	Lab
	14-18	Set #
	21-28	Date_Spk
	31-38	Date_Ext
	41-48	Date_Ana
	51-56	Site #
	59-64	Column
8	1-6	enter SAMPLE IDENTIFICATION NUMBER
	9-11	enter LAB ABBREVIATION
	14-18	enter SET NUMBER
	21-28	enter DATE SPIKED
	31-38	enter DATE EXTRACTED
	41-48	enter DATE ANALYZED
	51-56	enter SITE NUMBER
	59-64	enter ANALYSIS COLUMN

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) DATA (cont.)

LINE	COLUMNS	DESCRIPTION
9	BLANK	
10	1-4	Type
	8-13	Spiker
	16-22	Extract
	25-31	Analyst
	34-40	Sam_Vol
	43-49	Ext_Vol
	52-60	Int. Std.
	65-70	% Surr
11	1-5	enter SAMPLE TYPE
	8-13	enter SPIKER'S INITIALS
	16-22	enter EXTRACTOR'S INITIALS
	25-31	enter ANALYST'S INITIALS
	34-40	enter VOLUME OF SAMPLE
	43-49	enter VOLUME OF EXTRACT
	52-62	enter INTERNAL STANDARD
	65-70	enter PERCENT RECOVERY OF SURROGATE
12	BLANK	
13	1-8	Comments
14	1-80	enter ANY PERTINENT COMMENTS ON SAMPLE AND ANALYSIS
15	BLANK	
16	1-7	Analyte
	29-33	Conc.
	39-45	Analyte
	67-71	Conc.
17-?	1-25	enter ANALYTE'S NAME
	28-34	enter CONCENTRATION OR PERCENT RECOVERY
	39-63	enter ANALYTE'S NAME
	66-72	enter CONCENTRATION OR PERCENT RECOVERY

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) INSTRUMENT CONTROL DATA

LINE	COLUMNS	DESCRIPTION
1	1-3	Lab
	6-11	Method
	14-21	Date_Ana
	24-30	Analyst
	35-37	S/N
	42-44	PSF
	49-51	PGF
	55-58	Res.
2	BLANK	
3-?	1-3	enter LAB ABBREVIATION
	6-11	enter METHOD NUMBER
	14-21	enter DATE ANALYZED
	24-30	enter ANALYST'S INITIALS
	33-37	enter SIGNAL TO NOISE RATIO
	40-44	enter PEAK SYMMETRY FACTOR
	47-51	enter PEAK GEOMETRY FACTOR
	54-58	enter RESOLUTION

**** TSO FOREGROUND HARDCOPY ****
DSNAME=CPSFSOD.NPS.FORMAT.DATA (METHOD3)

I_Temp	S_Temp	Date_Sam	Date_Shp	Date_Rec	Time_Sam	Time_Ice
.	.	01/01/60	01/01/60	01/01/60	.	.

Receipt Condition

.

Samp #	Lab	Set #	Date_Spk	Date_Ext	Date_Ana	Column
.	TSD	01	01/01/60	04/30/87	05/03/87	PRIM

Type	Spiker	Extract	Analyst	Sam_Vol	Ext_Vol	Int. Std.	% Surr
...	.	.	...	1000	5	35	101.3

Comments
NONE.

Analyte	Conc.	Analyte	Conc.
Acifluorfen	-999	Dichloroprop	-999
2,4-DB	-999	Dinoseb	-999
Bentazon	-999	5-Hydroxy Dicamba	-999
Chloramben	-999	4-Nitrophenol	-999
2,4-D	-999	PCP	-999
Dalapon	-999	Pichoram	-999
DCPA acid metabolites	-999	2,4,5-T	-999
Dicamba	-999	2,4,5-TP	-999
3,5-Dichlorbenzoic acid	-999		

I_Temp	S_Temp	Date_Sam	Date_Shp	Date_Rec	Time_Sam	Time_Ice
.	.	01/01/60	01/01/60	01/01/60	.	.

Receipt Condition

.

Samp #	Lab	Set #	Date_Spk	Date_Ext	Date_Ana	Column
.	TSD	01	04/30/87	04/30/87	05/03/87	PRIM

Type	Spiker	Extract	Analyst	Sam_Vol	Ext_Vol	Int. Std.	% Surr
LCSA	CM	CM	CM	1000	5	31	99.4

Comments
NONE.

Analyte	Conc.	Analyte	Conc.
Acifluorfen	100.6	Dichloroprop	98.9
2,4-DB	.	Dinoseb	94.5
Bentazon	.	5-Hydroxy Dicamba	89.9
Chloramben	.	4-Nitrophenol	.
2,4-D	.	PCP	91.1
Dalapon	94.7	Pichoram	93.3
DCPA acid metabolites	.	2,4,5-T	.
Dicamba	.	2,4,5-TP	85.5
3,5-Dichlorbenzoic acid	97.5		

I_Temp S_Temp Date_Sam Date_Shp Date_Rec Time_Sam Time_Ice

APPENDIX E

SIGNIFICANT FIGURES AND ROUNDING OF NUMBERS

1 Introduction

To obtain meaningful data on water quality, the sample collector must obtain a representative sample and then deliver it unchanged for analysis. The analyst must perform the proper analysis in the prescribed fashion, complete calculations, and convert results to final form for permanent recording of the analytical data in meaningful, exact terms. These results are transferred to a storage facility for future interpretation and use.

The following sections discuss processing of actual values, recording and reporting of data in the proper way, some means of quality control of data, and the storage and retrieval of data.

2 The Analytical Value

3 Significant Figures

The term "significant figure" is used, sometimes rather loosely, to describe a judgment of the reportable digits in a result. When the judgment is not soundly based, meaningful digits are lost or meaningless digits are reported. On the other hand, proper use of significant figures gives an indication of the reliability of the analytical method used.

The following discussion describes the process of retention of significant figures.

A number is an expression of quantity. A figure or digit is any of the characters 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone or in combination, serve to express a number. A significant figure is a digit that denotes the amount of the quantity in the particular decimal place in which it stands. Reported analytical values should contain only significant figures. A value is made up of significant figures when it contains all digits known to be true and one last digit in doubt. For example, if a value is reported as 18.8 mg/l, the 18 must be firm while the 0.8 is somewhat uncertain, but presumably better than one of the values 0.7 or 0.9 would be.

The number zero may or may not be a significant figure depending on the situation.

Final zeros after a decimal point are always meant to be significant figures. For example, to the nearest milligram, 9.8 g is reported as 9.800 g.

Zeros before a decimal point with nonzero digits preceding them are significant. With no preceding nonzero digit, a zero before the decimal point is not significant.

If there are no nonzero digits preceding a decimal point, the zeros after the decimal point but preceding other nonzero digits are not significant. These zeros only indicate the position of the decimal point.

Final zeros in a whole number may or may not be significant. In a conductivity measurement of 1,000 μmho/cm, there is no implication by convention that the conductivity is 1,000 ± 1 μmho. Rather, the zeros only indicate the magnitude of the number.

A good measure of the significance of one or more zeros interspersed in a number is to determine whether the zeros can be dropped by expressing the number in exponential form. If they can, the zeros may not be significant. For example, no zeros can be dropped when expressing a weight of 100.08 g in exponential form; therefore the zeros are significant. However, a weight of 0.0008 g can be expressed in exponential form as 8×10^{-4} g, so the zeros are not significant. Significant figures reflect the limits in accuracy of the particular method of analysis. It must be decided whether the number of significant digits obtained for resulting values is sufficient for interpretation purposes. If not, there is little that can be done within the limits of the given laboratory operations to improve these values. If more significant figures are needed, a further improvement in method or selection of another method will be required.

Once the number of significant figures obtainable from a type of analysis is established, data resulting from such analyses are reduced according to set rules for rounding off.

4 Rounding Off Numbers

Rounding off of numbers is a necessary operation in all analytical areas. It is automatically applied by the limits of measurement of every instrument and all glassware. However, when it is applied in chemical calculations incorrectly or prematurely, it can adversely affect the final results. Rounding off should be applied only as described in the following sections.

5 Rounding-Off Rules

If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

6 Rounding Off Arithmetic Operations

When a series of numbers is added, the sum should be rounded off to the same number of decimal places as the addend with the smallest number of places. However, the operation is completed with all decimal places intact, and rounding off is done afterward. As an example,

$$\begin{array}{r} 11.1 \\ 11.12 \\ +11.13 \\ \hline 33.35 \end{array}$$

The sum must be rounded off to 33.4.

When one number is subtracted from another, rounding off should be completed after the subtraction operation, to avoid possible invalidation of the operation.

When two numbers are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the multiplier with the fewer significant digits.

When two numbers are to be divided, the division is carried out on the two numbers using .. digits. Then the quotient is rounded off to the number of significant digits of the divisor or dividend, whichever has the fewer.

When a number contains *n* significant digits, its root can be relied on for *n* digits, but its power can rarely be relied on for *n* digits.

7 Rounding Off the Results of a Series of Arithmetic Operations

The preceding rules for rounding off are reasonable for most calculations; however, when dealing with two nearly equal numbers, there is a danger of loss of all significance when applied to a series of computations that rely on a relatively small difference in two values. Examples are calculation of variance and standard deviation. The recommended procedure is to carry several extra figures through the calculations and then to round off the final answer to the proper number of significant figures.

APPENDIX F

STORAGE OF NPS HARDCOPY DATA FILES AT ECL

STORAGE OF NPS HARDCOPY DATA FILES AT ECL

The HARDCOPY DATA FILES and all related reports will be filed according to NPS Method No., and then by Sample Set.

ECL has a RECORDS ROOM available for this purpose. It is equipped with shelving for storage, a smoke alarm, and a sprinkler system. Activation of the smoke alarm is monitored 24 hours a day by the NSTL fire department which can respond within 2 minutes to an alarm. ECL will take precautions to protect from sprinkler system water damage all files stored in this room.

The RECORDS ROOM is also the office of the ECL QAC and is locked when the room is unoccupied. Access is limited to the ECL Laboratory Manager, the ECL QAC and Project/Team Leaders.

The STORED RECORDS LOG is used to log files into the RECORDS ROOM and to record removal and subsequent return of these files.

NPS STORED RECORDS LOG

RECORD IDENTIFICATION	INITIAL STORAGE	REMOVED	RETURNED	REMOVED	RETURNED	REMOVED	RETURNED	REMARKS
Method/Set No.	Date/By	Date/By	Date/By	Date/By	Date/By	Date/By	Date/By	

APPENDIX G
DIXON'S TEST

DIXON'S TEST

Dixon's test is used to confirm the suspicion of outliers of a set of data (for example, control chart data points). It is based on ranking the data points and testing the extreme values for credibility. Dixon's test is based on the ratios of differences between observations and does not involve the calculation of standard deviations.

The procedure for Dixon's test is as follows (from Taylor, 1987):

1) The data is ranked in order of increasing numerical value. For example:

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

2) Decide whether the smallest, X_1, or the largest, X_n, is suspected to be an outlier.

3) Select the risk you are willing to take for false rejection. For use in this QAPP we will be using a 5% risk of false rejection.

4) Compute one of the ratios in Table 1. For use in this QAPP we will be using ratio r_{22}, since we will be using between 20 and 17 points for the control charts.

5) Compare the ratio calculated in Step 4 with the appropriate values in Table 2. If the calculated ratio is greater than the tabulated value, rejection may be made with the tbulated risk. Fort his QAPP we will be using the 5% risk values (bolded).

Example (from Taylor)

Given the following set of ranked data:

10.45, 10.47, 10.47, 10.48, 10.49, 10.50, 10.50, 10.53, 10.58

The value 10.58 is suspected of being an outlier.

1) Calculate r_{11}

$$r_{11} = \frac{10.58 - 10.53}{10.58 - 10.47} = \frac{0.05}{0.11} = 0.454$$

2) A 5% risk of false rejection (Table 2), $r_{11} = 0.477$

3) Therefore there is no reason to reject the value 10.58.

4) Note that at a 10% risk of false rejection $r_{11} = 0.409$, and the value 10.58 would be rejected.

TABLE 1

CALCULATION OF RATIOS

Ratio	For use if n is between	if X_n is suspect	if X_1 is suspect
r_{10}	3 - 7	$\frac{(X_n - X_{n-1})}{(X_n - X_1)}$	$\frac{(X_2 - X_1)}{(X_n - X_1)}$
r_{11}	8 - 10	$\frac{(X_n - X_{n-1})}{(X_n - X_2)}$	$\frac{(X_2 - X_1)}{(X_{n-1} - X_1)}$
r_{21}	11 - 13	$\frac{(X_n - X_{n-2})}{(X_n - X_2)}$	$\frac{(X_3 - X_1)}{(X_{n-1} - X_1)}$
r_{22}	14 - 25	$\frac{(X_n - X_{n-2})}{(X_n - X_3)}$	$\frac{(X_3 - X_1)}{(X_{n-2} - X_1)}$

Note that for use in this QAPjP ratio r_{22} will be used.

TABLE 2

VALUES FOR USE WITH THE DIXON TEST FOR OUTLIERS

		Risk of False Rejection			
Ratio	n	0.5%	1%	5%	10%
	3	0.994	0.988	0.941	0.806
	4	0.926	0.889	0.765	0.679
r_{10}	5	0.821	0.780	0.642	0.557
	6	0.740	0.698	0.560	0.482
	7	0.080	0.637	0.507	0.434
	8	0.725	0.683	0.554	0.479
r_{11}	9	0.677	0.635	0.512	0.441
	10	0.639	0.597	0.477	0.409
	11	0.713	0.679	0.576	0.517
r_{21}	12	0.675	0.642	0.546	0.490
	13	0.649	0.615	0.521	0.467
	14	0.674	0.641	0.546	0.492
	15	0.647	0.616	0.525	0.472
	16	0.624	0.595	0.507	0.454
	17	0.605	0.577	0.490	0.438
	18	0.589	0.561	0.475	0.424
	19	0.575	0.547	0.462	0.412
r_{22}	20	0.562	0.535	0.450	0.401
	21		0.524	0.440	0.391
	22		0.514	0.430	0.382
	23		0.505	0.421	0.374
	24		0.497	0.413	0.367
	25		0.489	0.406	0.360

Note that for this QAPjP the 5% risk level will be used for ratio r_{22}.

Reference:

John K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI, 1987.

APPENDIX H

ADDITIONAL QUALITY CONTROL CHECKS

QUALITY ASSURANCE DATA FORM
NPS GROUND WATER

Sampling Date(s)_____ Method_____

Arrival Date(s) at ECL_____ Set No._____

Set Composition

	sample wt. (gms)	pH		sample wt. (gms)	pH
1.			9.		
2.			10.		
3.			11.		
4.			12.		
5.			13.		
6.			14.		
7.			15.		
8.			16.		

Standards and Set Controls Data

		Name / Date of Std. Used	Amt. Spiked	Initials
Method Blank	( )			
Shipping Blank	( )			
Shipping Blank	( )			
LCS	( )			
LCS	( )			
LCS	( )			
LSS	( )			
LSS	( )			
LSS	( )			
LSS	( )			
LSS	( )			
LSS	( )			
Surrogate	( )			
Column Check	( )			
Column Check	( )			

*** STOP!! . Has Sample Control Record been completed for both distribution and return of samples? _____

. Has Set Composition Form been attached? _____

*** . Has ECL/NPS Sample Tracking Form been attached? _____

Signature:_____ **Date:**_____

Sample Preparation

Procedure	Accomplished	Initials of Employee(s) Doing Work	Comments
Hydrolysis			
pH Adjustment			
Extraction			
Derivatization			
Cleanup:			
-Florisil			

Extracts Relinquished By: _____ Date: _____

Extracts Received By: _____ Date: _____

GC Analysis

Date Begun: _____ Analyst(s): _____ Date Completed: _____

Internal Std. Spike Data:

Spiked By: _____ Date: _____ Amt. Used: _____

Name / Date of Std. Used: _____

I.D. of Instrument Used for Analysis: _____

Analysis Dates

1.	4.	7.	10.	13.	16.
2.	5.	8.	11.	14.	
3.	6.	9.	12.	15.	

STOP!!
- Is GC work complete? _____
- Have NPS Data Report Forms on each sample been completed for each GC column? _____
- Has remedial QC work been carried out with results attached? _____
- If any sample in this set will be reextracted, list the 9 digit - code no. of the sample. _____
- Is any sample in this set a reextracted sample? _____

Signature: _____ Date: _____ Disposition of Extracts: _____

Data Reviewed By: _____ Date: _____

Final Disposition of Extracts: _____ Signature: _____

Date of Final Disposition: _____

EXCEPTIONS TO QC REQUIREMENTS

NPS Method_____ Set_____

State exception, when noticed, who notified, remedial action required, action taken; sign and date for each separate incident. Attach to this QUALITY ASSURANCE DATA FORM verification that the QC problem was resolved and the date it was resolved.

QUALITY ASSURANCE DATA FORM INSTRUCTIONS

To fill out the QA Data Form, refer to the Assignment Sheet and Sample Tracking Form for the set.

Sampling Date(s):

This information is on the Sample Tracking Form.

Arrival Date(s) at ECL:

This information is on the bottom of the Sample Tracking Form under Date Received.

Set No.:

This information is in the title of the Assignment Sheet.

Set Composition:

The correct order of the controls and samples is copied from the Assignment Sheet onto the Set Composition portion of the Quality Assurance Data Form. For each sample, write both the sample name and 9 digit sample-code number. The number to the left of each control name or sample name in this section is the Set Composition Number. It, in conjunction with the Set Number, will be used to identify the controls and samples throughout the extraction and G.C. Analysis. Set Composition Numbers are initially assigned on the Assignment Sheet for each set. After determination, the weight in grams and pH is recorded for each water sample. The weight for all controls is 1000 gms. No pH is recorded for controls. Column Checks are simply listed next to their Set Composition Numbers, pH and weight data being inapplicable.

In the event that a Ground Water Sample is a reextraction, place an R before the 9 digit sample - code number and follow it with the Set Number and Set Composition Number, in parenthesis, of the original Ground Water Sample.

Standards and Set Controls Data:

The purpose of this section is to provide information about the spiking standards used in the set. Copy this information from the Assignment Sheet. In the empty brackets to the right of the Method Blank, Laboratory Control Spikes, Surrogate and Column Checks, write the date the control was originated. This is the date of extraction for all but the Column Checks. The Column Checks are originated on the date the florisil columns are begun. For the Shipping Blanks and Laboratory Sample Spikes, the 9 digit sample - code numbers are placed in the empty brackets.

The information for the Name / Date of Std. Used and Amt. Spiked section can be copied from the Assignment Sheet. The date in parenthesis following the standard name indicates the date the standard was prepared.

The person who spikes a standard should write his initials behind it in the Initials section.

Questions:

Has Sample Control Record been completed for both distribution and return of samples?

The Sample Control Record is kept in the Receiving Room. When NPS water samples are removed from the cooler for extraction, they are signed out on the Sample Control Record. The empty sample bottles are later returned to the Receiving Room and signed in on the Sample Control Record.

Has Set Composition Form been attached?

The Assignment Sheet is prepared at EPA/ECL by the Project Manager and sent to the Processing Laboratory at the start of each set extraction.

Has ECL/NPS Tracking Form been attached?

The ECL/NPS Sample Tracking Form tracks the samples from storage through extraction, and G.C. Analysis.

Signature:

The person completing this page of the form should sign and date the form here.

Sample Preparation:

The NPS Method #3 Extraction Procedure is broken down into six parts in this section. The Date Accomplished and Initials of Employee(s) Doing Work should be provided for each. There is a section provided for comments (exceptions to routine) if applicable.

Signatures:

When sample extracts are delivered for GC analysis, the employee relinquishing the extracts and the employee receiving the extracts should sign and date the QA Data Form.

G.C. Analysis

Date Begun:

Write the date the extracts are spiked with the Internal Standard.

Analyst(s):

Write the name of the person(s) who analyzed the samples on the instrument(s) and performed the calculations on the set.

Date Completed:

Write the date all calculations and data forms for the G.C. analysis are completed and submitted for review.

Internal Std. Spike Data:

This section provides information concerning the Internal Std., the date the set was spiked, amount used and the name and date of standard used. This date is the date the Internal Std. was prepared.

I.D. of Instrument Used for Analysis:

Write in the serial no(s). of the G.C.(s) used.

Analysis Dates:

In this section, the controls and samples are referred to by their Set Composition numbers as written on the first page of this form. Beside each set composition number, record the date of the last injection on a Gas Chromatograph for each control or sample.

Questions:

Is G.C. work complete?

Is all analysis on the instrument completed?

Have NPS Data Report Forms on samples been completed for each G.C. column

This includes the primary and confirmatory G.C. columns.

Has remedial QC work been carried out with results attached?

The analyst is responsible for conducting QC checks. If any portion of the data falls out of the acceptable QC limits, remedial QC work must be done. All QC checks and QC remedial work is outlined in the QC Requirements and Criteria Attachment.

If any sample in this set will be reextracted, list the 9 digit - code no. of the sample.

Refer to the Set Composition section of this form to find the 9 digit - code no. of the sample.

Is any sample in this set a reextracted sample?

If the answer is Yes and additional information on the original sample is needed, refer to the Set Composition section of this form. Any reextracted sample will have an R preceding the 9 digit sample- code number and be followed by the bracketed Set Number and Set Composition Number of the original sample.

Signature:

The person completing this page of the form should sign and date the form here.

Disposition of Extracts:

Following review of the G.C. Analysis Data, sample tubes are quantitatively transferred to culture tubes and volumes marked. All information on concentrator tubes is transferred to the culture tubes, which are then stored in a cooler. At this time, the "EXTRACT STORAGE DATA SHEET",(See Appendix A), is completed by recording all pertinent extract information.

Data Reviewed By:

Signature of person who reviewed completed data set. This must be someone other than the person who analyzed the set.

Date:

Write the date the review was completed.

Final Disposition of Extracts:

Sample extracts will be held until the Technical Monitor approves of their disposal (See 7.23 of the QAPP).

NPS METHOD #3 QUALITY CONTROL DATA SHEET

		SAMPLE PREPARATION AND HYDROLYSIS						
Set	Date	Mercuric Chloride (10 mg/ml) Grade Lot #	New Solution? Date Person	DISPOSAL Date Prep. Date Disp. Person	NaCL Grade Lot #	NaOH (6N) Grade Lot #	New Solution? Date Person	DISPOSAL Date Prep. Date Disp. Person
Storage Conditions		Hood Room Temp.			Desiccator	Hood Room Temp		
Disposal Conditions				Lab. Sink	Dry Waste to NSTL Dump			Lab Sink

92

Set	Date	EXTRACTION							
		$MeCl_2$ Grade Lot #	H_2SO_4 (12N) Grade Lot#	New Solution? Date Person	DISPOSAL Date Prep Date Disp Person	Ether Grade Lot#	Na_2SO_4 (acidified) Grade Lot #	New Solution? Date Person	DISPOSAL Date Prep Date Disp Person
• Storage Conditions		Hood Room Temp.	Hood Room Temp.			Hood Room Temp.	Hood Room Temp.		
~~Ch~~ aal		Lab. Sink			Lab. Sink	Lab. Sink			Lab. Sink

		METHYLATION AND CONCENTRATION				FLORISIL CLEANUP			
Set	Date	Diazo-methane Batch Date	DISPOSAL Batch Date Date Disp. Person	MTBE Grade Lot #	Methanol Grade Lot #	MTBE/ Methanol Solution Grade Lot #	New Solution? Date Person	DISPOSAL Date Prep. Date Disp. Person	MTBE (Final Dil.) Date Person
Storage Conditions		Freezer		Hood Room Temp.	Hood Room Temp.	Hood Room Temp.			Hood Room Temp.
Disposal			Lab.	Lab.	Lab.			Lab.	Lab.

INTERNAL QUALITY CONTROL CHECKLIST

Method 03/ Extraction Set #_____

CRITERIA FOR RESULTS	ACCEPTABLE LIMITS*
SURROGATE RECOVERY:	PASS_____ FAIL_____
DCAA recovery must be within ± 30% of mean recovery determined during the initial demonstration of capabilities.	Mean: 84.6% Range: 54.6 to 114.6%
INTERNAL STANDARD AREA:	PASS_____ FAIL _____
Peak area for internal standard in any sample must not deviate by more than 20% from the mean peak area for the calibration standards it was analyzed against.	Mean:_____ Mean:_____ Mean:_____
LABORATORY CONTAMINATION:	PASS_____ FAIL_____
Method blank should not contain a peak greater than or equal to one-half MRL for each analyte.	Blank date_____ Analyte_____ Amount found_____
INSTRUMENT PERFORMANCE:	PASS_____ FAIL_____
See Section 11.1 of Method 3.	R: >0.4 S/N: >3.0 PSF: 0.70 to 1.05 PGF: 0.70 to 1.05
CALIBRATION STANDARD INTEGRITY:	PASS_____ FAIL_____
A calibration curve based on newly prepared standards must give results which are within 20% of the expected value for the most recently prepared calibration solutions.	Calib. Curve_____ (date) Calib. Level_____

*Note any exceptions to the Acceptable Limits.

Prepared by_____ Date_____

CONTROL CHARTS:

LCSA (date)_____ LCSB (date)_____

Recoveries from the Laboratory Control Standards must be within the limits of the current Control Chart.

COMPOUND NAME	UPPER CONTROL LIMIT	UPPER WARNING LIMIT	LOWER WARNING LIMIT	LOWER CONTROL LIMIT
DICAMBASOH	133	121	73	61
ACIFLUORFEN	74	67	39	32
AKIBEN	74	68	40	34
BENTAZON	105	102	89	86
D24	114	107	79	73
DACTHAL	109	104	82	77
DB24	110	105	85	81
DCAA	105	99	74	68
DCB35	97	88	50	40
DICAMBA	106	99	73	67
DINOSEB	80	70	31	21
DP24	110	104	80	74
PCP	95	88	58	51
PICLORAM	106	99	73	67
PNP	165	140	40	14
SILVEX	111	103	73	66
T245	109	104	83	77

Out of Control conditions: More than 15% of the analytes are outside $\pm$ 3 σ, or the same analyte is out twice in a row.

Alert conditions: Three or more consecutive points for an analyte are outside $\pm$ 2 σ, but inside $\pm$ 3 σ, or seven consecutive points for an analyte are in increasing or decreasing order.

APPENDIX I

ECL COMPUTER PROGRAMS

BASIC PROGRAM: REGVAR

MAR 23, 1988 15:43:27

```
5REM***REGVAR,WRITTEN FOR ECL BY WWD, OCT 1,1986
10LETN=T=C1=C2=D1=D2=0
20PRINT"ENTER COMPOUND NAME";
30DIMA$[40]
35DIMU[100]
36DIMP[100]
37DIMX[100]
38DIMD[100]
39DIMG[100]
40INPUTA$
50PRINT"ENTER -1 AFTER YOUR LAST DATA POINT"
60FORI=1TO30
70PRINTI
80PRINT"ENTER YOUR VALUE FOR X";
90INPUTU[I]
100IFU[I]=-1THEN150
110LETN=N+1
120PRINT"ENTER YOUR VALUE FOR Y ";
130INPUTP[I]
140NEXTI
150PRINT
160PRINT"ARE ALL VALUES CORRECT? (Y/N)";
170INPUTB$
180IFB$="Y"THEN260
190PRINT"ENTER THE NUMBER OF THE PAIR IN ERROR";
200INPUTI
210PRINT"ENTER THE CORRECT X";
220INPUTU[I]
230PRINT"ENTER THE CORRECT Y";
240INPUTP[I]
250GOTO160
260FORI=1TON
270LETC1=C1+U[I]
280LETC2=C2+(U[I]^2)
290LETD1=D1+P[I]
300LETD2=D2+(U[I]*P[I])
310NEXTI
320LETS=(N*D2-C1*D1)/(N*C2-(C1^2))
330LETY=(D1-(S*C1))/N
340PRINT
350FORI=1TON
360LETX[I]=S*U[I]+Y
370LETD[I]=P[I]-X[I]
380LETG[I]=D[I]^2
390NEXTI
400LETZ=0
410GOTO440
420OUTDVC"L1",E
430IFZ=2GOTO600
440PRINTA$
450PRINT"Y INTERCEPT IS ";Y
460PRINT"SLOPE IS ";S
470PRINT"X      ";"      Y ";"     CALC. Y     ";"  DIFF ";
480PRINTTAB(48);" DIFF^2"
490FORI=1TON
500PRINTU[I];TAB(12);P[I];TAB(20);X[I];TAB(33);D[I];
510PRINTTAB(48);G[I]
520LETT=T+G[I]
530NEXTI
540PRINT"THE SUM
550PRINT
```

```
560PRINT
570PRINT
580LETZ=Z+1
590GOTO420
600OUTDVC"T1",E
610PRINT"INPUT A Y VALUE. USE A -1 TO END THE OPERATION."
620INPUTT
630IFT=-1THEN720
640LETV=(T-Y)/S
650PRINT"YOUR X VALUE IS "V
660PRINT"YOUR Y VALUE IS "T
670OUTDVC"L1",E
680PRINT
690PRINT"YOUR X VALUE IS "V
700PRINT"YOUR Y VALUE IS "T
710GOTO600
720PRINT
730OUTDVC"T1",E
740IFL$="MANY"THEN10
750PRINT"IF YOU HAVE SEVERAL GROUPS AND WOULD LIKE TO OMIT";
760PRINT"THE NEXT QUESTION, ENTER MANY INSTEAD OF Y OR N."
770PRINT
780PRINT"DO YOU WANT TO ENTER ANOTHER GROUP? (Y/N/MANY)"
790INPUTL$
800IFL$="MANY"THEN10
810IFL$="Y"THEN10
820END

END OF FILE
```

APPENDIX J

RAPID REPORTING NOTIFICATION

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 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. They will need to have this information in hand prior to their conducting the dry run.

Attachment

Addressees:

A. Dupuy
L. Kamphake
C. Madding
R. Maxey
R. Sorrell
R. Thomas

cc:

J. Kotas
H. Brass
A. Kroner
J. Orme

METHOD #3

ANALYTE	RAPID REPORTING LEVEL
Acifluorfen	130 ug/L
Bentazon	87.5 ug/L
2,4-D	100 ug/L
Dalapon	800 ug/L
Dicamba	13 ug/L
Dinoseb	3.5 ug/L
Pentachlorophenol	300 ug/L
Picloram	700 ug/L
2,4,5-T	105 ug/L
2,4,5-TP	70 ug/L

METHOD 6

ANALYTE	Rapid Reporting Level (ppb)	Analytical Results		
		Primary GC Column (ppb)	Secondary GC Column (ppb)	GC/MS (pos. or neg. or N/R*)

* = NOT ANALYZED

QA Assessment:

Is there any QC problem(s) with the set or the sample for either Method that may adversely impact the identification or quantitation of the above analytes? If yes, describe.

R. Maxey, Project Leader

NPS RAPID REPORTING NOTIFICATION
NPS METHODS 1,3 AND 6

Date:_____

Set No.:_____

NPS Field Sample No.:_____

BSL Lab. I.D. No.:_____

METHOD 1

ANALYTE	Rapid Reporting Level (ppb)	Analytical Results		
		Primary GC Column (ppb)	Secondary GC Column (ppb)	GC/MS (pos. or neg. or N/R

METHOD 3

ANALYTE	Rapid Reporting Level (ppb)	Analytical Results		
		Primary GC Column (ppb)	Secondary GC Column (ppb)	GC/MS (pos., neg., or N/R[1]

* = NOT ANALYZED

APPENDIX K

GC/MS CHARACTERISTIC IONS FOR METHOD 3

TABLE 1. (continued)

ANALYTE	METHOD NUMBER	AMOUNT INJECTED, NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
ACIFLUORFEN	3	80	374.6	2590	75	375	223	A50	346	376	244	B106
BENTAZON	3	60	254.3	2072	212	254	105	A48	255	213	241	B104
CHLORAMBEN (A)	3		-	-	-	-	-	-	-	-	-	-
2,4-D METHYL ESTER	3	40	235.0	1374	199	234	236	A14	235	237	175	B69
DALAPON (D)	3	80	157.0	-	-	-	-	-	-	-	-	-
2,4-DB	3	20	263.1	1932	101	162	59	A47	101	263	231	B103
DCPA DIACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DCPA MONOACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DICAMBA	3	40	235.0	1165	203	234	205	A31	203	235	205	B87
DICAMBA METABOLITE (B)	3	80	222.0	-	-	-	-	-	-	-	-	-
DICAMBA METHYL ESTER	3	40	235.0	1165	203	234	205	A31	203	235	205	B87
3,5-DICHLOROBENZOATE	3	10	205.0	917	173	204	206	A12	205	207	173	B67
3,5-DICHLOROBENZOIC ACID	3	10	205.0	917	173	204	206	A12	205	207	173	B67
DICHLORPROP	3	160	249.1	1537	162	248	250	A44	189	249	251	B100
DINOSEB	3	60	254.2	2047	225	254	195	A46	255	225	195	B102
DINOSEB METHYL ESTER	3	60	254.2	2047	225	254	195	A46	255	225	195	B102
5-HYDROXY DICAMBA	3	80	251.0	1840	233	264	266	A45	233	265	251	B101
4-NITROPHENOL	3	1	139.1	1228	153	137	123	A43	154	124	138	B99
PCP	3	10	280.3	1499	280	282	265	A33	281	283	245	B89
PCP METHYL ESTER	3	10	280.3	1499	280	282	265	A33	281	283	245	B89
PICLORAM	3	80	255.5	2242	196	254	256	A49	255	257	223	B105
2,4,5-T	3	10	269.5	1619	233	268	270	A36	269	271	209	B91
2,4,5-T METHYL ESTER	3	10	269.5	1619	233	268	270	A36	269	271	209	B91
2,4,5-TP	3	80	283.5	1577	196	282	284	A35	223	283	285	B92
2,4,5-TP METHYL ESTER	3	80	283.5	1577	196	282	284	A35	223	283	285	B92

(A) COMPOUND OMITTED FROM MS MIXTURES.

(B) 3,6-DICHLORO-2-HYDROXYBENZOIC ACID; DATA BEING COMPILED.

(C) DISULFOTON SULFONE AND STIROFOS COELUTED ON THE DB-5 COLUMN; EI MASS SPECTRA NOT AVAILABLE.

(D) DALAPON ELUTED IN SOLVENT PEAK; MS SPECTRA NOT AVAILABLE.

APPENDIX L

ADDENDA TO METHOD 3 - JUNE 1988 TO DECEMBER 1989

05/01/89

Environmental Chemistry Section
Addendum - Method 3

Revision to Section 4, page 1, paragraph 1, sentence 4

- Change "Dr. Y. A. Yonan, ECL-QAO . . ." to "Mr. Danny McDaniel, Acting ECS-QAC. . ."

Revision to Section 4, page 1, paragraph 2, sentence 2

- Change "..handled by Ms. Jan Watkins." to "...handled by Ms. Jan Watkins backed up by Ms. Elizabeth Flynt."

Revision to Section 4, page 1, paragraph 2, sentence 3

- Change ". . . M. George Sand." to ". . .Mr. William Mitchell and Mr. Joe Ferrario."

Revision to Section 4, page 1, paragraph 2, sentence 4

- Change "Data handling and reporting will be handled by Ms. Watkins backed up by Mr. Mecomber and Ms. Flynt." to "Data handling and reporting will be handled by Ms. Watkins backed up by Ms. Flynt."

Revision to Section 4, Figure 4-1 - ECS ANALYTICAL TEAM - Method 3

- Delete ECS ANALYTICAL TEAM diagram from Figure 4-1.

- Replace with revised diagram on following page.

Approved Robert A. Money
EPA/ECS-NPS Project Leader/
ECS Analytical Coordinator

Approved Tony S. Johnson
QAO-NPS

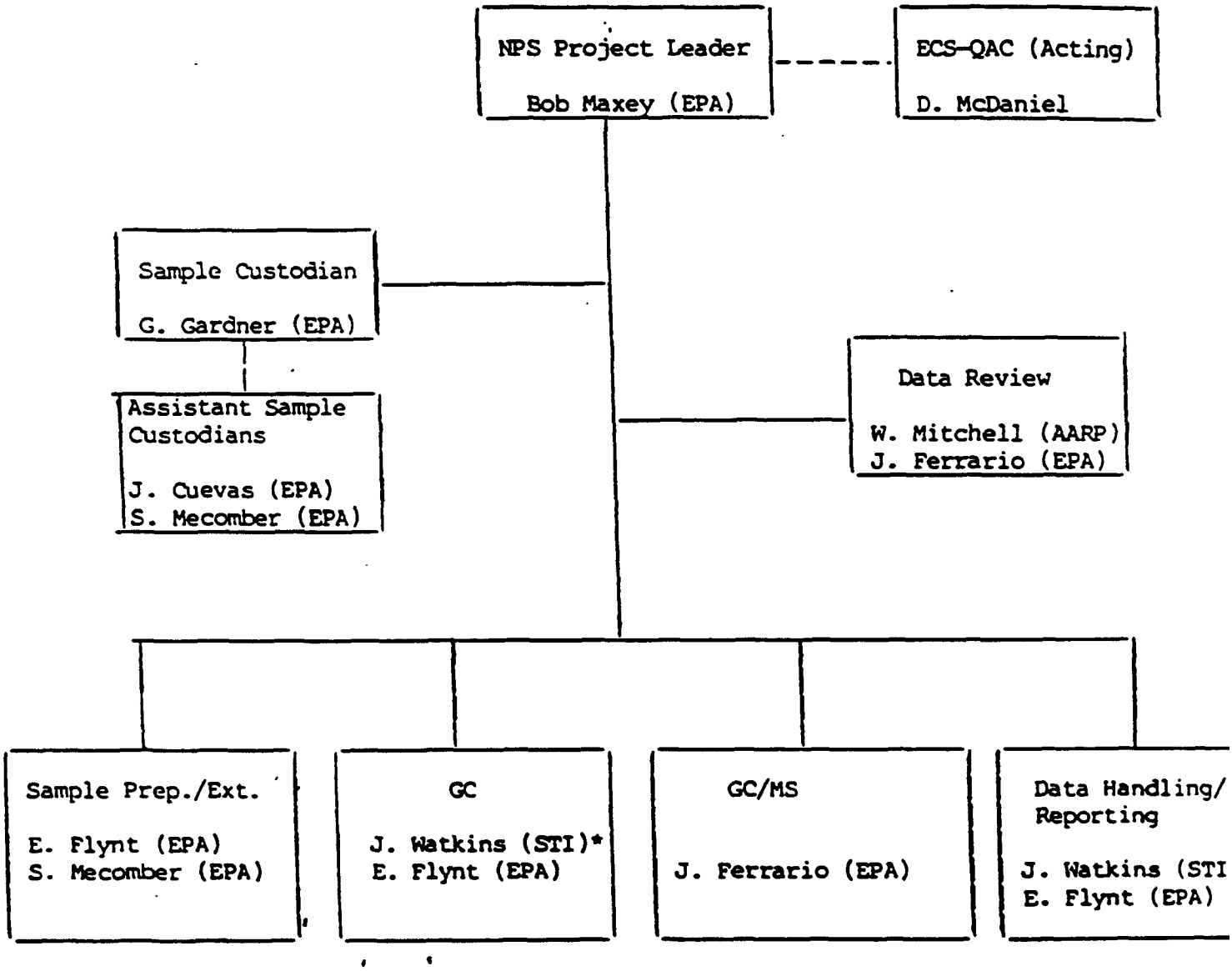
Approved
QAO-OPP

Approved Maria Flores-Taylor
QAO-ODW

Approved Jeanne Bustin
NPS Director

ECS ANALYTICAL TEAM

METHOD 3



* = Sverdrup Technology Inc. (In-house Contractor for ECS)
ECS provides overall technical direction to Sverdrup Technology, Inc.

FIGURE 4-1: ECS ANALYTICAL TEAM - METHOD 3

8/12/88

ENVIRONMENTAL CHEMISTRY LABORATORY
ADDENDUM - METHOD 3

Addition to Section 4, page 1, paragraph 2, sentence 3

-Add "Data review has been assigned to Mr. George Sand."

Addition to Section 4, page 1, paragraph 3

-Change "NASA/NSTL Bldg. 1105
NSTL,MS 39529"

to

"NASA/SSC Bldg. 1105
STENNIS SPACE CENTER, MS 39529-6000"

Addition to Section 4, page 1, paragraph 4

-Change "The Assistant Sample Custodian for NPS is:

Mr. John Cuevas
(601)688-3170 (or 3217)"

to

"The Assistant Sample Custodians for NPS are:

Mr. John Cuevas
(601)688-3170 (or 3217)

Mr. Stanley Mecomber
(601)688-3170 (or 3217)"

Figure 4-1: ECL ANALYTICAL TEAM was revised. The new chart is enclosed.

Approved _____
QAO-ODW

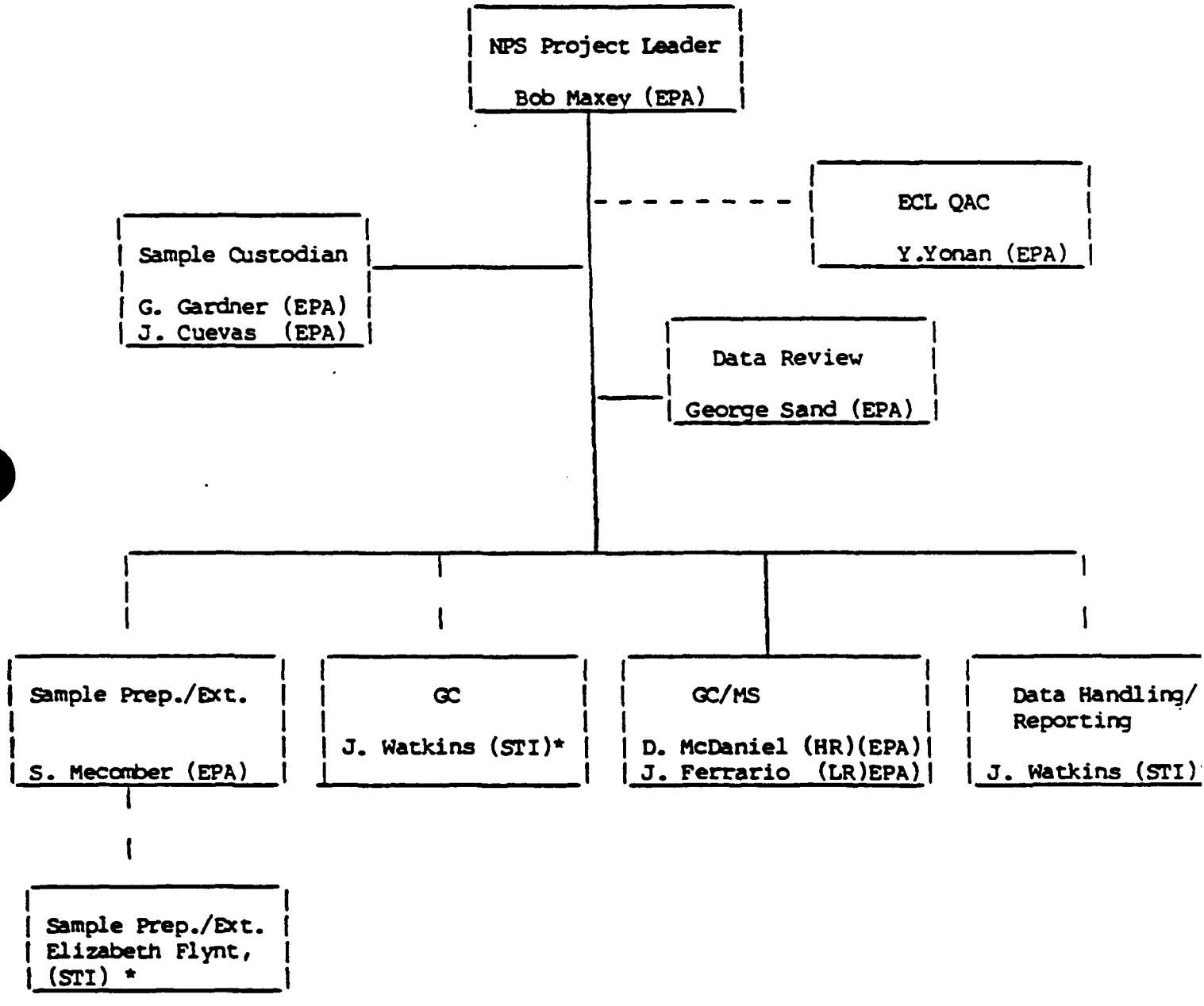
Approved _____
QAO-OPP

Approved _____
NPS Director

Approved _____
EPA/ECS-NPS Project Leader/
ECS Analytical Coordinator

ECL ANALYTICAL TEAM

METHOD 3



* STI = Sverdrup Technology Inc. (In-house Contractor for ECL)
Sverdrup is providing the ECL several person years of support.
ECL provides overall technical direction to Sverdrup Technology, Inc.

FIGURE 4-1: ECL ANALYTICAL TEAM - METHOD 3

7/21/88

Environmental Chemistry Laboratory
Addendum - Method 3

Addition to Section 2, page 7, Appendix H

-Add "Internal Quality Control Checklist" below "QC Data Sheet"

-Add an Appendix "K: GC/MS CHARACTERISTIC IONS FOR METHOD 3"

Addition to Section 5, page 1, number 8, end of paragraph

-Add "See Appendix K for a Table of the three ions for each analyte"

Addition to Appendices

-Add Internal Quality Control Checklist (enclosed) to end of Appendix G

-Add a cover sheet for Appendix K: GC/MS CARACTERISTIC IONS FOR METHOD 3. (For the appendix contents, see the enclosed GC/MS Characteristic Ions Table.)

Approved _____
QAO-ODW

Approved _____
QAO-OPP

Approved _____
NPS Director

INTERNAL QUALITY CONTROL CHECKLIST

Method 03/ Extraction Set #_____

CRITERIA FOR RESULTS	ACCEPTABLE LIMITS*
SURROGATE RECOVERY:	PASS_____ FAIL_____
DCAA recovery must be within ± 30% of mean recovery determined during the initial demonstration of capabilities.	Mean: 84.6% Range: 54.6 to 114.6%
INTERNAL STANDARD AREA:	PASS_____ FAIL _____
Peak area for internal standard in any sample must not deviate by more than 20% from the mean peak area for the calibration standards it was analyzed against.	Mean:_____ Mean:_____ Mean:_____
LABORATORY CONTAMINATION:	PASS_____ FAIL_____
Method blank should not contain a peak greater than or equal to one-half MRL for each analyte.	Blank date_____ Analyte_____ Amount found_____
INSTRUMENT PERFORMANCE:	PASS_____ FAIL_____
See Section 11.1 of Method 3.	R: >0.4 S/N: >3.0 PSF: 0.70 to 1.05 PGF: 0.70 to 1.05
CALIBRATION STANDARD INTEGRITY:	PASS_____ FAIL_____
A calibration curve based on newly prepared standards must give results which are within 20% of the expected value for the most recently prepared calibration solutions.	Calib. Curve_____ (date) Calib. Level_____

*Note any exceptions to the Acceptable Limits.

Prepared by_____ Date_____

CONTROL CHARTS:

LCSA (date)_____ LCSB (date)_____

Recoveries from the Laboratory Control Standards must be within the limits of the current Control Chart.

COMPOUND NAME	UPPER CONTROL LIMIT	UPPER WARNING LIMIT	LOWER WARNING LIMIT	LOWER CONTROL LIMIT
DICAMBA5OH	133	121	73	61
ACIFLUORFEN	74	67	39	32
AMIBEN	74	68	40	34
BENTAZON	105	102	89	86
D24	114	107	79	73
DACTHAL	109	104	82	77
DB24	110	105	85	81
DCAA	105	99	74	68
DCB35	97	88	50	40
DICAMBA	106	99	73	67
DINOSEB	80	70	31	21
DP24	110	104	80	74
PCP	95	88	58	51
PICLORAM	106	99	73	67
PNP	165	140	40	14
SILVEX	111	103	73	66
T245	109	104	83	77

Out of Control conditions: More than 15% of the analytes are outside $\pm$ 3 σ, or the same analyte is out twice in a row.

Alert conditions: Three or more consecutive points for an analyte are outside $\pm$ 2 σ, but inside $\pm$ 3 σ, or seven consecutive points for an analyte are in increasing or decreasing order.

TABLE 1. (continued)

ANALYTE	METHOD NUMBER	AMOUNT INJECTED, NG	MW	MS SCAN	EI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	EI SPECTRUM NUMBER	CI CHARACTERISTIC IONS, m/z PRIMARY	2ND	3RD	CI SPECTRUM NUMBER
ACIFLUORFEN	3	80	374.6	2590	75	375	223	A50	346	376	244	B106
BENTAZON	3	60	254.3	2072	212	254	105	A48	255	213	241	B104
CHLORAMBEN (A)	3		-	-	-	-	-	-	-	-	-	-
2,4-D METHYL ESTER	3	40	235.0	1374	199	234	236	A14	235	237	175	B69
DALAPON (D)	3	80	157.0	-	-	-	-	-	-	-	-	-
2,4-DB	3	20	263.1	1932	101	162	59	A47	101	263	231	B103
DCPA DIACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DCPA MONOACID METABOLITE	3	10	332.0	1936	301	332	330	A39	333	331	299	B95
DICAMBA	3	40	235.0	1165	203	234	205	A31	203	235	205	B87
DICAMBA METABOLITE (B)	3	80	222.0	-	-	-	-	-	-	-	-	-
DICAMBA METHYL ESTER	3	40	235.0	1165	203	234	205	A31	203	235	205	B87
3,5-DICHLOROBENZOATE	3	10	205.0	917	173	204	206	A12	205	207	173	B67
3,5-DICHLOROBENZOIC ACID	3	10	205.0	917	173	204	206	A12	205	207	173	B67
DICHLORPROP	3	160	249.1	1537	162	248	250	A44	189	249	251	B100
DINOSEB	3	60	254.2	2047	225	254	195	A46	255	225	195	B102
DINOSEB METHYL ESTER	3	60	254.2	2047	225	254	195	A46	255	225	195	B102
3-HYDROXY DICAMBA	3	80	251.0	1840	233	264	266	A45	233	265	251	B101
4-NITROPHENOL	3	1	139.1	1228	153	137	123	A43	154	124	138	B99
PCP	3	10	280.3	1499	280	282	265	A33	281	283	245	B89
PCP METHYL ESTER	3	10	280.3	1499	280	282	265	A33	281	283	245	B89
PICLORAM	3	80	255.5	2242	196	254	256	A49	255	257	223	B105
2,4,5-T	3	10	269.5	1619	233	268	270	A36	269	271	209	B91
2,4,5-T METHYL ESTER	3	10	269.5	1619	233	268	270	A36	269	271	209	B91
2,4,5-TP	3	80	283.5	1577	196	282	284	A35	223	283	285	B92
2,4,5-TP METHYL ESTER	3	80	283.5	1577	196	282	284	A35	223	283	285	B92

(A) COMPOUND OMITTED FROM MS MIXTURES.

(B) 3,6-DICHLORO-2-HYDROXYBENZOIC ACID; DATA BEING COMPILED.

(C) DISULFOTON SULFONE AND STIROPOS COELUTED ON THE DB-5 COLUMN; EI MASS SPECTRA NOT AVAILABLE.

(D) DALAPON ELUTED IN SOLVENT PEAK; MS SPECTRA NOT AVAILABLE.