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QUALITY ASSURANCE PROJECT PLAN FOR THE NATIONAL PESTICIDE SURVEY OF DRINKING WATER WELLS: ANALYTICAL METHOD 7 - FUMIGANTS

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OLS # 1991-

NATIONAL PESTICIDE SURVEY
QUALITY ASSURANCE PROJECT PLAN FOR
ANALYTICAL METHOD 7 - FUMIGANTS

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3. PROJECT DESCRIPTION

The National Pesticide Survey is intended to assess the extent and nature of pesticide presence in well waters used in private and community water supply systems. The statistical design of the survey will suggest from a manageable number of samples and analyses the nature of pesticide presence in such water supplies throughout the nation.

Environmental Science and Engineering, Inc. (ESE) of Gainesville, Florida, has contracted with the U.S. Environmental Protection Agency (EPA) to analyze the collected water samples for carbamates (Method 5) and halogenated fumigants (Method 7). This project plan applies to Method 7, the determination of ethylene dibromide (EDB), dibromochloropropane (DBCP), 1,2-dichloropropane, and cis- and trans-1,3-dichloropropene in ground waters. Method 7 involves extraction of the analytes from water, capillary gas chromatographic separation, and electron capture detection and quantitation. Positive results will be confirmed by the same method using a second GC column analysis. GC/MS will be used to verify confirmed positive results above the reporting limits. Method 7 is an adaptation of EMSL method 504, "1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) in Water by Microextraction and Gas chromatography" (Appendix A).

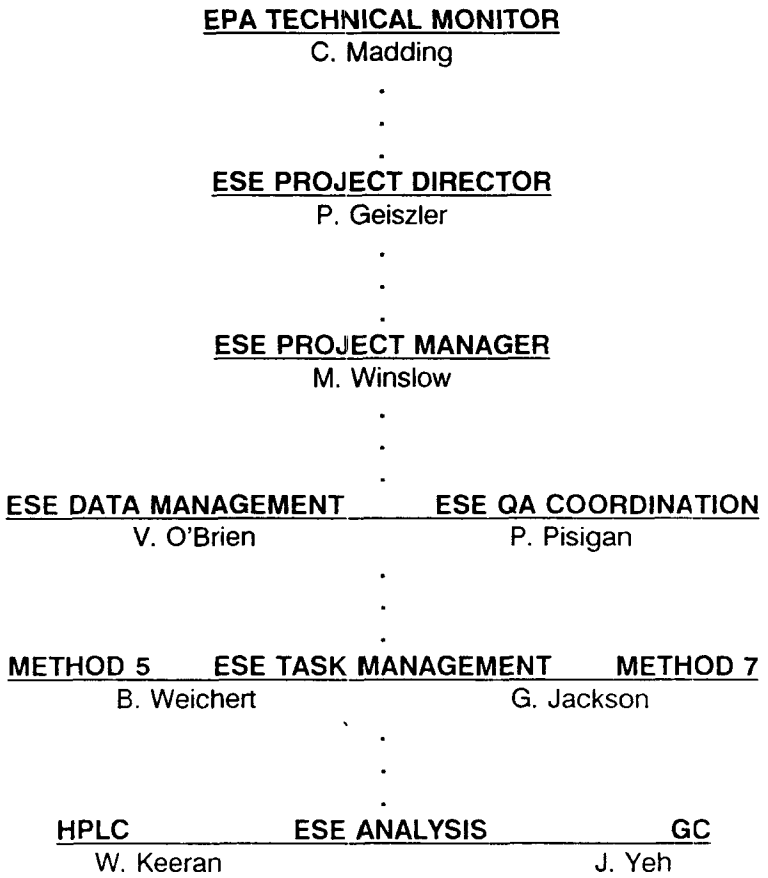
4. PROJECT ORGANIZATION AND RESPONSIBILITIES

The project organization chart is presented in Exhibit 4-1. The managing staff are:

Paul C. Geiszler	Project Director
Michael G. Winslow	Project Manager and Technical Contact
Portia O. Pisigan	Quality Assurance Coordinator
Virgina C. O'Brien	Data Management and Sample Control
Glenn T. Jackson	Manager, GC Volatiles Department
T. James Yeh	Associate Scientist, Lead Chemist

EXHIBIT 4-1

PROJECT ORGANIZATION CHART



Certain specific project assignments are handled by others:

Vince Prem-Das	Sample Check-in
D. Michael Ritter	Computer Sample Check-in and Data File Generation
Richard Ross	Sample Custody and Coldroom Support

Samples will generally be received by Vince Prem-Das, ESE, 14220 Newberry Road, Gainesville, FL, 32607; phone (904) 332-3318. It will generally be necessary to ask the ESE switchboard to page Mr. Prem-Das. In his absence, ask for Michael G. Winslow, Project Manager.

The EPA Technical Monitor (primary contact) for Method 7 matters is Caroline Madding, phone (513) 569-7945. The EPA Project Officer is David J. Munch.

5. QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The "estimated detection limit "(EDL) for Method 7 will be determined as follows:

1. Determine the concentration of each analyte which, when injected, yields a 5:1 signal-to-noise ratio, measured as the ratio of the center chromatographic peak height to the edge-to-edge height of the noise envelope.

2. Spike eight HPLC-grade water samples at the concentration determined in 1. and analyze together.

3. Calculate the Estimated Detection Limit (EDL) by multiplying the standard deviation of the concentrations from 2. by the Student t-value 2.998 (7 degrees of freedom, alpha = 0.99, one-sided).

4. The EDL is the greater of the values calculated in 1. and 3.

5. The EDL shall be evaluated by the Technical Monitor.

6. Acceptance of ESE's calculated EDL's shall be judged by the Technical Monitor based upon health effects data and the technical feasibility of achieving EDL's suggested by such data.

7. Analyze the eight sample aliquots of 2. on the confirmatory column and calculate EDLs as in 1 and 3. The resulting EDLs must roughly equal those of the primary column.

8. Perform up to six GC/MS analyses on the five analytes to determine the 5:1 signal-to-noise ratio for the least intense ion, using the following ions for each:

Analyte	Masses (amu)
EDB (ethylene dibromide)	107, 109
DBCP (dibromochloropropane)	115, 157, 159
1,2-Dichloropropane	62, 63, 64, 65
cis-1,3-Dichloropropene	75, 77, 110, 112
trans-1,3-Dichloropropene	75, 77, 110, 112

For sample analysis:

1. Minimum Reporting Levels (MRL) are 3 times the EDL for each analyte.

2. Report as an occurrence (code -111) any peak matching an analyte retention time at responses between one-half the MRL and the MRL. Such frequent occurrences may lead to confirmations and/or adjustment in the reporting limit. Frequent occurrences of non-analyte peaks will be reported to the Technical Monitor. Criteria for reporting these non-analyte peaks will be supplied by the EPA (Appendix B).

3. The lowest standard solution concentration will approximately equal the MRL for all analytes.

4. Initial demonstration of method performance will be accomplished by the analysis of 20 spiked samples at 10 times the MRL over a four day period (five spiked samples per day). Mean recovery, variance and the standard deviation will be calculated. Relative standard deviation (RSD) will be used to evaluate the precision of the method using the acceptance criteria provided by the EPA.

5. Method performance data will be reviewed by the Technical Monitor.

6. Samples having any analyte concentration above that analyte's reporting limit will be confirmed on a different GC column (see Section 8).

7. Samples found in the confirmatory analysis to have any analyte concentration above that analyte's reporting limit will be qualitatively analyzed by GC/MS. If this cannot be done by quadrupole GC/MS, the sample extracts will be shipped on ice to TSD (Appendix C). The shipping blank will be analyzed for any samples meeting second-column confirmation.

8. Performance evaluation samples will be analyzed quarterly.

Results from all of the above procedures in this Section will be reported to the Technical Monitor for approval. Data from the Initial Demonstration of Method Performance will be appended to this Plan (Appendix D).

During the survey, EPA will conduct a time-storage study and will provide extra field samples (10% of sites) for ESE to assess analyte recoveries from a variety of matrices. Each sample will be spiked with a stock solution in methanol to yield sample concentrations of 2, 10 or 20 times the reporting limit for each analyte (the surrogate will also be added) (Appendix E). This sample will be extracted and analyzed, and the data reported as a percent recovery. This data is not for laboratory control, and the analysis will be judged to have failed only if the extra sample's surrogate recovery fails the criterion for a regular sample.

6. SAMPLING PROCEDURES

All samples for Method 7 will be received in 60-mL amber bottles. Samples for Method 7 will include 10 mg/L mercuric chloride and will be shipped iced for overnight delivery. Each set received from a field site will include the following: primary samples and one backup sample for each primary sample, and one shipping blank sample for each primary sample. Matrix spikes will be performed on 10 percent of the sample sites. Some sets will include time-storage samples. Quarterly, sets will include performance-evaluation samples provided by the NPS QAO.

Analysis types and frequency are described on the next page.

The analysis types for Method 7 are:

Primary Analysis:		
Method Blank	1 per set	Not chargeable
Calibration Standards	daily	Not chargeable
Field Sample	1 per ESE sample no.	Chargeable
Lab Spike (ESE Matrix Spike)	10%	Chargeable
Day 0 Time-Storage Sample	10%	Chargeable
Day 14 Time-Storage Sample	10%	Chargeable
Day 14 Time-Storage Extract	10%	Chargeable
Shipping Blank	(a)	
Performance Evaluation Sample	Quarterly	Chargeable
Backup Sample	(b)	(b)
Confirmational Analysis:		
Method Blank	1 per set	Not chargeable
Calibration Standards	daily (when conf. is performed)	Not chargeable
Field Sample	(a)	Chargeable
Shipping Blank	(a)	Chargeable
GC/MS Confirmation:		
Method Blank	1 per set	Not chargeable
Calibration Standards	daily (when conf. is performed)	Not chargeable
Field Sample	(c)	Chargeable
Shipping Blank	(a)	Chargeable

(a) Analyzed when results of primary analyses are above one half the minimum reporting limit.

(b) Analyzed when results of initial analysis fails (not chargeable) or at the request of the Technical Monitor (chargeable).

(c) Analyzed when results of confirmational analyses are above one half the minimum reporting limit.

Each sample's shipping label will be of the form below.

FIGURE 2

NATIONAL PESTICIDE SURVEY - NPS

PD-0415-4-7-6 DATE 2-11-88

ESE - #7 - T/S

SAMPLER NAME _____

The sample bottle number (**PD-0415-4-7-6** in the above example) is constructed as follows:

PD Pesticide Survey Domestic Well

PC Pesticide Survey Community Well

PR Pesticide Survey Resampled Site

PB Pesticide Survey Performance Evaluation Sample

0415 is the site number

4 is the ESE lab number

7 is the fumigants method number

6 is the bottle number within this site number

The analysis type codes are given below:

FS Field Sample

FD Field Duplicate

SB Shipping Blank

BU Backup Sample

LS Lab Spike (The ESE Matrix Spike; "LS" will be followed by a numeric digit which indicates spike level; 0=2xMRL, 1=5xMRL, 2=10xMRL. These samples also serve as samples for time storage, t = 0 days.)

T/S Time Storage (t = 14 days)

T/S_0 Time Storage Duplicate (t = 0 days)

T/S_{14} Time Storage Duplicate (t = 14 days)

The sampling contractor will supply a copy of the field sample tracking sheet used for NPS samples.

7. SAMPLE CUSTODY

The sampling contractor (ICF) will supply information about sample shipments and the protocol ESE will follow to notify the sampling contractor about sample receipt and any problems associated with samples received. The project Technical Monitor will also be notified concerning problems with the receipt of samples from the sampling contractor (eg. no ice, etc).

Holding times for samples to be analyzed by Method 7 are: 14 days maximum holding time for samples, counting day of sampling as Day 0; and 14 days maximum holding time for extracts, counting the day of extraction as day 0. Sample disposal will be handled in accordance with Florida regulation.

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

Four extra aliquots of the samples for the time storage studies will be collected. Two of the four replicate aliquots will be spiked, extracted, and analyzed within a four-day time frame. They will then be reanalyzed 14 $\pm$ 4 days after the first analysis. The remaining two duplicates will be spiked at the same time as the first two duplicates, but will be allowed to sit 14 days before extraction. These samples will then be analyzed within four days of extraction.

Each sample will be spiked at the 10X MRL level. Results of the time storage samples will be reported to EPA along with the corresponding regular sample. For data reporting purposes, Day-0 samples (spiked, extracted and analyzed within 4 days of extraction) will be referred to as Day-0 Time Storage (DTS). These samples serve a dual role, as lab spikes and DTS. Extracts from these Day-0 samples reanalyzed within 10 to 18 days will be referred to as Holding Time Extracts (HTE). Day-14 time storage samples (spiked, held for + 14 days, extracted and analyzed within 4 days) will be referred to as Holding Time Samples (HTS). All of the holding time samples will be extracted and analyzed in duplicate. Any statistical analysis of the time storage data will be conducted by EPA.

When samples are received at the ESE Receiving Station, 14420 Newberry Road, Gainesville, FL, the receiving employee will deliver the samples to Vince Prem-Das at the sample check-in station, the Hendrickson building. Mr. Prem-Das will then (1) mark the NPS sample tracking form with the required information, (2) move the samples into a lockable refrigerator in ESE's volatile organic analysis laboratory, and (3) submit the logsheets to Data Management. A Data Management employee will enter the sample information to ESE's database, a process which automatically generates Sample Arrival Notices for the Method 7 Task Manager, Glenn Jackson. Mr. Jackson then schedules the analyses with the analyst, James Yeh, who analyzes them within the holding times, and enters the analytical data into the ESE database. Samples and extracts will be stored between 0°C and 6°C in the dark. At the end of the holding times, the water samples will be disposed in accordance with Florida regulation. Extracts will be held in a freezer until EPA releases them for

disposal. Sample extracts will be shipped to TSD next day, on ice, if GC/MS confirmation of GC confirmed positives is not possible at ESE. The shipping protocol will be appended.

The implementation contractors, ICF, will provide data on returning sample kits.

All ESE coldrooms, refrigerators, and freezers holding samples for chemical analysis are monitored daily by ESE personnel, and records are kept daily. Samples are signed out of the coldroom when removed to the laboratory and signed in when returned. The ESE coldrooms use a "library" system where samples are returned to a Return Shelf, and Data Management personnel only place samples on storage shelves. The coldroom is locked when no one is inside. ESE plans to keep NPS samples on a separate shelf from other samples during the analytical effort (about 18 months).

8. CALIBRATION PROCEDURES AND FREQUENCY

The instrumental analysis for Method 7 will be performed on a Hewlett-Packard 5890A gas chromatograph. Primary analytical separations will be performed on a DB-1 fused silica capillary column, 30 meters long, 0.32 millimeters internal diameter, and 0.25 micron film thickness. Secondary analytical separations will be performed on a DB-17 fused silica capillary column, 30 meters long, 0.32 millimeters internal diameter, and 0.25 micron film thickness. Helium will be used as a carrier gas.

ESE analysts will prepare standard solutions in methanol from EPA concentrate solutions and will keep detailed records of the means used to prepare them on each occasion. Spiking concentrates will be generated by separate dilutions from those used to generate standard solutions. Records of the generation of standards will be kept by the analyst in his permanent notebook. Each set's analytical records will refer to the standard solutions actually used on that day. New standard dilutions will be checked to insure that the QC criteria, $\pm$ 20% of initial calibration, is met. Standard and spiking solutions will be stored in the dark at 0° to 4°C in a standards refrigerator.

ESE plans to calibrate the instrument each day a set is analyzed. For primary analysis, five standards of various concentrations will be spaced periodically in the sample analysis set. The lowest calibration standard will be near the MRL. A solvent blank will also be analyzed. The correlation coefficient between concentrations and response will be 0.995 or greater.

For second column confirmation, a single calibration standard will be used for quantitation. The standard will contain analytes at concentrations near that detected during primary analysis. Results of second column confirmation will be within $\pm$ 25% of the primary analysis result. If this criteria is not met the project Technical Monitor will be advised.

For GC/MS confirmation, a single calibration standard will be used which is prepared at the concentration determined for the sample, on either the primary or secondary column, whichever concentration is lower. If additional sample extract treatment is performed for the GC/MS analysis, the calibration standard must also undergo the same treatment.

9. ANALYTICAL PROCEDURES

The primary analysis begins with the extraction of a 20-mL aliquot of water sample (to which the surrogate, bromochloropropane, has been added) by 1-mL of hexane solvent. Elution through a capillary column separates the analytes and other components, and electron-capture detection quantitates the analytes and surrogate. In confirmatory analysis, the extract is chromatographed through a somewhat different column, and electron-capture detection is used to verify any positive results from the primary analysis. GC/MS confirmation is similar to GC confirmatory analysis except that detection by mass spectrometry is used.

Primary and confirmatory analyses are performed using a Hewlett-Packard 5890A gas chromatograph equipped with two electron-capture detectors and a Hewlett-Packard 3393A integrator. Any GC/MS confirmations at ESE will be performed using a Hewlett-Packard 5987 gas chromatograph/mass spectrometer.

All data will be transferred to the Chemistry Division database running on 65 AT-class computers served by a 3-drive, 1600-Mbyte Novell network housed in the Chemistry Division.

ESE plans to include no more than 20 field samples in a set, and generally fewer.

ESE plans no significant differences from Method 504, revision dated October 27, 1987 as provided to ESE in glassware cleaning, reagents, or data reduction. Three additional analytes will be included in the determinations using Method 504, they are; 1,2-dichloropropane, cis- and trans-dichloropropene. Differences in equipment are listed above in this Section. In the analytical procedure, ESE plans to use a DB-1 column for the primary analysis and DB-1701 column for the confirmatory analysis. ESE plans to extract 20-mL of sample with 1-mL hexane rather that 35-mL of sample with 2-mL of hexane. Because of contamination risk, salt was not used in the extraction process. These changes are for the convenience of our analysts and causes no degradation in the data quality or detection limits. Any deviations from these procedures or QC requirements after the Plan is approved will only be used if approved by the EPA Technical Monitor in advance. Changes will be documented, signed by the Technical Monitor and appended to the Plan.

10. DATA REDUCTION, VALIDATION REPORTING

Calibration standard concentrations and raw instrument responses for calibration standards and sample aliquots are entered into the ESE Chemistry Division's database. ESE data management will support new in-house sample type codes that the numerous EPA sample types require. The analyst will generate ESE set reports and will verify correct entry and QC data compliance with project criteria. The Method 7 Task Manager will review data set reports before submission to the Data Management department. When Data Management receives a signed copy of the set report, they will generate a data file on floppy disk in the NPS format. The project manager will then examine a listing or summary of the file and approve delivery of the floppy disk to EPA.

All data for a set of samples (including QC and confirmatory data) will be reported to the EPA no later than two months from the date of sample collection. Any GC/MS confirmatory data will be reported as "presence" or "absence" of target analytes.

The NPS file format is appended to this Plan (Appendices G, H and I).

Fast Track Reporting (immediate telephone call to the Technical monitor) will be needed for confirmed positive sample concentrations of selected EPA analytes detected above known health effect levels (Appendix J). When results from confirmation columns do not agree with results from primary columns within criteria set by EPA ($\pm$ 25%), or shipping blanks are found to be contaminated, the Technical Monitor will be notified immediately. (Contaminated means a peak response at the correct retention time for an NPS analyte at one-half the MRL or greater.)

Storage of laboratory data will be by ESE standard procedures. Standards and reagent preparation data will reside in the analyst's permanent laboratory notebook. Chromatograms, calibration data, and corrective action records, etc. will reside in an analysis set folder which will be stored permanently in ESE's laboratory central filing system. ESE set folders currently reside in archival files in ESE's central filing system.

11. INTERNAL QUALITY CONTROL CHECKS

No lab control spikes are required for Method 7. Analytical quality will be controlled largely by the following means, which are summarized in Exhibit 11-1:

- If the responses of the analytes in each set's standard chromatograms have changed by ± 20 percent (%) of the previous calibration, the analyst will make new standard solutions from the EPA concentrates. These new dilutions must be within 20 percent of the previous set. Each set must include a chromatogram of a standard at or near the MRL for each analyte.

- Each set's method blank must have analyte responses less than half the minimum reporting limit. If any analyte is present at half or more of the MRL, a new method blank will be generated and analyzed. A second method blank failure will require the determination of the source of contamination before the analysis of samples begins.

- Surrogate recovery for each sample must be within 30 percent (absolute percentage) of the mean surrogate recovery of the data generated in the initial demonstration of capability and used in the control chart criterion generation or the updated control chart. Failure to meet the criterion will require that the situation be corrected before the sample data is accepted. Evaluation of calibration standards and/or reanalysis of sample may be required.

- Surrogate recovery in each set's method blank will be used as the set's control point in the control chart and will be compared against the criterion developed in the initial demonstration of capabilities or the current updated control chart. Thus, there will be one control chart point for each set of samples extracted. The control boundaries on surrogate control chart points will be originally determined from the 20 spiked samples analyzed during the initial demonstration of capability. The mean and standard deviation of the 20 surrogate recovery percentages will be calculated, then the relative standard deviation (RSD) will be calculated. The control limits on the accuracy chart will be ±3 RSD about the mean. The warning limits will be ±2 RSD about the mean. Dixons' test at the 99 percent confidence level will be used to determine outliers (Appendix K). There can be no more than 3 outliers in the original spiked controls.

- Following establishment of the control chart, the surrogate recovery from the method blank is determined with each analytical set. The percent recovery is then checked on the chart. When 5 such controls have been run, these surrogate recoveries will be incorporated into the control charts. From the 20 most recent good points, accuracy will be recalculated as above and the chart will be redrawn. The newly drawn chart will then apply to surrogate recoveries in the next five sample sets. If a field sample qualifies as a blank and it's surrogate recovery meets surrogate control chart limits, it can be substituted for the blank, if the blank recovery does not meet criteria.

- Analysis will be considered "out-of-control" if the surrogate recovery is outside ±3 RSD once. Analysis must be stopped until an "in-control" situation is reestablished. An "alert" situation will arise if a run of 7 consecutive points is above or below the mean, or a run of 7 consecutive points is increasing or decreasing. Also an "alert" situation will arise if 3 or more consecutive percent recoveries are outside the warning limits (±2 RSD).

EXHIBIT 11-1

INTERNAL QC CHECKS FOR METHOD 7

QC Type	Frequency	Concentration	Criteria
Method Blank	Each Set	---	up to 1/2 MRL
Shipping Blank	Positives in Sample	---	up to 1/2 MRL
Calibration Curve	Daily	---	+/- 20%
Surrogate Recovery	Each Sample	0.5 ug/L	+/- 30% mean R
Surrogate Recovery	Method Blank Each Set	0.5 ug/L	in CL on Chart
Second Column Confirmation	All Positives	Calibration Std. +/- 20% Prime Conc.	+/- 25% of Prime Conc.
GC/MS Qualitative Confirmation	All Confirmed Positives	---	+/- 10% of SIR Masses at Retention Times

EXHIBIT 11-1 (continued)

INTERNAL QC CHECKS FOR METHOD 7

QC Type	Purpose and Corrective Action
Method Blank	Method Blank determines if system is free of contamination. Action: Determine the source of contamination.
Shipping Blank	Determine if samples are free of contamination. If fails, inform monitor.
Calibration Curve	Determine validity of standard curve. Action: Check system, make new standard.
Surrogate Recovery/BCP	Monitors method efficiency for all samples. Action: Step-wise review of sample extraction concentration and chromatography to source of the error.
Second Column Confirmation	Report failure to technical monitor for next action.
GC/MS Qualitative Confirmation	Report failure to technical monitor for next action.

- If any positives are determined in the samples, the shipping blank will be analyzed.
- Second column confirmation must be within $\pm$25 percent of the concentration determined with the primary column.
- GC/MS qualitative confirmation must be performed with a standard that is approximately equal to the lowest concentration determined in the primary and confirmation GC analyses. If quadrupole GC/MS is not sensitive enough, the sample extracts will then be shipped on ice to TSD for analysis by magnetic sector GC/MS.

Exhibit 11-2 shows ESE's Internal Quality Control Checklist which will be included with each set file.

EXHIBIT 11-2

INTERNAL QUALITY CONTROL CHECKLIST

U. S. ENVIRONMENTAL PROTECTION AGENCY
NATIONAL PESTICIDE SURVEY
METHOD 7

INTERNAL QUALITY CONTROL CHECKS

EPA SET No._____ ESE BATCH No._____

DATE ANALYZED_____ ANALYST_____

		YES	NO
1.	DAILY STANDARD CALIBRATION RESPONSES (each analyte ±20% of previous day)	_____	_____
2.	CHROMATOGRAM NEAR MRL INCLUDED	_____	_____
3.	METHOD BLANK (less than 1/2MRL for each analyte)	_____	_____
4.	SHIPPING BLANK (less than 1/2MRL for each analyte - only if positives are found in samples)	_____	_____
5.	SECOND COLUMN CONFIRMATION (±25% of primary analysis)	_____	_____
6.	SAMPLE SURROGATE RECOVERY (within ±30% of control chart mean)	_____	_____
7.	METHOD BLANK SURROGATE RECOVERY (within ±3RSD on control chart)	_____	_____

COMMENTS:_____

_____

_____

_____

QUALITY ASSURANCE COORDINATOR_____ DATE_____

PROJECT MANAGER_____ DATE_____

12. PERFORMANCE and SYSTEM AUDITS

ESE's Quality Assurance Coordinator, independent of the Project Manager and reporting directly to the ESE Laboratory Director, will perform audits of the following types:

- Observation of the analyst analyzing samples during the initial demonstration of capabilities and approximately quarterly thereafter. This audit will include verification that no significant changes have occurred in procedure, instrumentation, analytical environment, or in sample and reagent storage and labelling. The auditor will select items for audit from this QA Plan at his discretion and generally without warning to the analyst. Retrievable errors (those affecting no data yet sent to EPA), will be corrected immediately and a means of assuring its long-term rectification established. Irretrievable errors will prompt written notice to the EPA Technical Monitor.

- Examination of a data set, especially QC and instrument performance parameters. This will be performed in detail during the initial demonstration of capabilities and approximately quarterly thereafter. The latter examinations will be performed on randomly selected data sets. The auditor may question the analyst at his discretion. However, the analyst may postpone for up to 10 working days a prolonged conference with the auditor if (1) the analyst or his department manager considers the current backlog of samples, especially those near holding times, to be too great to allow immediate consideration of the auditor's questions AND (2) if the auditor's questions do not concern data due within a few working days of generation.

- Discussion of QA reports when EPA conducts on-site audits.

13. PREVENTIVE MAINTENANCE

The instrumentation ESE specifies for the performance of Method 7 requires the following preventive maintenance.

- The injection septum will be replaced when daily inspection shows significant wear, after 7 days of use, when analyte or surrogate retention times vary more than 2 percent between consecutive chromatograms, or daily when the instrument is in heavy use (more than 50 injections per day).

- The detector will be cleaned by heating when the analyst detects irreproducible or otherwise irregular responses. This behavior is unusual for groundwater sample extracts and is not expected during the duration of this project.

- Gas cylinders will be changed when the cylinder pressure drops below 100 psig. Molecular sieves and oxygen traps in the gas supply lines will be changed per manufacturers recommendations.

- Spare columns, instrument cables, and some PC boards are kept to minimize instrument downtime.

- The injection port liner will be replaced or cleaned if found to be contaminated. However, this is not expected from the analysis of groundwater sample extracts.

14. SPECIFIC PROCEDURES FOR ASSESSING MEASUREMENT SYSTEM DATA

Instrument performance control standards are not required for Method 7. As mentioned in Section 10, a standard at or near the MRL will be analyzed daily and must have a response distinguishable from the instrument background, measured as 15 times the signal-to-noise ratio. This is not expected to be a problem for Method 7.

Each method blank surrogate percent recovery will be calculated as 100 times the measured concentration divided by the nominal concentration. This recovery will be compared to control chart criteria from the initial demonstration of capabilities to determine validity. The control chart criteria for the surrogate compound will be calculated from the initial 20 spiked samples as follows:

- The mean recovery is calculated as the sum of recoveries divided by the number of recoveries included in the sum.
- RSD is calculated as the standard deviation divided by the mean, where the standard deviation is the square root of the variance. The variance is calculated as the sum of the squares of differences between each recovery and the mean recovery, divided by the number of recoveries less one.
- The control chart limits are three times the RSD added to and subtracted from the mean recovery; the warning limits are plus and minus two times the RSD about the mean.
- The control limits for SAMPLE surrogate recoveries are 30 percent (absolute) added to and subtracted from the mean recovery.
- Acceptability of the above will be determined by the Technical Monitor.

15. CORRECTIVE ACTION

In general, bench-level corrective actions fall into three categories each with differing required action.

- Short-Term Action - Major and minor problems which can be corrected immediately. Examples include failure to date or sign a field form and date entry errors. Generally, the analyst or other employee committing the error can simply correct it, and the record of this corrective action will directly reflect the error and its resolution. This record will be kept with the analysis set file in ESE's central filing system.

- Long-Term Corrective Action - Minor and major problems which require a series of actions to resolve the problem. Examples include a discovery that part of the analytical or data-handling procedures were not being followed correctly. The actions to be taken are coordinated by the QA Supervisor or his designate, and a QA corrective action and routing form (Exhibit 15-1) is used to track the action. These corrective actions and their resolutions will be included in monthly reports to EPA.

- Quality-Control Corrective Actions - Failure to meet QC criteria specified in this QA plan. Actions consist of two kinds: Those resolved within each analytical department by reanalysis, etc.; and those resolved outside the department. Records of all QC corrective actions will be recorded in the analyst's notebook and in the analysis set file and reported to EPA's Technical Monitor in the monthly reports.

EXHIBIT 15-1

QUALITY ASSURANCE CORRECTIVE ACTION AND REQUEST FORM

QUALITY ASSURANCE CORRECTIVE ACTION REQUEST AND ROUTING FORM

1. Identification of a Problem: Date:
   Originator:
   Nature of Problem:

2. Determination of Required Action:
   Responsibility Assigned to: Due Date:
   Recommended Action:

3. Implementation of Required Action:
   Responsibility Assigned to: Due Date:

4. Assuring Effectiveness of Action:
   Responsibility Assigned to : Due Date:
   Procedure to assure Effectiveness:

16. QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA activities are reported to management by the QA Coordinator in three ways:

1. Verbal notification of significant QA deficiencies immediately upon discovering the problem,

2. Written interim QA reports, and

3. Written final QA reports.

A final QA report will be prepared for this project. Interim reports will be prepared at the request of ESE management, the Project Manager, or the Contracting Officer.

The contents of interim and final QA reports will be similar except final reports will include summaries of the interim reports.

The following items will be addressed in the reports:

1. An assessment of the precision and accuracy data associated with sample data generated during the report period.

2. Results of all QA audits performed during the report period.

3. Results of the QA data validations performed during the report period.

ESE will send monthly reports to the EPA Technical Monitor. These reports will be in the following format:

- Summary of progress - number of samples received and samples analyzed, (but not necessarily validated) and status of data processing for analyzed sets of samples, and numbers for sets of data sent to the EPA.

- Summary list of bench-level corrective actions (as in Sections 10 and 14 of this Plan).

- Identification of problems about any phase of the project.

- Copies of representative and, if applicable, unusual chromatograms.

- Any other chromatograms or information requested by the Technical Monitor because of specific methodology or problems encountered.

- Changes in personnel.

- Comments

17. ARCHIVAL OF RAW DATA

In order to assure the continued availability of all documentation necessary to defend NPS Method 7 analytical results, the documentation for each analytical set will be contained in a separate green file folder and will be comprised of the following:

- GC set documentation checklist
- Method 7 internal quality control checklist
- A hard copy of the NPS formatted results
- A hard copy of ESE's formatted results
- All chromatograms and quantitation reports for the following:
  - Solvent blank
  - Field samples and shipping blank (if analyzed)
  - Method blanks
  - Calibration standards
  - Time-storage samples
  - Lab spike samples
- Chromatographic analysis logs (Instrument logsheet)
- Chromatographic logsheet(s)
- Extraction logsheet(s)
- Surrogate Control Chart
- Copies of NPS sample tracking forms
- Copies of pertinent analyst notebook pages

All set file folders will be stored in banker's boxes. Each box will be labeled with number, a description of its contents (NPS Method 7 set files), a listing of ESE internal batch numbers corresponding to NPS well numbers, (sorted by NPS well number), the date placed in storage, and the date to be destroyed.

A separate banker's box will contain the following, and be labeled as described above:

- A copy of the QA Project Plan
- Monthly reports to the Technical Monitor
- Original NPS sample tracking forms with original Fed Ex airbills
- Correspondence to and from EPA
- Laboratory data from initial demonstration of capabilities and demonstration of accuracy and precision

- Miscellaneous documentation such as audit reports, internal memos, temperature logs, etc.
- Resumes of NPS participants

All banker's boxes containing the NPS files will be stored for a period of seven years in the Dead File Storage room located in the Maintenance building at ESE's Gainesville location. This room is kept locked at all times and access is limited to its custodian, Virginia O'Brien, Manager of the Information Services Department of ESE's Gainesville laboratory.

A Dead File Storage logsheet listing the same information that is written on bankers boxes will be kept with the storage room custodian and a copy will be sent to the EPA Technical Monitor. In addition, a list of all samples analyzed will be prepared, with cross references to the NPS set number, the ESE batch number, and the ESE internal sample number. Appendix L provides a copy of ESE's standard operating procedures for batch storage of data.

Any changes to the archival procedures described above will be communicated in writing to the Technical Monitor.

18. ADDENDUM TO ESE QUALITY ASSURANCE PROJECT PLAN FOR METHOD 7

1. Shipping Blanks - If any target analytes are found in a shipping blank by primary analysis, ESE will call the Technical Monitor prior to performing confirmational analyses. (pp. 7, 23)

2. Preservative - Mercuric chloride will be added to all method blanks. Use the supply of the compound provided by ICF and add to give the same concentration as in field samples. (p. 20)

3. Analyte and Other Peaks Below the MRL - The procedures provided by EPA (6/1/88 Memo, "NPS Analyte Reporting Below MRL and Identifying Unknown Peaks") will be referenced and appended to the plan. (pp. 7, 20)

4. Sample Shipments - The procedures provided by ICF (4/5/88 packet "NPSIS Sample Receipt Software for Laboratories") will be referenced and appended to the plan. (p. 14)

5. Data Report Format - The format provided by EPA in February will be referenced and appended to the plan along with the 4/18/88 Update Memo, "Data Reporting Format Changes". (p. 21)

6. Surrogate Recovery - The Surrogate in the method blank will be the only control blank that is used for control chart monitoring. (p. 23)

7. Outliers in Control Samples - Dixon's Test will also be used for the "observed" and "background" terms in the calculation. Only background peaks greater than one-half the MRL need to be subtracted. To calculate recovery, the concentration of the spike will be used to divide the difference of the peaks. Percent recovery equals the observed concentration minus the background concentration times 100 divided by the concentration of the spike added. (p. 23)

"NPS Rapid Reporting System" memo of 4/12/88 will be referenced and appended. (p 21)

Confirmation Column will be DB-1701. (p. 17)

APPENDICES

APPENDIX A

NPS METHOD 7

(EPA METHOD 504). MEASUREMENT OF 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

METHOD 504. 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY (1985, Ed. Rev. 1986)

1. SCOPE AND APPLICATION

1.1 This method (1,2,3) is applicable to the determination of the following compounds in finished drinking water and unfinished groundwater:

Analyte	CAS No.
1,2-Dibromoethane	106-93-4
1,2-Dibromo-3-Chloropropane	96-12-8

1.2 For compounds other than the above mentioned analytes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples (4) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (5).

1.3 The experimentally determined method detection limits (MDL) (6) for EDB and DBCP were calculated to be 0.01 µg/L. The method has been shown to be useful for these analytes over a concentration range from approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. SUMMARY OF METHOD

2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 minutes per sample depending upon the analytical conditions chosen. (See Table 1 and Figure 1.)

2.3 Confirmatory evidence can be obtained using a dissimilar column (see Table 1). When component concentrations are sufficiently high (> 50 µg/L), Method 524.1 (7) may be employed for improved specificity.

3. INTERFERENCES

3.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be

analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the sample blanks (7.1.1). Whenever an interference is noted in the sample blank, the analyst should reanalyze the extracting solvent. Low level interferences generally can be removed by distillation or column chromatography (3); however, it is generally more economical to obtain a new source solvent. Interference-free solvent is defined as a solvent containing less than 0.1 ug/L individual analyte interference. Protect interference-free solvents by storing in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. The sample blank (7.1.1) is used to monitor for this problem.

3.3 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds and, in addition, extracts polar organic components of the sample with varying efficiencies.

3.4 EDB at low concentrations may be masked by very high levels of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column (Sect. 5.8.2.2).

4. SAFETY

4.1 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (8-10) for the information of the analyst.

4.2 EDB and DBCP have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

5.1 SAMPLE CONTAINERS - 40-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.2 VIALS, auto sampler, screw cap with PTFE-faced septa, 1.8 mL, Varian #96-000099-00 or equivalent.

5.3 MICRO SYRINGES - 10 and 100 uL.

5.4 MICRO SYRINGE - 25 uL with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.

5.5 PIPETTES - 2.0 and 5.0 mL transfer.

5.6 VOLUMETRIC FLASKS - 10 and 100 mL, glass stoppered

5.7 STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.

5.8 GAS CHROMATOGRAPHY SYSTEM

5.8.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

5.8.2 Two gas chromatography columns are recommended. Column A is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes (Sect. 3.4). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

5.8.2.1 Column A - 0.32 mm ID x 30M long fused silica capillary with dimethyl silicone mixed phase (Durawax-DX3, 0.25 um film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 min, to increase to 190°C at 8°C/min, and hold at 190°C for 25 min or until all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. (See Figure 1 for a sample chromatogram and Table 1 for retention data).

5.8.2.2 Column B (confirmation column) - 0.32mm ID x 30M long fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 um film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 min, to increase to 270°C at 10°C/minute, and hold at 270°C for 10 min or until all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. (See Table 1 for retention data).

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 REAGENTS

6.1.1 Hexane extraction solvent - UV Grade, Burdick and Jackson #216 or equivalent.

6.1.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

6.1.3 Sodium chloride, NaCl - ACS Reagent Grade - For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Place in a bottle and cap.

6.2 STANDARD MATERIALS

6.2.1 1,2-Dibromoethane - 99%, available from Aldrich Chemical Company.

6.2.2 1,2-Dibromo-3-chloropropane - 99.4%, available from AMVAC Chemical Corporation, Los Angeles, California.

6.3 REAGENT WATER - Reagent water is defined as water free of interference when employed in the procedure described herein.

6.3.1 Reagent water can be generated by passing tap water through a filter bed containing activated carbon. Change the activated carbon whenever the criteria in Sect. 9.1.2 cannot be met.

6.3.2 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

6.3.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water at 100 mL/minute for 1 hour. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

6.3.4 Test reagent water each day it is used by analyzing it according to Sect. 10.

6.4 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

6.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min and weigh to the nearest 0.1 mg.

6.4.2 Use a 100-µL syringe and immediately add two or more drops of standard material to the flask. Be sure that the standard material falls directly into the alcohol without contacting the neck of the flask.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight.

6.4.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C.

6.5 SECONDARY DILUTION STANDARDS — Use standard stock solutions to prepare secondary dilution standard solutions that contain both analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Sect. 8.1.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions in Sect. 6.4.4 also applies to secondary dilution standard solutions.

6.6 QUALITY CONTROL (QC) CHECK SAMPLE CONCENTRATE (0.25 µg/mL) — Prepare a QC check sample concentrate of 0.25 µg/mL of each analyte from the standard stock solutions prepared in Sect. 6.4.

6.7 MDL CHECK SAMPLE CONCENTRATE (0.05 µg/mL) — Dilute 2 mL QC check sample concentrate (Sect. 6.6) to 10 mL with methanol.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Replicate field blanks must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample bottles with reagent water, seal, and ship to the sampling site along with sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by the field blanks.

7.1.2 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized

(usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.4 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill duplicate 40-mL sample bottles.

7.2 SAMPLE PRESERVATION

7.2.1 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be below 4°C on arrival at the laboratory.

7.2.2 The addition of sodium thiosulfate as a dechlorinating agent and/or acidification to pH 2 with 1:1 HCl, common preservation procedures for purgeable compounds, have been shown to have no effect on EDB and DBCP and, therefore, their use is not recommended for samples to be analyzed for these analytes.

7.3 SAMPLE STORAGE

7.3.1 Store samples and field blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

7.3.2 Analyze all samples within 28 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 CALIBRATION

8.1.1 At least three calibration standards are needed. One should contain EDB and DBCP at a concentration near to but greater than the method detection limit (Table 1) for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 µg/L, 0.10 µg/L, and 0.20 µg/L.

8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric flask. Do not add less than 20 µL of an alcoholic standard to the reagent water or poor precision will result. Use a 25-µL micro syringe and

rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Discard the contents contained in the neck of the flask. Aqueous standards should be prepared fresh daily unless sealed and stored without headspace as described in Sect. 7.

8.1.3 Analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.1.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

8.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent blanks, standards, duplicate samples, and the laboratory control standard (Sect. 9.2.2).

8.2.1 Peak tailing significantly in excess of that shown in the method chromatogram must be corrected. Tailing problems are generally traceable to active sites on the GC column or the detector operation.

8.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory detection limits capability and an ongoing analysis of spiked samples to evaluate and document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method

performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1. The analyst must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. =This is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed.

9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. The procedure for low level check samples is described in Sect. 9.4.

9.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst must perform the following operations:

9.2.1 Prepare seven MDL check samples at 0.05 µg/L by spiking 35 µg/L of the MDL check sample concentrate (Sect. 6.7) into 35-mL aliquots of reagent water in 40-mL bottles. Cap and mix well.

9.2.2 Analyze the well-mixed MDL check samples according to the method beginning in Section 10.

9.2.3 Calculate the average concentration found ($\bar{X}$) in µg/L, and the standard deviation of the concentrations (s) in µg/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates (6) as 3.143s.

9.2.4 For each analyte, $\bar{X}$ must be between 80% and 120% of the true value. Additionally, the MDL may not exceed the 0.05 µg/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to

meet a criterian, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

9.3 The laboratory must demonstrate on a frequency equivalent to 10% of the sample load that the measurement system is in control by analyzing a QC check sample of both analytes at 0.25 µg/L.

9.3.1 Prepare a QC check sample (0.25 µg/L) by adding 35 µL of QC check sample concentrate (Sect. 6.6) to 35 mL of reagent water in a 40-mL bottle.

9.3.2 Analyze the QC check sample according to Sect. 10 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.

9.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second check standard containing each analyte that failed must be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.

9.4.1 Prepare an MDL check sample (0.05 µg/L) as outlined in Sect. 9.2.1 and analyze according to the method in Sect. 10.

9.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If not, repeat the MDL test in Sect. 9.2.1. For each analyte, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

9.5 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 SAMPLE PREPARATION

10.1.1 Remove samples and standards from storage and allow them to reach room temperature.

10.1.2 For samples and field blanks, contained in 40-mL bottles, remove the container cap. Discard a 5-mL volume using a 5-mL transfer pipette. Replace the container cap and weigh the container with contents to the nearest 0.1g and record this weight for subsequent sample volume determination (Sect. 10.3).

10.1.3 For calibration standards, QC check standards and reagent blank, measure a 35-mL volume using a 50-mL graduated cylinder and transfer it to a 40-mL sample container.

10.2 MICROEXTRACTION AND ANALYSIS

10.2.1 Remove the container cap and add 7g NaCl (Sect. 6.1.3) to the sample.

10.2.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 sec.

10.2.3 Remove the cap and, using a transfer pipette, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Allow the water and hexane phases to separate. (If stored at this stage, keep the container upside down.)

10.2.4 Remove the cap and carefully transfer 0.5 mL of the hexane layer into an autosampler using a disposable glass pipette.

10.2.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler vial. Reserve this second vial at 4°C for a reanalysis if necessary.

10.2.6 Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be manually injected, although an autosampler is strongly recommended.

10.3 DETERMINATION OF SAMPLE VOLUME

10.3.1 For samples and field blanks, remove the cap from the sample container.

10.3.2 Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements.

10.3.3 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight is equivalent to the volume of water (in mL) extracted. (Sect. 11.3)

11. CALCULATIONS

11.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory control standard.

11.2 Use the calibration curve or calibration factor (Sect. 8.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response).

11.3 Calculate the sample volume (V_s) as equal to the net sample weight:

V_s = gross weight (Sect. 10.1.2) - bottle tare (Sect. 10.3.3).

11.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = C_i \times \frac{35}{V_s}$$

11.5 Report the results for the unknown samples in µg/L. Round off the results to the nearest 0.01 µg/L or two significant figures.

12. ACCURACY AND PRECISION

12.1 Single laboratory (EMSL-Cincinnati) accuracy and precision at several concentrations in tap water are presented in Table 2 (11). The method detection limits are presented in Table 1.

12.2 In a preservation study extending over a 4-week period, the average percent recoveries and relative standard deviations presented in Table 3 were observed for reagent water (acidified), tap water and groundwater. The results for acidified and non-acidified samples were not significantly different.

13. REFERENCES

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Table 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Min		MDL, ug/L
	Column A	Column B	
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A conditions: Durawax-DX 3 (0.25 µm film thickness) in a 30 m long x 0.32 mm ID fused silica capillary column with helium carrier gas at 25 cm/sec. Column temperature held isothermal at 40°C for 4 min, then programmed at 8°C/min to 180°C for final hold.

Column B conditions: DB-1 (0.25 µm film thickness) in a 30 m long x 0.32 mm ID fused silica capillary column with helium carrier gas at 25 cm/sec. Column temperature held isothermal at 40°C for 4 min, then programmed at 10°C/min to 270°C for final hold.

Table 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

Analyte	Number of Samples	Spike Level (ug/L)	Average Accuracy (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

Table 3. ACCURACY AND PRECISION AT 2.0 ug/L
OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Number of Samples	Average Accuracy (% Recovery)	Relative Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1]Matrix Identities
RW-A = Reagent water at pH 2
GW = Groundwater, ambient pH
GW-A = Groundwater at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2.

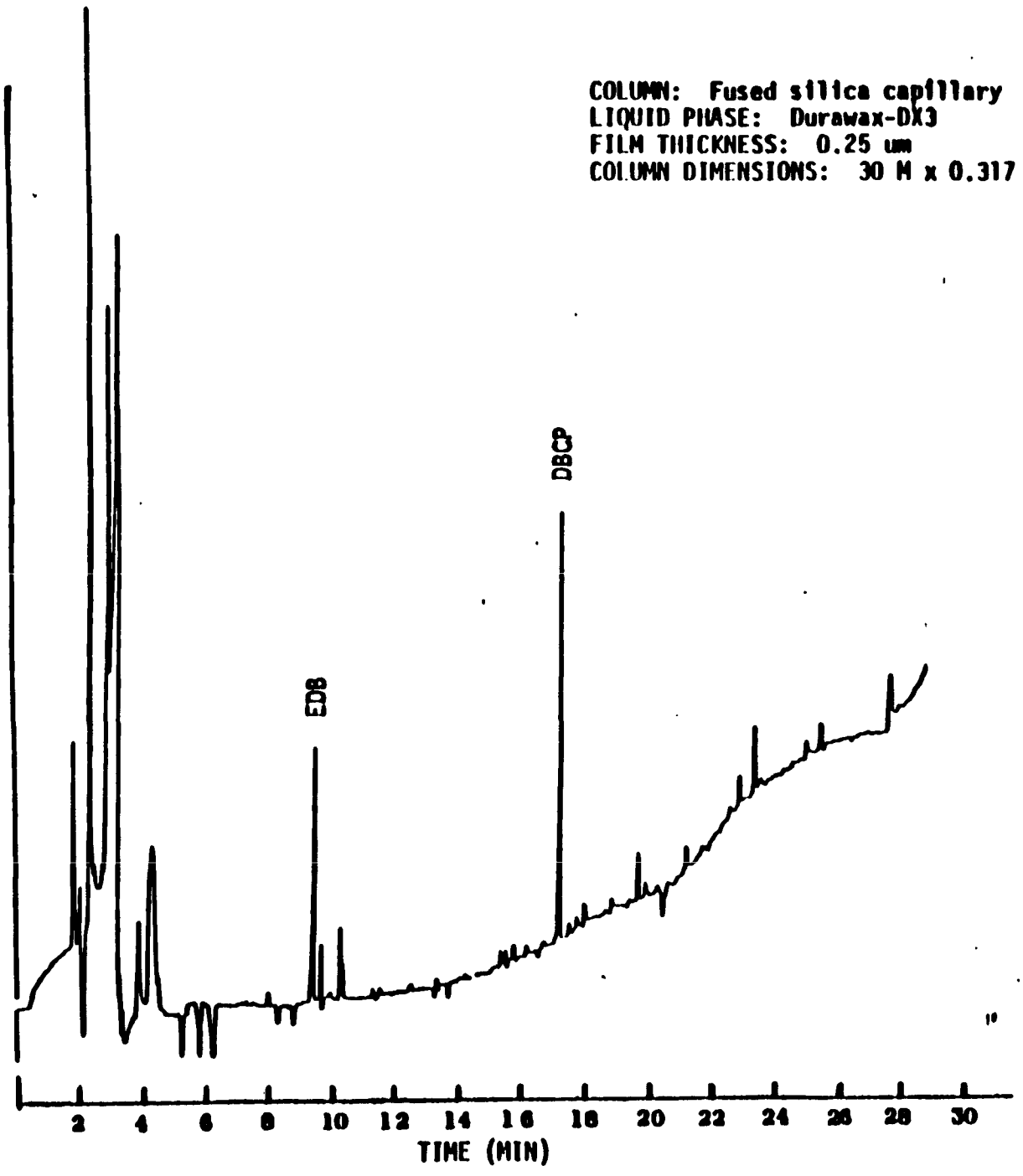


Figure 1. Extract of Reagent Water Spiked at 0.114 ug/L with EDB and DBCP

APPENDIX B

NPS ANALYTE REPORTING BELOW MRL AND IDENTIFYING UNKNOWN PEAKS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY LABORATORY, NASA/NSTL
BUILDING 1105, NSTL, MISSISSIPPI 39529

June 1, 1988

MEMORANDUM

SUBJECT: NPS Analyte Reporting Below MRL and Identifying Unknown Peaks

FROM: Bob Maxey, Analytical Coordinator
Environmental Chemistry Laboratory

Bob Maxey

TO: Dave Munch, Analytical Coordinator
TSD-Cincinnati

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

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

If you have any questions, give me a call.

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

Background Information

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

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

1. For methods 1-7, only peaks with responses of between one-half the establi ed MRL and the MRL [A/] on the primary column will be investigated. A respo on the "secondary" GC column, indicating the presence of the analyte, is a required for additional work.

2.a The first occurrence of a peak meeting the requirements of (1) is noted an reported to the Technical Monitor, but no action is taken [B/]. Upon a seco occurrence of the same suspect analyte, additional work is required as fol lows. After five successive failures to "confirm" on the secondary column the response on the primary column, discussions with OPP personnel will ta place before continuing low-level analytical work on the analyte(s).

b With methods 1,2,3, 6 and 7, for responses meeting the requirements of (1) and (2), the laboratory will attempt LR GC/MS [C/] confirmation if the GC/MS analyst feels it is within the capability of his instrument. If the confi mation is not within the capability of the laboratory, such extracts are sent weekly, under iced conditions by next-day air, to the appropriate referee laboratory having HR GC/MS [C/] capabilities. Copies of chromatograms and all pertinent sample information must be sent along with the extracts including extracts of the related Method Blank. (NPS will absorb the cost of these shipments.) It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tight seal and do not contribute interferences to the extracts. Volume level must be marked on the outside of the vial or ampule.

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

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

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

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

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

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

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

Procedure for Determining the Identity of Non-NPS Analytes

It is expected that, over the course of the NPS Program, numerous extraneous responses will be evident on chromatograms from the various methods The contractor or referee laboratories will be required to attempt identification of peaks or responses on the primary column exhibiting the minimal crite below.

1. For Methods 1, 2, 3, 6, and 7, if, upon initial analyses, the respons of an extraneous peak on the primary column is equal to or greater th the response of the nearest NPS analyte on that column at 10 x MRL (Minimal Reporting Level), an attempt must be made to identify that u known peak or response by GC/MS. Full scan spectra and subsequent library search are expected and must be followed by comparison of the spectra of the unknown compound with those of an authentic standard o the suspected compound.

2. The work in (1) must be attempted by the contractor and/or referee la oratories on the first occurrence of such a peak and the results of t attempt reported to the Technical Monitor for the Method. If the analytical contractor feels his system or instrument is not capable c the confirmatory work, he must send both that extract and that of the related Method Blank to the appropriate referee lab under iced conditions by next-day air.

It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tigh seal and do not contribute interferences to the extracts. Volume lev must be marked on the outside of the vial or ampule. (NPS will absor costs of these shipments.)

Specific sample and analytical information must accompany each such extract.

- o Sample i.d. number, weight of sample matrix contained in the ampule, copies of chromatograms from the primary GC column, identification of the retention window for the unknown response(s) as defined by the last NPS analyte to elute before the unknown peak or response and the first NPS analyte to elute following the unknown response.

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

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

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

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

APPENDIX C

GC/MS CONFIRMATION OF NPS SAMPLES

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

MEMORANDUM

DATE: July 19, 1988

SUBJECT: GC/MS Confirmation of NPS Samples

FROM: Caroline Madding, Chemist CVM
Drinking Water Quality Assessment Branch

TO: Robert F. Thomas, Chemist, DWQAB
Edward M. Glick, Chemist, DWQAB
Dan Hautman, Chemist, TAI

I will be qualitatively analyzing by GC/MS any sample for Methods 2 or 7 found in the confirmatory analysis to have any analyte concentration above that analyte's reporting limit. If you have a sample that needs confirmation, please forward to me the sample extract and the method blank extract for the appropriate set. I will also need a high standard of the allegedly present analyte/analytes and a standard near the sample's concentration.

APPENDIX D

IDC RESULTS

Determination of EPA-NPS Method 7
Estimated Detection Limits (EDL)

Signal to Noise Ratio - DB1 Column

Compound (ug/L)	Peak ht. (cm)	Average Noise (cm)	Signal to Noise Ration	EDL (ug/L
1,2-Dichloropropane (0.51)	0.5	0.10	5.00	0.51
Cis-1,3-Dichloropropene (0.015)	2.7	0.25	10.8	0.007
Trans-1,3-Dichloropropene (0.035)	0.7	0.25	2.80	0.063
EDB (0.005)	1.0	0.25	4.00	0.007
DBCP (0.005)	1.2	0.25	4.80	0.005

Replicate Spike Method - DB1 Column

Compound	1,2-DCP (0.51 ug/L) area counts	C13DCP (0.015 ug/L) cm	T13DCP (0.035 ug/L) cm	EDB (0.005 ug/L) cm	DBCP (0.005 ug/L) cm
Spike 1	2023	2.6	0.60	1.0	0.90
2	2371	2.6	0.70	1.0	1.1
3	1869	2.6	0.70	1.0	1.0
4	2212	2.7	0.60	1.0	0.90
5	1949	2.5	0.70	0.90	1.0
6	2613	2.6	0.60	0.90	0.90
7	2227	2.5	0.60	0.90	0.90
8	2160	2.4	0.50	0.90	0.90
Mean	2178	2.56	0.625	0.950	0.963
MDL Std. Dev.	240	.092	.071	.054	.074
EDL (ug/L)	0.17	.002	0.012	0.001	0.001
mRL	1.53	~~.01~~ .02	.19	.02	.02

APPENDIX E

CHANGES IN NPS LABORATORY PROCEDURES

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI OHIO 45268

MEMORANDUM

DATE: July 14, 1988

SUBJECT: Changes in NPS Laboratory Procedures

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

TO: NPS Technical Monitors (See below)

The following minor changes in laboratory operations are being made.

1. Spiking Levels (Methods 1-7)

Currently, selected NPS samples are being spiked at either Level 1 (5 times MRL), Level 2 (10 times MRL), or Level 3 (20 times MRL). In many cases, spiking at Level 3 has created analyte concentrations in samples which exceed the linear range of the instrumentation. Any Level 3 spiked samples currently on hand should be analyzed; however, no further requests will be made to spike samples at Level 3.

In order to maintain three spiking levels, a Level 0 (2 times MRL) is being added. Laboratory Control Standards and Time Storage Samples are to continue to be spiked at Level 2 (10 times MRL).

2. Spiking Levels (Method 9)

Currently, sample spiking levels used for Method 9 are, Level 1 (2 times MRL), Level 2 (10 times MRL), and Level 3 (10,000 ug/L). The spiking levels are to remain the same; however, Level 0 will now be 1 times MRL, Level 1 10 times MRL, and Level 3 10,000 ug/L.

3. Data Reporting Format

In order for the data reporting format to match the requirements for reporting suspected NPS analytes observed on the primary column, at a concentration between 1/2 MRL and MRL (see memorandum entitled "Determining and Reporting the Presence of NPS Analytes below the Minimum Reporting Levels and Identifying Unknown Peaks," by Bob Maxey 6/1/88), further clarification is required. In those cases where the presence of an NPS analyte at a concentration between 1/2 MRL and the MRL is successfully confirmed, the primary and confirmational column data for that analyte should be reported as "-111". In those cases where confirmational analyses are either not required, or the confirmational analyses did not confirm the presence of the analyte, the primary column data for that analyte should be reported as "-222".

Please transmit this information to both your contract and referee laboratories, as soon as possible. If you have any questions concerning these items, please let me know.

Addressees:

A. Dupuy
L. Kamphake (TSD)
C. Madding (TSD)
R. Maxey (OPP)
K. Sorrell (TSD)
R. Thomas (TSD)

cc:

H. Brass (TSD)
C. Freebis (CSD)
A. Kroner (TSD)

APPENDIX F

NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

MEMORANDUM 4/5/88

TO: DATA MANAGER, EPA/TSD LAB

FROM: CHIP LESTER, ICF INC. (703) 934-3431 Beth

RE: NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

ICF's National Pesticide Survey Information System (NPSIS) is ready to collect information from you regarding the receipt of well water samples and their condition. Please find enclosed the following items: 1) A users memo containing all operating instructions, and 2) A copy of Carbon Copy software which is necessary to establish communications with NPSIS over phone lines. As mentioned previously, the software allows you to report the receipt of a one or more sample kits. It also prompts you for details regarding the condition of the samples. Additional features include; a bulletin board whic allows you to interactively send messages to ICF staff via your computer keyboard, file transfer, and access to the ICF computerized mail system for sending memos. It is also possible for you to speak over the phone to an ICF staff member during your session.

It is important that you test the communications link between the NPSIS computer and yours. We have experienced trouble when using Carbon Copy software with a computer which has a Manzana 3.5 inch disk drive, and also with computers which have a non-Hercules or non-EGA compatible graphics card.

For testing purposes, your sample kit identification numbers and FedEx airbill numbers (respectively) are: PD-0000-711 and 1111111111, and PD-9999-711 and 2222222222. Use these sample kit identification numbers when trying out the NPSIS Sample Receipts Program.

We feel that it would be helpful to both parties if you could call us when you are ready to test the NPSIS system, and we will assist you over the phone during your session. If you would like to do this, please call Beth Estrada at (703) 934-3431. NPSIS will be available for access 24-hours a day seven days a week. We appreciate hearing any comments you have regarding NPSIS.

THE NPSIS SAMPLE RECEIPT PROGRAM

NPSIS is designed to keep track of the day to day operations of the National Pesticide Survey. You play an important role in NPS and your timely notification of receiving a kit of samples is essential to the success of NPS. We have designed the Sample Receipt Program with your busy schedule in mind. NPSIS will obtain the minimum amount of information necessary while still maintaining a secure system. You will be entering data into the NPSIS personal computer via your own computer, modem, and Carbon Copy software.

1.1 Hardware and Software Requirements.

The NPSIS Sample Receipt Program has a minimum hardware and software requirement. Here is a list of items you will need:

Hardware:

- One (1) IBM PC, XT, AT, or Personal System model with at least 640K memory.
- One (1) 2400 or 1200 baud Hayes or Hayes compatible modem with cables. (See Carbon Copy guide for cabling requirements and a description of usable modems)
- One (1) data transmission phone line.

Software:

- NPSIS Sample Receipt Program access provided for you by ICF.
- One (1) copy Carbon Copy software which is provided to yo by ICF for the duration of NPS.

1.2 Initial Installation Steps.

Before you can access and use NPSIS, you must first load the Carbon Cop software onto your PC. The directions are provided in the Carbon Copy manua One item you will want to include is an entry into the "Call Table". This entry will include a name, telephone number, and password for the NPSIS computer. To enter these items into the Call Table, press "2" from the Carb Copy Parameters' Screen. The information you must enter consists of the following:

- Name: NPS
- Telephone Number: 703-641-0629
- Password: NPS

1.3 Parameters for Communications.

NPSIS will maintain a set configuration throughout operation. Any changes due to updates in equipment or the system which will affect your ability to communicate through Carbon Copy will be forwarded to you. The parameters which will be maintained at this time are:

- 2400 baud modem speed.
- Answer ring count equal to one.
- Re-boot on exit after 5 minutes. (If there is a power failure or some other type of interruption, you can log back on to NPSIS and resume your session.)
- Five minute inactivity time constraint.
- Two password attempts.

2 REPORTING A SAMPLE RECEIPT TO NPSIS.

2.1 Establishing a Communications Link.

Once you have installed Carbon Copy and have all of the necessary hardware, you are ready to "log on" to the NPSIS computer at ICF. To do this

Type: C:> **CCHELP NPS** in your directory containing Carbon Copy.

This command will automatically dial the NPSIS computer, send your password for verification, and establish a data link between the two computers. You will be able to discern what is taking place by messages to your screen.

2.2 Entering A Sample Receipt Into NPSIS.

Once you have established a data link, (e.g., are "logged on"), you wil see on the screen exactly what is on the screen of the NPSIS computer. This screen you are viewing is the main menu for the Sample Receipt Program. Remember that you are controlling the NPSIS computer via a 2400 baud phone line and your typing will appear on the screen at a much slower rate than you are accustomed to. A few tips on how to use the system are outlined in the next section.

2.2.1 Useful Tips on How to Use NPSIS.

Before you start, a few things to remember are:

- Pressing the "Esc" key will cancel all changes for the screen you are currently in and return you to the previous screen. Pressing "Esc" at the Searching Screen returns you to the main menu.

- Pressing "PgDn" or "PgUp" will save the items you have entered in the current screen and place you in the next or previous screen, respectively. This feature is handy to use when you only have a f items to enter in a screen which prompts for several items.

- Pressing "Enter", "arrow up", or "arrow down" will move the cursor from field to field in each screen. Remember that using the sideways arrows will not work.

- Pressing the "Alt" and "Right Shift" keys together will place the Carbon Copy Control Screen over the NPSIS Sample Receipt Program. You can then use the communications features in Carbon Copy. Pressing "F10" again when you are through will replace the NPSIS Sample Receipt Program screen you were currently in back on your screen, and

- Because you will are most likely to be entering information regarding a number of kits at one time, after you save or cancel your entries for one kit, you will be placed at the initial Sample Searching Screen for a new kit. If you are finished with your dat entry, simply press "Esc" to exit the Sample Searching screen and placed in the main menu.

2.3 A Basic Outline of the Sample Receipt Program.

The NPSIS Sample Receipt Program has three basic features:

- Initial reporting of a NPS sample kit of sample bottles.

- Ability to edit or re-edit an existing report of a kit receipt, and

- Access to ICFs computerized mail system which provides t ability to send memoranda to ICF staff.

The information obtained in an entry for a kit of bottles is:

- The kit identification number, the FedEx airbill number and the last name of the person making the entry.

- Any damage to the kit as a whole such as melted ice or breakage of the cooler.

- Verification of which bottles belong in a kit or cooler, notification of any missing bottles or any additional bottles, and

- Any damage to each sample bottle which renders it unusab for analysis and testing.

2.4 NPSIS Sample Receipt Program Screens.

When you have completed the logon procedure, you will see the following main menu on your computer screen:

NATIONAL PESTICIDE SURVEY INFORMATION SYSTEM

SELECTION MENU FOR REPORTING SAMPLE RECEIPTS 04/05/88

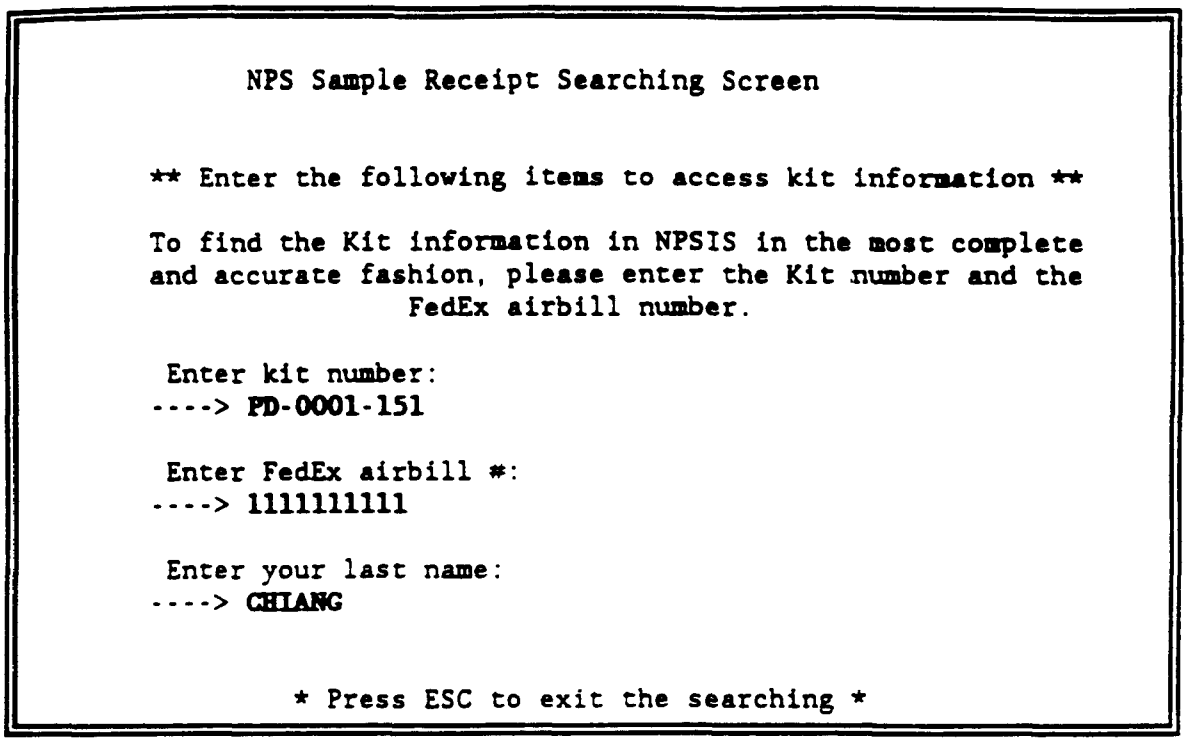
Report \ Edit a Sample Receipt
Send a Memo

Press <Alt><Right-Shift> to Logoff

use ↑ ↓ and ↵ to select option.

The screens provided in this memo will show all of the screens availab and thus represent the maximum number of screens you will encounter with NPSIS. It is most likely that you will not have the need to enter informat reporting damaged kits or samples. Therefore, not all of the screens depic below will appear in your normal session.

If you choose the first item on the menu, "Report \ Edit a Sample Receipt", you will then be prompted for the kit identification number and t FedEx airbill number associated with the specified kit. The screen will appear like this:



If the kit number you have entered is incorrect, or if the kit number ar FedEx airbill number combination is incorrect, NPSIS will prompt you to try t enter these number again, as illustrated on the next page. It is possible that the FedEx airbill number on the kit is not the same as the FedEx airbill number which was entered into the NPSIS system. This could happen if the field team loses or damages the airbill.

ERROR!! The kit you entered cannot be found. . .

Kit number: PD-0001-151
AND
FedEx airbill number: 1111111111

Please check these numbers and try again!

****
NPSIS is designed to track Kits and FedEx airbill numbers.
The Kit and FedEx airbill number combination you have entered
does not match what is currently in the system. Please enter
the correct combination. If you still have problems, try
leaving the FedEx airbill # BLANK. Only enter the Kit number.
****

Press any key to continue...

Then, you will encounter this screen insuring that you have entered the FedEx airbill number:

Kit No.: PD-0001-151

Did you enter the correct Kit number and FedEx airbill number?

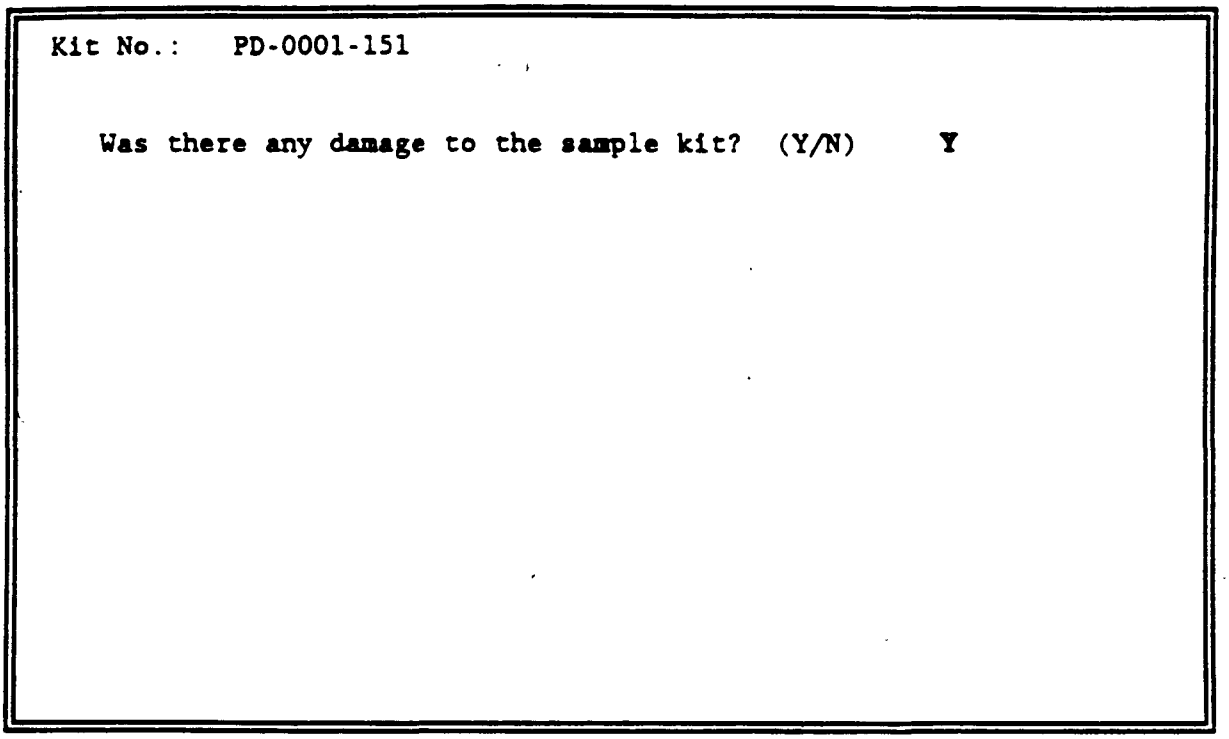
NPSIS is designed to store and track all FedEx airbill numbers. This Kit may have a different FedEx airbill number than the system, please enter the new FedEx airbill number:

---->

Note: if the correct airbill number was entered before, hit ENTER.

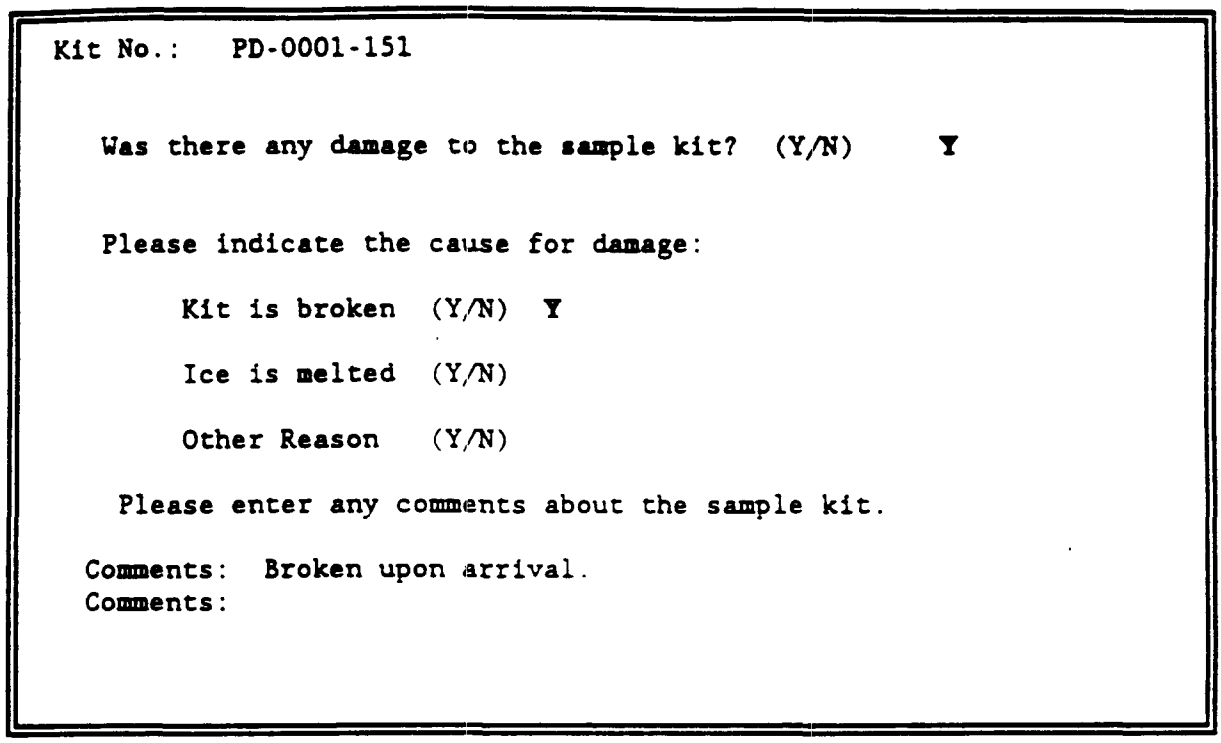
PgDn (Next page), PgUp (Previous page), Esc (Exit)

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



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

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



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

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

Next, NPSIS will ask you to survey the contents of the kit and check tha which bottles are contained within the kit. You should then look at the bottle labels and determine if any are missing. Don't forget to check and determine if any bottles have been included in the kit which do not appear on the list provided by NPSIS on this screen:

Kit No.: PD-0001-151

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

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

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

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

If you have pressed "N", indicating that you did not receive exactly wha NPSIS assumes you have received, you will be prompted to enter the appropriat information. This information includes pressing a "Y" or a "N" beside each bottle, and entering the bottle number found on the labels of any additional bottles you have received:

Kit No.: PD-0001-151

Please indicate which bottles you received:

Bottle No:	Received (Y/N)
PD-0001-1-1-01	N
PD-0001-1-1-03	N
PD-0001-1-3-01	Y
PD-0001-1-3-03	Y
PD-0001-1-9-01	Y
PD-0001-1-9-03	Y

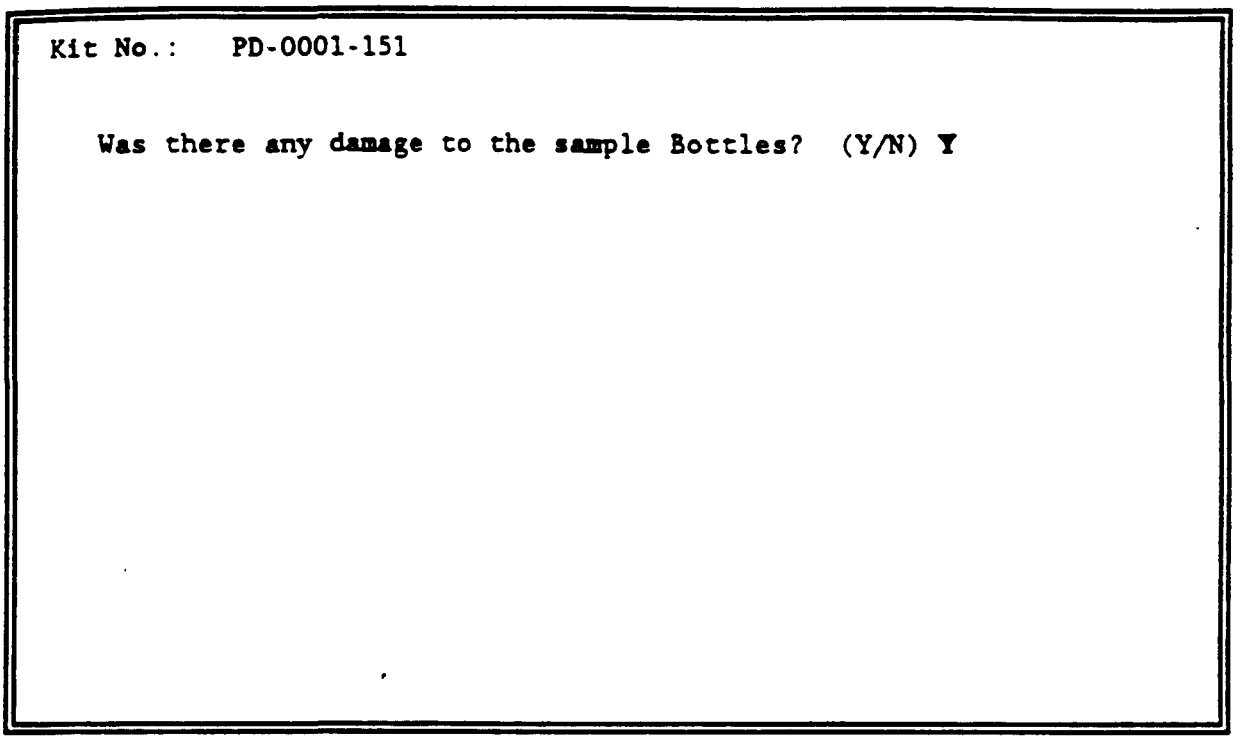
Please indicate any additional bottles you received:

1. Bottle No.:	PD-0002-1-1-05	2. Bottle No.:	PD-0002-2-2-01
3. Bottle No.:	PD-0004-4-4-01	4. Bottle No.:	- - - -
5. Bottle No.:	- - - -	6. Bottle No.:	- - - -
7. Bottle No.:	- - - -	8. Bottle No.:	- - - -

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

Notice that the user has indicated that he did not receive the first two bottles on the list. Also note that the user has indicated additional bottle which have come in the sample kit, but which were not on the list.

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



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

In order to complete the appropriate information on damaged samples, you must first press a "Y" or a "N" in the field labeled "Damaged Y/N". If you have entered a "Y" in this field, you must then identify what the cause of the damage is, to the best of your abilities. As noted on the computer screen below, the "Other" category should be used if the sample is unusable but is not broken. Please try to comment whenever possible.

Kit No.: PD-0001-151

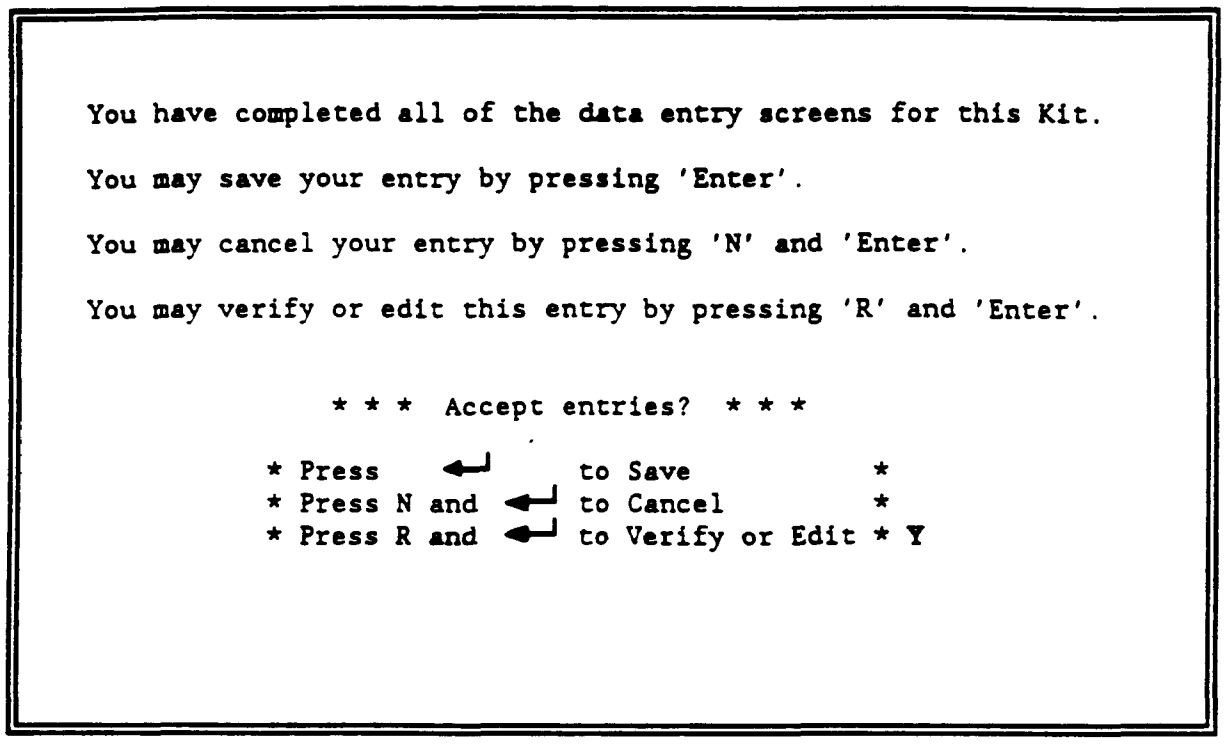
Please indicate which bottles are damaged by entering Y or N, and for those which are damaged, indicate the cause of damage.

Bottle No:	Damaged (Y/N)	--- CAUSE --- Broken (Y/N)	Other (Y/N)	Comment
PD-0001-1-3-01	N			
PD-0001-1-3-03	N			
PD-0001-1-9-01	N			
PD-0001-1-9-03	N			
PD-0002-1-1-05	N			
PD-0002-2-2-01	Y	Y		
PD-0004-4-4-01	N			

The 'Other' cause category is for reporting contamination of a sample, e.g. contamination noted on the Sample Tracking Form, air bubbles, or other reasons a sample is unusable.

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

Now you have completed all of the necessary information needed to verify that the proper samples have reached their final destination in usable condition. You may save your kit entry by pressing "Enter". If you wish to cancel your kit entry and try again, press "N" and "Enter". If you wish to view or edit the current kit entry, press "R" and "Enter" and NPSIS will plac you back at the beginning of your entry.



By pressing "Enter" , you have saved all of the information necessary fo a particular sample kit. NPSIS assumes that you will enter more than one kit entry per session. Therefore, you will be placed at the initial "Searching Screen". If you are finished, press "Esc" and you will be returned to the main menu. You can then log off of NPSIS by pressing "Alt" and "Right shift" at the same time. You may also send a memo through the ICF computerized mail system. To do this, cursor down to the second menu choice and press "Enter".

The next two pages of this memo describe how to use the ICF electronic mail system. Note that the password for you is NPS. The mail system softwar program will prompt you for this password before it will allow access to the system. Also, when you are selecting the recipients of your memo, please press the space bar beside the initials "NPS". This will send your memo to all ICF staff involved in the NPS project. If you wish to send memos to a particular ICF staff member, please call Beth Estrada for the identification number of the desired ICF employee.

ELECTRONIC MAIL

Function
Augment office communications with electronic transfer of notes and files.

Summary
Electronic Mail (E-Mail) allows you to send, receive, read, and subsequently save or discard notes and attached files.

When you power up your workstation you will automatically enter E-Mail if you have received any mail. Enter your password to check your mail, or press <ESC> twice to avoid E-Mail and continue to the Assist main menu.

Instructions
Operation of E-Mail is similar to Lotus 1-2-3. Press the F1 key to receive help at any time during operation. If any more help is needed contact workstation support to receive a manual.

For more information on any feature of electronic mail, use Network Courier's on-line help or refer to the User's Manual.

Passwords

Your password will be "password" until you change it yourself. Once you have given your password and entered E-Mail, you can change your password by selecting Options, then Password.

Reading Mail

1. Select "Read" from your menu Highlight read,then press <ENTER>.
2. Select the note to read:
   a. Highlight the note (using the arrow keys); and press <ENTER>.
   B. To save the note, select "Storage", then "Save". Enter the name of the file to which the note should be saved.
3. Press <ESC> to select another note.

Writing Mail

1. Select "Compose", then "edit".
2. Press <ENTER> when the highligh moves to "TO".
3. Select the recipients(s):
   a. Move the highlight to the first recipient's initials.
   b. Press the space bar. A small mark will appear.
   c. Repeat steps a and b for all recipients. Press the space ba twice to "de-select" recipients. The small mark will disappea
   d. Press <ESC> to cancel the entire list.
4. Select the initials of those who wil receive copies:
   a. Press the down arrow to mo to "CC".
   b. Select recipients as instructed above (step 3, a-d)

Writing Mail, continued

5. Enter a subject and priority. (optional)
6. Select attachments (optional):
   a. Press <ENTER> and type the path for the document(s).
   b. Press <ENTER> and select the document(s) to be attached.
   c. Repeat steps a and b for documents in another directory.
7. Enter the text of your message.
8. Press <ESC> when finished.
9. Select "Transmit" to post the note and attachments.

Quitting the Mail Program

1. Press <ESC> from the menu.
2. Select "YES".

APPENDIX G

FORMAT FOR NPS DATA

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) DATA

LINE	COLUMNS	DESCRIPTION
1	1-6	I_Temp
	9-14	S_Temp
	17-24	Date_Sam
	27-34	Date_Shp
	37-44	Date_Rec
	47-54	Time_Sam
	57-64	Time_Ice
		[FOR METHODS 5 AND 9 ONLY]
	68-69	pH
2	1-6	enter INITIAL TEMPERATURE OF WATER
	9-14	enter STABILIZED TEMPERATURE OF WATER
	17-24	enter DATE SAMPLED
	27-34	enter DATE SHIPPED
	37-44	enter DATE RECEIVED
	47-54	enter TIME SAMPLED
	57-64	enter TIME ICED
		[FOR METHODS 5 AND 9 ONLY]
	67-70	enter pH
3	BLANK	
4	1-17	Receipt Condition
5	1-80	enter CONDITION OF SAMPLE UPON RECEIPT AT LABORATORY
6	BLANK	
7	1-6	Samp #
	16-18	Lab
	21-25	Set #
	28-35	Date_Spk
	38-45	Date_Ext
	48-55	Date_Ana
	58-63	Column
8	1-13	enter SAMPLE IDENTIFICATION NUMBER
	16-18	enter LAB ABBREVIATION
	21-25	enter SET NUMBER
	28-35	enter DATE SPIKED
	38-45	enter DATE EXTRACTED
	48-55	enter DATE ANALYZED
	58-63	enter ANALYSIS COLUMN
9	BLANK	

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

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

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

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
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@
Day@Time Storage	DTS@

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

if only one mix use "A"

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	.
Not Detected (< Estimated Detection Limit)	-999
Saturated	-777
Other	-333
Below Reporting Limit, but above EDL	-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 >

APPENDIX H

DATA REPORTING FORMAT CHANGES

MEMORANDUM

DATE: April 18, 1988

SUBJECT: Data Reporting Format Changes

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

TO: NPS Technical Monitors (See below)

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

1. Line 2, columns 1-6 are to be used to record the pH measured in the field. This data will be found on the field sample tracking sheet.

2. Line 2, columns 67-70 are to be used to record the pH measured upon sample receipt at the laboratory. This only applies to methods 5 and 9.

3. Line 8, columns 1-13, Sample Identification Number, have been expanded to columns 1-14.

4. The data entered on line 10, columns 52-60, concerning the internal standard, it should be entered not as the peak area but as the "percent recovery" as compared to the mean observed for the calibration curve.

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

LCS@ = Laboratory Control Sample
LSS@$ = Laboratory Spiked Sample
DTS@ = Day 0 Time Storage Sample
HTE@ = Extract Time Storage Sample
HTS@ = Sample Time Storage Sample

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

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

Format for National Pesticide Survey (NPS) Data

LINE	COLUMNS	DESCRIPTION
1	1-6	~~[redacted]~~ Fld_pH
	9-14	S_Temp
	17-24	Date_Sam
	27-34	Date_Shp
	37-44	Date_Rec
	47-54	Time_Sam
	57-64	Time_Ice
	68-69	pH Note: Method 9 only
2	1-6	enter ~~INITIAL TEMPERATURE OF WATER~~ Field_pH
	9-14	enter STABILIZED TEMPERATURE OF WATER
	17-24	enter DATE SAMPLED
	27-34	enter DATE SHIPPED
	37-44	enter DATE RECEIVED
	47-54	enter TIME SAMPLED
	57-64	enter TIME ICED
	68-69	enter pH Note: Method 9 only
3	BLANK	
4	1-17	Receipt Condition
5	1-80	enter CONDITION OF SAMPLE UPON RECIEPT AT LABORATORY
6	BLANK	
7	1-6	Samp #
	16-18	Lab
	21-25	Set #
	28-35	Date_Spk
	38-45	Date_Ext
	48-55	Date_Ana
	58-63	Column
8	1-13	enter SAMPLE IDENTIFICATION NUMBER
	16-18	enter LAB ABBREVIATION (JMM)
	21-25	enter SET NUMBER
	28-35	enter DATE SPIKED
	38-45	enter DATE EXTRACTED
	48-55	enter DATE ANALYZED
	58-63	enter ANALYSIS COLUMN
9	BLANK	

APPENDIX I

DATA REPORTING CODES

DATE: September 9, 1988

SUBJECT: Data Reporting Codes

FROM: Christopher Frebis, CSC Statistician

TO: Distribution

The purpose of this memorandum is to discuss the reporting codes used in the National Pesticide Survey. There has been some confusion over these codes as to when and where to use them and their exact meaning.

Table 1 identifies the unique sample types (SAMP - field sample, MBLK - method blank, SBLK - shipping blank, LCS - lab control standard, and LSS, DTS, HTE, and HTS - spiked field samples — these last three are each a type of time storage sample). Under each unique sample type are the only possible codes that can appear for that sample type. (Note: -555 has been added for the situation where the contract lab sends the extract to the referee lab for GCMS analysis, and the code -222 has been deleted.) There is also a type of decision tree for field samples since they are a little more complicated with three analyses for confirmation and qualitative only analytes.

I hope this memorandum helps to put everyone on similar terms as well as clearing the muddy water. If there are any questions of different scenarios you wish to discuss, please call me at (513) 569-7498.

Distribution: Herb Brass, Technical Support Division
Aubry Dupuy, Environmental Chemistry Laboratory
Carol Madding, Technical Support Division
Bob Maxey, Environmental Chemistry Laboratory
Dave Munch, Technical Support Division
Kent Sorrell, Technical Support Division
Bob Thomas, Technical Support Division

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 etc., 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 or positive method blank or time to extraction or analysis is too long) 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 and therefore cannot be reported, however the analyte requires 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.

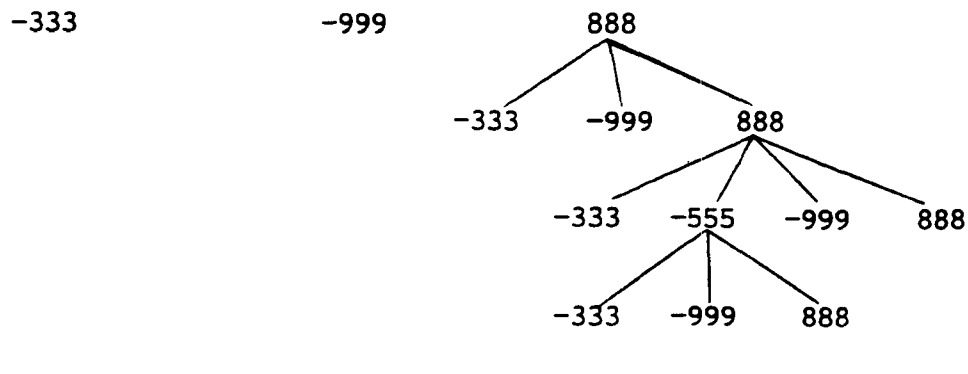
(j) Analyte's concentration below MRL/2.

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

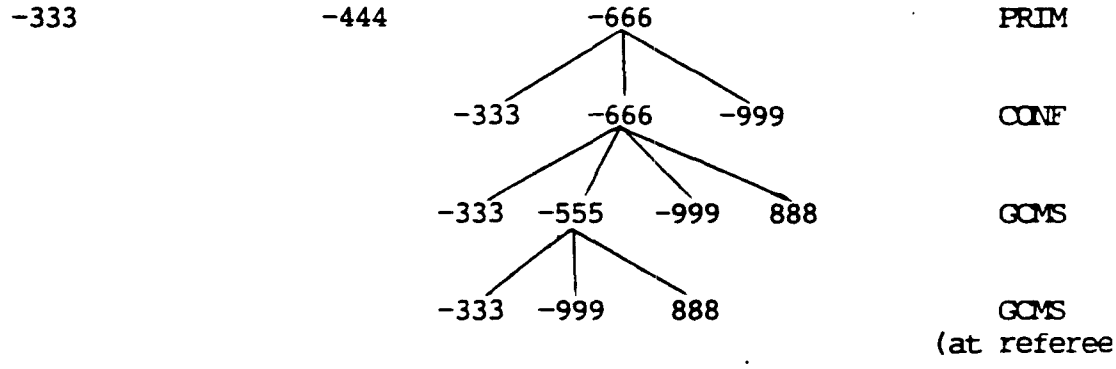
(l) Percent recovery, reported to one decimal place (even if recovery is 0.0%).

**** Code not applicable.

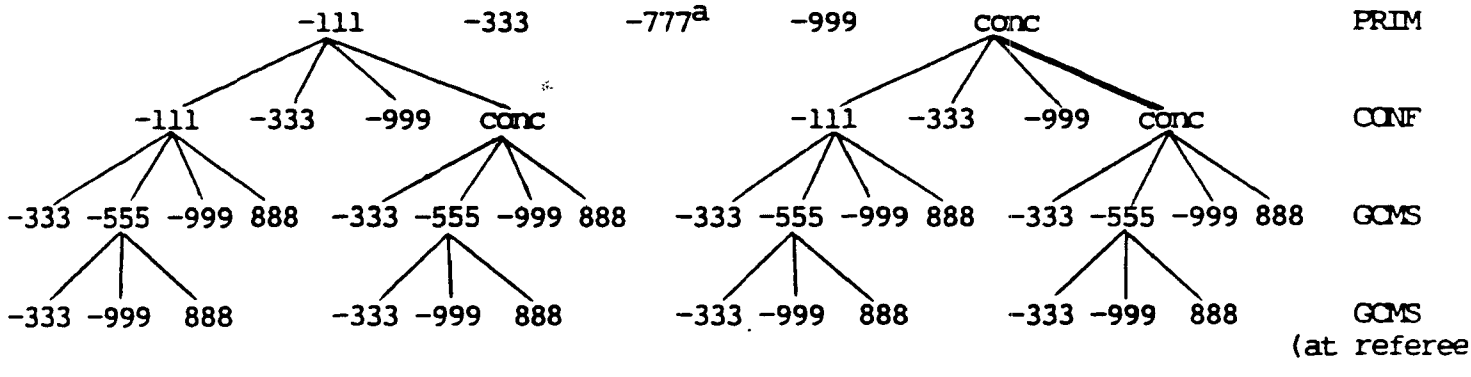
Sample (Qualitative only analyte)



Sample (Quantitative analyte with QC failure)



Sample (Quantitative analyte with no QC failure)



a = Dilute and reanalyze

APPENDIX J

NPS RAPID REPORTING SYSTEM

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 Coqrdinator 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 #1

ANALYTE	RAPID REPORTING LEVEL
Alachlor	44 ug/L
Ametryn	300 ug/L
Atrazine	35 ug/L
Bromacil	2,500 ug/L
Butylate	700 ug/L
Carboxin	1,000 ug/L
Diphenamid	300 ug/L
Fenamiphos	5.0 ug/L
Hexazinone	1,050 ug/L
Metolachlor	300 ug/L
Metribuzin	250 ug/L
Propazine	500 ug/L
Simazine	50 ug/L
Tebuthiuron	125 ug/L
Terbacil	250 ug/L

METHOD #2

ANALYTE	RAPID REPORTING LEVEL
alpha-Chlordane	0.5 ug/L
gamma-Chlordane	0.5 ug/L
Chlorothalonil	150 ug/L
Dacthal (DCPA)	5.000 ug/L
Dieldrin	0.5 ug/L
Propachlor	130 ug/L
Trifluralin	25 ug/L

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 #4

ANALYTE	RAPID REPORTING LEVEL
Cyanazine	13 ug/L
Diuron	70 ug/L
Fluometuron	438 ug/L
Propham	595 ug/L

METHOD #5

ANALYTE	RAPID REPORTING LEVEL
Aldicarb	10 ug/L
Baygon	40 ug/L
Carbaryl	1,000 ug/L
Carbofuran	50 ug/L
Methomyl	250 ug/L
Oxamyl	175 ug/L

METHOD #6

ANALYTE	RAPID REPORTING LEVEL
ethylene thiourea	1.05 ug/L

METHOD #7

ANALYTE	RAPID REPORTING LEVEL
dibromochloropropane	2.5 ug/L
1,2-dichloropropane	56 ug/L
cis/trans 1,3-dichloropropene	11 ug/L
ethylene dibromide	0.04 ug/L

METHOD #9

ANALYTE	RAPID REPORTING LEVEL
Nitrate/Nitrite	10,000 ug/L

APPENDIX K

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 L

STANDARD OPERATING PROCEDURES; BATCH FILING SYSTEM

APPENDIX L

STANDARD OPERATING PROCEDURE: BATCH FILING SYSTEM

PURPOSE

To centralize the storage of ESE analytical data batches and all associated documentation for each batch.

PROCEDURE

All data batches created by the various departments will be placed in departmentally assigned colored batch files. All associated documentation for each batch will be included in each folder as well as a documentation checklist. The checklist will be marked by the analyst noting everything included in the batch file and will be signed and dated by the analyst and a review person.

The batch file must also have the "Computer QC Checks" and the "Internal QA/QC Batch Checklist" section located at the end of each batch marked, signed and dated by the analyst. The batch then must be reviewed, signed and dated by the Department Manager. If the batch fails any of these checks, the corresponding Lab Coordinator(s) for all samples in the batch must also sign and date the batch and may add comments.

The batch file is then signed-in to Information Services to document chain-of-custody of the raw data.

Each batch will then be finalized and filed numerically by department in locked file cabinets located in the Information Services department. Each department manager will have a key to his/her file cabinet and Information Services will retain a key to all cabinets.

Since only the most recent batches can be filed in the file cabinets, all "older" batches are filed by department in a separate, locked storage room with access available only to Information Services.

All data batches including those in the storage room are available for checkout at any time. All batches are signed out to the individual with a hard copy as well as an electronic file kept of all checkouts.