Interim Guidance for the Preparation of Quality Assurance Project Plans for Chemical Tests in the Underground Injection Control Program

Prepared by the EPA UIC-QA
Workgroup
July 1985

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

AUG 2 1985

OFFICE OF
WATER

MEMORANDUM

SUBJECT: Guidance for the Preparation of Quality Assurance (QA) Project Plans for Chemical Tests (UICB #35)

FROM: Victor J. Kimm, Director
Office of Drinking Water

TO: Water Management Division Directors
Regions I-X

The attached document provides guidance on the preparation of quality assurance project plans for chemical tests and instructs the Regions to include in the grant agreement or workplan a statement by the States that they will submit a QA project plan within 120 days after receiving this guidance from EPA. This document is the product of months of meetings of the UIC-QA workgroup which is composed of representatives from EPA (RO, HQ, EMSL) and the States (TX, MS, NM).

The guidance document consists of a short guidance (5 pages) and attachments which are intended as technical assistance to the States. It should be introduced to the States ASAP in order for them to begin the preparation of QA project plans for all chemical tests done in support of the UIC program.

If you need additional information, feel free to call me on 382-5508 or Mario Salazar (Project Manager) on 382-5561.

Attachment

cc: Nancy Wentworth, QAMS
UIC Representatives, Regions I-X
Water Supply Branch Chiefs

Interim Guidance for the Preparation of Quality Assurance Project Plans for Chemical Tests in the Underground Injection Control Program

Prepared by the EPA UIC-QA Workgroup

July 1985

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

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* See list of abbreviations and glossary

GLOSSARY OF TERMS

AUDIT:

a systematic check to determine the quality of operation of some function or activity. Audits may be of two basic types: (1) performance audits in which quantitative data are independently obtained for comparison with routinely obtained data in a measurement system, or (2) system audits of a qualitative nature that consist of an on-site review of a laboratory's quality assurance system and physical facilities for sampling, calibration, and measurement.

DATA QUALITY:

The totality of features and characteristics of data that bears on its ability to satisfy a given purpose. The characteristics of major importance are accuracy, precision, completeness, representativeness, and comparability. These characteristics are defined as follows:

- Accuracy - the degree of agreement of a measurement (or an average of measurements of the same thing), X, with an accepted reference or true value, T, usually expressed as the difference between the two values, X-T, or the difference as a percentage of the reference or true value, 100 (X-T)/T, and sometimes expressed as a ratio, X/T. Accuracy is a measure of the bias in a system.

- Precision - a measure of mutual ageeement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation.

Various measures of precision exist depending upon the "prescribed similar conditions."

- Completeness - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions.

- Representativeness - expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Comparability - expresses the confidence with which one data set can be compared to another.

DATA VALIDATION

A system process for reviewing a body of data against a set of criteria to provide assurance tha the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verification, certification, and review.

ENVIRONMENTALLY RELATED MEASUREMENTS

A term used to describe essentially all field and laboratory investigations that generate data involving (1) the measurment of chemical, physical, or biological parameters in the environment, (2) the determination of the presence or absence of criteria or priority pollutants in waste streams, (3) assessment of health and ecological effect studies, (4) conduct of clinical and epidemiological investigation, (5) performance of engineering and process evaluations, (6) study of laboratory simulation of environmental events, and (7) study or measurement on pollutant transport and fate, including diffusion models.

PERFORMANCE AUDITS:

Procedures used to determine quantitatively the accuracy of the total measurement system or component parts thereof.

QUALITY ASSURANCE:

The total integrated program for assuring the reliability of monitoring measurement data. A system for integrating the quality planning, quality assessment, and quality improvement efforts to meet user requirements.

QUALITY ASSURANCE PROGRAM PLAN:

An orderly assembly of detailed and specific procedures which delineates how data of known and acceped quality data

is produced for a specific project. (A given agency or laboratory would have only one quality assurance program but would have a quality assurance project plan for each of its projects.)

QUALITY CONTROL:

The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process.

STANDARD OPERATING PROCEDURE (SOP):

A written document which details an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performaing certain routine or repetitive tasks.

ABBREVIATIONS

API - American Petroleum Institute

CERCLA - Comprehensive Emergency Response Compensation and Liability Act (Superfund)

CFR - Code of Federal Regulations

DI - Direct Implementation (States in which EPA has implemented a UIC Program).

FR - Federal Register

Lab - Laboratory

NPDES - National Pollutant Discharge Elimination System

O & G - Oil and Gas

PWSS - Public Water System Supervision

QA - Quality Assurance

QAMS - Quality Assurance Management Staff

QAO - Quality Assurance Officer

QC - Quality Control

RCRA - Resource Conservation and Recovery Act

RO - Regional Office

RQAO - Regional (Office) Quality Assurance Officer

SDWA - Safe Drinking Water Act of 1974 as amended

SOP - Standard Operating Procedure

SQAO - State Quality Assurance Officer

TDS - Total Dissolved Solids

UIC - Underground Injection Control

UIC-QA - Underground Injection Control Quality Assurance

USDW - Underground Source of Drinking Water

1425 - Oil and Gas programs. From §1425 of the SDWA which makes special provisions for delegation of the UIC program for Oil and Gas related injection wells.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OFFICE OF
WATER

MEMORANDUM

SUBJECT: Interim Guidance for the Preparation of QA Project Plans* for Chemical Tests, in the UIC** Program - (UICPG #35)

FROM: Victor J. Kimm, Director
Office of Drinking Water

TO: Water Supply Branch Chiefs/ Underground Injection Control Section Chiefs/QAOs - Regions I-X

Background

On September 30, 1983, the final version of the general grant regulations was published under 40 CFR Part 30. In §30.503(e) the regulations require that States and local governments receiving assistance from EPA implement a Quality Assurance (QA) program. The QA program must have: 1) a management plan identifying the State agency and/or office responsible, resources available and the person in charge of the program; and 2) a commitment on the part of the State to develop and implement QA project plans for environmental measurements, in accordance with scientific methods approved by EPA. This latter requirement would mean, among other things, that each entity administering a UIC program must structure all the components of its sampling and testing program, including sampling and testing by the operators, to insure that data is of known quality and to conform with EPA accepted procedures and State requirements.

In the case of Direct Implementation (DI) programs, the Director (RA) establishes criteria for QA of all environmentally related measurements submitted in support of UIC activities. The authority for QA in the UIC program is based on 40 CFR §144.28(g), §144.51 (e) and §144.52(a)(5), which require adequate QA to be used when submitting data mandated by the program. Data submitted by well operators also need to include QA elements.

* See glossary of terms (p.ii)
** See list of abbreviations (p.vii)

Due to the newness of some of the testing procedures used in the UIC program and the program itself, implementation will take place in three sequential phases. The first phase will address traditional chemical tests*. The second will address widely used physical tests, and the third, less well known geophysical tests.

Purpose

The purpose of a Quality Assurance program is to help assure that methods to obtain environmental measurement data are technically valid, scientifically defensible and of known quality. For this reason, EPA is requiring States to assess the adequacy of their present data gathering-activities and is offering technical help where needed to assist States in upgrading their programs to meet Federal QA standards. If a State already has a comprehensive, coordinated and effective QA program for which a QA project plan(s) have been prepared, it should submit the plan to the Regional Office (RO) for evaluation. The RO may recommend some revisions to assure that the QA project plans are in conformance with scientific methods approved by EPA.

This guidance will help recognized UIC agencies (i.e., State agencies, ROs) in the preparation of a QA project plan for chemical tests in the UIC program. It is not the intention of EPA to modify the existing UIC delegated program in any manner. This guidance does not change the parameters which are being tested for and does not change the frequency of these tests.

Specific QA project plans may deviate from this guidance with proper justification which is acceptable to the ROs. The EPA will evaluate those project plans in light of the overall QA program goal that environmental measurements be representative, accurate, comparable, complete and of known quality.

* These include analyses of injection fluids, formation fluids and any other aqueous solutions in their terminal stable form or any of their intermediary forms.

Guidance

This guidance is based on "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans." (QAMS 005/80, EPA-600/4-83-004, NTIS PB83-170514). Attachment A follows the same organization as the QAMs guidance and it is intended to aid in the preparation of UIC-QA project plans in states that have not developed their own. It contains directions and suggested language that can be be modified by the State for more relevance.

The QA project plan for chemical analysis must contain the elements listed below. However, if any of these are duplicated in other programs they can be incorporated by reference (e.g. NPDES, or RCRA QA programs). Furthermore, the preparer can, if warranted, consolidate some of the elements under generic headings. The RO should indicate to States what would be acceptable.

- Plan Overview
- Organization and Responsibility
- Sampling Procedures
- Sample Preservation, Stabilization and Chain of Custody
- Laboratory and Field Equipment Calibration Procedures
- Analytical Procedures
- Documentation, Data Reduction, Validation and Reporting
- Internal Quality Control Checks
- Performance and Systems Audits
- Preventive Maintenance
- Precision and Accuracy Protocols/Limits
- Data Representativeness, Comparability and Completeness
- Corrective Action
- Quality Assurance Reports
- Standard Operating Procedures (SOPs)

Attachment A gives guidance for each of the sections above. It also gives specific examples or "boiler plate" for some of the more generic sections. References are also given which would help the State in preparing the plan and obtaining useful information. Particularly useful documents which the States and EPA could use as models are: "Guidance for the Development of a QA Plan by Regional Team" (Regions 8,9,10) and "Guidance for the Preparation of Combined Work QA Project Plans for Environmental Monitoring" (OWRS QA-1). These are available from the RQAOs. Attachment E includes a QA project plan that addresses the analysis of environmental samples containing complex chemical mixtures.

In preparing the UIC-QA project plan for chemical tests, the UIC agency should consider only the needs and requirements of the State program. Some States, as in the case of a Class II program (oil & gas related) require very few chemical analyses by the operator, and may also include only a few chemical tests

by the UIC agency in support of UIC. In such States, only the tests that are actually done in support of the UIC program should be covered. However, the preparer of the plan should give consideration, not only to the primary use of the data, but also to secondary uses. For example, consideration could be given to possible applications in enforcement activities (secondary use) for any data submitted to support a permit application (primary use). In such cases, the SQAO should make sure that tests done to estimate certain parameters, such as TDS, are adequate to evaluate contamination episodes or for permit purposes.

EPA has not established a valid test for "compatibility" of injection fluids in injection formations. However, if a compatibility test is required under a State UIC program, it must be included in the QA plan. EPA will revise this guidance in the future as compatibility tests are studied. In general, operators perform some tests to evaluate the ease of injection (e.g., whether there is precipitation of solids in the formation). Attachment "C" gives a short discussion of compatibility and a test which can be done to determine ease of injection.

EPA has not developed or approved specific tests and protocols to deal with some complex injection fluids. These will be made available to the States as they are developed.

RCRA and CERCLA offices in the States or EPA Regions should be able to provide sampling guidance for "high hazard" samples taken to analyze Class I hazardous waste injection fluids. The ROs should include this information in the guidance to be given to States that have HW facilities.

Implementation

The ROs will distribute this guidance to the States. Upon receipt, the States will contact all persons (e.g., affected operators, laboratories and other State offices) involved in the sampling, testing, processing and reporting of UIC chemical data. The implementation of this plan in the States should be completed within the 1986 grant year. The RO's UIC section and QA officer will determine the adequacy of the State QA project plan. For DI States, the ROs must send the QA project plan to the Chief, Underground Injection Control Branch in Headquarters after concurrence from the Regional QA officer.

The ROs will include a condition in the grant agreement or workplan with respect to the full implementation of the UIC-QA project plan for chemical test. This condition should read:

"The State agrees to submit to EPA a QA project plan for chemical tests within 120 days after receiving guidance from EPA and to implement this plan within the 1986 grant year. The QA project plan will follow guidance provided by EPA on this subject."

The ROs will prepare a QA project plan for DI States and will send it to the Chief, Underground Injection Control Branch, EPA Headquarters, no later than 120 days from the receipt of guidance on the subject.

This guidance will be updated periodically in the future as warranted. Examples of programs or special situations will be incorporated in future guidances.

Since the primary purpose of QA is the improvement of the quality of the data generated by the States and EPA, the program should be viewed as a cooperative effort between these two parties. The ROs, as the overseeing authority, should remain flexible enough to encourage initiative on the part of the States and the regulated community. The bottom line however, is that a QA program is necessary to assure effective environmental programs and EPA, the States and the regulated community are responsible for implementing such a program. EPA has made the obtainment of data of known quality one of its biggest priorities.

Filing

This guidance should be filed under Underground Injection Control Program Guidance #35 (UICPG #35).

Responsibility

For additional information please contact:

Mario Salazar, Environmental Engineer
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Washington, D.C. 20460
Phone (202) or FTS 382-5561

Attachments

cc: UIC-QA workgroup

ATTACHMENT A

Instructions and Examples to Be Used in the Preparation of UIC-QA Project Plans for Chemical Tests

Based on QAMS 005/80 "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans"

Foreword

The original intent of Attachment A was to provide the States and the ROs with a "fill-in-the-blank" guidance document, which would minimize the effort expended by the States preparing a Quality Assurance project plan for chemical tests. However, as the workgroup became aware of the complexity and relative differences in the UIC programs, the consensus was reached to provide a general document with some specific instructions and illustrative examples.

As mentioned in the text of the guidance, the QA plan that each State and each RO develops should be designed to meet its needs. It is also intended to be a dynamic document which will change as the UIC program and technology evolve. It is not intended to duplicate work done in support of other EPA programs such as NPDES, PWSS and RCRA. The States are encouraged to coordinate their QA activities and to avoid redundancy.

I. PLAN OVERVIEW

Instructions

The preparer should list (or reference) in the QA project plans if relevant:

a) The reasons for preparing this plan. General grant regulations (40 CFR 30.503 (e)) require that the State prepare a QA project plan for all environmental measurements. These project plans establish a vehicle for assuring the generation of data of known quality through the documentation of the processes of sample collection, analyses and data handling.

b) The regulations relevant to the UIC QA program. The Federal regulations are: 40 CFR 30.503(e), 146.13(b)(1), and 146.33(b)(1) for primacy States; and 40 CFR 144.28(f) and 146.52(a)(3) for DI States. The preparer* of the QA project plan should list the applicable State statute and regulations/rules.

c) Measurements in the UIC program which will generate chemical data. Some such activities are: analyses of formation fluids, analyses of injection fluids, analyses of samples from monitoring wells, analyses of fluids for aquifer exemption justification, analyses involved in ground-water contamination episodes and others;

* The person in the State or RO who has been charged with preparing the UIC-QA project plan for chemical tests.

d) Participants in the program. Examples of these are: recognized UIC agencies, State laboratories, private laboratories, well operators, any contributing State offices and others.

e) To whom applicable. All entities required to submit data to the program should be described. Data of unknown quality are not acceptable for submission to the UIC program. At this time, there is no explicit regulation in the UIC program minimum requirements requiring the owner or operator to comply with specific QA practices outlined in this and subsequent guidance. However, there are several references in the UIC regulations requiring the submittal of data of known quality (see b) above). EPA and the State can assure compliance with the program by including QA requirements as a part of all permits issued.

f) How QA requirements will be disseminated to the regulated community. The preparer should indicate what plans have been made to disseminate information. Some vehicles that could be used are:

1. Newsletters
2. Statewide meetings
3. Fact Sheets
4. Information bulletins to accompany permit applications
5. Trade associations
6. Operator training

II. ORGANIZATION AND RESPONSIBILITY

Instructions

The preparer must name the office or offices responsible for UIC-QA chemical tests and indicate how the UIC-QA program will be implemented. A split responsibility situation can arise when the 1422 (Class I, III, IV and V) program and the 1425 (Class II) program choose to implement different UIC-QA programs.

Throughout this guidance many different responsibilities are assigned to the State Quality Assurance Officer (SQAO). Some of these responsibilities may be delegated to other program participants (e.g. laboratory personnel); however, the SQAO should be ultimately responsible for the adequacy of the QA program to the RO.

The preparer must also indicate the various offices and agencies involved in the generation and use of UIC fluid chemical data. In some States different environmental programs will integrate many or all their field activities. In these cases, sampling for the UIC program (surveillance) may fall under the responsibilities of a separate agency. The State (or the RO in DI States) must ensure that adequate QA practices are implemented in all offices contributing to the UIC effort.

The preparer (see footnote on page A.1) must also show how the State will ensure that all data generated by the operators will follow the State's QA requirements. As mentioned before,

all data submitted as part of permit application, self-monitoring and any other UIC activity are also required to be covered by the QA program. Either the State or the RO in DI States, must establish a program to periodically check on QA compliance by the operators.

III. SAMPLING PROCEDURES

Instructions

The State should specify in its QA plan how, when and where the sampling should be done, using permit and generic requirements as a base. Some useful examples of general sampling techniques should be mentioned. Specific recommendations should also be made. The State should develop a short fact sheet to be used by operators, which specifies the minimum amount of information to be included on the sample label. It should emphasize the importance of a specific description on how and where the sample was taken.

Attachment B includes: 1) examples of completed sample forms; 2) "Standard Procedures for the Collection of Ground Water Samples from Residential and Municipal Wells" which is applicable to a variety of investigations dealing with inorganic parameters; 3) "Required Containers, Preservation Techniques and Holding Times"; 4) an example of a "Chain of Custody" form; and 5) a chapter from a field handbook (under preparation) with instructions for sampling trace organic materials, including

volatile ones. Furthermore, the first reference in Section VI of this attachment, also elaborates on the types of sampler materials to be used. A survey of these documents should give the preparer of the QA project plan a fairly complete picture on sampling techniques to be used in the UIC program.

Some general recommendations that could be made in this section follow.

Example

The sampler should coordinate with the laboratory doing the analysis to ensure proper scheduling. Attachment C gives the specified containers, preservation techniques and holding times for selected samples. After collecting all samples they should be handled as few times as possible. All personnnel should use extreme care to ensure that samples are not contaminated.

Sample containers should be rinsed with sample water at least twice before use. The sampler should make sure that, when warranted, the well is evacuated prior to taking ground water samples. Extreme care shall be taken to ensure that all materials in pumps, tubing, bailers and sample containers do not contaminate the sample by releasing materials that would interfere with, add to, or react with the components being tested. The same precautions should be taken to prevent any adsorption of the sample components by the materials in the pumps, tubing, bailers and/or sample containers. The type of equipment and the sample

containers used in the collection and preservation of samples should be determined by investigating their compatibility with the expected components in the sample.

All samples should be taken at representative locations. If possible, injection fluid samples should be taken out of the injection line.

References

The plan preparer should reference or include relevant portions of useful publications (in accordance with copyright laws). Some particularly helpful publications are:

* "Manual of Ground Water Sampling Procedures," available from NWWA, phone (614) 846-9355.

* "Manual of Ground Water Quality: Monitoring Methodology," EPA-600/4-76-026.

* "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 - 2nd edition.

* "Sampling Ground Water for Organic Contaminants", EPA 600/5-80-022.

* "Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA-600/4-82-029, Order PB-83-/24-503, available from NTIS.

* U.S. Geological Survey 1977, "Handbook of Recommended Methods for Water Data Acquisition," USGS Office of Water Data Coordinators, Reston, Virginia.

* Wood, W.W., 1976 "Guidelines for Collection and Field Analyses of Ground Water Samples for Selected Unstable Constitutents," U.S. Geological Survey Techniques for Water Resources, Investigations Book 1, Chapter D-2.

* "Standard Methods for the Examination of Water and Wastewater," Current Edition

* "Suitability of Containers for Storage of Water Samples," Water Resources Council Technical Paper 16, 1976.

* Morrison, R.D., and Brewer, P.E., "Air-lift Samplers for Zone-of-Saturation Monitoring." Ground-Water Monitoring Review, No. 1, Vol 1, p.52, 1981.

* Claassen, H.C. "Guidelines and Techniques to Obtain Valid Ground-Water Quality Samples." Open-File Report USGS, 1978, 54 pages.

* Keith, S.V., Wilson, L.D. Sources of Spatial-Temporal Variability in Ground-Water Quality Data and Methods of Control" Ground-Water Monitoring Review, Number 3, Volume 2, p.21, 1983.

* Hunkin, G.G.; Reed, T.A.; Branch, G.N, Some Observations on Field Experiences with Monitoring Wells," Ground-Water Sampling, Englewood, CA.; Ground-Water Monitoring Review, No 1, Vol 1, p. 43, 1984.

* "Procedures for the Collection and Preservation of Ground Water and Surface Water Samples and for the Installation of Monitoring Wells," NTIS, DE84-007264, Bendix Field Engineering Corp., Grand Junction, CO. January 1984.

IV. SAMPLE PRESERVATION AND STABILIZATION AND CHAIN OF CUSTODY

Instructions

The handling of samples from the sampling point to the laboratory is very important. The preparer should define adequate preservation, storage and transportation procedures and make sure that documentation of the handling of the sample will take place. The plan should require a sampling label (see Figure 1) and a bound laboratory log book to ensure that all details associated with the sampling, transportation and analyses can be retraced. The sampler should also keep a weather-proof log book in which the relevant conditions of the sampling methods are recorded.

Appendix B includes an example of a chain of custody form as well

as information on preservation techniques. This chain of custody form is being used in EPA Region II for special samples to be used for enforcement cases.

Sample wording of this section follows.

Example

All samples must have a sampling label containing at least the information shown in Figure 1. This label must remain with the sample throughout its collection, storage, transportation and analysis. When the sampler (operator) reports the analysis to the State, the sampling label should be referenced by its "Sample ID No." and date of collection and analysis. The sampler and/or the laboratory should retain all sampling labels or the information on them for three years or as required by the State Quality Assurance Officer (SQAO). Where samples may be needed for legal purposes, "chain-of-custody" procedures (as defined by the enforcement agency in the State and/or EPA) must be used.

All laboratories performing analyses of samples must retain a "laboratory log" as part of their records. This log should show the dates of sample receipt, preparation, analysis and results of the sample as well as other relevant information.

(NAME OF SAMPLING ORGANIZATION)

SAMPLE DESCRIPTION _____

_____

FACILITY:_____ LOCATION: _____

WELLS: _____ _____

DATES: _____ _____

TIME: _____ _____

TYPE OF FACILITY:_____ SAMPLING LOCATION:_____

SAMPLE TYPE: _____ PRESERVATIVE: _____

SAMPLING METHOD: _____

SAMPLED BY: _____

SAMPLE ID NO.: _____ - - - - _____

LAB NAME _____

REMARKS

Figure 1. Example of General Sample Label

NOTE: To prevent problems if the label becomes detached from the sample container, each should be marked with the same symbol. The container can be marked with indelible ink, and if used again, the same number/symbol should be referenced on the label. There are certain types of label tape which are solvent resistant, can be ordered in a roll, preprinted, and written on or stamped with indelible ink. (Attachment "B" includes an example of a sample label.)

Instructions:
Sample description: Whether this is a formation, injection or combined fluid sample, etc.
Facility, Location: Self-explanatory
Wells: Number of the well sampled, number of wells at the facility
Dates, Time, Type of Facility, Sampling location: Self-explanatory
Sample type: Batch, composite, etc.
Sampling method: Air lift, bailer, swab, etc.
Sampled by, Sample ID No., Lab name, Remarks: Self-explanatory (See text).

V. LABORATORY AND FIELD EQUIPMENT OPERATION AND CALIBRATION PROCEDURES

Instructions

The preparer of the QA plan should include in it the appropriate SOP and methods which will aid in assuring that both field and laboratory equipment are functioning properly.

The plan should either include or reference the written calibration procedures, the reference standards, and QC samples used. The use of these standards and samples is essential to ensure system control and to measure operator performance. A description of a continuous review process over these control systems should also be included. These control functions should include the internal laboratory activities.

Provisions for equipment maintenance, inspection, and testing procedures must be implemented. This is necessary to ensure that all facility equipment, servicing instruments, and any other ancillary items are available, properly functioning and maintained. A description of how the responsible authority monitors and controls this vital function shall be included. Preventive maintenance and inspection procedures must cover such diverse items as ion chromotographs, gas chromotographs and other laboratory instruments, the facility high vacuum system, the water distillation or deionization unit, electronic thermometers, thermostats, pressure gauges and constant voltage transformers. An item of special importance is the academic

training and/or work experience of the analyst needed to operate the sophisticated equipment which may be required for some analysis.

The State should develop a SOP for operation of field equipment used to obtain preliminary water quality data. Some such equipment may include HACH Chloride kits, field conductivity meters, portable pH meters, etc. In the plan, the SQAOs should define the applicability of the field kits from their experience and manufacturers' literature. EPA intends to provide further guidance on this subject in the future.

A field and laboratory equipment check list(s) must be developed. The list(s) should include equipment operating parameters, such as temperature, pressure, flow rate, voltage, etc. In addition, to the check list(s), an equipment maintenance log book containing calibrations and repairs must be established, and it must remain with the piece of equipment in the lab, or in a safe location for field equipment. Maintenance schedules should also follow manufacturer's recommendations.

Some of the references in Section VI ("Analytical Procedures") include the calibration procedures and frequency for the equipment used. Each laboratory involved in the analysis of UIC-related samples should have a record showing the dates of calibration for the preceding three years or longer, as required by the SQAO. This record should be available for inspection by the SQAO.

To comply with this requirement, it is necessary for all laboratories doing tests required in the UIC program to agree to:

- Retain calibration logs for three years;
- Retain laboratory logs for three years;
- Retain sampling labels or information on them for three years;
- Perform all analytical tests in accordance with methods specified in this plan.

Example

[Due to the diversity of equipment used in laboratories, it would be impractical to present a representative example. The State should prepare this section in accordance with the type of laboratory equipment it has available. Field equipment, especially the so called "kits", should be periodically checked against more sophisticated lab equipment and calibrated every time they are taken out. For example, titration equipment used for chloride determination should be checked against amperometric titrators or more complex/accurate equipment.]

VI. ANALYTICAL PROCEDURES

Instructions

The preparer should use this section to give the operators the range of acceptable procedures. The laboratory analyst should use EPA approved procedures and, when these are not available, the best available techniques (see example).

The preparer of the project plan should keep in mind that some of the industrial injection streams may contain a wide variety of compounds and unusually complex analytical techniques may have to be used.

Example

All water quality tests required in the UIC program must be done in accordance with the permit or one of the following methods:

1. Organic and inorganic compounds, water quality measurements: 40 CFR Part 136 "Guidelines Establishing Test Procedures for the Analysis of Pollutants," (as revised on October 26, 1984 and January 4, 1985), §136.3, Table I. This list references the accepted methods to analyze waters for organic and inorganic contaminants. It also includes some physical tests (temperature, specific gravity, etc.). This document is available from the SQAO.

2. Organic compounds, water quality measurements: "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, available from the Center for Environmental Research Information (CERI) 26 West St. Clair Street, Cincinnati, Ohio 45268, Phone: (513) 684-7562 or FTS 684-7562.

   NOTE: This technical report provides procedures that are as uniform and cost effective as possible (with some

minor compromises) for the analysis of some organic pollutants. It also provides references that would be helpful to the analyst.

3. Methods for the analysis of inorganic compounds: "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1979; available from Center for Environmental Research (CERI), 26 West St. Clair Street, Cincinnati, Ohio 45268. NOTE: This reference is included in 1. above and provides acceptable analytical methods.

4.* Other analyses not covered above should be performed in accordance with the most recent edition of "Standard Methods for the Examination of Water and Wastewaters": American Public Health Association, American Water Works and the Water Pollution Control Federation. Other analyses not covered above should be performed by the best available methods.

5.* For Class II programs, analyses which require a high degree of accuracy must be done as explained above or in accordance with "API Recommended Practice for Analysis of Oil-Field Waters" API RP 45.

Note: Techniques already approved and used for other programs (RCRA, CERCLA, NPDES, PWSS, etc.) should be deemed acceptable for the same type of analyses.

* The preparer of the plan should make it clear that the use of the last two references above (Nos. 4 and 5) is adequate until EPA approves specific tests to be used.

VII. DOCUMENTATION, DATA REDUCTION, VALIDATION AND REPORTING Instructions

The QA project plan should include detailed documentation of all samples and methods of collection. The preparer of the QA plan should prepare SOPs in which the type of record to be maintained and the method of storage are defined.

The preparer should also include those mathematical and/or statistical procedures which are used by the generators of data to convert raw data into its final form. Cross-checking procedures should also be indicated. If the data are to be entered into a computer system, the SOP should be described.

Validation procedures can be incorporated into the State's data gathering effort by analyses of split samples, and replicate sample analyses, spiked addition recoveries and intra and inter laboratory comparisons. Validation procedures are described in the EPA document "Calculation of Precision, Bias and MDL for Chemical and Physical Measurements" (March 30, 1984) which is available from the RQAOs.

The State Quality Assurance Officer (SQAO) should prepare written instructions to validate data. Examining data for outliers* (as determined by the SQAO) should be done routinely.

*Data which are significantly different from the majority of the other results, as determined by valid statistical techniques.

An adequate matrix presentation or other graphic display of the data can help to identify outliers. There are a number of statistical methods for the identification of outliers. One which is widely used is the Standard Deviation method. The SQAO should consider the establishment of a formal laboratory certification program. This could be done either by the incorporation of UIC related laboratories into other certification programs such as the one for PWSS or the creation of a new program which could be expanded in the future to include all State environmental programs. The ROs must use labs certified for other programs (NPDES, PWSS), if available and applicable, to analyze samples taken to support DI programs. The States should also use these labs where applicable.

The State or RO should determine its needs in this area and include them in the project plan. The RQAO should be consulted for assistance.

VIII. INTERNAL QUALITY CONTROL CHECKS

Instructions

Checks of the data must be done as explained in standard EPA Quality Control publications (see references below) or by using other reliable methods. The establishment of control charts for instrument calibration is an important Internal Quality Control Check. Sample wording to this effect is shown in the following example.

Example

All laboratories performing analyses of UIC samples should maintain a program to frequently check their results. This could be done by selecting representative samples of analytical results for the particular area or type of injection fluid. Irregular or unusual data should be investigated. A regular program of instrument calibration should be developed and followed. Quality Control criteria are explained in "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA-600/4-79019, March 1979, available from the Center for Environmental Research Information (CERI), 26 West St. Clair Street, Cincinnati, Ohio 45268 Phone: (513) 684-7562 or FTS 684-7562.

NOTE: This publication provides information on quality control measures such as control of the quality of the reagents, standardization of titrants, monitoring of instruments' response, etc.

Practices such as those listed below must be implemented in laboratories to ensure adequate quality control.

1. Standard Curve Data - Where applicable, standard curves must be checked and calibrated at least monthly. This requirement applies to atomic emission, ion chromatographic and colorimetric methods. Atomic absorption curves should be obtained daily.

2. Standardization of Titrants - When standard solutions (titrants) are used for quantitative analyses to determine the concentration of pollutants, these titrants must be standardized monthly or more frequently if the method requires it. Traceability to the National Bureau of Standards should be established for all reagent chemicals used as standards in the calibration of equipment.

3. Electrochemical Methods - Electrochemical instruments must be standardized each day (or shift) in which they are used. These standardization procedures can be found either in the methods text used or manufacturer's instructions for the instrument.

4. Analytical Balances - Because the balances are the primary standard in the laboratory, care must be taken to ensure their accuracy. Each balance should be serviced annually. In addition, Class 'S' weights must be weighed quarterly to document accuracy or to detect problems so corrective action can be taken.

5. Duplicate Analyses - Duplicate analyses must be done on at least ten percent (10%) of the UIC samples received. If there are less than 10 samples in a batch, 1 duplicate analysis should be done.

   Results of these analyses must fall within the acceptance

limits for precision defined in the "Precision and Accuracy Protocols/Limits," Section XI.

6. Spiked Sample Analyses - Spiked sample analysis allows the laboratory personnel to evaluate the accuracy of the sampling method performed on a routine basis. A spiked sample is created by adding a known amount of the constituent being analyzed to a representative portion of the original sample. The amount of spike should be approximately equal to the concentration of the analyte in the original sample. At least 10% spikes or 1 per batch (if less than 10 samples per batch) must be run.

   The Regional Quality Assurance Office will make documents available outlining the instructions for preparation of spiked samples and to evaluate the results of such analyses. Section IX outlines how to obtain "QC Samples" to assess performance.

7. Preparation of a Quality Control Manual (QCM) - Each laboratory should prepare a QCM to document the responsibilities of the laboratory personnel. Also, all QC checks should include acceptance/rejection criteria.

IX. PERFORMANCE AND SYSTEMS AUDITS

Instructions

The SQAO should make periodic visits to laboratories doing analyses of UIC fluid samples. These visits may be done as

part of the evaluation audits for several programs (e.g., NPDES, PWSS, RCRA, etc.). The visits could include evaluation of laboratory quality control procedures as well as their interface with sampling practices. SQAO visits should be included in program work plans following recommendations by the RQAO. The laboratories should also analyze Q.C. samples periodically. These samples will be provided by EPA and made available to laboratories through the SQAOs. These samples would be reflective of everyday samples received in the laboratory and the concentrations would be known to the SQAO. The SQAO should request these QC samples from the RQAO. Appendix "D" includes an order form to obtain Q.C. Samples. This form should be sent to the RQAO.

The SQAO can also recommend candidates to the RQAO for the "Performance Evaluation Program." The Performance Evaluation Program sends "blind" samples to the participating labs. The labs perform the analysis and send the result to the Environmental Monitoring and Support Laboratory (EMSL). EMSL evaluates the results and informs the RQAO. Participation in this program is limited.

Example

All laboratories and other parties participating in the collecting, transporting and analyzing of chemical samples for the UIC program are subject to audit visits by the State QA Officer. These

visits would concentrate on assuring that the activity being performed is in accordance with the State's QA plan and scientific principles.

The SQAO should provide the laboratories with "QC Samples," for analysis and reporting of results. Evaluation would indicate to the lab and the SQAO the quality of the work done in the lab and any shortcomings.

The QA should pursue corrective action, if necessary and help any participant requiring assistance to improve performance. Please refer to the front of this plan for the name and address of the State Quality Assurance Officer.

X. PREVENTIVE MAINTENANCE

Instructions

The preparer of this plan should address procedures for preventive maintenance and associated documentation. The plan should at least call for laboratories and field units to perform the maintenance required in the operational manuals for the equipment used. Another important consideration would be the availability of critical spare parts for the equipment. The SQAO may want to require a list of such parts from each of the participating laboratories.

Example

[All laboratories and field units participating in the collection of environmentally related data for the State UIC program should have a preventive maintenance program. A log must be kept

documenting the maintenance. It would be a good practice to have a list of critical spare parts available to the SQAO.]

XI. PRECISION AND ACCURACY PROTOCOLS/LIMITS

Instructions

Estimates of data precision and accuracy must be developed in accordance with EPA guidelines entitled, "Calculating Data Quality Indicators" and "Establishing Achievable Data Quality Goals". These guidelines and updates are available from the RQAOs.

Laboratory personnel should be consulted with regard to the selection of analytical methods. Once the methods are selected, the detection, precision, and accuracy requirements for these should be developed and then incorporated into the QA project plan. Along with each requirement, there should be a protocol to monitor whether these requirements were met. For example, intra-laboratory precision can be monitored by using replicate samples. Accuracy can be monitored with the use of field blinds, spikes, surrogate spikes, National Bureau of Standards' Standard Reference Materials (SRMs), EPA QC reference samples, etc. Wherever possible, criteria should be set for the "total measurement". This could be accomplished, for example, with the use of field spikes and replicate samples. As a minimum, acceptance criteria should be within plus or minus two standard deviations of the precision and accuracy data published for the parameter by EPA.

The written and other material mentioned above are available from the Regional Quality Assurance Officer (RQAO).

XII. DATA REPRESENTATIVENESS COMPARABILITY AND COMPLETENESS

Instructions

Data "representativeness" is a qualitative element which refers to a sample or a group of samples that reflect the characteristic of the waste stream at the sampling point. It also includes how well the sampling point represents the parameters which are under study. For example, the representative point to sample the injection fluid is at the well head. The permit may specify sampling points at a facility. The preparer of the project plan should provide some guidelines on the proper sampling location in accordance with local treatment and construction practices. A SOP can be developed for this purpose.

"Comparability" is also a qualitative characteristic which must be considered in QA program planning. Depending on the end use of data, comparability must be assured for the project in terms of sampling plans, analytical methodology, quality control, data reporting, etc. For example, in the example above for representativeness, in order to have comparability, all samples must be taken from the same location in the waste stream and at the same relative time in the process. Another comparability issue would be that data should be reported in comparable units.

"Completeness" is defined as the amount of valid data obtained from a measurement system compared to the amount that was expected and needed to be obtained in meeting the project data goals. The determination of data completeness is the responsibility of the sampler (reporting party), as determined by guidance and requirements specified by the SQAO. For example, if unexpected events, such as breakdown of equipment, weather conditions and poor quality of reagents, caused 70% of the required test to be deleted, the reporting party (operator) should qualify the results obtained. This by no means releases the operator from the reporting requirements under the UIC program.

XIII. CORRECTIVE ACTION

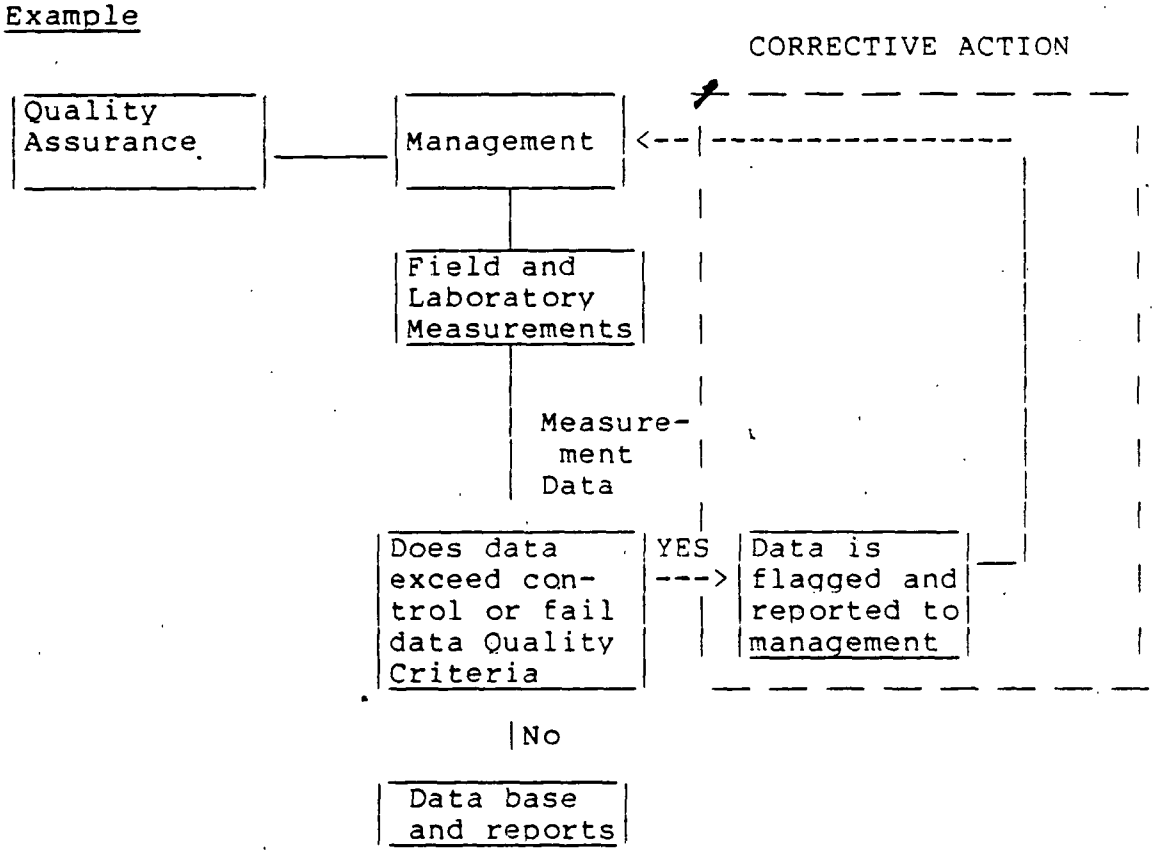
Instructions

Whenever data are generated, analyzed and reduced there is a possibility that some of them may not meet a limit for acceptability. This limit would have been established in accordance with the needs of the UIC program in the State. This limit would indicate the point at which corrective action is required.

The preparer of the UIC-QA projet plan should investigate, analyze and establish the limits for data acceptability beyond which corrective action is required. He/she should also offer some examples of what corrective action can be taken to solve the problem and offer assistance on a case-by-case basis.

Corrective action may also be required as a result of State or EPA performance audits, system audits, quality control sample results and laboratory comparision surveys. An example of the type of corrective action flow chart that should be developed follows.

Example



Corrective Actions Include: Revision of Quality Assurance Criteria; Recalibration or Repair of Equipment; Resampling; Revision of Measurement Procesures; Training of Personnel

XIV. QUALITY ASSURANCE REPORTS

Instructions

The preparer of this plan should obtain agreement from the SQAO

and the Director of the UIC program (State or RO) as to the schedule for reporting. A logical alternative would be to integrate QA reporting with annual UIC reporting by the State or to consolidate all QA reports for chemical tests for all environmental programs administered by a single agency. The report should indicate to EPA that the State is applying adequate QA techniques to all its environmentally related measurements. The State should agree to report to EPA on:

- o Program highlights;
- o Approximate number of participating laboratories;
- o Types of fluid quality tests performed;
- o Future plans;
- o Training;
- o Number of laboratories visited by the SQAO;
- o Evaluation of performance audit samples.

The reports should be sent to the Regional UIC program office and the RQAO. Ir order for the SQAOs to obtain the information required above, they should ask participating laboratories to report their activities. These reports should contain at least the following elements:

- o Name and location of unit;
- o Types of analysis done and samples taken;
- o Number and types of tests done in the reporting period;
- o Future plans;
- o Training;

o Evaluation of performance audit studies.

The laboratory reports should be sent to the SQAO (see beginning of plan) no later than January 31 of each year for the preceding year. The SQAO, in turn, would send the summarized State/Agency UIC report to the RO no later than February 28.

XV. STANDARD OPERATING PROCEDURES (SOPs)

Instructions

Standard Operating Procedures (SOPs) are very effective in assuring that certain complex and repetitive tasks are done in the same manner every time. The laboratories, samplers and/or operators should prepare SOPs. The State should decide which of these SOPs should be sanctioned by the SQAO.

The SOP should provide step-by-step instructions on the handling of the sample, chain of custody, preservation and analytical procedures, if warranted. It should be easily understood by the user and available at each working station. Appendix D includes an SOP which was prepared to test for sulfides in ground water. It has been modified from the last reference in Section III ("Sampling Procedures").

Example

An SOP should be prepared by the operators, samplers and laboratory personnel for each procedure that is done repeatedly or routinely. The SOP should be written in simple terms as to be understandable to the person doing the work.

The operator may develop as many SOPs as needed, however, all SOPs used to develop UIC reporting data should be available for inspection by the SQAO. The SQAO will, at the request of the operator, provide guidance on the preparation of specific SOPs. All SOPs should follow scientific and EPA-approved methods and procedures, as well as equipment recommendations when applicable.

ATTACHMENT B

I Examples of Completed Sample Labels

II Standard Procedures for the Collection of Ground-Water Samples from Residential and Municipal Wells

III Containers, Preservation Techniques and Holding Times (with summary page)

IV Chain of Custody Form

V Sampling, Preservation and Storage Considerations for Trace Organic Materials (Including Volatile Organics)

Example of Complete Sample Label (1)

(NAME OF SAMPLING ORGANIZATION)

SAMPLE DESCRIPTION Formation

STATE: MT COUNTY:

FACILITY OR FIELD: Cedar Creek Anticline

LEGAL LOCATION: SW, SE, Sect. 19, T4N, R62E

NAME OF SAMPLE SOURCE: Carter Oil

TYPE OF SOURCE: Potential Oil Reservoir

GEOLOGIC SOURCE: Darwin SAMPLE INTERVAL: 8320-8349 *

DATE: 11/14/41 TIME:

SAMPLING LOCATION: Insitu/Drill Stem SAMPLE TYPE: Formation Water

FIELD TEMP OF SAMPLE: 153° F FIELD PH:

Remarks: Drill stem test (DST) flowed for 1 1/2 hours sample appears to be contaminated with mud filtrate. See completion report for details of DST (attached).

* Depth below ground surface

Example of Complete Sample Label (2)

(NAME OF SAMPLING ORGANIZATION)

SAMPLE DESCRIPTION Produced Water

STATE: WY COUNTY: Carbon

FACILITY OR FIELD: Wertz Oil Field

LEGAL LOCATION: Section 6, T26N, R89W

NAME OF SAMPLE SOURCE: Wertz #47

TYPE OF SOURCE: Producing Oil Well

GEOLOGIC SOURCE: Tensleep, Amsden, Darwin, and Madison

SAMPLE INTERVAL: Multiple perforation from 5867 to 6587 *

DATE: 12/28/81 TIME: 2:30 pm

SAMPLING LOCATION: Heater Treater SAMPLE TYPE: Formtion Water

FIELD TEMP OF SAMPLE: 60°F FIELD PH: 7.2

PRESERVATIVE:

Comments: Heater Treater (HT) is receiving water and oil only from well #47. HT is pumped every 4-5 days. HT was pumped out 4 days prior to sampling (see attached sampling location description).

* Depth below ground surface

STANDARD PROCEDURES FOR THE COLLECTION OF GROUND-WATER SAMPLES FROM RESIDENTIAL AND MUNICIPAL WELLS*

INTRODUCTION

This document outlines procedures for the collection of representative ground-water samples from residential and municipal wells. It specifically addresses monitoring of ground-water quality in relation to the subsurface injection of salt water. As such, the procedures presented address only inorganic parameters and do not consider the more difficult task of sampling for organics.

The collection of representative ground-water samples is neither a straightforward or easily accomplished task. In fact, many feel that it is impossible to collect a ground-water sample that is truly representative of aquifer water quality conditions due to changes which may occur during sample collection, preparation, preservation and storage prior to analysis. However, certain procedures can be adopted that will maximize the integrity of the sample. This document presents in a step-by-step manner procedures which will ensure not only the collection of ground-water samples which are representative as possible but also allow for maximum efficiency in sample collection. The following procedures are divided into five sections. These are:

1. Obtaining background information.
2. Obtaining laboratory information and materials.

* This material was prepared for EPA Region V under contract with Engineering Enterprizes, Inc., of Norman, OK.

3. Sample collection, preparation, preservation and storage.

4. Field measurements of in situ parameters.

5. Chain of custody procedures.

1. OBTAINING BACKGROUND INFORMATION

The necessary first step in the collection of ground-water samples is to obtain background information on the liquid suspected of affecting the ground-water quality and specifics of the area and wells to be sampled. This information can then be used to design a sampling program which will provide the maximum efficiency of sampling and improve the quality of the collected data. Information to be obtained during this first phase includes:

- Identification of parameters for analysis:
  For salt water waste streams, the principal parameters of interest are pH, specific conductance, alkalinity, Ca, K, Mg, Na, Cl, and SO_4^{-2}. Additionally, salt water may contain various trace metals. Collection of samples for these metals will affect the sampling protocol with respect to preparation and preservation of the samples. If possible, any other constituents in the injected stream should be identified in advance. This will allow for development of an appropriate scheme for preparation and preservation of the samples for metal analysis if necessary. The procedures discussed in the following sections will differentiate between

the principal parameters of the wastes and the metals.

- Scheduling

Proper scheduling of sampling periods for residential municipal wells is important in obtaining representative samples. It is important that a municipal well be sampled while it is pumping, because water that has been held stagnant in the well casing will not be representative of the aquifer being sampled. Be sure to collect samples from residential wells when the water is at equilibrium with the aquifer. This will depend upon the water usage at the residence. It is best not to take a sample immediately after heavy usage (after morning showers) or after a long period of little or no usage (usually late to mid-afternoon). When sampling a group of residential wells in a particular area, be sure to sample them over a relatively short period of time. When collecting more than one round of samples, make the sample periods consistent with respect to the time of day the samples are taken.

- Accessibility

When sampling residential and municipal wells, site accessibility is normally not a problem, especially since only a limited amount of equipment has to be brought

on-site. However, accessibility of the well can cause major problems. Before attempting to sample a residential well, determine if the well is physically accessible for sampling. For municipal wells, check to see if a spigot or valve is available from which a sample can be taken. In both cases, be sure that the sampling port or spigot is positioned as close to the wellhead as possible and before any type of treatment unit, such as a water softener or filtration.

- Materials

  Contact the owner or operators of the wells to determine what tools, valves, hoses, etc., will be needed. Wrenches may be needed for opening and closing faucets or spigots. Often ports or valves on municipal wells may be too large and their use may result in a high volume flow which will make sampling difficult. In this case, it will be necessary to reduce the flow by using appropriate fittings. Obtain information from the operator on the size of the fittings required and on accessibility of the sampling spigot. It may be convenient to attach a section of hose to the line, especially in very cramped quarters.

2. OBTAINING LABORATORY INFORMATION AND MATERIALS

The importance of communicating with laboratory personnel responsible for analysis of the samples prior to sample collection cannot be overemphasized. They can be an important source of information and materials if they understand the specifics of the sampling program. This will not only improve the efficiency of the program, but also the accuracy and completeness of the results. It will be necessary to establish with the laboratory the procedures and analyses which you wish to conduct. The laboratory personnel may able to lend guidance or give suggestions pertaining to particular problem areas which may develop and provide written instructions from the laboratory for any nonroutine procedures pertaining to sample preparation, preservation and storage.

- o Sample bottles

  Once the laboratory knows the analyses to be conducted, they will be able to supply the appropriate bottles and preservatives or inform you as to what you should obtain. The size of the bottle will depend on the analysis to be conducted and the analytical methods to be employed. Be sure to collect sufficient samples for duplicate analyses should they be required. The type of bottles will depend upon the suspected constituents. For the constituents of salt water, linear polyethelene

bottles are best. Wide-mouth bottles will provide easy access during both sampling and analysis. The amount of the sample needed varies according to the method to be used in the analysis and the preservation methods.

- o Sample Care

  In choosing a laboratory it may be necessary to weigh the efficiency of using one near the sampling site versus the greater degree of reliability of a well-known but distant laboratory to which samples must be shipped. If the latter option is used, make sure that the logistics of transport, shipping, and pickup have been fully worked out so that the chain-of-custody is not compromised and that sample preservation times are not exceeded.

3. SAMPLE COLLECTION, PREPARATION, PRESERVATION, AND STORAGE

One important goal of sample collection is to obtain a representative sample of aquifer water by minimizing changes that may occur in the field while the sample is collected, preserved and stored. Seemingly small departures in collection techniques can significantly affect the results of the tests. Care in handling and cleanliness must be maintained from the time the sample is taken until it is delivered to the laboratory. Consistency is the key to quality control. The following outlined procedures, if adhered to, should produce

samples that are as close as practically possible to representative aquifer conditions.

- o Well Evacuation

  As previously mentioned, it is important to remove stagnant water from a well that has not recently been pumped prior to taking a sample. This is because standing water that has been exposed to the atmosphere or has been in contact with the well casing or pump, even for short periods of time, will react with these substances, and its chemical composition will be altered. Contact with air will affect pH, alkalinity, and specific conductance. Changes in these parameters will in turn oxidize certain metal constituents and cause them to precipitate.

  The amount of water that should be removed from the well is dependent on the diameter and depth of the well, the depth to ground water, and the yield of the well. A general rule is to evacuate three to five times the volume of water from a well which has been inoperative. To assure adequate evacuation it is a standard practice to measure pH, conductivity and temperature to insure stabilization. The measurement of the well volume and water level should be conducted in the following fashion:

  - Measure well casing inside diameter.

- Determine the static water level. This should be expressed as feet below ground surface or below casing elevation depending upon information available. (Note that the water indicator used may have to be cleaned before use in each well.)
- Determine the total depth of the well.
- Calculate the number of linear feet of static water (difference between static water level and total depth of well).
- Calculate the static volume.

The sample should be taken as the water level is rising in the well bore, i.e., as the well is filling with fresh water from the aquifer.

Sampling from residential/municipal wells can be a very straightforward procedure if the well is pumped regularly. For most residential wells, water should be run for two minutes prior to sample collection. In most cases, residential samples can be taken outside without entering the house. Besides being convenient, outdoor faucets usually supply a more representative sample by intercepting water from the well before it has entered the water tank or water softener. The faucet should be checked, however, to ensure that it is, in fact, the most direct outlet from the

Since municipal wells are high volume water producers, there is no necessity for evacuating the well. However, the lines from the wellhead to the sampling port must be evacuated. For most residential and municipal wells, the samples generally can be collected either directly into the sample bottles, or in cases where sample filtration is called for, samples can be placed directly into the filter apparatus.

- Sample Storage

  Choosing a sample container is of primary importance. The material of construction must be nonreactive with the sample and especially with the particular parameter to be tested. In general, there are three types of construction materials: plastic, glass, and teflon. Samples collected for metals and general water quality parameters are stored in plastic bottles. Samples collected for organic analysis are routinely placed in glass bottles of various types and sizes depending upon the particular analysis to be conducted. In most cases, bottles will be supplied by the laboratory conducting the analysis.

o Rinsing

Just prior to filling, the sample containers are rinsed with the water to be sampled. Enough water is run into the container to rinse the inside and is then dumped out. The lid is rinsed also. Care is taken not to rest the lid on the ground or touch the inside of the lid after rinsing. Rinsing is, of course, omitted if the container is pretreated with preservative. Care should be taken not to come in contact with the sample fluid.

o Filling Sample Containers

Bottles should be filled quickly to minimize mixing with air. It is helpful to allow the water to overfill the container to prevent small bubbles from forming.

o Filtering

Whether or not a sample is to be conditioned prior to preservation and storage depends upon the analyses to be conducted and the type of sample collected. Whether or not a sample is to be filtered will depend upon the analyses to be conducted. If dissolved metal constituent concentrations are to be measured,

ground-water samples must be filtered in the field immediately after collection. Ground waters tend to be in a more reducing environment than they would be under standard atmospheric conditions and, as such, precipitation will occur if the sample is not filtered and preserved with nitric acid immediately after withdrawal.

Filtering is necessary if the sample is to be analyzed for dissolved constituents. It is not required if a total analysis of the sample will be performed. Certain metals are adsorbed by suspended sediments and if filtering does not take place they tend to raise the concentration of these constituents in the analysis. The ions, Ca^{+2}, K^{+}, Mg^{+2}, Na^{+}, Cl^{-} and SO_4^{-2}, tend to be relatively stable; therefore, sampling for their presence does not require filtering. However, for certain sophisticated testing methods the sample should be filtered prior to analysis. Filtering through a 0.45 micron pore size membrane should be performed if the elements Fe, Mn, Mg, Cd, Cu, As, Se, or B are involved. This is done with a device called a vacuum filter. A funnel may be helpful to direct the flow of water into the filter unit. Once the sample has been filtered, it can be transferred to the sample container. Before taking the next sample, the filter unit is rinsed with a very dilute acid solution, followed with deionized water. Also, a new filter paper is inserted.

- Sample Preservation

  Complete preservation of any sample is difficult because it may be impossible to completely stabilize every constituent within a sample. At best, preservation techniques can only retard the chemical and biological changes that continue after the sample is removed from its environment. If the sample environment is significantly different from atmospheric conditions, the sample may undergo changes which will render it nonrepresentative of its original environment. Methods of preservation are relatively limited and are intended to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents. Generally, preservation methods are limited to pH control, chemical addition, refrigeration, and freezing. Table 1 in Attachment D gives recommended container types, preservatives, and holding times for a variety of standard water chemical parameters.

  Sample preservation should be performed in the field immediately after sample collection and preparation. In many cases where pH control or additions of reagents are required, separate bottles and chemical preservatives may be supplied by the laboratory. In other cases, the reagents or preservatives may be placed in the sample bottle prior to delivery to the site.

4. FIELD MEASUREMENTS OF IN SITU PARAMETERS

The parameters of temperature, pH, Eh (redox potential), and Ec (electrical conductivity) begin to change rapidly as soon as the sample is removed from the well. In some cases, it may be desirable to perform in situ measurements before the samples are brought to the lab. Field measurements of Eh and pH are made in a closed, air-tight flow-through cell whenever possible. The closed cell prevents the sample from reacting with the atmosphere and a stirring mechanism ensures that the sample is consistent throughout. Numerous devices for measuring field parameters are available from various manufacturers. Follow the equipment manual for the particular piece of equipment you are using. The required equipment is vulnerable to precontamination and physical abuse; thus, it is important that meters for measuring pH, Eh, and Ec are calibrated periodically as recommended by the manufacturer with the appropriate liquid standards. Allow sufficient time for the electrode to stabilize before recording the measurement. The probe or thermometer should be cleaned and rinsed with distilled water following each use.

5. CHAIN-OF-CUSTODY PROCEDURES

In any activity that may be used to support litigation, the sampler must be able to provide the chain-of-possession

and custody of any samples which either are offered as evidence or for which the samples for test results are introduced as evidence. Written procedures must be available and followed whenever evidence samples are collected, transferred, stored, analyzed or destroyed. The primary objective of these proceduress is to create an accurate written record which can be used to trace the possession and handling of a sample from the moment of its collection through analysis and its introduction as evidence.

A sample is defined as being in someone's "custody" if:

- It is in one's actual possession; or
- It is in one's view, after being in one's physical possession; or
- It is in one's physical possession and then locked up so that no one can tamper with it; or
- It is kept in a secured area, restricted to authorized personnel only.

The number of persons involved in collecting and handling samples should be kept to a minimum. Field records should be completed at the time the sample is collected and should be signed or initialed, including the date and time, by the sample collector(s). Field records should contain the following information:

- Unique sampling or log number;
- Date and time;
- Source of sample (including name, location and sample type);

- Preservative used;
- Analysis required;
- Name of collector (s);
- Pertinent field data (pH, DO, chlorine residual; specific conductance, temperature, redox potential, etc.);
- Serial number on seals and transportation cases.

Each sample must be labeled using waterproof ink and sealed immediately after it is collected. Labels should be filled out before collection to minimize handling of sample container.

The sample container should then be placed in a transportation case along with the chain-of-custody record form, pertinent field record, and analysis request form as needed. The transportation case should be sealed or locked. A locked or sealed chest eliminates the need for close control of individual samples. However, on those occasions when the use of a chest is inconvenient, the collector should seal the cap of the individual sample container with tape in a way that any tampering would be easy to detect.

When transferring the samples, the transferee must sign and record the date and time on the chain-of-custody record, which should have been prepared according to enforcement requirements. Custody transfers made to a sample custodian in the field should account for each sample, although samples may be transferred as a group. Every person who takes custody must fill in the appropriate section of the chain-of-custody record. To minimize custody records, the number of custodians in the chain-of-possession should be minimized.

Table I. Required Containers, Preservation Techniques, and Holding Times

	Measurement Table/Parameter	Container	Preservative	Maximum Holding Time
IA	Bacterial Tests			
	Coliform, fecal and total	P,	Cool, 4°C 0.008% $Na_2S_2O_2$[5]	6 hours
	Fecal streptococci	P, G	Cool 4°C 0.008% $Na_2S_2O_2$[5]	6 hours
IB	Inorganic Tests			
	Acidity	P, G	Cool, 4°C	14 days
	Alkalinity	P, G	Cool, 4°C	14 days
	Ammonia	P, G	Cool, 4°C H_2SO_4 to pH<2	28 days
	Biochemical oxygen demand	P, G	Cool, 4°C	48 hours
	Biochemical oxygen demand carbonaceous	P, G	Cool, 4°C	48 hours
	Bromide	P, G	None required	28 days
	Chemical oxygen demand	P, G	Cool, 4°C H_2SO_4 to pH<2	28 days

Table I. Required Containers, Preservation Techniques, and Holding Times

	Measurement Table/Parameter	Container	Preservative	Maximum Holding Time
IB (Cont.)	Inorganic Tests			
	Chloride	P, G	None required	28 days
	Chloride residual	P, G	None required	Analyze immediately
	Color	P, G	Cool 4°C	48 hours
	Cyanide, total and amenable to chlorination	P, G	Cool 4°C NaOH to pH> 12 0.6g ascorbic acid	14 days[6]
	Fluoride	P	None required	28 days
	Hardness	P, G	HNO_3 to pH<2	6 months
	Hydrogen ion (pH)	P, G	None required	Analyze immediately
	Kjeldahl and organic Nitrogen	P, G	Cool, 4°C H_2SO_4 to pH<2	28 days
	Metals			
	Chromium VI	P, G	Cool, 4°C	24 hours
	Mercury	P, G	HNO_3 to pH<2	28 days

Table I. Required Containers, Preservation Techniques, and Holding Times

	Measurement Table/Parameter	Container	Preservative	Maximum Holding Time
IB(Cont.)	Metals, except above	P, G	HNO_3 to pH<2	6 months
	Nitrate	P, G	Cool 4°C	48 hours
	Nitate-nitrite	P, G	Cool 4°C H_2SO_4 to pH<2	28 days
	Nitrite	P, G	Cool, 4°C	48 hours
	Oil and grease	P, G	Cool 4°C H_2SO_4 to pH<2	28 days
	Organic carbon	P, G	Cool, 4°C HCl or H_2SO_4 to pH<2	28 days
	Orthophosphate	P, G	Filter immediately Cool, 4°C	48 hours
	Oxygen, Dissolved Probe	G Bottle and Top	None required	Analyze immediately
	Winkler	G Bottle and Top	Fix on site and store in dark	8 hours
	Phenols	G only	Cool, 4°C H_2SO_4 to pH<2	28 days

Table I. Required Containers, Preservation Techniques, and Holding Times

	Measurement Table/Parameter	Container	Preservative	Maximum Holding Time
IB (Cont.)	Phosphorus (elemental)	G	Cool, 4°C	48 hours
	Phosphorus, total	P, G	Cool, 4°C H_2SO_4 to pH<2	20 days
	Residue, total	P, G	Cool, 4°C	7 days
	Residue, Filterable	P, G	Cool, 4°C	7 days
	Residue, Non-filterable(TSS)	P, G	Cool, 4°C	7 days
	Residue, settleable	P, G	Cool, 4°C	48 hours
	Residue, volatile	P, G	Cool, 4°C	7 days
	Silica	P	Cool, 4°C	28 days
	Specific conductance	P, G	Cool, 4°C	28 days
	Sulfate	P, G	Cool, 4°C	28 days
	Sulfate	P, G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH>9	7 days
	Sulfite	P, G	None required	Analyze immediately
	Surfactants	P, G	Cool, 4°C	48 hours
	Temperature	P, G	None required	Analyze immediately
	Turbidity	P, G	Cool, 4°C	48 hours

Sample Preservation and Maximum Holding Times Specific to Class II Well Samples

The sampling preservation and maximum holding times are defined to maintain the integrity of the samples so that accurate and reliable data will be generated by the laboratories analyzing such samples. It is incumbent on the sampling teams to understand these requirements and plan the sampling projects so that the requirements are met. It is also necessary that the laboratory personnel understand the requirements and notify clients when there are problems so that corrective action can be taken.

Sampling containers should be made from polyethylene with polyethylene lined lids. Glass is required only when dissolved oxygen samples are stabilized in the field and titrated later. Glass sample bottles may be used for all other sample types but polyethylene lined lids are necessary.

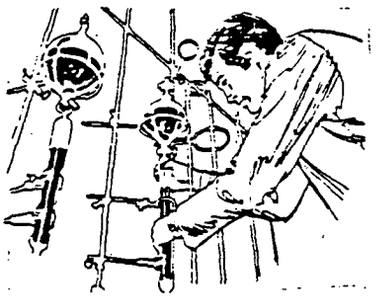
When filtration is required, it should be performed on-site. If conditions preclude field filtration, the samples must be delivered to facilities and filtered within four(4) hours. Samples should be chilled to 4°C during transit.

Table II summarizes preservation and holding times for some tests.

TABLE II

Parameter	Preservation Technique	Maximum Holding Time
Major Cations (Na^+, K^+, Ca^{+2}, Mg^{+2})	HNO_3 to pH<2.0	6 months
Major Anions (Cl^-, $SO_4^=$, F^-, Br^-)	Chill to 4°C	1 month
Trace Metals (Fe, Mn, Zn, Pb, Hg)	HNO_3 to pH < 2.0	6 months
Alkalinity	Chill to 4°C	14 days
Sulfide	Chill to 4°C 2nd Zn Acetate Reagent per liter, NaOH to pH>9.0	7 days
pH	None	1 hour maximum
Dissolved Oxygen	Meter method - none Winkler method - add $MnSO_4$ and Azide - NaOH reagents	determine on-site 8 hours
Specific Conductance	Chill to 4°C	28 days
Total Dissolved Solids	Chill to 4°C	7 days
Compatability	Chill to 4°C	48 hours

Note: Holding time and preservation requirements for other parameters may be obtained from the RQAOs.



REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter	Container[1]	Preservation[2,3]	Maximum holding time[4]
Bacterial Tests:			
Coliform, fecal and total	P,G	Cool 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours.
Fecal streptococci	P,G	Cool 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours.
Inorganic Tests:			
Acidity	P,G	Cool, 4°C	14 days.
Alkalinity	P,G	Cool, 4°C	14 days.
Ammonia	P,G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Biochemical oxygen demand	P,G	Cool, 4°C	48 hours.
Bromide	P,G	None required	28 days.
Biochemical oxygen demand, carbonaceous	P,G	Cool, 4°C	48 hours.
Chemical oxygen demand	P,G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Chloride	P,G	None required	28 days.
Chlorine, total residual	P,G	None required	Analyze immediately.
Color	P,G	Cool, 4°C	48 hours.
Cyanide, total and amenable to chlorination	P,G	Cool, 4°C, NaOH to pH>12, 0.6g ascorbic acid[5]	14 days.[6]
Fluoride	P	None required	28 days.
Hardness	P,G	HNO_3, to pH<2 or H_2SO_4 to pH<2	6 months.
Hydrogen ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and organic nitrogen	P,G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Metals:[7]			
Chromium VI	P,G	Cool, 4°C	24 hours.
Mercury	P,G	HNO_3, to pH<2	28 days.
Metals, except chromium VI and mercury	P,G	HNO_3, to pH<2	6 months.
Nitrate	P,G	Cool, 4°C	48 hours.
Nitrate-nitrite	P,G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Nitrite	P,G	Cool, 4°C	48 hours.
Oil and grease	G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Organic carbon	P,G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days.
Orthophosphate	P,G	Filter immediately, Cool, 4°C	48 hours.
Oxygen, Dissolved Probe	G Bottle and top	None required	Analyze immediately
Winkler	G Bottle and top	Fix on site and store in dark	8 hours.
Phenols	G only	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Phosphorus (elemental)	G	Cool, 4°C	48 hours.
Phosphorus, total	P,G	Cool, 4°C, H_2SO_4 to pH<2	28 days.
Residue, total	P,G	Cool, 4°C,	7 days.
Residue, Filterable	P,G	Cool, 4°C,	48 hours.
Residue, Nonfilterable (TSS)	P,G	Cool, 4°C,	7 days.
Residue, Settleable	P,G	Cool, 4°C,	48 hours.
Residue, volatile	P,G	Cool, 4°C,	7 days.
Silica	P	Cool, 4°C,	28 days.
Specific conductance	P,G	Cool, 4°C,	28 days.
Sulfate	P,G	Cool, 4°C,	28 days.
Sulfide	P,G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH>9.	7 days.
Sulfite	P,G	None required	Analyze immediately.
Surfactants	P,G	Cool, 4°C	48 hours.
Temperature	P,G	None required	Analyze immediately.
Turbidity	P,G	Cool, 4°C	48 hours.
Organic Tests:[8]			
Volatile Organics (EPA) method 624-See Table A	G, Teflon lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$,[5] HCl to pH2[9,10]	14 days.
Semi-Volatile Organics plus PCB/Pesticides (EPA) method 625-See Table B	G Teflon-lined cap	Cool, 4°C, $Na_2S_2O_3$,[5] Store in dark	7 days until extraction. 40 days after extraction.
Pesticides Tests:			
Pesticides[11]	G, Teflon-lined cap	Cool, 4°C, pH 5-9[15]	7 days until extraction. 40 days after extraction.
Radiological Tests:			
Alpha, beta and radium	P,G	HNO_3 to pH<2	6 months.

[1] Polyethylene (P) or Glass (G).

[2] Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

[3] When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater), Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater), Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater), and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administrator under § 136.3(e). Some samples may not be stable for the maximum time period given in the Table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See § 136.3(e) for details.

[5] Should only be used in the presence of residual chlorine.

[6] Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

[7] Samples should be filtered immediately on-site before adding preservative for dissolved metals.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9] Samples receiving no pH adjustment must be analyzed within seven days of sampling.

[10] The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

[12] If 2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

[13] Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$, and adjust pH to 7-10 with NaOH within 24 hours of sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

ATTACHMENT B-IV

CHAIN OF CUSTODY RECORD

ENVIRONMENTAL PROTECTION AGENCY - REGION II
Environmental Services Division
EDISON, NEW JERSEY 08817

Name of Unit and Address		
Sample Number	Number of Containers	Description of Samples

Person Assuming Responsibility for Sample:	Time	Date

Sample Number	Relinquished By:	Received By:	Time	Date	Reason for Change of Custody
Sample Number	Relinquished By:	Received By:	Time	Date	Reason for Change of Custody
Sample Number	Relinquished By:	Received By:	Time	Date	Reason for Change of Custody
Sample Number	Relinquished By:	Received By:	Time	Date	Reason for Change of Custody

SAMPLING, PRESERVATION AND STORAGE CONSIDERATIONS

FOR TRACE ORGANIC MATERIALS

Organic compounds in water and wastewater are regulated by the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

The SDWA has established maximum contaminant levels (1)(2) for the following organic chemicals:

a) Chlorinated hydrocarbons:

Endrin	Methoxychlor
Lindane	Toxaphene

b) Chlorophenoxys:

2,4-D	2,4,5-TP (Silvex)

c) Trihalomethanes:

Trichloromethane	Bromodichloromethane
Dibromochloromethane	Tribromomethane

Listed in Table 12.1 are chemicals which have been detected in drinking water supplies and for which the possibility of adverse health effects exists. The presence of these chemicals is indicative of chemical pollution; this list is not exhaustive, but serves merely as a guide.(3)

A court settlement agreement involving the Natural Resources Defense Council, et al. and the U.S. Environmental Protection Agency (EPA Consent Decree) resulted in EPA publishing a list of 65 compounds and classes of compounds (Table 12.2). The Consent Decree required that EPA regulate these compounds via the Federal Water Pollution Control Act (subsequently amended by the Clean Water Act). EPA's expanded list of organic priority pollutants (Table 12.3) is an outgrowth of the Consent Decree's list of 65.

Specific toxic pollutant effluent standards will be promulgated for the organic priority pollutants, thus far they have been promulgated (4)(5)(6) for the following:

Aldrin/Dieldrin	Endrin
Benzidine	Toxaphene
DDT (DDD, DDE)	PCB's

TABLE 12.1 CHEMICAL INDICATORS OF INDUSTRIAL CONTAMINATION (23)

I. Aliphatic halogenated hydrocarbons:

Methane derivatives:

Dichloromethane	Dichlorodifluoromethane
Trichlorofluoromethane	Carbon Tetrachloride

Ethane derivatives:

1,1-dichloroethane	1,1,1-trichloroethane
1,2-dichloroethane	1,1,2-trichloroethane
hexachloroethane	1,1,2,2-tetrachloroethane

Unsaturated hydrocarbons:

Trichloroethylene	1,2-dichloroethene
Tetrachloroethylene	1,3-dichloropropene
Vinyl chloride	Hexachlorobutadiene
1,1-dichloroethene	2-chlorovinyl ether

Other halogenated compounds:

1,1-dichloropropane	Bis(2-chloroethyl) ether
bis(2-chloroisopropyl) ether	

II. Cyclic aliphatic compounds:

Chlorinated hydrocarbons:

Lindane	Kepone
BHC	Toxaphene

Cyclodienes:

Chlordane	Heptachlor
Aldrin	Heptachlor epoxide
Dieldrin	Endrin
Hexachlorocyclopentadiene	

III. Aromatic hydrocarbons:

3,4-benzofluoranthene	fluoranthene
benzo(k)fluoranthene	indeno(1,2,3,c,d)pyrene
1,12-benzoperylene	benzo(a)pyrene

Benzenes:

Benzene	Ethylbenzene
Toluene	Propylbenzene
Xylenes	Styrene

Halogenated aromatics:

Chlorinated naphthalenes	DDE
Chlorobenzene	DDD

TABLE 12.1 (continued)

Halogenated aromatics:(continued)	
Dichlorobenzenes	Chlorophenols
Polychlorinated biphenyls	Trichlorobenzenes
Pentachlorophenol	4-bromophenylphenyl ether
Bromobenzene	4-chlorphenylphenyl ether
DDT	Hexachlorobenzene
Other aromatic hydrocarbons:	
Nitrobenzene	Phthalate esters
Dinitrotoluene	Atrazine

TABLE 12.2 65 TOXIC POLLUTANTS OR CLASSES OF TOXIC POLLUTANTS (21)

Acenaphthene
Acrolein
Acrylonitrile
Aldrin/Dieldrin
Antimony and compounds
Arsenic and compounds
Asbestos
Benzene
Benzidine
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane (technical mixture and metabolites)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorinated ethanes (including 1,2 dichloroethane 1,1,1-trichloroethane, and hexachloroethane)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
Chlorinated naphthalene
Chlorinated phenols
Chloroform
2-chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites
Dichlorobenzenes (1,2-,1,3- and 1,4-dichlorobenzenes)
Dichlorobenzidine
Dichloroethylenes (1,1- and 1,2-dichloroethylenes)
2,4-dichlorophenol
Dichloropropane and dichloropropene
2,4 Dimethylphenol
Dinitrotoluene
Diphenylhydrazine
Endosulfan and metabolites
Endrin and metabolites
Ethylbenzene
Fluoranthene
Haloethers
Halomethanes
Heptachlor and metabolites
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Isophorone
Lead and compounds
Mercury and compounds
Naphthalene
Nickel and compounds
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
Nitrosamines
Pentachlorophenol
Phenol
Phthalate esters
Polychlorinated biphenyls (PCB's)
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes and indenopyrenes)
Selenium and compounds
Silver and compounds
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene
Trichloroethylene
Vinyl Chloride
Zinc and compounds

TABLE 12.3 PRIORITY POLLUTANTS

I. Phthalate esters:

Dimethyl phthalate	Di-*n*-octyl phthalate
Diethyl phthalate	Bis(2-ethylhexyl)phthalate
Di-*n*-butyl phthalate	Butylbenzyl phthalate

II. Haloethers

Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane
Bis(2-chloroisopropyl)ether	4-chlorophenylphenyl ether
2-chloroethylvinyl ether	4-bromophenylphenyl ether

III. Chlorinated hydrocarbons:

Hexachloroethane	1,3-dichlorobenzene
Hexachlorobutadiene	1,4-dichlorobenzene
Hexachlorocyclopentadiene	1,2,4-trichlorobenzene
1,2-dichlorobenzene	Hexachlorobenzene

2-chloronaphthalene

IV. Nitroaromatics and Isophorone:

Nitrobenzene	2,4-dinitrotoluene
2,6-dinitrotoluene	Isophorone

V. Nitrosoamines:

N-nitrosodimethylamine	N-nitrosodipropylamine

N-nitrosodiphenylamine

VI. Dioxin:

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

VII. Benzidines:

Benzidine	3,3-dichlorobenzidine

VIII. Phenols:

Phenol	Pentachlorophenol
2,4-dimethylphenol	4-chloro-3-methylphenol
2-chlorophenol	2-nitrophenol
2,4-dichlorophenol	4-nitrophenol
2,4,6-trichlorophenol	2,4-dinitrophenol

4,6-dinitro-2-methylphenol

TABLE 12.3 (continued)

IX. Polynuclear aromatics:

Acenaphthene	Acenaphthylene
Fluoranthene	Anthracene
Naphthalene	Benzo(g,h,i)perylene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Phenanthrene
Benzo(b)fluoranthene	Dibenzo(a,h)anthracene
Benzo(k)fluoranthene	Indeno(1,2,3-cd)pyrene
Chrysene	Pyrene

X. Pesticides & PCB's:

Aldrin	Heptachlor epoxide
Dieldrin	Alpha-BHC
Chlordane	Beta-BHC
DDD	Delta-BHC
DDE	Gamma-BHC
DDT	Toxaphene
A-endosulfan	Aroclor 1242
B-endosulfan	Aroclor 1254
Endosulfan	Aroclor 1221
Endrin	Aroclor 1232
Endrin aldehyde	Aroclor 1248
Heptachlor	Aroclor 1260
Toxaphene	Aroclor 1016

XI. Purgeables:

Benzene	Chloroform
Chlorobenzene	1,1-dichloroethylene
Toluene	1,2-transdichloroethylene
Ethylbenzene	1,2-dichloropropane
Carbon tetrachloride	1,1-dichloropropyiene
1,2-dichloroethane	Methylchloride
1,1,1-trichloroethane	Methylenechloride
1,1-dichloroethane	Methylbromide
1,1,2-trichloroethane	Bromoform
1,1,2,2-tetrachloroethane	Dichlorobromomethane
Chloroethane	
Chlorodibromomethane	Trichloroethylene
Tetrachloroethylene	Vinyl chloride

XII. Acrolein & Acrylonitrile:

Acrolein	Acrylonitrile

Analytical procedures for the identification of organic compounds can be found in a number of publications.(7 - 22) However, analytical results are only meaningful if the sample analyzed is truly a representative sample of the media you are testing. Chemical analysis for organics present at trace levels places high demands on sampling techniques.

12.1 SAMPLE COLLECTION METHOD

The method of sampling can either be manual or automatic. Sampling practices, as specified in Chapter 2, should be followed, except as indicated in this chapter.

12.1.1 Manual Sampling

The considerations outlined in Chapter 2 are applicable. However, the sample collector and container should be constructed of borosilicate glass to minimize sample contamination. Grab samples obtained for analyses of purgeable organics are sealed to eliminate entrapped air.(7) This sample collected without headspace, is illustrated in Figure 12.1.

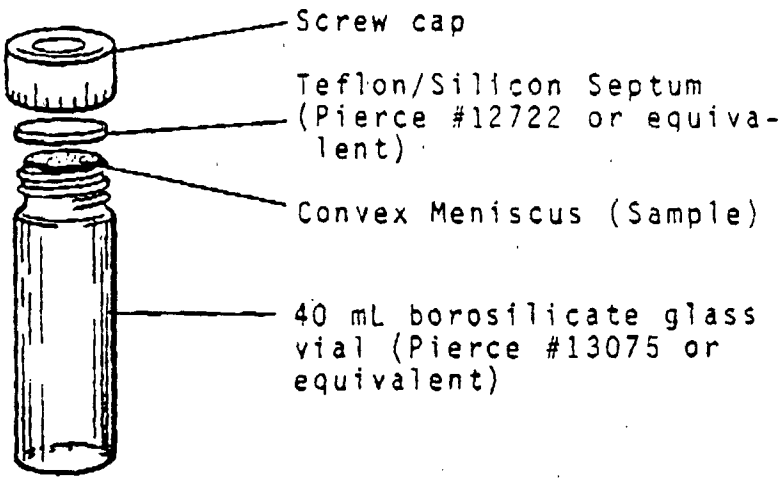


Figure 12.1 Collection Bottle (21,22)

12.5 SAMPLING PROCEDURE AND PRETREATMENT OF SAMPLE EQUIPMENT

12.5.1 Pretreatment of Equipment

The pretreatment technique should be dictated by the analysis to be performed. The general pretreatment technique for sample and storage containers is to:

1. Wash bottles with hot detergent water.
2. Rinse thoroughly with tap water followed by three or more rinses with orgainic-free water.

3. Rinse with interference free redistilled solvent such as acetone or methylene chloride and dry in contaminant free air at room temperature. Protect from atmospheric or other sources of contamination. Caps and liners for bottles must also be solvent rinsed as above.

If automatic samplers are to be employed, use the peristaltic pump type with a single 8 - 10 liter (2.5 - 3.0 gallons) glass container. Vacuum type automatic samplers can be used if sample containers are glass. The procedure outlined above should be followed for the pretreatment of the containers. In addition all tubing and other parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with interference free acetone or methylene chloride is advised when tubing and other parts permit, i.e., are not susceptible to dissolution by the solvent.

12.5.2 Sampling Procedure

Purgeables (22)(31)(32)

Collect grab samples in glass containers. The procedure for filling and sealing sample containers is as follows: Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum Teflon side down on the convex sample meniscus. Seal the sample with the screw cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal (in same manner as stated above). The sample must remain hermetically sealed until it is analyzed. Maintain samples at 4°C (39°F) during transport and storage prior to analysis. If the sample is taken from a water tap, turn on the water and permit the system to flush. When the temperature of the water has stabilized, adjust the flow to about 500-mL/minute and collect samples as outlined above.

Non-Purgeables (22)(32)

Collect grab samples in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of Tygon and other potential sources of contamination.

12.6 SAMPLE PRESERVATION AND STORAGE (32)

Analyze samples as soon as possible. Preserve and store samples collected for analyses via EPA's 600 Method Series as described below:

Method 601 - Purgeable Halocarbons

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thoisulfate preservative (10 mg/40 mL will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site.

All samples must be analyzed within 14 days of collection.

Method 602 - Purgeable Aromatics

Collect about 500 mL sample in a clean container. Adjust the pH of the sample to about 2 by adding 1:1 diluted HCl while stirring vigorously. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site.

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

All samples must be analyzed within 14 days of collection.

Method 603 - Acrolein and Acrylonitrile

The samples must be iced or refrigerated at 4° from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site.

If acrolein is to be analyzed, collect about 500 mL sample in a clean glass conatiner. Adjust the pH of the sample to 4 to 5 using acid or base, measuring with narrow range pH paper. Samples for acrolein analyses receiving no pH adjustment must be analyzed within three days of sampling.

All samples must be analyzed within 14 days of collection.

Method 604 - Phenols

The samples must be iced or refrigerated at 4° from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 605 - Benzidines

The samples must be iced or refrigerated at 4°C from the time of collection to extraction. Benzidine and dichlorobenzidine are easily oxidized by materials such as free chlorine. For chlorinated wastes, immediately add 80 mg sodium thiosulfate per liter of sample.

If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4 ± 0.2 units to prevent rearrangement to benzidine. The sample pH should be adjusted to 2-7 with sodium hydroxide or sulfuric acid.

All samples must be extracted within seven days. Extracts may be held up to seven days before analysis if stored under an inert (oxidant free) atmosphere. The extract must be protected from light.

Method 606 - Phthalate Esters

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

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 607 - Nitrosamines

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample. And, if diphenylnitrosamine is to be determined, adjust the pH of the water sample to pH 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base added.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 608 - Organochlorine Pesticides and PCB's

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 - 9.0 with sodium hydroxide or sulfuric acid. If aldrin is to be determined, and if residual chlorine is present, add sodium thiosulfate.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 609 - Nitroaromatics and Isophorone

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

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 610 - Polynuclear Aromatic Hydrocarbons

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. PAHs are known to be light sensitive, therefore, samples, extracts and standards should be stored in amber or foil wrapped bottles in order to minimize photolytic decomposition. Fill the sample bottle and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days, and analysis completely analyzed within 40 days of extraction.

Method 611 - Haloethers

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of water.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 612 - Chlorinated Hydrocarbons

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

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 613 - 2,3,7,8-Tetrachlorodibenzo-p-dioxin

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of water. Protect the sample from light from the time of collection until analysis.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 624 - Purgeables (GC/MS)

The sample must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for one minute.

Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethylbenzene are susceptible to rapid biological degradation under certain environmental conditions.(3) Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2. If chlorine residual is present, add sodium thiosulfate to another sample container and fill as in Section 9.2 and mix thoroughly.

All samples must be analyzed within 14 days of collection.

Method 625 - Base/Neutrals, Acids and Pesticides (GC/MS)

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. The sample must be protected from light. If the sample contains residual chlorine, add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

ATTACHMENT C

COMPATIBILITY

I Compatibility in the Hydrogeological Environment

II Compatibility for Ease of Injection

I. COMPATIBILITY IN THE HYDROGEOLOGICAL ENVIRONMENT*

In designing an injection well, injection fluid and formation fluid interactions must be accounted for. These interactions may lead to severe reduction in formation permeability or to a loss of structural integrity within the formation itself. Fluid and formation compatibility problems are specific to the particular formation and waste involved. Their prediction and solution require site-specific studies. Specific problems associated with such compatibility include plugging of the injection formation with suspended solids, precipitation and polymerization of the waste fluid, growth of biologic organisms within the formation, and dissolution of the formation matrix.

In some cases, the injection fluid may react directly with the rock matrix. One common problem is the swelling of clays from contact with the injection fluid. Affected clays can significantly reduce the permeability of the formation. In other instances, polar-organic compounds can be adsorbed by the rocks, particularly silicates, and can significantly reduce the permeability of the formation.

The injection of acids may result in dissolution of the rock matrix. In the case of certain cemented material, dissolution can result in the migration of particles which then block pore spaces and reduce permeability. Dissolution of the confining

* This material was extracted from various reports prepared by Geraghty and Miller, Inc. for EPA-ODW under contract #68-01-5971. This material only addresses compatibility in what relates to "ease of injection". It does not address more complex problems such as waste interactions, chemical gradients, etc. EPA will develop criteria on these in the future.

formation can allow the migration of injection fluid from out of the injection formation. In addition, under certain conditions CO_2 gas can be formed, which may interfere with injection and may cause "blow-outs".

To avoid interaction problems, the injection and confining formations should have their respective formation fluid and rock matricies tested for compatibility with the proposed injection (or similar) fluid. Drilling a borehole offers an excellent opportunity to collect data relevant to a number of important parameters of the formations penetrated. The following are the major fluid and rock matrix sampling techniques:

A. Drill Cuttings

Drilling techniques produce cuttings which can be collected and analyzed. Cuttings produced during drilling accumulate in the hole and are removed at intervals by bailing. In rotary drilling, the cuttings are collected from the "shaleshaker". The cuttings obtained provide samples representative of the formations penetrated.

Cuttings are normally examined at the site under low-power magnification to identify rock type, grain size, color, and mineralogy. Testing the samples with acid can be used to determine carbonate material. Exposing cuttings to the injection fluid will allow other useful observations regarding compatibility.

Cuttings must be disposed of properly once they have outlived their usefulness.

B. Coring

Geologic cores taken while drilling provide lithologic and hydrologic information superior to that obtained from the analysis of drill cuttings. Coring is accomplished through the use of a special drilling bit and a coring barrel which is attached to the end of the drill pipe. As the bit cuts into the rock, an inner core is left intact and pushed into the core barrel.

Techniques are also available to take cores from the sides of a borehole after drilling is completed. These sidewall cores are generally taken to provide information about formations from which cores were not taken during drilling. Sidewall coring is accomplished by driving a wireline coring device which contains small hollow cylinders into the formation by an explosive charge. Sidewall coring is limited to relatively soft materials.

Examination of conventional cores can provide substantial amounts of data valuable to the design and the construction of injection wells. Visual examination of cores can reveal fractures, bedding features, and solution cavities; laboratory examination can determine porosity, grain size, permeability, and formation-fluid quality. In situ behavior of the injection and confining formations can be simulated in the laboratory using conventional core samples and representative injection fluid.

Data obtained from sidewall cores are not as reliable as those obtained from conventional cores due partly to the relatively small size of the sample. Formations are disturbed substantially during coring, and the more permeable formations sampled have generally been invaded with drilling fluid.

C. Fluid Sampling

Some of the methods for obtaining formation-fluid samples are drill-stem testing, swabbing, bailing, and air-lift.

Drill-stem testing is a technique whereby a zone in an open borehole is isolated by an expandable packer or packers and fluid from the formation allowed to flow through a valve into a drill pipe. Similar to this, there is a device which can be lowered into the borehole on a wire line rather than on a drill pipe. In this case, the sample is limited to the amount that can be contained in the testing device (no more than 5 gallons).

Swabbing is a method of producing fluid similar to pumping a well. In swabbing, fluid is lifted from the borehole through drill pipe, casing, or tubing by a swab that falls freely downward through the pipe and its contained fluid, but which seats against the pipe walls on the up-stroke, drawing a volume of fluid above it as it is raised. Swabbing is preferable to drill-stem testing where unconsolidated formations cause testing to be difficult. Swabbing may also be used in conjunction with drill-stem testing

to increase the volume of fluid obtained. The advantage of swabbing is that it can be continued until all drilling mud has been drawn from the pipe, thus allowing the chemistry of the formation water sampled to reach a steady state. This procedure helps to insure that a representative sample of formation water is obtained.

Bailing may be used to obtain formation water samples, but care must be taken to insure that the water sample is representative of the formation of interest and not of another formation also draining into the borehole. This problem is reduced in holes in which casing is driven since the casing acts to isolate the lowest formation from the other water-producing formations.

In air-lift (or gas-lift) sampling, fluid can be obtained by injecting gas under pressure into the well. The gas forces the fluids in the well to rise to the surface. This air-lift sampling has limits similar to those encountered with bailing.

II. COMPATIBILITY TEST FOR EASE OF INJECTION*

A. Scope and Application

1. This method is designed to qualitatively determine the compatibility of waters by mixing two representative samples and evaluating the effects over a specific time.

2. The method is only applicable to the UIC program and is an approximation of the interactions which may occur in the injection zone.

B. Summary of Method

1. Equal volumes of injection and formation fluids are mixed together under controlled laboratory conditions The mix is then allowed to stand undisturbed for 20 days and is visually observed periodically. In addition, portions of the samples are analyzed for iron and calcium before mixing to determine if these constituents are being precipitated.

C. Comments

1. Because this is a qualitative method, experience in performing the test is invaluable.

D. Sample Handling and Preservation

* Prepared by Tom Steibel, EPA Region VIII.

1. Samples must be taken in one liter polyethylene or glass containers and care should be taken to eliminate air spaces in the bottles;
2. Samples must be refrigerated or chilled to 4°C with ice during storage or transit, and maximum holding times prior to beginning analysis is 48 hours;
3. The subsurface environment should be simulated to reflect actual conditions as much as possible.

E. Equipment

1. pH meter;
2. Refrigerator;
3. Three or four liter glass beaker with watch glass;
4. The equipment and reagents necessary for the analysis of iron and calcium.

F. Procedure

Before mixing the pH and the concentration of iron and calcium should be determined.

1. Carefully pour one liter of each sample of water together in the three or four liter beaker. Mix thoroughly with a glass rod. Allow solids to settle.
2. Using a serological pipette, remove enough of the mixture from the supernatant to analyze pH, iron and calcium. Cover mixture with watch glass.
3. Obtain the pH, iron and calcium concentrations by an acceptable technique and enter these values on the sample record form along with any observations of the mixture.

4. Carefully place beaker in refrigerator.

5. On days 3, 7, 11, 14, and 20, repeat steps 2 and 3.

H. Precision and Accuracy

There are no proven methods for evaluating the precision or accuracy for compatability. The precision and accuracy for pH, iron and calcium determinations is listed in Section VI of the UI Quality Assurance Criteria.

COMPATIBILITY

SAMPLE RECORD FORM

Injection Water Sample Number:

Aquifer Water Sample Number:

Date Sampled: Time Sampled:

Date Test Began: Time Test Began:

Analyst:

	Date	pH	Ca	Fe	Observations
Day 1					
Day 3					
Day 7					
Day 14					
Day 20					

Refrigerator Temperature:= (Acceptable range = 2-5°C)

ATTACHMENT D

I. Quality Control Sample Request Form

II. Example of an SOP

PLEASE PRINT OR TYPE.

Form Approved O.M.B. 2000-0139
Exp. 4-30-86

QUALITY CONTROL SAMPLE REQUEST

Name _____ Telephone _____

Company _____

Laboratory _____

Address _____

City _____ State _____ Zip Code _____

Approval of Laboratory Director _____

Please indicate Programs for which QC samples are requested: ☐ Ambient Monitoring
☐ Drinking Water ☐ Wastewater ☐ Toxics (TSCA) ☐ Solid Waste/Hazardous Wastes (RCRA)

WATER QUALITY/WATER POLLUTION SAMPLES

_____ Demand
EPA/API Reference Oils
_____ Arabian Light Crude
_____ Prudhoe Bay Crude
_____ South Louisiana Crude
_____ No. 2 Fuel (high arom.)
_____ No. 6 Fuel (high visc.) Bunker C
_____ LAS
_____ Mineral
_____ Mun. Digested Sludge
_____ Nutrients
_____ Oil & Grease
_____ Pesticides in Fish
_____ PCBs in Fish
_____ PCBs in Sediments
_____ Phenols (4AAP Method)
_____ Residues
_____ Other _____

PCBs in Oils
_____ Aro. 1016 in Capac.
_____ Aro. 1016 in Hydraul.
_____ Aro. 1016 in Trans.
_____ Aro. 1242 in Capac.
_____ Aro. 1242 in Hydraul.
_____ Aro. 1242 in Trans.
_____ Aro. 1254 in Capac.
_____ Aro. 1254 in Hydraul.
_____ Aro. 1254 in Trans.
_____ Aro. 1260 in Capac.
_____ Aro. 1260 in Hydraul.
_____ Aro. 1260 in Trans.
_____ Trace Metals WP - I
_____ Trace Metals WP - II
_____ Trace Metals WP - III
_____ Trace Metals in Fish
_____ Volatile Organics
_____ Other _____

WATER SUPPLY SAMPLES

_____ WS Corrosivity/Sodium
_____ WS Herbicides
_____ WS Nitrate/Fluoride
_____ WS Chl. Hyd. Pest. I
_____ WS Chl. Hyd. Pest. II
_____ WS Res. Free Chlorine
_____ WS Temik
_____ WS Trace Metals
_____ WS Trihalomethanes
_____ WS Turbidity
_____ Other _____
_____ Other _____

PRIORITY POLLUTANTS/HAZARDOUS WASTES/TOXIC CHEMICALS

_____ n-Alkanes
_____ Aromatic Purgeables
_____ Chlorinated Hydrocarbons
_____ Chl. Hyd. Pest. WP - I
_____ Chl. Hyd. Pest. WP - II
_____ Chl. Hyd. Pest. WP - III
_____ Cyanide
_____ Dichlorobenzenes
_____ EP Metals
_____ GC/MS Acids
_____ GC/MS Base Neutrals - I
_____ GC/MS Base Neutrals - II
_____ GC/MS Base Neutrals - III
_____ GC/MS Pesticides - I
_____ GC/MS Pesticides - II
_____ GC/MS Purgeables - I
_____ GC/MS Purgeables - II
_____ GC/MS Purgeables - III
_____ GC/MS Purgeables - IV

_____ Haloethers
_____ Halo. Purgeables - I
_____ Nitroaro. & Isophorone
PCBs (specific Aroclors)
_____ Aroclor 1016
_____ Aroclor 1221
_____ Aroclor 1232
_____ Aroclor 1242
_____ Aroclor 1248
_____ Aroclor 1254
_____ Aroclor 1260
_____ Aroclor 1262
_____ Phenols (GC)
_____ Phthalate Esters
_____ Polynuclear Aromatics I
_____ Polynuclear Aromatics II
_____ Polynuclear Aro. SRM 1647
_____ Other _____
_____ Other _____

BIOLOGICAL SAMPLES

_____ Chlorophyll Fluoro.
_____ Chlorophyll Spectro.
_____ Phytoplankton
_____ Simulated Plankton
_____ Other _____
_____ Other _____

DATE REQUESTED: _____ DATE SHIPPED: _____

EPA-360 (Cin) (Rev. 6/83, Pt. 1)

APPENDIX D-II

Example of a SOP

Sampling for Sulfide

The following procedure is recommended for collecting samples for sulfide analysis:

1. Have reagent-grade zinc acetate and 1N NaOH available in the field.

2. Add 2 g of reagent-grade zinc acetate to a 100-ml polyethylene bottle.

3. Measure the pH of the sample (see Korte and Ealey, 1983).

4. Collect the sample by flowing it through the filter holder and directly into the sample bottle as described previously. If the sample pH is >7, fill sample bottle to top and close tightly.

5. If the sample pH is <7, neutralize with NaOH solution. The final pH should be >7.

6. Store sample away from natural light, and analyze as soon as possible.

ATTACHMENT E

DRAFT OUTLINE OF ITEMS TO BE ADDRESSED IN THE QUALITY ASSURANCE PROJECT PLAN FOR THE NATIONAL PESTICIDE SURVEY

QUALITY ASSURANCE PROJECT PLAN GROUND WATER SUPPLY SURVEY

FINAL REPORT -- DETERMINATION OF THE QUALITY OF GROUND WATER SUPPLIES

DRAFT OUTLINE OF ITEMS TO BE ADDRESSED

IN THE

QUALITY ASSURANCE PROJECT PLAN

FOR THE

NATIONAL PESTICIDE SURVEY

By

Task Group Leaders

Office of Pesticide Programs
and
Office of Drinking Water

OPP PROJECT NUMBER _____

ODW PROJECT NUMBER _____

PROJECT PERIOD _____

APPROVALS:

Director, Hazard Evaluation Division, OPP ?

_____ DATE _____

Quality Assurance Officer, OPP:

_____ DATE _____

Director, Criteria and Standards Division, ODW ?

_____ DATE _____

Quality Assurance Officer, ODW:

_____ DATE _____

SECTION 2

TABLE OF CONTENTS

DISTRIBUTION

Steering Committe for the NPS:

Stuart Cohen (OPP), Co-chairman
Arthur Perler (ODW), Co-chariman
Peter Kuch (OPP)
George Denning (ODW)
Herbert Brass (ODW)

Task Group Chairpersons for the NPS:

Stuart Cohen (OPP): Analyte Selection, Geophysical Characterization
Peter Kuch (OPP): Pesticide Usage Information
George Denning (ODW): Sample Sites Location, OMB Submission
William Coniglio (ODW): Occurrence Data
Kris Khanna (ODW): Health Advisories
John Trax (ODW): State Liaison
Herbert Brass (ODW): Analytical Methods and Sampling, Analytical Contractor Selection and Management
Irwin Pomerantz (ODW): Quality Assurance Project Plan
Elizabeth Leovey (OPP): Quality Assurance Project Plan
James Westrick (ODW): Survey Sampling, Data Handling

HED Ground Water Team:

David Severn (OPP)
Gary Ballard (OPP)
Thomas Dixon (OPP)
Paul Price (OPP)
Patricia Ott (OPP)
Elizabeth Leovey (OPP)
James Conlon (ODW)
Irwin Pomerantz (ODW)

Joseph Cotruvo (ODW)

Edward Ohanian (ODW)

Others ???

SECTION 3

PROJECT DESCRIPTION

3.1 Data Quality Objectives for the Project

A summary of the statement of the Data Quality Objectives (DQOs) for the National Pesticide Survey (NPS) should be in this section. The DQO statement includes:

- Statement of Project Objectives (intended use of the data)
- Design of the Data Collection Scheme (selection of analytes, of types of samples, of sites, etc.)
- Statement of the Data Quality Objectives (precision, accuracy, representativeness, comparability, completeness in relation to the data collection plan)

3.2 Quality Assurance Project Plan for the Project

Development of the DQO statement precedes the development of a QA Project Plan. After decisions are made about project objectives, project design, and data collection quality objectives, plans can be made to conduct the project in a manner to assure that the collected data does meet the stated needs.

3.3 Outline of the QA Project Plan for the NPS

The following outline of issues/procedures that need to be addressed in order to plan for the conduct of the NPS was developed according to the EPA QAMS Guidelines (QAMS-005/80) and the recent experience of the Office of Drinking Water in planning and conducting the National Inorganics and

Radionuclides Survey (NIRS). It is to be reviewed by ODW/OPP Managers, Task Group Chairpersons, HED Ground Water Team, and QA personnel for clarity, accuracy and completeness. The final outline will include their input and will serve as a comprehensive check list for those who plan the operational phases of the project.

3.4 Documentation of the QA Project Plan for the NPS

EPA Quality Assurance Policy requires documentation of the QA plans for environmental data collection projects, and the identification of the key persons who will be responsible for the associated activities. The QAMS-005/80 format includes the various activities that require planning. Documentation of the plans can be in various forms.

3.4.1 Direct Presentation

Information about the planned conduct of an activity can be presented in the text of the QA Project Plan.

3.4.2 Reference to Work Plan Documents

Presentation of information in a Project Work Plan document can be referenced in the applicable section of the master QA Project Plan. The Work Plan document should be readily available in a permanent file of survey records, through a designated custodian. The cover page of the document should be appended to the plan to facilitate retrieval. The reference in the master QA plan must be very clear (page number and location in the work plan).

Additionally, a "QA Project Plan locator page" should be inserted at the beginning of the Work Plan document to assure traceability of the applicable section. Appendix A, (Section) "6.0 Quality Assurance Project Plans Versus Project Work Plans" from the QAMS-005/80 Guidelines, contains information about relating project planning documents to sections in a master QA Project Plan.

3.4.3 References to Standard Operating Procedures (SOPs)

Presentation of information in an SOP document can be referenced in the applicable section of the master QA Project Plan. The SOP should be readily available in a permanent file of survey records, through a designated custodian. The cover page should be appended to the plan to facilitate locating/retrieving it in the file of survey records. Appendix B, "Standard Operating Procedures," contains information about relating SOPs to sections in a master QA Project Plan.

SECTION 4

PROJECT ORGANIZATION AND RESPONSIBILITIES

This section should present the roles of the Office of Pesticide Programs and the Office of Drinking Water for this project. It should include the roles of the Divisions and/or Branches and/or groups within each Office that have been assigned key responsibilities, and also the functions of QA personnel in each Office. Names of Directors, Chiefs, Group Chairpersons, and QA Officers should appear with their respective organizational listings. Tables or Charts should be developed to show line authority for the conduct of the project.

SECTION 5

QA OBJECTIVES FOR MEASUREMENT DATA

This section addresses the analytical methods selected to measure the analytes of interest, the minimum reporting limits to be used for analytical results, and the precision, accuracy, comparability, representativeness and completeness objectives for the measurement data to be generated during the survey. Following is an outline of issues to be addressed/information to be obtained for these aspects of project planning.

5.1 Methodology

- Criteria used to select methodology for the analytes chosen during the development of the Data Quality Objectives (DQOs) for the NPS.
- Status of selected methods as standard or non-standard for pesticides in water or in drinking water.
- Generation of precision and accuracy data for non-standard or non-approved methods may be required so the EMSL-CI Equivalency Staff can statistically compare the new method to an accepted method. If a totally new method is required for any NPS analytes, the criteria for acceptable precision and accuracy needs to be set. The precision and accuracy objectives stated in the DQOs for the NPS can serve as a guideline to needs.
- Tables for Section 5 should include a listing of the types of methodology to be used, the analytes to be measured with each type,

the source of each method and its (numerical) identification in the referenced source. An example format is shown in Table 5.1.

5.2 Minimum Reporting Limits

- Until survey analysts can generate minimum report limits, the method statements of detection limits might be used as guideline analytical information for survey designers.
- Prior to the survey, participating analysts should generate the minimum reporting limits they can achieve for survey analytes with the selected methodology and the equipment they will use during the survey. (All the NIRS analysts used the procedure in Appendix A of EPA-600/4-82-057, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.")
- Minimum reporting limits for each analyte are included in the format shown in Table 5.1.

5.3 Precision and Accuracy

- Until survey analysts can generate precision and accuracy data, the method statements of precision and accuracy might be used as guideline analytical information for survey designers.
- Prior to the survey, participating analysts should analyze standard solutions to generate precision and accuracy data, and calculate statistics to indicate the quality of data they can achieve for survey analytes with the selected methodology and the equipment they will

use during the survey. The solutions should undergo any pre-treatments (e.g., concentration procedures) that are planned for survey samples. The concentrations of the standard solutions used to generate the data should be reported and should be at the level expected in survey samples. Estimates of expected concentrations might be available from survey designers.

- At least one concentration was analyzed on seven different days by NIRS analysts. For most types of analyses, two concentration levels were analyzed and reported. Survey planners designated the statistics to be calculated. The Table 5.1 format includes precision and accuracy statistics and the concentration(s) of the standard solution(s) used to generate the data for each analyte.

5.4 Comparability

5.4.1 Comparable Application of Selected Methodology

- Standard Operating Procedures (SOPs) Required and Reviewed (See Appendix B)
  - Any deviations from a selected method should be known.
  - If more than one laboratory is using a method, significant differences can be resolved.
- Precision and Accuracy Data Required
  - Serves as a check on acceptable application of analytical method.

5.4.2 Comparable Generation of Criteria Data Prior to Survey

All analysts should use the same procedures to generate data and to calculate minimum reporting limits and precision and accuracy statistics, regardless of the type of analytical method used.

5.4.3 Comparable Pre-Treatments of Samples

- Familiarity with the methodologies and review of the SOPs from the laboratories will help identify issues about pre-treatments.
- If a pre-treatment is presented as an option in any of the analytical procedures, it may be possible to establish a protocol to minimize analytical time, to ensure a consistent response to the variant, and to provide for the treatment only as necessary.
- Data handlers need to be alerted about segregating data representing treated samples from data reported for non-treated samples for the same analyte(s).
- Pre-treatments conducted by more than one laboratory should be conducted in a comparable manner. Review of the SOPs and, to some extent, comparison of the precision and accuracy data generated from pre-treated solutions by the laboratories can provide a basis for planning/ensuring comparability.

5.4.4 Comparable Spiking Concentrations

- Since the amount of spike used affects the magnitude of a subsequent percent recovery calculation, standardization of the

amount that will be used by the laboratories for survey samples should be established. This will provide a comparable basis for using the recovery data to characterize the quality of survey data at the end of the project.

- NIRS analysts report detailed information about spiking operations. An example of the bench sheet for reporting the information is in Table 5.2.

5.4.5 Comparable Acquisition of Reported Data

The data user should be informed about how a reported analytical result was obtained. Laboratory SOPs should include this information and it should be included in reports of the data to the user. Is the result routinely:

- from one analysis of one sample?
- an average from one analysis each of field replicates?
- an average from one analysis each of two or more extracts from one sample?
- an average of two or more quantifications (e.g., GC runs) of aliquots from one processed sample?
- or other possibilities, depending on the nature of the analysis?

5.4.6 Comparable Reporting Standards

- Identification of the type of data if some is produced from pre-treated samples and some is not for the same analyte.
- Units to be used.

- Significant figures to be reported.
- Correction factors may be an issue. If so, should they be reported with the raw data or be applied prior to reporting?
- Other issues pertinent to the methodology to be used.

5.5 Representativeness During Analytical Operations

Analysts are responsible for ensuring that they use a representative aliquot of any sample(s) they analyze.

5.6 Completeness of Valid Data Obtained

Participating analysts should submit their estimate of the percentage of samples they receive for which they can obtain valid data. Estimates should be based on their previous experience in conducting the analyses they will perform on survey samples.

TABLE 5.1

INORGANICS*

Parameter and EPA Methodology[a]	Minimum Reporting Limit (mg/L)[b]	Conc. (mg/L) for P&A Statistics[c]	Precision (% RSD)[d]	Accuracy (% RE)[e]
FOUR ELEMENTS, Atomic Absorption-Furnace Technique:				
Arsenic (206.2)				
Cadmium (213.2)				
Lead (239.2)				
Selenium (270.2)				
ONE ELEMENT, Atomic Absorption-Cold Vapor Technique:				
Mercury, Total (245.1)				
THIRTY-TWO ELEMENTS AND SILICA, Inductively Coupled Plasma-Atomic Emission Spectrometry:				
Aluminum (200.7)				
Antimony (200.7)				
Barium (200.7)				
Beryllium (200.7)				

*
Footnotes for Table 5.1 are at the end of Table 5.2.

TABLE 5.2

SAMPLE # _____

Spiked
Data

	Arsenic	Selenium	Lead	Cadmium
Analyst				
Date of Analysis				
Concentration of Unspiked Sample mg/L				
Spike Volume				
Spike Concentration				
Concentration Sample Plus Spike mg/L				
Concentration of Spiked Sample Found				
Volume of Sample				
Calculated % Recovery				

Date Reviewed by: Date:

Additional Comments:

SECTION 6

SAMPLING PROCEDURES

6.1 Sites

A description of the criteria used to select sampling sites. If this is included in Section 3, that section can be referenced.

6.2 Type of Samples

Grab? Raw? Finished? Ground? Surface?

6.3 Number of Samples Per Site

Survey samples required from each site, including any duplicates required for individual analytical methods.

6.4 Collection of Duplicate Samples

The rate of collection and procedure to select sites for collection of duplicate samples to be analyzed for quality control purposes. (If the procedure to select the sites is in Section 3, that section can be referenced.)

6.5 Sample Collectors

- Who will collect the samples?
- How will sample collectors be "recruited"?
- Do collectors need special training?

6.6 Scheduling System for Sample Collection

- The analytical capacities of participating laboratories and the allowable holding times for samples govern the rate at which samples should be scheduled for collection.
- A system for control of the rate should be planned.

6.7 Sampling Materials

- Required supplies: containers, preservation equipment for collectors, preservation chemicals, etc.
- Required preparation of containers or equipment (e.g., special cleaning, rinses, etc.)
- Pre-survey checks on quality of supplies.

6.8 Field Blanks

- Preparation and rate of usage.
- Any treatments to be done in the field (e.g., addition of a preservative).

6.9 Shipment of Sampling Materials

- Contents of sampling kits
- Destination
- Any arrangements for second-party distribution to collectors

6.10 Collection Procedures

- Reference the source(s) of the description(s) of collection procedure(s):
  - Analytical Method
  - EPA 600/4-82-029, "Handbook for Sampling and Sample Preservation of Water and Wastewater"
  - EPA 600/8-80-038, "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples"
  - ASTM Annual Book of Standards Part 31, D3370-76 "Standard Practices for Sampling Water"
  - Other

- If a non-standard procedure is to be used, it should be described either in an Appendix to the Plan or in Task Group records that are readily available in a permanent file of survey records, through a designated custodian. In the latter case, a traceable reference to the Task Group record is sufficient for this item in the Plan. (See Appendix A).
- Pre-survey tests of the comparability of collection procedures in cases where alternatives are expedient or when a non-standard procedure is under consideration.
- Development of a "Sampling Instructions" packet for sample collectors.

6.11 Preservation

- Chemical additions required for analytes of interest.
- Department of Transportation regulations may affect plans or require a waiver for shipment of preservatives or preserved samples.
- Icing requirements.

6.12 Transport of Samples and Field Blanks to Laboratories

- Mode (holding times may affect choice).
- Information and shipping materials needed by field personnel.
- Arrangements for payment of shipping charges.
- Decision on destination - All sent to TSD for distribution or some/all sent directly from the field to the analytical laboratories?

6.13 Checks or Treatments of Samples Prior to Distribution to Analysts

- There may be a need to check some common condition of samples, e.g., the pH if samples are acidified in the field. In this case, plans could be made for a central laboratory to check the condition and keep records for all the samples, or else for designated persons in each analytical laboratory to check and keep records.
- Checks (e.g., for residual chlorine) or pre-treatments that are only required for some types of analyses would probably be done in the laboratory responsible for those analyses. These method-specific checks or pre-treatments should be discussed elsewhere (Section 9) in the Plan.

6.14 Storage of Samples and Field Blanks Prior to Analysis

- Any special conditions required.

6.15 Holding Times

- Maximum holding times according to analytes from time of collection to beginning of analyses.

6.16 Disposal of Samples

- Who will be responsible for disposal?
- Who will be responsible for releasing samples for disposal?
- Are special techniques required for disposal of pesticide samples?
- Are containers to be returned to TSD?

SECTION 7

SAMPLE CUSTODY

If samples are needed for legal purposes (e.g., enforcement), "chain-of-custody" procedures as defined by the Office of Enforcement should be planned. A manual describing the required procedures is available from that Office. Survey designers should specify if the procedures are necessary.

For any project, plans need to be made to document the identity of each sample and to keep records that describe each sample and trace each through the collection-to-disposal processes presented in Section 6, "Sampling Procedures." Persons should be designated to be responsible for the samples, to keep suitable records about the samples while in their custody, and to move them along to the next process. All records should be made in ink and, whenever feasible, kept in permanently-bound books. Dates and signatures should be required.

Survey planners should also devise a system for tracking the entire sample stream during the project so they can arrange a steady flow of samples to the laboratories within holding times, and ensure the timely completion of the project.

7.1 Field Operations

- System and person(s) responsible for record-keeping about the sources of collected samples. If information is required from the private sector (plant manager, well owner, etc.), OMB approval is probably required.

- System for sample identification.
- System for record-keeping by the sample collector about sample collection information and, as appropriate, field measurement and preservation information. Signature of sample collector should be required.
- System and person(s) responsible for any transport records that need to be kept, or if signatures are required.

7.2 Laboratory Operations

- Designation of person(s) to receive samples and log them in. Specify information to be recorded.
- System and person(s) responsible for re-labeling audit samples (field blanks, duplicates, blinds) if they are to be disguised as regular survey samples. Include a system to notify handlers of survey data so they can distinguish audit data from survey sample data.
- System, person(s) responsible, and record-keeping for any checks on some condition common to all samples (e.g., pH), if required, and for reporting the results to analysts, if necessary.
- System, person(s) responsible, and record-keeping for any storage of samples and/or for their distribution to analysts or to other laboratories. If samples are distributed to other laboratories, each should have a Sample Custodian who maintains a log of samples received and is responsible for their distribution to analysts and for their final deposition.

- Analysts are responsible for maintaining traceable records about any treatments of a sample while it is in their custody.
- System, person(s) responsible, and record-keeping for storage/disposal of any unused sample matter and for sample containers and any other sampling equipment.

7.3 Overall Sample Tracking System

- A system for tracking sample-handling operations from the shipment of collection kits through disposal of analyzed samples is highly recommended. Such a system is in use for the NIRS. It requires input from key survey personnel, and has proven to be very effective in controlling the rate of sample collection according to the analytical capacities of participating laboratories, in assuring that back-logged samples can be analyzed within holding times, in keeping laboratory supervisors informed about the progress of their analysts in processing samples, and in presenting reports to ODW management about the status of survey operations.
- Figure 7.1 is an example of the monthly progress report for NIRS that is sent to all analysts, laboratory chiefs and QA officers, and TSD survey managers. It communicates information about shipment of sample kits, the number of samples received to date by each laboratory, the number of samples processed by each laboratory through data transmittal to TSD, and the sample receipts anticipated for the next month.

- Figure 16.1 is an example of a TSD quarterly report on the NIRS that includes summary statistics about sampling operations.

7.4 Permanent Filing of Sample Handling Records

- All records should be made in ink and, whenever feasible, kept in permanently-bound books.
- Record books should be filed along with other survey records and identified in a manner to facilitate their later use, if required. References to the location of analysts' notebooks may be used if participating laboratories maintain their own permanent file of analytical records.
- A person should be identified in the final project report as custodian of the records, in case access to the records is needed at some future time.

FIGURE 7.1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

CINCINNATI, OHIO 45268

Technical Support Division
Office of Drinking Water
OFFICE OF WATER
26 W. St. Clair Street, Cincinnati, OH 45268

DATE: August 16, 1984

SUBJECT: First Monthly Progress Report of the NIRS

FROM: Edward M. Glick, Chemist EMG
Drinking Water Quality Assessment Branch

TO: Addressees

This is the first monthly progress report (of many) for the NIR survey. This report will hopefully keep you aware of the status of sample shipments and reciepts on a monthly basis.

The following table will detail the current status of the survey relating to the shipment/receipt of samples and the analytical data that has been submitted for verification and input into the computer. The effective date of this memo is 8-6-84.

LABORATORY	SAMPLES RECEIVED	DATA RECEIVED	DATA VALIDATED
TSD	27	11	0
MERL	27	0	0
EMSL-IAS-ICP	25	0	0
EMSL-ES-ICP	2	0	0
EMSL-IAS-RAD	27	0	0
EERF-RAD	0	0	0

To date, 91 shipment sets have been sent to the states for later sampling. The anticipated sample load for the month of August is 29. The anticipated sample load for the month of September, at this time, is 65.

As always, if I can be of assistance, don't hesitate to call or stop by.

Addressees:

SECTION 8

CALIBRATION PROCEDURES AND FREQUENCY

The participating laboratory(ies) should provide information about the calibration of any piece of equipment that will be used for measurement procedures during a project.

8.1 Type of Information to be Provided

- Information about any solutions that will be used to calibrate or check the performance of the equipment (e.g., calibration solutions, internal standard spiking solutions, equipment performance check solutions). Traceability to a recognized source of standard materials is also of interest.
- A description of the procedure(s) that will be used to perform the calibration or performance check.
- The criteria or the planned frequency for recalibrations.

8.2 Location of the Information

A written Standard Operating Procedure (SOP) that includes the cited information for equipment that will be used may be referenced rather than repeating the information here. Each referenced SOP should be:

- the one that will be used during the project;
- readily available in a permanent file of survey records, through a designated custodian.

See Appendix B, "Standard Operating Procedures."

SECTION 9

ANALYTICAL METHODS

Although standard measurement methods are usually selected for a data collection project, they often contain options because of sample matrix variables, the availability of alternative equipment, etc. Some selected methodology may be for state-of-the-art analyses that are subject to continuous analyst improvement. A copy of a selected method, then, cannot serve as an unequivocal description of how an analyst will conduct an analysis on project samples. The participating laboratory(ies) should provide information about how each analyte or characteristic (e.g., pH) will be measured.

9.1 Type of Information to be Provided

- Information about reagents that will be used.
- Identification of equipment that will be used.
- The stepwise procedure for any pre-treatment of samples (e.g., extraction, digestion).
- The stepwise procedure that the analyst will use for measurements on project samples, including any pre-analysis checks (e.g., for residual chlorine) that will be made.
- Criteria that will be used if judgements about optional steps need to be made.

9.2 Location of the Information

A written Standard Operating Procedure (SOP) that includes the cited information for an analyte or characteristic that will be measured may be referenced rather than repeating the information here. Each referenced SOP should be:

- the one that will be used during the project;
- readily available in a permanent file of survey records, through a designated custodian.

See Appendix B, "Standard Operating Procedures."

SECTION 10

DATA REDUCTION, VALIDATION AND REPORTING

Survey planners need to develop processing and management systems for each type of data required for a project.

10.1 Types of Data That Require Processing and Management

10.1.1 Data Collected Prior to Collection/Analyses of Project Samples

- Measurements required to plan the design of the sampling program.
- Measurements for procedure or method equivalency checks for field and/or analytical operations.
- Measurements to establish minimum reporting limits for measurements on project samples.
- Measurements to establish precision and accuracy capabilities for measurements on project samples.

10.1.2 Sample Background Data

- Information about the source of the sample (e.g., plant treatments, well information).

10.1.3 Sample Collection Data

- Results from any measurements made in the field.
- Outcomes from adding preservatives.
- Information specific to the project.

10.1.4 Sample Treatment Data

- Measurements made because of pre-analytical checks or treatments of samples.

10.1.5 Analytical Data for Samples

Data handling (reduction, validation and reporting) procedures for analytical results are usually documented in a laboratory's Standard Operating Procedure (SOP) for each measurement method and/or in their Laboratory QA Program statement. These documents may be referenced for analytical data rather than repeating the information in this section. See Appendix B, "Standard Operating Procedures."

10.1.6 Analytical Data for QC Check Samples

- Data handling procedures within a laboratory for results from internal QC check samples are usually documented in an SOP for a measurement method. See the above item about referencing SOPs.
- Results from internal QC check samples reported by laboratories to external project managers.
- Results reported for audit QC check samples provided by external sources (e.g., EPA performance evaluation samples; blanks, duplicates or blinds provided by project managers to look like "regular" samples).

10.2 Data Handling for Each Type of Data

10.2.1 Reduction of the Data

- Standard for significant figures.
- Standard procedure for rounding-off operations.
- Equations to calculate values from data (e.g., concentration of an analyte).
- Any other treatments specific to the type of data.

10.2.2 Validation of the Data

- Criteria or cross-checks to validate the integrity of the data during collection, transfer, reduction, storage and reporting operations.
- System to ensure that data obtained/generated from non-uniform procedures is segregated from "regular" data. An example is tagging data from a digested sample if data for the analyte is usually obtained from non-digested samples.
- Methods to screen data for conformity to specified standards (e.g., significant figures, units to be used for reporting).
- System to check for completeness of data.
- Methods to identify and treat outliers, inconsistent data, etc.
- System for originators of data to check interim records or outputs for error.

- ° System of periodic audits of data bases for error and the cause of the error.
- ° Identification of the person(s) responsible for any of the planned validations.

10.2.3 Reporting of the Data

- ° Identification of reports to be made.
  - Immediate reports to appropriate officials when analytical results exceed established "alert" criteria (e.g., MCLs, Health Advisory action levels).
  - Interim reports of project data to management.
  - Reports to officials associated with the sites sampled during the survey.
  - Final report of data from the project.
  - Other reports appropriate to the project.
- ° Formats for reporting the data to ensure that uniform and complete information is reported.
- ° Identification of the person(s) who are to prepare reports.
- ° Identification of the person(s) who are to receive reports.

10.3 Managing the Data Flow for a Project

The overall scheme of data flow for a project should be planned starting with its collectors or generators through its receipt by the data user. (A flow chart is usually needed.)

- ° Include the names of key individuals who reduce the data, validate the data or deal with the data in any manner.
- ° Completely identify computers and data bases that will be used.

SECTION 11

INTERNAL QUALITY CONTROL CHECKS

For each measurement method that will be used during a project, the participating laboratory(ies) should provide information about the internal quality control checks that the analyst will apply to check the quality of the measurements made on project samples.

11.1 Checks That Might be Planned

- Analysis of various types of blanks or treated sample aliquots to monitor for interferences.
- Analysis of duplicate aliquots from one sample to assess precision.
- Analysis of QC samples, laboratory control standards, spiked samples, etc., to assess accuracy.
- Other checks appropriate for monitoring variables pertinent to a particular measurement method.

11.2 Information to be Provided for Each Check

- The purpose of the check.
- The planned frequency of the check.
- As applicable, the source and/or the concentration of the solution used.
- The criteria for acceptability of results of the check.
- The course of action if acceptance criteria are not met (corrective action in the laboratory).

- The system for reporting results from the checks to laboratory supervisors (QC reports to laboratory management).
- The location of records about the checks.

11.3 Location of the Information

A written Standard Operating Procedure (SOP) that includes the cited information for a measurement method that will be used may be referenced rather than repeating the information here. Each referenced SOP should be:

- the one that will be used during the project;
- readily available in a permanent file of survey records, through a designated custodian.

See Appendix B, "Standard Operating Procedures."

SECTION 12

PERFORMANCE AND SYSTEM AUDITS

Survey planners need to provide audit materials and/or the resources to evaluate the performance of critical project operations. (Section 14 deals with procedures to assess audit data after it is collected.)

12.1 Audits for Field Operations

- Field (shipping) blanks
- Checks on the addition of preservative(s)
- Collection of duplicate samples for analyses, especially if volatile compounds are of interest

12.2 Audits for Analytical Operations

12.2.1 Audit Samples Disguised as Field Samples (Blinds)

- Field (shipping) blanks
- Duplicate samples
- Laboratory-prepared blanks
- Standard solutions from EPA, NBS, etc., sources

12.2.2 Analyses by an Independent Laboratory

- Duplicate samples collected in the field.
- Splits of audit samples provided by survey managers to principal laboratories.

12.2.3 Performance Evaluation Studies

- Participation in EPA Studies or other evaluation programs.

12.3 Audits for Data Management Operations

- Second party audits at any level of operations that include data handling.
- Types of systems that might be checked are listed in Section 10.2.2, "Validation of the Data."

12.4 System Audits

12.4.1 In-house Laboratories

Supervisors and/or QA personnel should conduct system audits as part of the routine QA activities for the laboratory. Types and frequency would be included in the laboratory's QA Program statement. (See Appendix B).

12.4.2 Contract Laboratories

An on-site system audit of the laboratory is usually a pre-award requirement. Additional system audits may be conducted by the project officer during the term of the contract.

SECTION 13

PREVENTIVE MAINTENANCE

Any equipment used for measurement procedures should be subjected to any kind of maintenance that will help assure its continued, quality operation. The participating laboratory(ies) should provide maintenance information for any equipment that will be used for a project.

13.1 Type of Information to be Provided

- Maintenance procedures that will be conducted.
- The person responsible for conducting the maintenance.
- The schedule or frequency of the maintenance.
- Critical spare parts on hand and/or back-up equipment that is available to assure continuous operations.

13.2 Location of the Information

A written Standard Operating Procedure (SOP) or a Laboratory QA Program statement that includes the cited information for equipment that will be used may be referenced rather than repeating the information here. Each referenced SOP or QA Program should be:

- the one that will be used during the project;
- readily available in a permanent file of survey records, through a designated custodian.

See Appendix B, "Standard Operating Procedures."

13.3 Equipment Failures During a Project

- Survey planners should establish a system for the immediate report of significant equipment downtime that becomes necessary during a project. The scheduling of sample collection may need adjustment because of allowable holding times.

SECTION 14

SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

Survey planners need to choose the procedures they will use to assess the precision and accuracy of project data and its completeness in reference to the data collection scheme. Statements for all three of these data quality indicators should accompany any report of data from project samples.

14.1 Types of Data to be Assessed

(Section 10.1 includes subdivisions of these types.)

14.1.1 Data collected prior to the main project.

14.1.2 Data about the sample source.

14.1.3 Data from field operations.

14.1.4 Data from pre-analytical checks or treatments of samples.

14.1.5 Data from analysis or measurements of samples.

14.1.6 Data from QC check and audit samples.

14.2 Types of Assessments

14.2.1 Precision, accuracy and completeness of data.

14.2.2 Other Statistical Treatments

- Tests of significance
- Confidence limits
- Testing for outliers

14.3 Procedures to be Selected

14.3.1 Methods used to gather the data for calculations.

14.3.2 Equations to calculate the assessments.

14.3.3 Standards for significant figures in data used to calculate the assessments.

14.3.4 Standards for significant figures used to report assessment statistics.

SECTION 15

CORRECTIVE ACTION

As decisions are made about the requirements for sampling, analyses, and data handling, plans should be made to provide checks and procedures for corrective action to ensure that activities are conducted as envisioned.

15.1 Elements of Plans for Corrective Action

- What is the standard for acceptable performance? (See 15.2).
- What check can be made?
- Who is responsible for monitoring the system or operation?
- Who needs to know about the problem so it can be corrected (communication chain)?
- What procedure can be used to correct the problem?
- Who is responsible for oversight to assure that the problem is corrected?

15.2 Standards for Common Operations

15.2.1 Sampling Operations

- Collection Techniques
  - Type of sample required
  - Type of analyte of interest
- Rate of Sample Collection
  - Holding times required
  - Laboratory capabilities

- ° Measurements in the field
  - Precision, accuracy, completeness
- ° Addition of Preservatives
  - Outcome required
- ° Transportation
  - Preservation required
  - Holding times
  - Availability of mode
- ° Storage of Samples
  - Preservation condition required

15.2.2 Laboratory Operations

- ° Analyses and Measurements
  - Standard methodology (comparability)
  - Minimum reporting limits
  - Precision, accuracy, completeness. [Laboratory Standard Operating procedures usually include a plan for corrective action based on internal QC checks (see Appendix B). An additional system for external (audit) checks on these standards should be planned by project managers (Section 12).]

15.2.3 Data Management Operations

- Reduction, Validation, Reporting
  - Integrity
  - Comparability (standards for rounding, calculating, etc.)
  - Completeness
  - User needs
- Section 10.2.2 includes checks to be planned for data handling.

SECTION 16

QUALITY ASSURANCE REPORTS TO MANAGEMENT

16.1 Content of Periodic Reports

- Assessment of measurement data in terms of accuracy, precision, and completeness.
- Results of performance audits.
- Results of system audits, as appropriate.
- Significant QA problems and their resolution or, if appropriate, recommended solutions.
- Figure 16.1 is an example copy of a TSD quarterly report on the NIRS.

16.2 Mechanism for Periodic Reports

- How often will reports be made?
- Who prepares the report?
- Who receives the report?

16.3 Content for Final Report on Project

- A separate section on QA should be included in the final report.
- The QA section should include a summary of the data quality information contained in the periodic reports.

FIGURE 16.1

Project 82A: National Inorganics and Radionuclides Survey (NIRS)

Description:

The project is primarily designed to provide, through a national sampling survey, information on the occurrence in drinking water of several radionuclides (especially radium-228) and on gross alpha and beta radiation levels. Radium-228 data will also be used to investigate the feasibility of using a geological model to predict the occurrence of radium-228. In addition to the radionuclide determinations, occurrence information for thirty-seven inorganic species will be gathered. This information is needed to provide sound guidance to the Office of Drinking Water in making regulatory decisions.

Status:

The sampling phase of the survey was started on July 1, 1984. Summary statistics, as of September 22, 1984, describing the current status are presented in Table 1.

Table 1

National Inorganics and Radionuclides Survey
Project Status (as of 9/21/84)

Number of weeks into survey	12
Number of sites sampled	92
Number duplicates received	13
Number field blanks received	1
Total samples received	106
Number sampling kits shipped	>300
Number acid shipments	62
Turn-around documents mailed	294
Turn-around documents returned*	56
Number schedule forms returned by states	29

*New York, which has sampled 48 sites, will be returning turn-around documents at a later time.

2

To date, sampling materials (bottles, cubitainers, shipping containers, instructions, etc.) for over 300 sites have been distributed. This translates into about 25% of sampling materials having been distributed during the first 11% of the project period. No shipments of sampling materials to states have been significantly delayed or lost. Thus, all indications are that there will be no significant problems in the distribution of sampling materials for the NIRS project.

The return of samples to TSD is progressing very well. There have been no samples lost or seriously delayed, and all samples received have been in good condition. All samples received to date have been adequately acidified in the field. Thus, there are no problems anticipated with sample preservation. In addition, no samples have leaked or been lost due to improperly fitting or tightened cubitainer caps. This is probably due in part to the use of the "CAPLUG" insert. One sample leaked slightly due to a small perforation of unknown origin in the cubitainer wall, but sufficient sample remained for analysis.

Several computer programs have been completed which are designed to input, store, and process sampling schedule information. The organization of these programs allow both a historical listing of what happened and a future projection of anticipated sampling. The high priority candidates (i.e., those that are targeted to be sampled in the month or quarter in which the project week falls) are identified and listed for convenience in arranging schedules. These listings have become very valuable in controlling the number of samples that might go astray and/or in quickly resolving problems.

A pair of programs has been developed which permit the generation of data entry screen forms for inputting a wide variety of data. These programs can be used for many different projects and applications including the data entry for the NIRS project.

Cooperation from the states has been excellent and far exceeds expectations. While there are about 15 states that have not yet been in contact with TSD, most of the others have sent back schedule forms or indicated that they were flexible and would be willing to adjust their schedule to accommodate our needs. At this point, there are enough sites scheduled to maintain a relatively uniform sample flow for at least three months.

A status report on the NIRS project has been prepared which contains additional information on the project.

Anticipated Activity:

1. Continue the sampling program, analysis, data entry, and state and regional contacts.

3

2. Continue software development for scheduling and data handling, including development of user documentation for the generalized data entry programs.

3. Continue to monitor the quality assurance of the survey. Specifically, to undertake a study of the quality and completeness of information being returned on NIRS survey forms and to prepare a report describing results, conclusions, and recommendations by December 31, 1984.

J.P. Longtin
J.B. Walasek

6.0 QUALITY ASSURANCE PROJECT PLANS VERSUS PROJECT WORK PLANS

This document provides guidance for the preparation of QA Project Plans and describes 16 components which must be included. Historically, most project managers have routinely included the majority of these 16 elements in their project work plans. In practice, it is frequently difficult to separate important quality assurance and quality control functions and to isolate these functions from technical performance activities. For those projects where this is the case, it is not deemed necessary to replicate the narrative in the Quality Assurance Project Plan section.

In instances where specific QA/QC protocols are addressed as an integral part of the technical work plan, it is only necessary to cite the page number and location in the work plan in the specific subsection designated for this purpose.

It must be stressed, however, that whenever this approach is used a "QA Project Plan locator page" must be inserted into the project work plan immediately following the table of contents. This locator page must list each of the items required for the QA Project Plan and state the section and pages in the project plan where the item is described. If a QA Project Plan item is not applicable to the work plan in question, the words "not applicable" should be inserted next to the appropriate component on the locator page and the reason why this component is not applicable should be briefly stated in the appropriate subsection in the QA Project Plan proper.

FROM: EPA-QAMS Guidelines (QAMS-005/80)

STANDARD OPERATING PROCEDURES

Several sections in the QAMS-005/80 guideline format for QA Project Plans deal with activities that are exclusively part of analytical or measurement activities. These are:

Section 8, Calibration Procedures and Frequency
Section 9, Analytical Procedures
Section 11, Internal Quality Control Checks
Section 13, Preventive Maintenance

Other sections deal with activities that are also conducted as part of either the analytical process or the internal quality control check system for analyses. These are:

Section 10, Data Reduction, Validation, Reporting
Section 14, Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness
Section 15, Corrective Action
Section 16, QA Reports to Management

The information that is cited in the outlines for these eight sections, as required for analytical procedures, is usually included in Standard Operating Procedure (SOP) documents that a laboratory develops for analyses conducted by their staff or for the QA program conducted by the laboratory.

The SOP for an analysis might be a totally original write-up, even though a standard analytical method is addressed. Another approach to SOP documentation is the thorough annotation of a copy of the standard method, with original sections added to document laboratory-specific protocols.

Standard methods usually include sections dealing with:

- Calibrations
- Stepwise Analytical Procedures
- Internal Quality Control Checks
- Data Reduction (calculation of results)

These sections can be annotated by the analyst to describe how the analysis will be conducted for a project.

Additional SOP information that usually requires specific, added input by the analyst or other laboratory personnel is:

- Preventive Maintenance
- Data Validation and Reporting
- Specific Procedures to Assess Data Precision, Accuracy, and Completeness
- Corrective Action
- QA Reports to Management

Some laboratories have these operations standardized and documented in a statement of the laboratory QA Program.

Copies of SOP information should be provided by the participating laboratory(ies) to project managers well before the operational phase of a project. Those responsible for oversight of analytical operations need time to review each SOP in case any changes are required in the operations.

Ideally, each laboratory will have SOPs on file and available when the participation commitment is made. If laboratories are secured by contract, SOP information can be required in the request for proposals by requiring a QA Project Plan on the mandatory "QA Form QAR-C" (copy attached). The type of information that should be included in each section of the submitted plan

is itemized in each corresponding section of this outlined project plan. If the proposer has SOPs that contain the required information, the person can reference the SOPs in the appropriate sections of the project plan and attach the entire SOPs as appendices.

QUALITY ASSURANCE REVIEW FOR EXTRAMURAL PROJECTS

(CONTRACTS)

I. GENERAL INFORMATION

Descriptive Title:

Sponsoring Program Office:

Approximate Dollar Amount:

Duration:

II. THIS CONTRACT REQUIRES ENVIRONMENTAL MEASUREMENTS (If yes, complete form; if no, sign form and submit with procurement request)	Yes	No

---

III. QUALITY ASSURANCE REQUIREMENTS (Projects involving environmental measurements)	Yes	No
a. Submission of a written quality assurance (QA) program plan (commitment of the offeror's management to meet the QA requirements of the scope of work) is to be included in the contract proposal.	____	____
b. Submission of a written QA project plan is to be included in the contract proposal.	____	____
c. A written QA project plan is required as a part of the contract.	____	____
d. Performance on available audit samples or devices shall be required as part of the evaluation criteria (see list on reverse side).	____	____
e. An on-site evaluation of proposer's facilities will be made to ensure that a QA system is operational and exhibits the capability for successful completion of this project (see schedule on reverse side).	____	____
f. QA reports will be required (see schedule on reverse side).		

QA Form QAP-C, Revision No. 1, 1981

IV. DETERMINATION (Projects involving environmental measurements)

Percentage of technical evaluation points assigned to QA _____%

Project Officer estimate of percentage of cost allocated to environmental measurements _____%

Parameter Measured	QC Reference Sampling or Device Available (Yes or No)	Split Samples for Cross-Comparison (Yes or No)	Required for Preaward (Yes or No)	FREQUENCY During Contract

QA System Audits are required: Preaward _____; during contract: _____.

QA Reports are required: With Progress Reports _____: with Final Report ____.

The signatures below verify that the QA requirements have been established.

QA Officer: Project Officer:

Signature Date Signature Date

After signatures, a copy of this form must be included with the Request for Proposal and sent to the Contracts Office and a copy placed on file with the QA Officer.

QA Form QAR-C

QUALITY ASSURANCE PROJECT PLAN

GROUND WATER SUPPLY SURVEY

by

Mary Ann Feige, Quality Assurance Coordinator
and
J. Wayne Mello, Project Engineer

Water Supply Technology Branch
Technical Support Division
Office of Drinking Water
Office of Water
U.S. Environmental Protection Agency
Cincinnati, Ohio

Project Number: FY '81 - 81, FY '82 - 82B, FY '83 - 82B

Project Period: October 1980 - February 1983

APPROVALS:

Branch Chief, WSTB James J. Westrick Date 7/28/83

Branch Chief, DWQRB Herbert J. Brass Date 7/27/83

Division QA Coordinator Audrey Kresner Date 7/27/83

CONTENTS

APPENDICES:

SECTION 1

DISTRIBUTION

James J. Westrick, Chief, WSTB, TSD
J. Wayne Mello, Project Engineer, WSTB, TSD
Herbert J. Brass, Chief, DWQAB, TSD
Robert F. Thomas, Contract Project Officer, DWQAB, TSD
Mary Ann Feige, Quality Assurance Coordinator (until 1/82), TSD
Audrey D. Kroner, Quality Assurance Coordinator (after 1/82), TSD
Lowell A. Van Den Berg, Director, TSD
Irwin Pomerantz, Quality Assurance Officer, ODW

SECTION 2

INTRODUCTION

Volatile organic contaminants (VOCs) are a general category of synthetic organic chemicals which include low molecular weight, volatile halogenated aliphatic and aromatic compounds. Many VOCs are commonly used industrial, commercial, and household solvents which have been detected frequently in ground water supplies. Numerous incidents of contamination of well water by such VOCs as trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, benzene, xylene, etc., have been reported across the country.

Many of the VOCs are adverse to human health in some measure; some VOCs are known or suspected carcinogens. Therefore, the Environmental Protection Agency is considering various regulatory alternatives for limiting public exposure to VOCs in drinking water. In order to develop a sensible, technically sound regulatory posture, the Agency must have a strong base of data on the occurrence of VOCs in drinking water. To supplement the data which have been gathered in previous EPA surveys and various State investigations, the EPA, Office of Drinking Water (ODW), Technical Support Division (TSD), Cincinnati, Ohio, conducted an extensive sampling and analysis program to examine the occurrence of VOCs in drinking water from ground water sources.

The following Quality Assurance Project Plan covering the sampling and measuring activity requirements for the survey is in accordance with EPA policy requirements that each office or laboratory generating environmental data has the responsibility to implement minimum procedures which assure that the precision, accuracy, completeness, representativeness, and comparability of its data are known and documented.

SECTION 3

PROJECT DESCRIPTION

The Technical Support Division (TSD), Office of Drinking Water, conducted a national survey of water supplies using ground water sources. Samples from approximately 1,000 ground water systems were to be analyzed to determine total organic carbon (TOC) levels and the presence of purgeable volatile organic chemicals (VOCs). The major objectives of the survey were:

(1) to provide data on the frequency and magnitude of occurrence of VOCs in systems using ground water; and

(2) to provide the states information on systems suspected of being contaminated by purgeable VOCs.

The survey was divided into two parts. A random sample of 500 systems was selected for sampling from the national inventory of public water systems. In the second part of the survey, the states were asked to select 500 suspect supplies for inclusion in the program (see Appendix A).

Information packages were distributed to all the states and Puerto Rico. All regions and participating states were contacted to discuss and schedule the sampling efforts. TSD supplied sampling kits and arranged with the regions, states or local utilities to have the samples collected. Appendix B is a copy of the instructions for sampling and shipping.

Samples were analyzed for purgeable halocarbons and aromatics and for total organic carbon. Residual chlorine was also measured in samples from chlorinated supplies to provide information supplemental to the trihalomethane data. The analyses were conducted by SRI International under contract #68-03-3031, "Determination of the Water Quality of Ground Water

Supplies" (Appendix C). TSD analyzed some duplicate samples for quality control, and supplied the contractor with blind samples, shipping blanks and standards for quality assurance purposes.

TSD prepared periodic reports of data for submission to the cognizant regional offices, states, and local utilities.

EPA response on samples containing VOCs depended on the risk associated with the level of contamination (see Appendix A). This ranged from simply reporting the data to the utility, state and region in periodic reports in the case of very low risk contamination, to immediate reporting to the state and region in the case of high risk levels. TSD personnel were available on a limited basis to assist states and utilities in the investigation of contamination incidents. This assistance was in the form of advice on sampling and analytical procedures, treatment methods, ground water investigation techniques, and analytical assistance. Resampling on request to assist a state was also available on a limited basis during the first phase of the survey.

Selected sites found to be contaminated during the first phase of sampling were resampled. This resample consisted of collecting water samples from the original sample point and at a number of well heads, if possible. The number of resamples was negotiated by the Project Engineer and the state contact person.

At the end of the project, TSD conducted appropriate statistical analyses of the data and prepared a summary report for submittal to the Director, Office of Drinking Water. The contractor prepared a final report on the analytical and quality control program for the survey (Appendix D).

SECTION 4

PROJECT ORGANIZATION AND RESPONSIBILITIES

A schematic showing project organization and line authority is shown in Figure 1.

The Ground Water Supply Survey was conducted under the c·erall management of Lowell Van Den Berg, Director, Technical Support Division. This management function consisted of coordination of the efforts of various Divisions of the Office of Drinking Water and reporting progress to the Director, Office of Drinking Water.

James Westrick, Chief, Water Supply Technology Branch (WSTB), was responsible for the work performed by WSTB staff in conducting the survey and for preparing the final reports. Wayne Mello, Project Engineer (WSTB), was responsible for scheduling the sampling with state personnel, supplying sampling materials, receiving samples, shipping samples to the analytical contractor, preparing periodic reports of the data for distribution to participating regions, states, and utilities, responding immediately to evidence of serious contamination (including prompt notification and any resampling), conducting statistical analyses of the data, and assisting in the preparation of the final report and papers for presentation and publication in the technical literature.

Herbert Brass, Chief, Drinking Water Quality Assessment Branch (DWQAB), was responsible for the work performed by DWQAB staff during the conduct of the survey. Robert Thomas, Contract Project Officer (DWQAB), was responsible for overseeing the contract laboratory activities to assure the quality of the analytical data. The chemists (DWQAB) who prepared blind samples and conducted the analyses of quality control check samples upon direction by the Contract Project Officer were:

Michael Weisner - preparation of blind samples at beginning of survey; analysis of purgeable halocarbons and aromatics

Candy Miller - analysis of purgeable halocarbons and aromatics
Robert Streicher - analysis of purgeable halocarbons and aromatics
Kerry Sweeney - analysis of total organic carbon

Richard Johnston and Waymon Wallace (WSTB) prepared the shipping blanks.

Barbara Kingsley, Contract Project Manager for SRI, International, was directly responsible for all analytical data generated for survey samples, for reporting (monthly) technical progress and quality control results, for reporting sample data, and for preparing a final report on the analytical and quality control program of SRI, International for the survey. The chemists (SRI, International) who conducted the analyses of survey samples and quality control check samples were:

Barbara Kingsley - analysis of purgeable halocarbons and aromatics
Christina Gin Avanzino - analysis of purgeable halocarbons and aromatics
Curtis Beeman - confirmatory analysis of purgeable halocarbons and aromatics
Robert Emerson - analysis of total organic carbon and residual chlorine

The Office of Program Development and Evaluation had the responsibility for generating and updating the random sample and for providing input to the statistical analysis phase of the project. The Health Effects Branch of the Criteria and Standards Division provided health effects guidance to regions and states upon the discovery during this survey of a serious contamination problem.

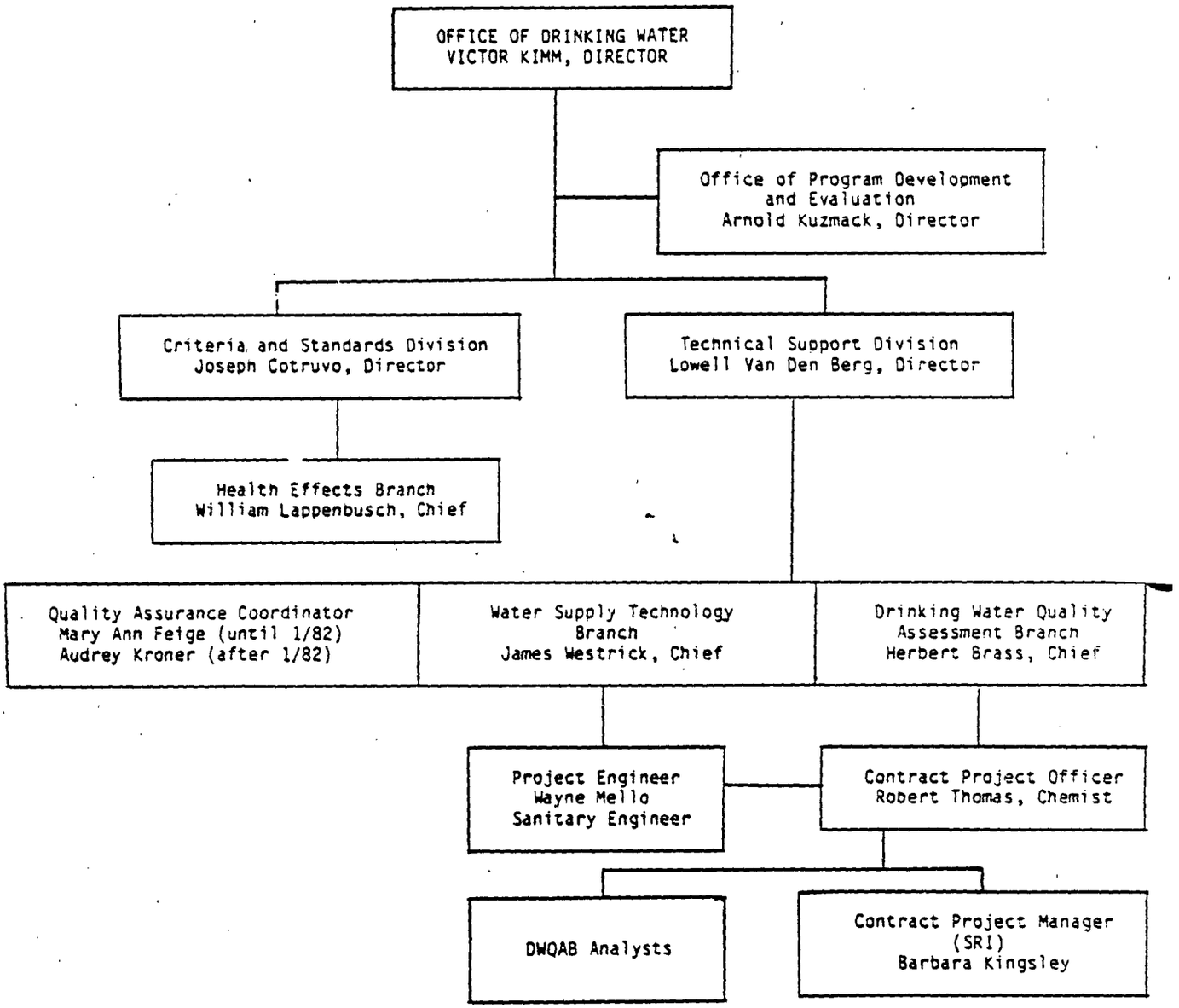


Figure 1. Project Organization

SECTION 5

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

A. Methodology

Purgeable Halocarbons were analyzed using EPA Method 502.1, "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," (1981). See Section 9.

Purgeable Aromatics were analyzed using EPA Method 503.1, "The Analysis of Aromatic Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," (1981). See Section 9.

Total Organic Carbon was determined using EPA's "Total Organic Carbon, Low Level Method" (1978) and the "Dohrmann DC-54 Ultra Low Level Total Organic Carbon Analyzer System Equipment Manual," 2nd ed. (1978).

Residual Chlorine was determined with the Hach CN-70 Test Kit. This testing was a check for the presence of chlorine in samples from supplies that practice chlorination.

B. Precision

The contract stipulated the precision requirement for analyses of replicate samples for purgeable organics at ± 40% difference when compound concentrations determined were below 5 µg/L and ± 20% for concentrations above 5 µg/L. Precision for analyses of replicate samples for TOC initially was to be within ± 10% for concentrations below 200 µg/L and ± 5% for concentrations above 200 µg/L. By mutual agreement between the TSD Contract Project Officer and the SRI Contract Project Manager, the precision for TOC analyses could be within ± 20% for concentrations below 300 µg/L and ± 10% for concentrations above 300 µg/L.

C. Accuracy

The accuracy requirement for EMSL QC samples for purgeable organics was ± 40% and ± 20% difference for concentrations below and above 5 µg/L, respectively. Accuracy for EMSL QC samples for TOC initially was to be ± 20% and ± 10% for concentrations below and above 200 µg/L, respectively. By mutual agreement between T&D and SRI, the final accuracy requirement for TOC was ± 20% for concentrations below 300 µg/L and ± 10% for concentrations above 300 µg/L.

D. Completeness

The quantity of data generated during this project should provide a high degree of confidence that estimates of nationwide occurrence of synthetic volatile organic contaminants made from these data are accurate. Sample sizes of 200 systems that serve more than 10,000 persons and of 300 systems that serve less than 10,000 persons were selected on the basis of occurrence frequencies found in the Community Water Supply Survey (CWSS) of 1978. Those sample sizes should allow at least 95% confidence that errors of the estimates of occurrence frequencies would be no more than ± 15% for the larger systems and ± 30% for the smaller systems.

E. Representativeness

The total number of samples to be analyzed was limited by the contract funds available, and a balance was struck between random samples for nationwide occurrence estimates and suspect sites for investigating the upper range of contamination levels. To obtain information from a maximum number of supplies within the available resources, it was decided to collect one sample of finished water from each utility at a point near the entrance to the distribution system. The VOC concentrations in water supplies from a single well that is not pumped continuously can vary depending on pumping rate and schedule, and the hydrodynamics of the plume of contamination. If multiple wells supply a system at a single entry point and some wells are

contaminated while others are not, the VOC concentration in the sample at the entry point could vary greatly, depending on which wells were in operation at the time of sampling. In systems with more than one entry point, a single sample would obviously represent only those wells contributing to that entry point. With these limitations in mind, a sample of finished water taken at or near a point of entry provides a reasonable compromise between the information obtained from a single sample from a single well and that from multiple samples taken throughout the system.

E. Comparability

Sampling, analysis, and reporting units are those in the approved methodology.

SECTION 6

SAMPLING PROCEDURES

A sampling kit was prepared at TSD for each sampling location. Amber bottles of 60 mL and 250 mL capacity were dosed with a preservative (mercuric chloride at 10 mg/L), capped with teflon septa and screw caps, labeled with preprinted labels which had been stamped with the sample identification numbers, and secured in "styrofoam" boxes. The styrofoam boxes had been custom molded to hold the proper number of bottles. A shipping blank (250 mL bottle containing organic-free water and preservative) was also included with the sampling kit. The shipping blanks were to remain with the sampling kit through all stages of transportation and storage. Any possibilities of contamination from the surroundings could be investigated by analysis of these blanks.

The bottles, along with a plastic bag and tie, a sampling site data sheet (Appendix B), sampling and shipping instructions (Appendix B), and shipping labels and forms were shipped to the sample collectors on a schedule which had been prearranged with the states. The sample collectors took the samples, filled in the labels and site data sheets, iced and secured the boxes, and delivered them to an overnight freight delivery service. The samples were shipped to TSD except for a few samples collected during the second phase of the survey from sites located near the contract laboratory. Those samples were shipped directly to the contractor. All shipping costs were paid by EPA.

When samples arrived at TSD, they were unpacked, logged in, and any unusual circumstances were noted. The sample bottles were then placed in storage in a cold room free of organic vapor contamination until they were repacked in ice for overnight shipment to the chemical analysis contract laboratory. Replicate samples were collected at each site so half the bottles were shipped to the contract laboratory and half were held in cold storage at TSD. This was necessary for occasional analysis of sample duplicates by TSD chemists or for quick-response, in-house verification of contract laboratory results.

When samples were received at the contract laboratory, they were logged and inspected, then immediately stored in a walk-in refrigerator maintained at 4°C. All primary analyses were completed within one month of sample collection.

SECTION 7

SAMPLE CUSTODY

Samples were collected by plant, state or EPA personnel. The sample collector signed the identification label on each sample bottle. His name was also recorded on the Ground Water Survey Data Sheet (see Appendix B) which was part of the sampling kit sent to each sampling location. The data sheet was stamped with the same identification number as that on the sample bottles in the kit. Either the sample collector or utility personnel completed the form and returned it to the Project Engineer.

The Project Engineer maintained a log of receipt of these data sheets and kept the forms in labeled binders. He also entered information from these sheets for each sample into the EPA computer system, an IBM 360 at Research Triangle Park. These items included date sampled, location of sample point, the number of wells in the system, the number of wells contributing to the sample, the depth of the wells, treatment, proximity to industry, etc.

The Project Engineer maintained a log of all survey samples received at TSD. He was responsible for shipping samples to the contract laboratory and maintained a file of all shipping records. He also was the custodian of the replicate samples held in cold storage at TSD.

When the samples were shipped to the contract laboratory, the TSD Project Officer logged pertinent sample information into the TSD laboratory data system (HP 3354) for tracking purposes.

When samples arrived at the contract laboratory, the Contract Project Manager logged their receipt, served as custodian of the samples during storage, and distributed them to the analysts. Disposal of the samples after analysis was at the direction of the TSD Contract Project Officer.

Replicates of samples stored at TSD that were chosen for quality control check analysis were distributed to the analysts by the Project Engineer at the direction of the TSD Contract Project Officer. The latter also directed disposal of samples after analysis.

After sample analyses were confirmed, one 60 mL vial and one 250 mL vial of sample from each site were retained in 4°C storage at TSD. These will remain in storage until the TSD Contract Project Officer releases them for disposal.

All the survey data sheets and TSD sample handling records are in files kept by the TSD Project Engineer.

SECTION 8

CALIBRATION PROCEDURES AND FREQUENCY

The methods used to analyze survey samples are listed in Section 5. Each method includes specific calibration procedures and the frequency for performance. The Contract Project Manager was responsible for meeting this contract provision to assure that the analytical systems were in control. The TSD Contract Project Officer used the data reported by SRI, International for the required quality control analyses (Section 11) to check that the analytical systems of the contract laboratory were indeed in control during analyses of survey samples.

SECTION 9

ANALYTICAL PROCEDURES

The analytical procedures were those approved by the EPA; they are listed in Section 5. For this survey, the procedures for purgeable halocarbons (502.1) and aromatics (503.1) were combined by placing the respective detectors in series (the PID, then the Coulson) and using one gas chromatograph. This cut the analysis time almost in half. It also provided additional confirmatory analytical data. This method had been shown by SRI to be comparable to the individually-applied EPA methods. The procedure is included in a paper "Gas Chromatographic Analysis of Purgeable Halocarbon and Aromatic Compounds in Drinking Water Using Two Detectors in Series," Kingsley, et al., in "Water Chlorination, Environmental Impact and Health Effects," Vol. 4, Book 1, R.L. Jolley, Ed., Ann Arbor Science Publishers, Ann Arbor, MI (1983), p. 593. A copy is in the TSD files for contract #68-03-3031.

SECTION 10

DATA REDUCTION, VALIDATION, AND REPORTING

A. Sample Background Data

Information from the data sheets submitted by the sample collectors was entered into the computer by the TSD Project Engineer. After entry, the printouts were checked against the handwritten copy. After all the field data were entered into the EPA computer system, several checks were made to test its validity. One test performed was to determine if the population figure given was the total population served or if it was the number of service connections. This was done by dividing the total production (MGD) by the total population figure. If the result was below 25 gallons per day per person (gpdc) or over 200 gpdc, the state was called to verify the population figures. Any necessary corrections were made in the data file.

The other field data, such as number of wells, depth of wells, treatment, or proximity to industry will not be double checked at this time.

B. Analytical Data

Results from each analysis were calculated by the contractor's individual analysts and submitted to the Contract Project Manager for review. The data were objectively reviewed for completeness, calculation accuracy, and conformity to specific standards, for example, significant figures. The contract laboratory was provided access to the EPA computer system (IBM 360 at Research Triangle Park), so their Project Manager could enter the data in a format specified by the TSD Contract Project Officer. After data entry and before permanent storage in a data file, all new entries were printed on the Project Manager's data terminal and checked for accuracy. Appropriate changes were made if necessary. Then the sample data were stored in the designated data file.

The TSD Contract Project Officer periodically reviewed all data entered by the contractor into the EPA data system. These data included the results of duplicate analyses, duplicate samples also analyzed by TSD, confirmatory analyses, "blind" unknowns sent to the contractor by TSD, and analyses of shipping blanks. Furthermore, monthly reports were submitted by the contractor which contained the results of EMSL quality control samples that were analyzed twice monthly for each analytical system employed. From all of these data, the Project Officer determined: (1) any potential problem areas; (2) the precision and accuracy of the analyses; and (3) the adherence to quality assurance guidelines set forth in the written contract. The sample results were then accepted or rejected on the basis of these determinations. If accepted, the results were finalized and verified again by the Contract Project Manager as being final. If rejected, then the compound or parameter in question was listed as being "not analyzed," and corrective action was initiated.

C. Collating Sample Background Data and Analytical Data

After sample and analytical data had been entered and validated, the program to collate the site data and the analytical data was performed. Every 100th data line was checked to see if the analytical data for that sample matched with its site information. If the match was correct, the data processing for that group of data was considered correct.

D. Reporting Survey Results

The validated sample background data and analytical results for the thirty-four organic compounds selected for analysis in the survey were compiled and reported at the end of the project in "The Ground Water Supply Survey, Summary of Volatile Organic Contaminant Occurrence Data," January 1983. (The Total Organic Carbon data were of secondary interest so are not included in this report.) The report also contains the results of tests of significance of the differences in frequency of occurrence of compounds, point estimates of the probability of VOC occurrence and the confidence limits of the estimates.

Any additional access to the sample background data and analytical results in the IBM 360 data base will be through the Project Engineer.

SECTION 11

INTERNAL QUALITY CONTROL CHECKS

Internal quality control was tracked by SRI, International by duplicate analysis of survey samples and by analyzing quality control samples as stipulated in the analytical contract (Appendix C). All samples found or suspected to contain the organics of interest were reanalyzed for confirmation. The results from duplicate analyses were entered into the EPA computer system by the Contract Project Manager. The results of analyses of quality control samples were reported to the TSD Contract Project Officer in monthly progress reports. The TSD Contract Project Officer used these data as described in Section 10. In addition, quality control was tracked by TSD with duplicate samples and blinds which were analyzed by both SRI and TSD. The use of these data is also described in Section 10.

At the conclusion of the survey, the contractor prepared a report on the quality control applied during the project (Appendix D), in order to substantiate the quality of the data generated.

SECTION 12

PERFORMANCE AND SYSTEM AUDITS

Performance evaluation samples were analyzed by SRI, International and the data evaluated by TSD before the analytical contract was awarded. A pre-award site visit was made by Herb Brass, Chief, DWQAB, in combination with a meeting to finalize aspects of the Community Water Supply Survey contract. Site visits by the TSD Contract Project Officer continued on an annual basis after the contract was awarded.

SECTION 13

PREVENTIVE MAINTENANCE

The Project Manager for SRI, International was responsible for assuring that the equipment used for the required analytical work was properly maintained. The TSD Contract Project Officer used the data from the quality control analyses reported by the contractor and TSD analysts (Section 11) to check that the analytical systems of the contract laboratory were in control during analyses of survey samples.

SECTION 14

SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

A. Analytical Data

The analytical contract (Appendix C) stipulated % difference (relative range) between duplicates as the precision statistic to be used. For most of the quality control checks, enough data were generated to justify using % relative standard deviation as the precision statistic. The accuracy statistic used was % error, with signed results to distinguish positive and negative error. The formulas for these statistics are included in the final report (Appendix D) prepared by the contract laboratory about the quality assurance program they conducted during the generation of analytical data for this survey.

B. Survey Results

The survey was conducted to gather occurrence data. Treatment of the results was a matter of sorting the data (random - nonrandom, population categories, etc.) to report the results. See the January 1983 report, "Summary of Volatile Organic Contaminant Occurrence Data." Statistical inferences (tests of significance, etc.) drawn from the data were calculated according to Miller, I. and Freund, J.E., Probability and Statistics for Engineers, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965.

SECTION 15

CORRECTIVE ACTION

Any questions or problems about sample collection were handled on a case-by-case basis by the Project Engineer. If a shipping blank contained detectable levels of organics, the Contract Project Manager contacted the TSD Contract Project Officer and a joint decision was made concerning the sample collected at the same time.

If the TSD Contract Project Officer determined that sample results should be rejected based on quality assurance guidelines, the TSD Project Officer and the Contract Project Manager determined the proper course of corrective action. The contract laboratory took whatever steps were necessary to correct any analytical problems. Samples held in reserve at the contractor's laboratory or at TSD were then reanalyzed if the storage time was not excessive. If the reserve samples were not usable, the site was resampled if possible.

SECTION 16

QUALITY ASSURANCE REPORTS TO MANAGEMENT

Monthly reports on technical progress and quality control were submitted by the Contract Project Manager through the SRI, International Laboratory Director to the TSD Contract Project Officer. After completion of the analyses of survey samples, the contractor submitted a summary report (Appendix D) about the analytical procedures used to perform the analyses and the results obtained from the analytical quality control program. The summary report prepared by TSD at the completion of the project contains a section on the quality assurance program for the survey.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
Technical Support Division
Office of Drinking Water
OFFICE OF WATER AND WASTE MANAGEMENT
5555 Ridge Road, Cincinnati, OH 45268

GROUND WATER SUPPLY SURVEY

STATUS REPORT #1
(February 1981)

The national Ground Water Supply Survey (GWSS) is now underway and this is the first of several planned status reports on its progress. The GWSS has four objectives. It will be used to describe the national occurrence levels and frequency of synthetic organic pollution found in drinking water supplied from the ground. It will improve Federal and State responses to newly identified contamination incidents. It will stimulate and enhance State ground water contamination detection and control activities. And, it should improve our ability to predict where ground water pollution is likely to be found in the future.

In early November 1980 the Office of Drinking Water (ODW) announced its proposal for a ground water supply survey and requested the advice and cooperation of all fifty States and Puerto Rico. By mid December, most of the States had sent written comments and all had been contacted. Over forty States are cooperating in the implementation of the survey, and all but four intend to take part in follow-up activites when a contaminated supply is identified.

Of the 1,000 systems to be surveyed, nearly 13% have been sent the sampling package. By the first week in February, 82 sample sets had been forwarded to the analytical laboratory. At present, 152 systems have been scheduled to take

samples, filling up the analytical schedule through the first week in March. The sampling schedule is continuing to fill, and if your State has a particular future date in mind, please call us to ensure adequate planning. When a schedule is established, please make every effort to collect samples within that time period. If you must change the schedule, let us know as soon as possible. The laboratory can analyze only a certain number of samples per week so scheduling for a relatively uniform work load is extremely important.

The analytical results of the sampling will be forwarded routinely on a bimonthly basis. The first analytical report is expected out in April. Pertinent results will be forwarded to each State and Region. Special actions will be taken if a high level of contamination is found. Those actions are discussed toward the end of this report.

Questions and Answers

As a result of the comments received in December, and from early experience from the first several sample collections, a number of specific questions have come up. Although not every State or Region is affected by these issues, quite a few are, and attention to them is important. The questions are:

Q - The survey design allows for only one sampling point for each system. There are many shortcomings with this type of survey design. For example, if a supply uses multiple wells, from what point should the sample be drawn? What are the reasons for the single sample design, and can it be changed?

A - Extensive discussion preceded the decision to use the single sample design. The most compelling argument in favor of the selected design is resources. Only 1,000 water samples can be analyzed. Considering the multi-objective nature of the GWSS, the single sample per system approach best serves to support a broad initiative on ground water quality. With

respect to the multiple well question, a sampling point should be chosen which represents the largest possible number of wells. The analytical methods in use are very sensitive, so that if one of several wells contributing to the sampling point is significantly contaminated, some contamination will be found. As described later, the single sample is being used as a screening device and confirmatory analysis will be carried out when significant pollution is found.

Q - What is the purpose of doing both a random and a nonrandom sample, and are the results going to be combined?

A - The random sample is being done for the express purpose of determining the national occurrence of drinking water contamination by synthetic organic chemicals. Only this data will be used in the development of national economic impacts and estimates of national occurrence needed to help decide whether or not to write a regulation, and how a regulation might be designed.

The nonrandom sample has different purposes. It should provide information on the upper range of contamination levels, help States to provide added public health protection by searching for contamination, assist EPA and States in developing a predictive capability for locating contaminated sites, and may help in structuring future national guidance and regulations.

Q - What is the purpose of the primary and secondary lists of systems, and how are they used?

A - The random sample was drawn nationally, and consists of about 500 systems. Naturally, not every system will be able to participate, so a second list of 250 systems was drawn to back up the primary list. These systems were drawn randomly from the whole nation, so it is possible that a particular State will have a listing which is not very representative within that State. This is to be expected. In terms of the use of these lists, the primary list should be fully used if at all possible. However, when a name cannot be used from the primary list, one from the secondary list should be used. Only in this way can the "randomness" be maintained. Another feature of the random sample is that the sample is broken into subgroups. One is the group of systems which serve fewer than 10,000 people, the other is systems which serve more than 10,000 people. When replacing a system from the primary list by a system from the secondary list, the size breakdown must be maintained. Replace a small system with a small system; replace a large system with a large system. If you run out of replacements, please let us know.

Q - A small number of criteria were suggested for use when selecting water supplies as part of the nonrandom sample. Are these to be the only criteria, or can a State use others as well?

A - By no means should a State feel constrained by the criteria ODW suggested. We recognize that State personnel are far more knowledgeable on conditions that may lead to contamination of ground water, and expect other criteria to be used as well. An essential point we would like maintained is that the systems chosen be those for which there is no existing water quality data, but which are suspected to be contaminated by organic chemicals. In addition, we want to know just what criteria actually were used to select the systems. When you have completed selection of the nonrandom systems in your State, please briefly describe the selection process to us.

Q - State and Regional resources for surveys and follow-up of contamination found are not unlimited, and usually are allocated well ahead of time. This survey will, in some cases, place severe burdens on States resources. What can EPA provide to ease these burdens?

A - We have a genuine concern about the impact on resources, and this survey has required ODW to reprogram some work as well. In terms of assistance, half of the samples being examined are being selected by the States but analyzed by EPA. This is an expensive task which may support work a State otherwise would have to do, or may not be able to do. Beyond analytical support for initial and confirmatory samples, we are unable to help financially.

However, contamination of drinking water supplies by harmful organic chemicals is an important public health matter. Where detected, serious incidents of contamination must be dealt with to protect public health. Such responses will require a concerted State-Federal effort. We must all plan to take part in this work, especially on follow up in incidents of detected contamination.

Follow-up When Contamination Is Found

One of the important aspects of the GWSS is follow-up when a case of ground water contamination is found. The local response will vary from State to State and system to system, depending on many factors. This issue is so important that a draft guidance on the matter will be circulated for comment soon. Final

guidance will be issued separately. In the meantime, ODW has developed an approach for timely notification of Regions and States, based on the degree of risk imposed by the contamination found.

In essence, when a sample is found to have high levels of contamination, EPA or the State will analyze an additional water sample taken from the identical original sampling point. Additional EPA follow-up analysis on the water system will usually not be possible, and should be discussed by the State and Region on a case-by-case basis. Generally, system level follow-up is a State responsibility.

Specifically EPA response to a high level will be as follows. For contaminants which are known or suspected carcinogens, and when the concentration found is associated with a lifetime risk to the community at the level shown in the column titled "Risk Level," the actions shown in the "Action" column below will be taken by EPA. The lifetime risk is the probability of illness over a 70-year period. A 10^{-5} risk level is equal to a one in one-hundred-thousand chance of illness.

Risk Level	Action
10^{-5} (moderate risk)	Alert call from laboratory to ODW; immediate Regional and State notification.
10^{-5} - 10^{6} (relatively low risk)	Notification by laboratory to ODW in its weekly report: Regional and State notification within one week.
Less than 10^{-6} (very low risk)	Notification to ODW, Regions and States in bimonthly report.

For contaminants which are noncarcinogenic toxins, and when the risk to the community is at the level shown in the column titled "Risk Level," the actions shown in the "Action" column will be taken by EPA.

Risk Level	Action
At or near 10-day SNARL (Suggested No Adverse Response Level)	Alert call from laboratory; immediate Regional and State notification; development of new SNARL (if necessary).
Between ADI (Acceptable Daily Intake) and 10-day SNARL	Notification by laboratory to ODW in its weekly report; Regional and State notification within one week.
Less than ADI	Notification to ODW, Regions and States in bimonthly report.

When there is a mixture of two or more chemicals which are potential carcinogens, the risk will be treated additively. For noncarcinogens no additive assumption will be made, for purpose of notification.

The water analyses will measure the concentration of the chemicals listed below. The status of formal health advisories is indicated in the group headings.

Chemicals Covered by TTHM MCL

bromoform
bromodichloromethane
chloroform
dibromochloromethane

SNARLS Presently Available

carbon tetrachloride
methylene chloride
tetrachloroethylene
1,1,1-trichloroethane
trichloroethylene

Health Effects Criteria Documents

vinyl chloride

SNARLS Or Criteria Documents To Be Available By August 1981

1,2-dibromo-3-chloropropane (June)
1,2-dichloroethane (March)
1,1-dichloroethylene (March)
cis-1,2-dichloroethylene (March)
trans-1,2-dichloroethylene (April)
benzene (March)
toluene (August)
o-xylene (March)
m-xylene (March)

Chemicals Rarely Found And Which May Be Evaluated After August 1981

dichloroiodomethane
bromobenzene
o-chlorotoluene
p-chlorotoluene
ethylbenzene
iso-propylbenzene
n-propylbenzene
styrene
1,1-dichloroethane

p-xylene (March)
chlorobenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
1,2-dichloropropane
1,1,2,2-tetrachloroethane
1,1,1,2-tetrachloroethane
1,1,2-trichloroethane
trichlorobenzene isomers

If you have further questions, please contact Lowell A. Van Den Berg, Director, TSD, ODW, 5555 Ridge Road, Cincinnati, OH 45268 (513-684-4374). For questions concerning sampling and scheduling contact J. Wayne Mello at 513-684-4445.

Lowell A. Van Den Berg, Director
Technical Support Division

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
Technical Support Division
Office of Drinking Water
OFFICE OF WATER AND WASTE MANAGEMENT
5555 Ridge Avenue, Cincinnati OH 45268

DATE: December 22, 1980

SUBJECT: Sampling and Shipping Instructions for the Ground Water Supply Survey

FROM: Lowell A. Van Den Berg, Director, Technical Support Division

TO: Ground Water Supply Survey Sample Collectors

Attached are instructions for collection and shipment of water samples for the Ground Water Supply Survey. This survey is being conducted by the Office of Drinking Water, US EPA, in cooperation with state agencies and Regional offices of EPA. It is important to read the sampling instructions thoroughly to become familiar with the procedures and requirements.

You will also find a data sheet which, when completed, will provide information on the sampling site and on the water system. Please fill in the information as completely and accurately as you can, or have someone knowledgeable about the system provide the information. The data will be useful in identifying the sample and describing the system from which the sample was taken. This information, combined with the analytical results, will provide an assessment of the state of the nation's ground water supplies.

The contamination of ground water by man-made organic chemicals is a problem that has only recently been recognized. We hope the data developed by this survey will greatly increase our knowledge of the extent of the problem.

We are grateful for your help in providing the samples and the system information. Your assistance in these matters is essential to the success of the project.

NATIONAL GROUND WATER SURVEY DATA SHEET

SAMPLE ID:_____ PWS ID_____
SAMPLING DATE:_____ SAMPLING TIME:_____
NAME OF SAMPLER:_____ TELEPHONE NO:_____

NAME AND ADDRESS OF SYSTEM BEING SAMPLED:	NAME AND ADDRESS OF OWNER:
PLANT CONTACT PERSON: TELEPHONE NO:	TELEPHONE NO:

FIELD DATA: COUNTY:_____

TURBIDITY:_____ pH:_____ COLOR:_____

CHLORINE RESIDUAL: FREE _____ TOTAL _____

IDENTIFY THE EXACT POINT OF SAMPLING:
(ADDRESS IF APPROPRIATE)

---

1. APPROXIMATELY HOW MANY PEOPLE DOES THE WATER SYSTEM SERVE (INCLUDING PURCHASED WATER CUSTOMERS)? _____

2. IN TOTAL, HOW MANY WELLS DOES THE WATER SYSTEM OWN? _____

3. FOR EACH WELL, INDICATE:

	DEPTH (FT.)	PUMP CAPACITY (GPM)	FREQUENCY OF USE (MONTHS/YEAR)	AQUIFER TYPE (WATER TABLE OR CONFINED)
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				

CONTINUE ON BACK IF NEEDED

4. CIRCLE THE NUMBER OF THE WELLS WHICH CONTRIBUTE THE MAJORITY OF WATER TO THE SAMPLING POINT.

5. FOR WELLS NOT USED AT LEAST SIX MONTHS EACH YEAR, WHY ARE THEY NOT USED REGULARLY? (E.G. SEASONAL VARIATION IN DEMAND, CONTAMINATION, EQUIPMENT PROBLEMS, ETC.)

6. WHAT TYPE OF SOIL IS THE MAJOR OVERBURDEN ABOVE THE AQUIFERS FROM WHICH WATER IS DRAWN? (E.G. CLAY, SAND, LOAM, OTHER)

7. WHAT IS THE AVERAGE DAILY PRODUCTION OF THE SYSTEM? _____ THOUSANDS OF GALLONS PER DAY

8. ARE ALL WELLS IN ONE GENERAL LOCATION (WITHIN A FE BLOCKS)? ___YES ___NO

IF NOT, HOW MANY GROUPS OF WELLS ARE THERE IN THE SYSTEM? _____

WHAT IS THE DISTANCE BETWEEN THE TWO CLOSEST GROUPS: _____

WHAT IS THE DISTANCE BETWEEN THE TWO FARTHEST GROUPS: _____

9. AT HOW MANY LOCATIONS DOES THE WATER ENTER THE DISTRIBUTION SYSTEM? _____

10. ARE THERE RESERVOIRS OR HOLDING FACILITIES TO WHICH THE WATER IS PUMPED BEFORE IT IS DISTRIBUTED? ___YES ___NO

11. DOES THE WATER SYSTEM CHLORINATE? ___YES ___NO

IF SO, AT WHAT POINTS IN THE TREATMENT PROCESS IS CHLORINATION DONE, AND WHAT FORM OF CHLORINE IS USED AT EACH POINT?

12. OTHER THAN CHLORINATION, WHAT TREATMENTS ARE USED?

A. ___DISINFECTION (OTHER THAN CHLORINE)
(SPECIFY)_____
B. ___COAGULATION
C. ___SEDIMENTATION
D. ___FILTRATION
E. ___LIME SODA SOFTENING
F. ___ION EXCHANGE SOFTENING
G. ___AERATION
H. ___AMMONIATION
I. ___IRON REMOVAL
J. ___ACTIVATED ALUMINA
K. ___CORROSION CONTROL
L. ___FLUORIDE ADDITION
M. ___FLUORIDE REMOVAL
N. ___GRANULAR ACTIVATED CARBON
O. ___OTHER (SPECIFY) _____

13. WHAT PERCENTAGE OF THE WATER IS TREATED? _____

14. IS TREATMENT CONDUCTED AT EACH WELL OR ARE THERE CENTRAL TREATMENT LOCATIONS? EACH WELL / CENTRAL LOCATIONS

IF CENTRAL TREATMENT LOCATIONS, HOW MANY? _____

15. IS THERE ANY COMMERCIAL OR INDUSTRIAL ACTIVITY IN CLOSE PROXIMITY TO ANY OF THE WELLS? ___YES ___NO
(WITHIN 10 MILES)

IF SO, INDICATE THE DISTANCE BETWEEN THAT ACTIVITY AND THE WELLS:

HOW MANY WELLS ARE WITHIN THE FOLLOWING DISTANCES FROM COMMERCIAL OR INDUSTRIAL ACTIVITY?	WITHIN 1/2 MILES	1/2 - 1 MILES	1 - 3 MILES	3 - 10 MILES

WHAT IS THE NATURE OF THE COMMERCIAL OR INDUSTRIAL ACTIVITY?
(INDICATE HOW DISTANT THE ACTIVITY IS FROM THE NEAREST WELL)

	WITHIN 3 MILES	3 - 10 MILES
A. DRY CLEANING BUSINESS	_____	_____
B. AVIATION FACILITIES	_____	_____
C. MACHINE SHOPS	_____	_____
D. METAL FABRICATION	_____	_____
E. ELECTROPLATING	_____	_____
F. REFINERIES	_____	_____
G. CHEMICAL PLANTS	_____	_____
H. DUMPS/LANDFILLS	_____	_____
I. HAZARDOUS WASTE TREATMENT STORAGE OR DISPOSAL	_____	_____
J. INDUSTRIAL SEPTIC TANKS	_____	_____
K. HOME SEPTIC TANKS	_____	_____
L. INDUSTRIAL PITS, PONDS AND LAGOONS	_____	_____
M. OTHER (SPECIFY)_____	_____	_____
_____	_____	_____
_____	_____	_____

16. HAS THERE BEEN ANY CONCERN REGARDING THE QUALITY OF THE DRINKING WATER? ___YES ___NO
(INCLUDING TASTE AND ODOR)

IF SO, WHAT WERE THE CHARACTERISTICS OF THE WATER QUALITY PROBLEM?

PLACE THIS DATA SHEET IN THE ATTACHED ENVELOPE AND MAIL IT AS CLOSE TO THE DATE OF SAMPLING AS POSSIBLE. IF YOU WOULD LIKE A SUMMARY OF THE STUDY RESULTS CHECK HERE ___.

December 16, 1980

SAMPLING INSTRUCTIONS

A sample of the finished drinking water should be collected at a point as close as possible to the entrance to the distribution system (such as after the clear well, or distribution manifold) but also at a convenient point for sample collection. The time of collection will depend on the operation of the facility. If pumping is continuous, the collection can be at any time; but if pumping only occurs during a certain time of day, say 8:00 am to 5:00 pm, collect the sample during the last hours of pumping (4:00 - 5:00 pm) if possible. This procedure will produce a water sample representing a larger area of the aquifer.

The procedures for the collection of drinking water samples to be analyzed for organic contamination may be different from those with which you are familiar. First, the sample bottles should not be rinsed, because they contain preservatives. Second, all sample bottles should be filled completely, so a few drops of water run over the top. Carefully put the cap and teflon septum back over the top and seal. CAUTIONS:

1. The white, shiny side of the septum should not be visible when the vial is capped.

2. No air bubble should be present when the vial is turned over. If an air bubble is present, remove the cap and septum and make up the difference with additional water, then recap.

3. Do not tighten caps too much, they break easily.

The sampling box contains the following items:

3-60 ml vials: Preserved with 0.5 ml of mercuric chloride. These will be analyzed for 11 aromatic compounds.

4-60 ml vials: These will be analyzed for 26 volatile halocarbons.

1-60 ml vial: Preserved with 0.5 ml of sodium thiosulfate. This vial may be analyzed at a future date for the quenched trihalomethanes.

3-250 ml vials: Preserved with 1 ml of mercuric chloride. These will be analyzed for total organic carbon (TOC).

1-250 ml vial: This vial contains blank water. This vial should not be opened, but it should be carried along with the other vials. This is done to determine the possibility of contamination from the surrounding environment.

- Data Sheet
- Pictorial Sheet on the Collection of Organics
- Return Shipment Labels
- Return Envelope

Before sample collection, fill out the sample labels, using a waterproof pen (if nothing else, a hard ball point pen will work). A dry label is easier to fill in than a wet one.

Also, either before or after collection, please ask the person you are working with at the utility to fill in the enclosed data sheet. Some of the questions he/she may not be able to answer. Please encourage him/her to provide as much of the information as possible. Completeness in filling out this data sheet will help greatly in the interpretation of the resultant data.

After all samples are collected, repack them into the Styrofoam box and fill with ice. The smaller size ice works better than the larger cubes. Close the plastic bag around the Styrofoam box using the enclosed twist tie. Before the box is to be shipped, tightly tape the box shut.

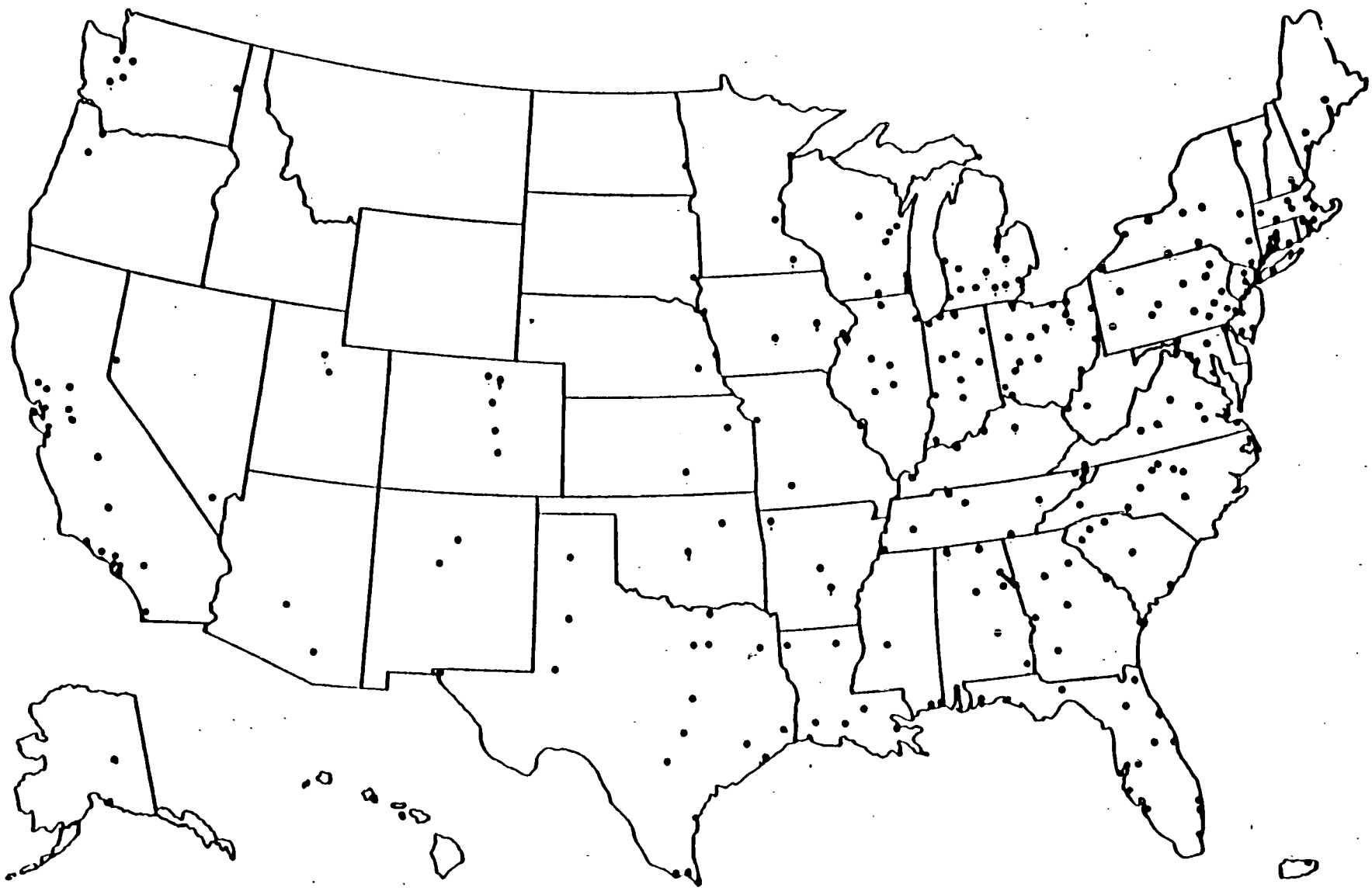
Shipping:

To reduce the cost of shipping these samples back to the Cincinnati Lab, combined shipments are recommended, i.e., if more than one site can be collected within 1-3 days, wait until all are collected and tape the boxes together before shipping them. If samples can be collected over several days, don't seal the first samples collected until they are ready for shipment. All samples should be kept iced until then. Also, if samples are to be collected on a Friday, wait until Monday to ship them. This will avoid samples setting on some loading dock over the weekend. Again, make sure all samples are kept iced and stored in an organics-free area (do not store with solvents, paints, or other organic chemicals).

All shipments should be sent collect to the Cincinnati Lab via either Federal Express or Purolator to avoid billing problems. We have accounts with either of these firms and they are very cooperative. Also, If you are collecting samples in an area that isn't served by either, if at all possible wait until you are in one of those cities before shipping the samples to us. A list of cities serviced by Federal Express and Purolator in your State is enclosed. If time will not permit you to do so, ship the sample collect to me by any air freight service that will get the sample to me overnight. Again, if samples have to be held, keep them iced and stored in an organics-free area.

The data packet should be mailed in the enclosed envelope.

Your cooperation in this effort will be greatly appreciated. If at any time you have questions, please call, Wayne Mello, collect, at (513) 684-4445.



LOCATION OF CITIES
SERVICED BY EITHER
FEDERAL EXPRESS OR PUROLATOR

CITIES SERVICED BY EITHER FEDERAL EXPRESS OR PUROLATOR

AREA SERVED	TELEPHONE NUMBERS FOR PICK UP SERVICE	
	PUROLATOR	FEDERAL EXPRESS
Alabama		
Anniston		800-238-9070
Birmingham	205-328-8370	205-591-7745
Midland City/Dothan	205-983-3602	
Florence		800-238-9070
Gadsden	205-328-8370	800-238-9070
Huntsville	205-328-8370	205-772-0131
Mobile	205-666-3947	205-342-7990
Montgomery	205-265-7208	205-288-8274
Alaska		
Anchorage		907-243-3322 (Info)
Fairbanks		907-452-1186 (Info)
Arizona		
Phoenix	602-267-1467	602-894-9681
Tucson	602-792-0290	602-294-2691
Arkansas		
Fayetteville	501-664-8100	
Little Rock	501-664-8100	501-372-7201
Pine Bluff		800-238-9070
California		
Anaheim		213-594-6813
Bakersfield		805-393-5580
Burbank		213-849-3191
Fresno		209-252-4091
Long Beach		213-594-6813
Los Angeles	213-673-1200	213-776-4111
Modesto		209-982-5781
Napa		800-852-7707
Oakland		415-568-2380
Ontario		213-331-0768
Oxnard		800-852-7707
Sacramento		916-392-9360
San Diego	213-673-1200	714-297-0386
San Francisco	415-952-0880	415-877-9000
San Jose		408-279-8870
Santa Barbara		805-964-0736
Santa Cruz		800-852-7707
Santa Rosa		800-852-7707
Stockton		209-982-5781
Colorado		
Colorado Springs		303-574-6850
Denver	303-287-0395	303-320-8320
Fort Collins		800-824-7831
Greeley		800-824-7831
Pueblo		800-824-7831

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Connecticut		
Bridgeport		203-579-1911
Bristol		203-728-1221
Hartford	203-527-2100	203-728-1221
New Britain		203-728-1221
New Haven		203-469-2347
New London		800-526-3900
Norwalk	203-847-3888	800-431-1186
Stamford		800-431-1186
Waterbury		203-753-4087
Delaware		
Wilmington		302-652-1803
District of Columbia	703-836-4542	703-691-1901
Florida		
Daytona Beach		800-238-9070
Fort Lauderdale	305-525-3339	305-525-4287
Fort Myers	813-332-3132	
Gainesville		800-238-9070
Jacksonville	904-389-5524	904-757-0800
Lakeland		813-682-6076
Melbourne/Titusville		800-238-9070
Miami	305-949-2226	305-371-8500
Orlando	305-896-1676	305-857-3420
Pensacola	904-477-2276	800-238-9070
Sarasota		813-746-9211
St. Petersburg	813-823-5806	813-821-4572
Tallahassee	904-576-7174	
Tampa	813-879-5960	813-885-2783
West Palm Beach		800-238-9070
Georgia		
Albany	912-883-5223	
Athens		800-238-9070
Atlanta	404-763-8500	404-452-0314
Augusta	404-793-2189	
Columbus	404-323-6071	
Macon	912-788-5152	912-781-8794
Savannah	912-964-6174	912-964-9261
Hawaii		
Honolulu		808-836-2303

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Idaho	None	None
Illinois		
Bloomington/Normal		800-526-3940
Chicago	312-738-6480	312-686-6886
Decatur		800-526-3940
Moline	309-788-0428	309-797-9706
Peoria	309-829-4366	309-697-5910
Rockford	815-965-4377	815-874-9591
Springfield		217-753-3626
Indiana		
Bloomington		800-526-3940
Evansville	812-424-7516	812-426-1461
Fort Wayne	219-484-5724	219-747-1637
Gary		312-686-6886
Indianapolis	317-634-1161	317-248-1251
Kokomo		800-526-3940
Lafayette/West Lafayette		800-526-3940
Michigan City		800-526-3940
Muncie/Anderson		800-526-3940
South Bend	219-233-1406	219-234-0023
Terre Haute		800-526-3940
Iowa		
Cedar Rapids	319-366-8635	319-366-8613
Davenport		309-797-9706
Des Moines	515-287-4000	515-280-8001
Sioux City	712-252-2729	
Kansas		
Topeka	816-471-0057	800-526-3940
Wichita	816-471-0057	316-945-5201
Kentucky		
Lexington	606-259-0406	606-253-2488
Louisville	502-637-9791	502-361-2326
Owensboro		812-426-1461
Paducah	502-442-9555	
Louisiana		
Baton Rouge		504-924-0347
Lafayette		800-238-9070
Lake Charles		800-238-9070
Monroe	318-322-2309	
New Orleans	504-466-6256	504-733-3724
Shreveport	318-742-7268	318-227-1903

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Maine		
Bangor		207-947-6749
Lewiston	207-784-0110	
Portland		207-775-7755
Maryland		
Baltimore	301-488-2020	301-760-8750
Gaithersburg		703-691-1901
Hagerstown		800-526-390[illegible]
Massachusetts		
Boston	617-269-7000	617-662-0200
Brockton		617-662-0200
Fall River		800-556-6553
Fitchburg		617-662-0200
Pittsfield		800-526-3900
Springfield		413-736-3220
Worcester	617-853-2458	617-393-6166
Michigan		
Ann Arbor		313-941-7010
Battle Creek/Kalamazoo		616-968-0385
Benton Harbor		800-526-3940
Detroit	313-542-6223	313-941-7010
Flint		313-767-4003
Grand Rapids	616-698-9500	616-455-1012
Jackson		800-526-3940
Lansing	517-321-6184	517-394-6440
Muskegon		800-526-3940
Saginaw/Bay City		517-695-6150
Minnesota		
Duluth	218-727-2798	
Minneapolis/St. Paul	612-721-6201	612-340-0887
Rochester	507-282-2559	
Mississippi		
Biloxi/Gulfport		800-238-9070
Jackson	601-939-6080	601-932-3310
Pascagoula		800-238-9070
Missouri		
Kansas City	816-471-0057	816-471-7110
St. Louis	314-776-1110	314-367-8278
Springfield		417-869-8422

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Montana	None	None
Nebrasks		
Lincoln		800-526-3940
Omaha	712-323-1678	712-347-6890
Nevada		
Las Vegas		702-736-6161
Reno		702-323-3664
New Hampshire		
Manchester	603-668-1773	603-669-6672
Nashua		603-669-6672
New Jersey		
Atlantic City		800-942-7717
Camden		609-662-5682
Edison		201-923-6000
Jersey City		201-923-6000
New Brunswick		201-923-6000
Newark	201-967-9474	201-923-6000
Paterson		201-923-6000
Teterboro		201-923-6000
Trenton		609-587-7678
Vineland/Millville		800-942-7717
New Mexico		
Albuquerque	505-345-7777	505-344-2321
Sante Fe		505-344-2321
New York		
Albany	518-785-3676	518-783-1155
Binghamton		607-729-5218
Buffalo	716-685-4911	716-632-6200
Elmira		800-526-3900
Farmingdale		516-454-0300
Garden City		516-454-0300
Long Island	516-349-8383	
New York City	212-392-6150	212-777-6500
Newburgh/Poughkeepsie		914-564-6850
Rochester	716-225-1505	716-546-8080
Syracuse	315-437-7361	315-463-6647
Utica		800-526-3900
White Plains	914-592-2171	914-835-0030

6

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
North Carolina		
Asheville	704-525-1127	800-238-9070
Burlington		919-855-5340
Charlotte	704-525-1127	704-394-5101
Fayetteville		800-238-9070
Greensboro	919-467-2241	919-855-5340
Raleigh/Durham	919-467-2241	919-781-9060
Salisbury		800-238-9070
North Dakota		
Fargo	701-237-3239	
Ohio		
Akron		216-733-8341
Belpre	614-423-9580	
Canton	216-456-7188	216-494-3691
Cincinnati	513-621-3720	606-283-2922
Cleveland	216-431-0500	216-361-0872
Columbus	614-471-4126	614-475-8314
Dayton	513-898-1070	513-898-1693
Hamilton		606-283-2922
Lima		800-526-3940
Lorain		216-361-0872
Mansfield		419-524-2143
Marion		800-526-3940
Springfield		513-898-1693
Steubenville		412-923-2130
Toledo	419-865-8200	419-865-0265
Youngstown		216-759-8222
Oklahoma		
Oklahoma City	405-672-5539	405-682-3681
Tulsa	918-836-8719	918-836-0241
Oregon		
Portland	503-283-1220	503-257-6611
Salem		800-824-7831

TELEPHONE NUMBERS FOR PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Pennsylvania		
Allentown	215-791-1621	215-435-7651
Altoona		800-526-3900
Erie	814-453-6032	814-833-5660
Harrisburg	717-939-1351	717-944-0401
King of Prussia		215-923-3085
Lancaster		717-944-0401
Philadelphia	215-825-5710	215-923-3085
Pittsburgh	412-366-7970	412-923-2130
Reading		215-435-7651
Seneca	814-676-0606	
Tyrone	814-684-0729	
Wilkes-Barre/Scranton	717-655-8696	717-346-7011
Williamsport	717-326-1303	800-526-3900
Puerto Rico		
San Juan		800-238-3064
Rhode Island		
Providence	401-463-6720	401-738-4401
South Carolina		
Anderson		800-238-9070
Charleston	803-791-5800	800-238-9070
Columbia	803-791-5800	803-254-0201
Greenville/Spartanburg	803-791-5800	803-288-8191
South Dakota		
Sioux Falls	605-339-9110	
Tennessee		
Bristol		615-323-7117
Chattanooga	615-629-9736	615-892-2760
Clarksville		800-542-5171
Jackson	901-423-0605	
Johnson City		615-323-7117
Kingsport		615-323-7117
Knoxville	615-525-5181	615-970-2761
Memphis	901-365-1670	901-345-3810
Nashville	615-226-0930	615-361-4121

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Texas		
Amarillo	806-374-4930	806-335-1641
Austin	512-928-4970	512-474-8029
Beaumont		713-842-5892
Brownsville		512-541-6721
Corpus Christi		512-851-2836
Dallas	214-438-4713	214-358-5271
El Paso	915-565-2256	915-778-5435
Fort Worth	214-438-4713	817-332-6293
Galveston		800-238-9070
Harlingen		512-423-8835
Houston	713-869-6405	713-667-2500
Longview		800-238-9070
Lubbock	806-747-3601	806-747-1752
McAllen		512-687-4792
Midland/Odessa		800-238-5355 (Info)
San Antonio	512-227-5113	512-824-9488
Sherman		214-358-5271
Temple		512-474-8029
Utah		
Provo/Orem		800-824-7831
Salt Lake City		801-532-6590
Vermont		
Burlington		802-864-0074
Virginia		
Bristol		615-323-7117
Charlottesville		800-238-5355 (Info)
Lynchburg		800-238-9070
Newport News		804-857-5967
Norfolk	804-853-6754	804-857-5967
Petersburg		804-222-6765
Richmond	804-644-4086	804-222-6765
Roanoke	703-985-0525	703-342-7851
Washington		
Bremerton		206-762-5811
Olympia		206-762-5811
Seattle	206-325-5400	206-762-5811
Spokane	509-535-3521	800-238-5355 (Info)
Tacoma		206-762-5811
West Virginia		
Charleston/Dunbar	304-768-9796	
Huntington	304-768-9796	

9

TELEPHONE NUMBERS FOR
PICK UP SERVICE

AREA SERVED	PUROLATOR	FEDERAL EXPRESS
Wisconsin		
Appleton/Oshkosh	414-731-5769	414-739-8033
Green Bay	414-468-7159	414-432-3260
Janesville/Beloit		608-241-2825
Kenosha		414-481-8680
Madison	608-241-4106	608-241-2825
Milwaukee	414-342-9330	414-481-8680
Racine		414-481-8680
Schofield	715-359-4210	
Wyoming	None	None

SF 26 FORM 26 JULY 1966
GENERAL SERVICES ADMINISTRATION
FED. PROC. REG. (41CFR) 1-16.101

AWARD/CONTRACT

1 CONTRACT (Prim. Inst. Ident.) NO.	2 EFFECTIVE DATE	3. REQUISITION/PURCHASE REQUEST/PROJECT NO	4 CERTIFIED FOR NA REG. 2 AND/OR DA RATING
[redacted]-03-3031	SEP 2 9 1980	CI 80-0428	

5 ISSUED BY CODE
Negotiated Contracts Branch
Contracts Management Division
Environmental Protection Agency
Cincinnati, Ohio 45268

6 ADMINISTERED BY (If other than block 5) CODE

7 DELIVERY FOR DESTINATION [X]
OTHER (See below) [ ]

8 CONTRACTOR NAME AND ADDRESS (Street, city, county, State, and ZIP code) CODE FACILITY CODE
SRI INTERNATIONAL
333 Ravenswood Avenue
Menlo Park, CA

9 DISCOUNT FOR PROMPT PAYMENT
N/A

10 SUBMIT INVOICES (4 copies unless otherwise specified) TO ADDRESS SHOWN IN BLOCK 12

11 SHIP TO/MARK FOR CODE

12 PAYMENT WILL BE MADE BY CODE
ACCOUNTING OPERATIONS OFFICE
Environmental Protection Agency
Cincinnati, OH 45268

13 THIS PROCUREMENT WAS [ ] ADVERTISED, [X] NEGOTIATED, PURSUANT TO: [ ] 10 U.S.C. 2304 (a)( ) [X] 41 U.S.C. 252 (c)(10) FIRM FIXED PRICE - INDEFINITE QUANTITY

14 ACCOUNTING AND APPROPRIATION DATA
2-1 680/10108 B00004 68033031 0R6440M051 25.32 $275,000 060812140 AP27

15 ITEM NO	16 SUPPLIES/SERVICES	17 QUANTITY	18 UNIT	19 UNIT PRICE	20 AMOUNT
	TITLE: DETERMINATION OF THE WATER QUALITY OF GROUND WATER SUPPLIES	5000	ANALYSES	(MINIMUM)	$275,000*
		8500	ANALYSES	(MAXIMUM)	$570,725*

*The figures were arrived at on an average basis, however, the Contractor is responsible for the number of analyses.

Order of Precedence - In the event of an inconsistency between the provisions of this contract, the inconsistency shall be resolved by giving precedence in the following order: (a) the schedule including the Statement or Scope of Work; (b) the General Provisions; (c) the other provisions of the contract whether incorporated by reference or otherwise; and (d) the specifications.

21 TOTAL AMOUNT OF CONTRACT $ 275,000

CONTRACTING OFFICER WILL COMPLETE BLOCK 22 OR 26 AS APPLICABLE

22. [X] CONTRACTOR'S NEGOTIATED AGREEMENT (Contractor is required to sign this document and return 3 copies to issuing office.) Contractor agrees to furnish and deliver all items or perform all the services set forth or otherwise identified above and on any continuation sheets for the consideration stated herein. The rights and obligations of the parties to this contract shall be subject to and governed by the following documents: (a) this award/contract, (b) the solicitation, if any, and (c) such provisions, representations, certifications, and specifications, as are attached or incorporated by reference herein. (Attachments are listed herein.)

26 [ ] AWARD (Contractor is not required to sign this document.) Your offer on Solicitation Number _____, including the additions or changes made by you which additions or changes are set forth in full above, is hereby accepted as to the items listed above and on any continuation sheets. This award consummates the contract which consists of the following documents: (a) the Government's solicitation and your offer, and (b) this award/contract. No further contractual document is necessary.

23 NAME OF CONTRACTOR
BY Spencer Floyd
(Signature of person authorized to sign)

27 UNITED STATES OF AMERICA
BY James W. Geiser
(Signature of Contracting Officer)

24. NAME AND TITLE OF SIGNER (Type or print)
Spencer Floyd
Manager
Contract Administration

25 DATE SIGNED
SEP 26 1980

28 NAME OF CONTRACTING OFFICER (Type or print)
JAMES W. GEISER

29 DATE SIGNED
SEP 29 1980

ARTICLE VII - PAYMENTS

The contractor shall be paid, upon submission of proper invoices or vouchers, the prices stipulated below for the following items delivered and accepted less deductions, if any, as herein provided:

TABLE 1

Base Period

Sample Set	Parameters to be Determined	Price Per Analysis
1. Source of supply raw water/finished water Halocarbons	1 - Bromoform 2 - Bromodichloromethane 3 - Carbon Tetrachloride 4 - Chlorobenzene 5 - Chloroform 6 - Dibromochloromethane 7 - 1,2-Dibromo-3-chloropropane 8 - 1,2-Dichlorobenzene 9 - 1,3-Dichlorobenzene 10 - 1,4-Dichlorobenzene 11 - 1,1-Dichloroethane 12 - 1,2-Dichloroethane 13 - 1,1-Dichloroethylene 14 - cis-1,2-Dichloroethylene 15 - trans-1,2-Dichloroethylene 16 - 1,2-Dichloropropane 17 - Methylene Chloride 18 - 1,1,2,2-Tetrachloroethane 19 - 1,1,1,2-Tetrachloroethane 20 - Tetrachloroethylene 21 - 1,1,1-Trichloroethane 22 - 1,1,2-Trichloroethane 23 - Trichloroethylene 24 - Vinyl Chloride 25 - Dichloroiodomethane[c] 26 - Bromobenzine	$50.00
2. Source of supply raw water/finished water Aromatics	1 - Benzene 2 - o-chlorotoluene 3 - p-chlorotoluene 4 - Ethylbenzene 5 - iso-propylbenzene 6 - n-propylbenzene 7 - Styrene 8 - Toluene 9 - o-Xylene 10 - m-Xylene 11 - p-Xylene 12 - Trichlorobenzene Isomers	$50.00
3. Source of supply raw water/finished water	Total organic carbon	$45.00

Contract No. 68-03-3031	SPECIAL PROVISIONS	PAGE 5

4.	Source of supply raw water/finished water	Free and combined chlorine residual	$ 8.70
5.	Confirmatory Analysis (Dual Column - 10%)	Halocarbons	$ 60.00
		Aromatics	$ 60.00
6.	Confirmatory (GC/MS)	Halocarbons	$ 245.00
		Aromatics	$ 245.00
7.	Quality Control (Duplicate-10%)	Halocarbons	$ 50.00
		Aromatics	$ 50.00
		Total Organic Carbon	$ [illegible]
		Free and Combined chlorine residual	$ 8.70
8.	Quality Control (reference samples)	Halocarbons	$ 55.00
		Aromatics	$ 55.00
		Total Organic Carbon	$ 50.00
		Free and Combined chlorine residual	$ 8.70

An original and 3 copies of each voucher shall be submitted to the Accounting Operations Office set forth in Block #12 on Page 1 (Standard Form 26).

ARTICLE VIII - PROJECT DIRECTOR

The performance of the work required by this contract shall be conducted under the direction of Dr. Dale M. Coulson. The Government reserves the right to approve any successor to Dr. Coulson.

STATEMENT OF WORK

The contractor, employing gas chromatography, will analyze raw and finished ground water samples.

Samples shall be provided by EPA to the contractor. Samples to be analyzed for aromatic compounds will have a suitable preservative such as nitric acid or mercuric chloride added at the time of sample collection. Samples will be stored at 4°C after collection and must be stored at this temperature until analysis. Samples will be provided to the contract laboratory within seven (7) days after collection and must be analyzed within thirty (30) calendar days after collection.

The goal of the program is to provide quantitative data on a broad range of purgeable organic compounds. Total organic carbon and free and combined chlorine residual measurements are also to be performed. Additional purgeable compounds are to be reported, though not necessarily identified, by comparison to internal standard(s) and the development of retention indicies. The relative peak area compared to that of a known concentration of an internal standard should also be reported.

During the period of performance delivery orders will be issued for the following types of analyses. (Reference Payment Article Items 1 thru 4). The purge and trap gas chromatographic procedure employing an electrolytic conductivity detector is to be used for the analyses of halocarbons. Attachment I (paragraphs 4,5,6,7, 8 & 9). The more selective and sensitive photoionazation detector should be employed for the analyses of aromatic compounds rather than a flame ionization detector (FID) --sample measurements. Attachment I (10).

During the period of performance delivery orders will be issued for the following types of analyses. (Reference Payment Article Items 5 and 6). It is realized that in certain cases, a second gas chromatographic column will be required for confirmatory analyses and in some cases gas chromatography/mass spectrometry (GC/MS) will be required for positive identifications. These analyses should be quantitative in nature and be restricted to sample sets 1 and 2 and to specific compounds identified in Table I. Dual column confirmatory determinations shall be performed on 10% of the samples. Gas chromatography/mass spectrometry confirmatory analyses shall be performed on 5% of the samples. The project officer in conjunction with the contractor will select samples to be analyzed by GC/MS. Detection and quantification limits for the organic compounds listed in Table I must be equal to or less than 0.1 - 0.5 ug/l and 0.5 ug/l respectively. Generally, detection limits for additional compounds reported must be equal or less than 0.5 ug/l. However, during the course of the contract, the detection and quantitation limits should be expected to be improved.

Low-level total organic carbon determinations shall be made according to the specified method. Attachment I (11) Samples will be preserved by EPA at the time of collection. Minimum detection and quantification limits of 50 and 100 ug/l must be achieved.

Free and combined residual chlorine measurements shall be made according to the specified method. Attachment I (12) Minimum detection and quantification limits of 50 and 100 ug/l must be achieved.

Quality Assurance

During the period of performance delivery orders will be issued for the following types of analyses. (Reference Payment Article Items 7 & 8). The following items shall be performed by the contractor for quality assurance purposes:

a. The contractor shall analyze in duplicate a total of 10% of each sample set listed in Table I. The initial 10 samples in each set shall be analyzed in duplicate to better define precision of the analytical laboratory. Precision for all compounds quantitatively analyzed for shall be as given in Table II. In addition, EPA may collect (in duplicate) and analyze 5-10% of all samples.

b. During the contract period, when analytical data are being obtained, the contractor will quantitatively analyze, twice per month and in duplicate, reference samples supplied by EPA. This requirement will apply for each instrument being employed by the contractor in the study. Four samples are required as outlined in Table III. Precision requirements will be as stated in Table II. Accuracy requirements (Table III) will be based on the averages obtained by qualified testing laboratories who have previously analyzed the reference samples.

EXHIBIT A
Contract No. 68-03-3031
4/7/80
Page 2 of 2

REPORTS OF WORK

Compilation of Data

All generated data will be inputed by the contractor into a data handling system that is compatible with a 370/168 IBM System. The contractor will also submit monthly to EPA interim and final printouts of all data plus a magnetic tape of interim and final data.

Reports

The major reporting effort, Analytical Results are to be submitted to the project officer on a monthly basis. Six copies of the monthly report are to be provided within 15 (calendar days) after the end of the period being reported. The contractor, for each preceding month, shall provide the project officer with the following:

a. Entry of data into an appropriate data system

b. A copy of the computer printout.
c. Duplicate determination data.
d. Confirmatory analyses data.
e. Quality control data -- precision and accuracy.
f. Details of progress, accomplishments, and problem areas.
g. Examples of analog outputs of data gathered in the preceding month.

At the direction of the project officer, the contractor shall provide an example of how final reported values for specific samples are obtained. The contractor must save all raw data outputs for a period of one year after completion of the contract. All or part of these data shall be made available to EPA on request. All data may be transferred to EPA on request.

A summarized report is to be submitted to the project officer consisting of: confirmatory analyses, quality control, and any additional pertinent experimental data. The report shall include a detailed description of the methods used, modifications made to established procedures, difficulties encountered, and, if any, recommendations for future analytical development work.

Reports shall be prepared in accordance with EPA Manual entitled, "Science and Technical Publicaiton" TN3 dated May 14, 1974.

EXHIBIT B
Contract No. 68-03-3031
4/7/80
Page 1 of 1

Attachment I

1. US Environmental Protection Agency, "National Interim Primary Drinking Water Regulations," Fed. Register, 40(248), 59566-59588 (December 24, 1975).

2. US Environmental Protection Agency, "Interim Primary Drinking Water Regulations; Control of Organic Chemical Contaminants in Drinking Water," Fed. Register 43(28), 5756-5780 (February 9, 1978).

3. US Environmental Protection Agency, "National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drimking Water; Final Rule," Fed. Register 44(231), 68624-68707 (November 29, 1979).

4. US Environmental Protection Agency, "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio (April 1977).

5. Ballar, T. A. and J. J. Lichtenberg, "Determining Volatile Organics at the Microgram-per Litre Level in Water by Gas Chromatography," J. AWWA, 66 739 (1974).

6. Bellar, T. A., J. J. Lichtenberg and R. C. Kroner, "The Occurrence of Organohalides in Chlorinated Drinking Water," J. AWWA 66 703 (1974).

7. Brass, H. J., M. A. Feige, T. Halloran, J. W. Mello, D. Munch and R. F. Thomas, "The National Organic Monitoring Survey: Samplings and Analyses for Purgeable Organic Compounds," in "Drinking Water Quality Enhancement Through Source Protection," Robert Pojasek, Editor, Ann Arbor Science Publishers, Ann Arbor, MI (1977).

8. US Environmental Protection Agency "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations," Fed. Register 44(233), 69464-69575 (December 3, 1979), Methods 601 and 602.

9. US Environmental Protection Agency "The Analysis of Halogenated Chemical Indicators of Industrial Contamination by the Purge and Trap Method," Environmental Monitoring and Support Laboratory, Cincinnati, OH (April 1980) (DRAFT).

10. US Environmental Protection Agency "The Analysis of Aromatic Indicators of Industrial Contamination in Water by the Purge and Trap Method," Environmental Monitoring and Support Laboratory, Cincinnati, OH (April 1980) (DRAFT).

11. US Environmental Protection Agency "Method for the Low Level Determination of Total Organic Carbon," Environmental Monitoring and Support Laboratory, Cincinnati, OH (April 1978).

12. US Environmental Protection Agency, "Methods for Chemical Analyses of Water and Wastes," Environmental Monitoring and Support Laboratory, Cincinnati, OH (1978).

ATTACHMENT I
Contract No. 68-03-3031
4/7/80
Page 2 of 2

TABLE II

Minimum Precision Requirements

Sample Set[a]	Precision Requirements[b]
1	20% above 5 ug/l 40% below 5 ug/l
2	20% above 5 ug/l 40% below 5 ug/l
3	5% above 200 ug/l 10% below 200 ug/l
4	10% above 100 ug/l

a - See Table I.

b - Measured as the percent difference between the two values obtained. The average of the two values shall be used to base the percentage difference. Thus,

$$\text{Percentage Difference} = \left| \frac{V_2 - V_1 \times 100}{\frac{V_1 + V_2}{2}} \right|$$

where V_1 and V_2 are the experimentally determined concentrations.

TABLE II
Contract No. 68-03-3031
4/7/80
Page 1 of 1

TABLE III

Required Reference Sample Analyses and Accuracy Requirements[a-c]

1.	Purgeable Organic Halocarbons -- two samples each containing compounds at different concentrations; accuracy requirements ± 20% above 5 ug/l and ± 40% below 5 ug/l.
2.	Purgeable Aromatic Compounds -- two samples each containing compounds at different concentrations; accuracy requirements ± 20% above 5 ug/l and ± 40% below 5 ug/l.
3.	Total Organic Carbon -- two samples, each containing different TOC concentrations; accuracy requirements ± 10% above 200 ug/l and ± 20% below 200 ug/l.
4.	Free and combined chlorine residual -- one sample; accuracy requirements ± 10%.

a. To be analyzed twice a month in duplicate.
b. For each analytical system being employed.
c. Accuracy based on the averages of testing laboratories who have previously analyzed these reference samples.

TABLE III
Contract No. 68-03-3031
4/7/80
Page 1 of 1

January 19, 1983

Final Report

DETERMINATION OF THE QUALITY OF GROUND WATER SUPPLIES

By: B. A. Kingsley, C. Gin Avanzino,
C. W. Beeman, and R. M. Emerson

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Technical Support Division-Office of Water Supply
26 West St. Clair Street
Cincinnati, Ohio 45268

Attention: Mr. Robert Thomas
Project Officer

EPA Contract No. 68-03-3031
SRI International Project No. PYU-2250

Approved:

M. E. Hill, Laboratory Director
Chemistry Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

EPA Report No.
January 1983

DETERMINATION OF THE QUALITY OF GROUND WATER SUPPLIES

BY

B. A. Kingsley, C. Gin Avanzino, C. W. Beeman, and R. M. Emerson

SRI International
Menlo Park, California 94025

EPA Contract No. 68-03-3031

Project Officer

Robert Thomas
Technical Support Division
Office of Water Supply
26 West St. Clair Street
Cincinnati, Ohio 45268

Office of Water and Waste Management
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

DISCLAIMER

This report has been reviewed by the Technical Support Division, Office of Drinking Water, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWARD

(to be supplied by USEPA)

ABSTRACT

The Ground Water Supply Survey was initiated to assess the quality of ground-source drinking water with respect to purgeable halocarbon and aromatic compounds and total organic carbon. In the first phase of this survey, the U.S. Environmental Protection Agency, in cooperation with the States, collected samples from approximately 1000 water supplies. Half of these supplies were randomly selected to provide a representative survey of the nation's ground water sources. Of these sources, 40% were systems serving populations of 10,000 or more, and 60% were smaller systems. The remaining water supplies were selected because of suspected chemical contamination. Many of the supplies found to contain purgeable organic compounds will be resampled during a second phase of this survey, now in progress.

Purge and trap preconcentration methods were used for the purgeables gas chromatographic analyses. A serially interfaced photoionization/electrolytic conductivity detector system was developed and used to detect and quantify 37 target compounds. An extensive quality assurance program was incorporated into the analytical scheme. All data were entered directly from SRI International into an EPA-maintained data file.

This final report, covering the first phase of the survey, summarizes the procedures used to perform these analyses and the results obtained as part of the quality assurance program. Results of sample analyses are not discussed.

This report was submitted in fulfillment of EPA Contract No. 68-03-3031 by SRI International under sponsorship of the U.S. Environmental Protection Agency, Office of Drinking Water, Technical Support Division. This report covers the period from October 1, 1980, to January 31, 1982. Work was completed on February 15, 1982.

CONTENTS

FIGURES

TABLES

ACKNOWLEDGMENTS

The authors would like to acknowledge the staff members at SRI International and the Technical Support Division, Office of Drinking Water of the U.S. Environmnetal Protection Agency, for their efforts, comments, and criticisms of this work. At SRI we extend special recognition to Dr. Dale M. Coulson for his guidance and support in this work.

At EPA we especially appreciate the guidance of the Project Officer, Robert Thomas, and Wayne Mello for providing some of the statistical analyses included in this report.

In addition, we extend our thanks to the personnel of the fifty states who provided the samples used for this study.

SECTION 1

INTRODUCTION

The Office of Drinking Water of the U.S. Environmental Protection Agency (EPA), in cooperation with the States, has undertaken a survey of the quality of the nation's drinking water derived from ground water sources. The goals of the Ground Water Supply Survey (GWSS) are to (1) augment the current pollution occurrence data base for ground water supplies, (2) improve Federal and State responses to pollution incidents, (3) stimulate State ground water quality activities, and (4) develop improved identification of heavily polluted ground water sources.

For the first phase of the GWSS, approximately 1000 ground water supplies were sampled. Half of these supplies were randomly selected, with 200 representing systems serving populations of 10,000 or more and 300 systems serving smaller populations. The remaining water supplies were selected by the States and EPA because of suspected contamination.

All samples were analyzed for purgeable halogenated and aromatic organic chemicals and for total organic carbon. Residual chlorine concentrations were measured at the time of analysis for those systems that add a disinfectant. These analyses were performed at SRI International under contract to the EPA, Office of Drinking Water, Technical Support Division (TSD), Cincinnati, Ohio.

Phase 1 of this survey has now been completed. Sixteen monthly reports have been submitted describing in detail the analytical procedures used, problems encountered, data acquired, and results obtained from the quality assurance program. This final report is intended to summarize the work done during this phase of the GWSS.

Phase 2, now under way, will continue these analyses, resampling many of the systems where contamination was identified during this initial phase in an effort to locate the specific sites of contamination and to monitor any changes in types or concentrations of pollutants.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

All data generated in this survey were analyzed by the EPA Technical Support Division (TSD). Although conclusions regarding the results of the sample analyses are beyond the scope of this project, SRI International can make certain recommendations based on its experience with these analyses:

(1) Resampling of contaminated supplies, now under way, should provide the information necessary to pinpoint the location of the offending well(s) in a ground water system. It is recommended that, whenever possible, samples from heavily contaminated wells be obtained and analyzed for the semivolatile (extractable) organics using gas chromatography/mass spectrometry (GC/MS) techniques, since the purgeables data obtained may be a good indication of further contamination.

(2) The serial gas chromatography/photoionization detector/electrolytic conductivity detector (GC/PID/ElCD) system developed for these analyses provided significantly more information for compound identification than is available from separate GC/PID and GC/ElCD analyses. This system is recommended for future work of this type.

(3) It is recommended that dichloromethane be eliminated from the list of target compounds or that its quantification limit be raised significantly. This compound is present in the environments of most laboratories involved in water analyses, including some water utilities. Low level occurrence data are almost meaningless. Field blanks analyzed in this work routinely contained 2-3 ppb of this compound.

SECTION 3

EXPERIMENTAL PROCEDURES

ANALYTICAL PROCEDURES

All water samples collected for this phase of the survey were analyzed for purgeable halocarbon and aromatic compounds and for total organic carbon (TOC). The concentrations of residual free and total chlorine were determined at the time of purgeables analysis for those samples to which disinfectant had been added. Second column confirmatory analyses were performed for all samples found to contain compounds other than the trihalomethanes (THMs) and for other samples as necessary. Selected samples were also analyzed by GC/MS. These confirmatory analyses are discussed in detail in Section 4 as a part of the quality assurance program.

SAMPLE COLLECTION AND STORAGE

Samples were collected in 60- and 250-ml headspace-free, screw cap septum-sealed bottles with Teflon-lined septa. Samples intended for purgeables and TOC analyses were preserved with mercuric chloride (10 ppm) to inhibit bacterial growth, since some data indicate losses of aromatic compounds by biodegradation (1). Additional bottles of sample containing no preservative were collected for residual chlorine measurements. Field blanks (TSD generated Milli-Q processed water) accompanied the water samples at all times.

Field collected samples were first shipped iced by overnight air express to TSD, where they were inspected, sorted, and temporarily stored. Backup samples were kept at TSD. Sample sets were then replaced in ice before shipment to SRI, again by overnight air express. A standard sample set for a ground water site consisted of one 250-ml and two 60-ml sample bottles containing mercuric chloride preservative, one 60-ml bottle without mercuric chloride preservative, and a 250-ml field blank. After being logged and inspected, the samples were immediately stored in a walk-in refrigerator maintained at 4°C. Additional bottles of SRI-generated blank water were stored in this refrigerator to monitor for contamination during storage. This refrigerator is equipped with alarm and automatic shutoff systems to prevent accidental freezing or overheating of the samples.

All primary analyses were completed within one month of sample collection.

PURGEABLE HALOCARBON AND AROMATIC COMPOUNDS

General Procedures and Instrumentation

The purge/trap technique (2-4) was used to concentrate the purgeables from 25-ml water samples before gas chromatographic analysis.

The original analytical scheme specified separate purge/trap GC analyses for halocarbon and for aromatic compounds, using electrolytic conductivity detection (ElCD) and photoionization detection (PID), respectively. However, at the initial project meeting before beginning the analyses, SRI proposed the use of a serially interfaced PID/ElCD system that allows detection of all these compounds in a single analysis. Data obtained from analyses of EPA supplied Reference Samples using this system were presented, showing the required accuracy and precision with no loss of sensitivity. Further, SRI agreed to analyze an initial batch of samples using both the serial detector procedure and separate ElCD analyses for halocarbons. The results of these analyses demonstrated that data obtained using the GC/PID/ElCD system was equivalent to the data derived from separate analyses. Subsequently, all analyses were performed using the dual detector system (5).

Over the period of this study, a number of samples have been analyzed by both SRI and TSD as a part of the quality assurance program. (The data obtained from these analyses are presented in Tables 8 and 9 of Section 4.) The SRI values were obtained using the serial detectors, and the TSD data were obtained from separate analyses for halocarbon and aromatic compounds. These data also demonstrate the equivalence of the procedures.

The instrumentation used, shown in Figure 1, consisted of the following components: a Tekmar LSC-II purge/trap unit; a Hewlett-Packard 5840A gas chromatograph with recording integrator; an HNU high temperature photoionization detector (PID), model PI-51-02, with a 10.2-eV lamp; a detector interface unit; a Coulson electrolytic conductivity detector (ElCD); and an additional Hewlett-Packard model 3380A recording integrator. The sorbent trap in the LSC-II was filled with two-thirds Tenax GC/one-third coconut charcoal (6, 7). The glass vessel was wrapped with heating tape to allow complete drying of the vessel during the trap bake-out cycle.

The photoionization detector was modified to eliminate leaks. The modifications made, shown as shaded areas in Figure 2, provided the leak-tight system necessary to allow the gas stream to pass to the second detector. The transfer line from the GC column is connected directly to the detector inlet tube by a 1/16-in. Swagelok union. The Swagelok nut attached to the inlet tube is held rigidly in place by a hexagonal opening in the plate attached firmly to the detector base, preventing damage to the glass-lined inlet tube when the transfer line is attached. A Teflon O-ring is inserted at the base of the UV lamp window to provide a better seal between the lamp and the detector cell. The PID was operated at 200°C.

A modified heated transfer block was also installed between the PID and the ElCD. A glass transfer tube delivers the effluent from the PID into the heated zone of the ElCD furnace. Additional helium (35 cm^3/min) is added within the transfer block to sweep the PID effluent into the glass transfer tube.

Two identical systems were used for these analyses: one for the primary analyses and the other for second-column confirmations.

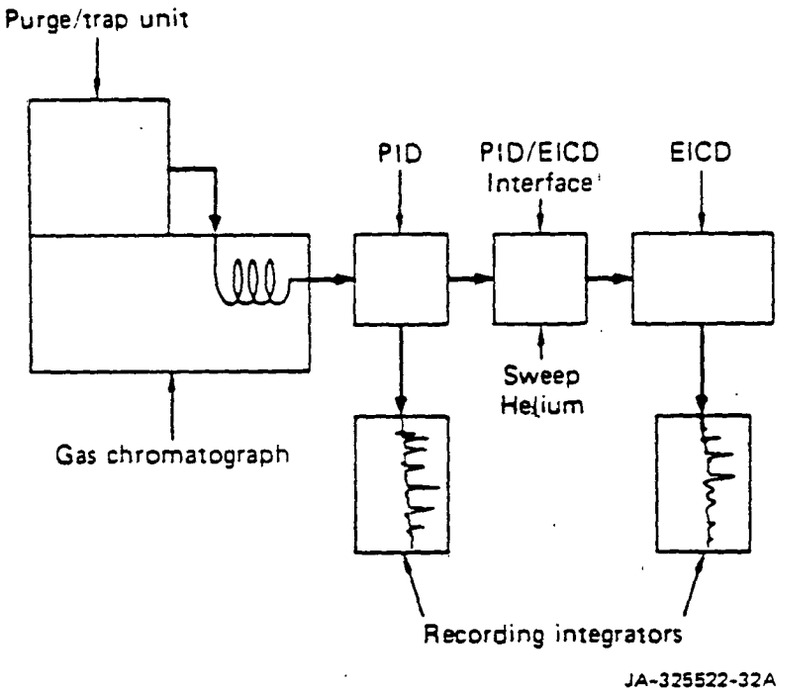


FIGURE 1 DIAGRAM OF GC/PID/EICD INSTRUMENTATION

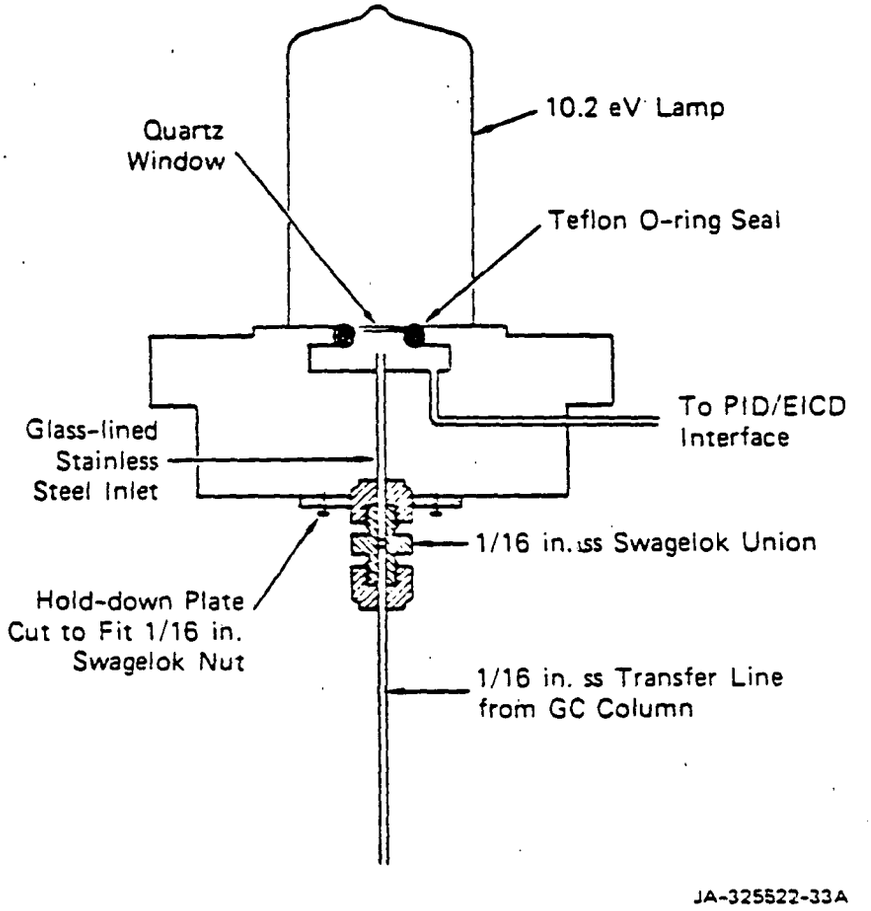


FIGURE 2 DIAGRAM OF MODIFIED PHOTOIONIZATION DETECTOR CONNECTIONS

Standards Preparation

All standard solutions were prepared in methanol (Burdick & Jackson, distilled-in-glass). An aliquot of this methanol was tested for contamination before use by spiking ~10 µl into water and analyzing the solution by the procedures described below for sample and standard analyses.

Stock standards were prepared by placing about 9 ml of methanol in a 10-ml volumetric flask, which was then stoppered and weighed. One to two drops of the desired compound were added to the flask, using a disposable pipette with the tip barely above the surface of the methanol. The stopper was replaced and the flask was reweighed. The concentration of the standard was calculated from the weight difference. The flask was then filled to the mark with methanol, and the contents were mixed by inverting the flask three times. These stock standards, at concentrations of 1 to 2 mg/ml (µg/µl), were transferred to 10-ml crimp-top vials and stored refrigerated in dessicators containing activated carbon. Stock standards of vinyl chloride were purchased in sealed glass vials containing 0.1 mg/ml of vinyl chloride in methanol (Chem Service, West Chester, Pennsylvania) to avoid problems associated with handling and preparing standards of this gas.

Working standard mixes were prepared by adding aliquots of the desired stock standards to methanol. Several different mixes were used to avoid interferences. The concentration of each compound in these working standard mixes was 6.0 ± 0.2 ng/µl. These standards were used until they failed to give satisfactory results when compared with the Reference Samples. Vinyl chloride working standards were prepared immediately before use because radical changes in concentration of this compound could be noticed within one hour of preparation. The remaining stock standard was discarded once the glass seal was broken.

Blank water was generated using a Milli-Q reverse osmosis system (Millipore, Bedford, MA). The blank water used for purgeables standards was kept under continuous nitrogen purge.

Analytical Procedures

The same procedures (2-4) were used for analysis of samples and of standards. Standards were prepared by spiking the desired amount of working standard mixture into 25 ml of blank water in a 30-ml gas-tight syringe with an inert valve.

Samples were carefully poured into a 30-ml gas-tight syringe. After the headspace was eliminated, the volume was adjusted to 25 ml. Five microliters of the internal standard mixture containing 10 ng/µl each of 2-bromo-1-chloropropane (BCP) and α,α,α-trifluorotoluene (TFT) in methanol was added through the syringe valve using a 10-µl syringe. Sample syringes were rinsed with blank water and dried in a 110°C oven between samples.

Analytical Conditions—The conditions used for the primary purgeables analyses are shown in Table 1.

TABLE 1. ANALYTICAL CONDITIONS FOR PRIMARY ANALYSIS OF HALOCARBONS AND AROMATICS

Sample volume:	25 ml
Internal standards:	50 ng 2-Bromo-1-chloropropane (2 ppb) 50 ng α,α,α-Trifluorotoluene (2 ppb)
Purge:	Helium at 40 cm^3/min for 10 min
Desorption:	4 minutes at 180°C
Chromatographic system	
Column:	1.8-m by 2-mm I.D. glass packed with 1% SP-1000 on 60/80 Carbopack B
Carrier:	Helium at 35 cm^3/min (26 cm^3/min through the LSC-II, 9 cm^3/min directly into injector)*
Temperature program:	Initial temperature 60°C for 10 min (including the 4-min desorption), programmed at 7°C/min for 10 min, then 12°C/min to final temperature of 200°C
Analysis time:	55 min

At the beginning of an analysis, the purge vessel of the LSC-II was filled with 25 ml of sample or standard, and the purge cycle, the GC program, and the second recording integrator were started simultaneously. The sample was purged with helium for 10 minutes while the purged organics were collected on the sorbent trap. At the end of the purge cycle, the sorbent trap was sealed off and rapidly heated to 100°C, then switched into the GC carrier stream and heated to 180°C, while the collected sample was thermally desorbed onto the head of the gas chromatographic column. At the end of 4 min, the sorbent trap was switched out of the GC carrier stream. The GC column was then temperature programmed as shown in Table 1 and held at the final temperature until after the expected elution time of p-dichlorobenzene (55 min).

During the desorption period, the sample was drained from the vessel. At the completion of desorption, the sorbent trap was heated to 220°C, and the purge vessel was heated to 110°C while the vessel and trap were purged with helium (~100 cm^3/min) for 20 min. All valve switching and heating were performed automatically by the LSC-II and an auxiliary timer and heater.

*Use of the extra helium sweep in the injector significantly improved the shape of early-eluting peaks using this gas chromatograph.

Chromatograms obtained from analysis of a 1 ppb standard mixture of halocarbon and aromatic compounds using the GC/PID/ElCD system are shown in Figure 3. The circled numbers refer to ID numbers in Tables 2 and 3. These chromatograms indicate a number of opportunities for compound misidentification as a result of either coelution or close retention times. For example, vinyl chloride (No. 3) and dichlorodifluoromethane (No. 4) are not resolved. Dichloroiodomethane (No. 22) is poorly resolved from the internal standard BCP (No. 21). Tetrachloroethylene (No. 25) and 1,1,2,2-tetrachloroethane (No. 26), and n-propylbenzene (No. 38) and o-chlorotoluene (No. 37) are also unresolved. Trichloroethylene (No. 17) and benzene (No. 18) elute very closely. However, in each case, one of the pair causes a response on only one detector, while the other causes both detectors to respond. In addition, for compounds that cause both ElCD and PID response, the difference in retention times between the two detectors is very reproducible. This information has been very helpful in identifiying compounds in complex samples.

Calibration--The system was calibrated by analyzing spiked standards. Calibration factors were determined by analysis of standards spiked into blank water at concentrations of 0.5, 1, 2, 3, and 10 ppb. At least two analyses were performed at each level. For each compound, area counts were plotted versus concentration (ppb). The slope of the regression line was then calculated, and the inverse was used as a calibration factor (R), having the units ppb/area count.

In general, calibration factors for the halogenated alkanes and alkenes and chlorobenzene were calculated from the ElCD calibration, whereas the PID calibration was used for the aromatic compounds, including the other halogenated aromatics. Dichloroiodomethane was an exception. At low concentrations, this THM was poorly resolved from the internal standard BCP in the ElCD chromatogram, and its concentration was frequently determined using a calibration factor calculated from the PID, where BCP caused no interference. Calibration factors from both detectors were used for the applicable compounds if needed for clarification.

Typical calibration data are shown in Table 2. Quantification limits were at least two times the minimum detectable concentration. The 0.2-ppb quantification limit was set as a reasonable and convenient minimum for the halocarbon compounds. However, for many of the halgenated compounds, detection limits were much lower than 0.1 ppb. The 0.5-ppb limits for the aromatic compounds were set to accommodate fluctuations in the PID lamp intensity over time. There were a number of exceptions. For example, the quantification limit for vinyl chloride was set at 1 ppb even though much smaller amounts of this compound could be easily detected in the ElCD chromatogram. However, because of the frequently observed coeluting freon (dichlorodifluoromethane), detection of a peak in the less sensitive PID chromatogram was necessary for identification of vinyl chloride.

There were several cases of anomolous response in the halocarbon data. The tetrachloroethane isomers show a 4:1 ratio in ElCD response factors, and the trichloroethane isomers have a nearly 2:1 response factor ratio. This problem was noted early in the contract period, and standards prepared by TSD were analyzed, giving the same results. TSD had reported 1:1 ratios for each of these isomeric pairs. Although these differences have never been resolved,

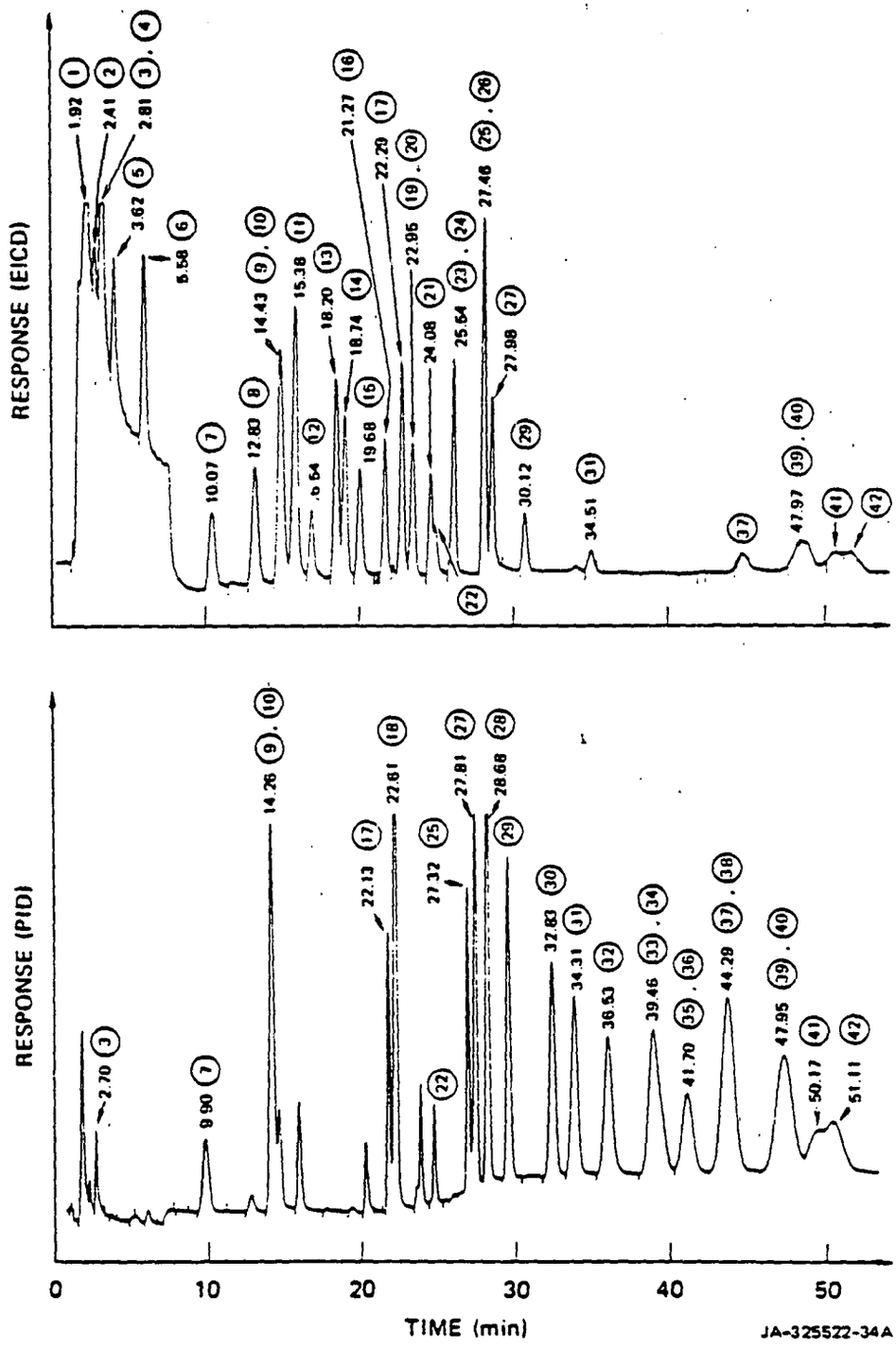


FIGURE 3 CHROMATOGRAMS OBTAINED BY PURGE/TRAP GC/PID/EICD ANALYSIS OF 1 ppb STANDARD MIXTURE OF HALOCARBON AND AROMATIC COMPOUNDS USING 1% SP1000 ON CARBOPACK B COLUMN

Numbers in circles refer to ID numbers in Tables 2 and 3.

TABLE 2. CALIBRATION DATA AND QUANTIFICATION LIMITS FOR GC/PID/ElCS PRIMARY SYSTEM

ID Number	Compound	R[a] (x10^6)	Quantification Limit (ppb)
Electrolytic conductivity detector			
3	Vinyl chloride	9.8	1
6	Dichloromethane	4.5	1[b]
7	1,1-Dichloroethylene	9.8	0.2
8	1,1-Dichloroethane	3.7	0.2
9,10	cis-, trans-Dichloroethylene	7.6	0.2
11	Chloroform	3.4	0.2
12	1,2-Dichloroethane	8.3	0.5
13	1,1,1-Trichloroethane	5.2	0.2
14	Carbon tetrachloride	3.5	0.2
15	Bromodichloromethane	5.6	0.2
16	1,2-Dichloropropane	5.8	0.2
17	Trichloroethylene	3.7	0.2
19	Dibromochloromethane	10	0.5
20	1,1,2-Trichloroethane	9.8	0.5
21	2-Bromo-1-chloropropane (ISTD)	-	-
22	Dichloroiodomethane	22	1.0
23	Bromoform	29	1.0
24	1,1,1,2-Tetrachloroethane	4.2	0.2
25	Tetrachloroethylene	3.1	0.2
26	1,1,2,2-Tetrachloroethane	16	0.5
29	Chlorobenzene	9.2	0.5
-	1,2-Dibromo-3-chloropropane	150	5
Photoionization detector		R (x10^5)	
18	Benzene	1.7	0.5
27	α,α,α-Trifluorotoluene (ISTD)	-	-
28	Toluene	1.6	0.5
30	Ethylbenzene	1.9	0.5
31	Bromobenzene	2.4	0.5
32	Isopropylbenzene		0.5
33	m-Xylene	1.6	0.5
35,36	o-, p-Xylenes	1.7	0.5
37	o-Chlorotoluene	c	0.5
38	n-Propylbenzene	c	0.5
39	p-Chlorotoluene	c	0.5
40	m-Dichlorobenzene	c	0.5
41	o-Dichlorobenzene	c	0.5
42	p-Dichlorobenzene	c	0.5

[a]Calibration factors calculated as described in text have units ppb/area counts.

[b]No quantification limit was set for dichloromethane because of possible background contamination.

[c]Because of poor integration of these late-eluting compounds, concentrations of these rarely observed compounds were determined by manual integration with a standard analyzed the same day.

TABLE 3. RETENTION ORDER AND DETECTOR RESPONSE OF SELECTED PURGEABLES USING GC/PID/ElCD SYSTEM

ID No.	Compound	Relative Retention Time on Column[a]			Detector Response[b]	
		A[c]	B[d]	C[e]	PID	ElCD
1	Chloromethane	0.069	0.177	ND[f]	-	+
2	Bromomethane	0.086	0.294	ND	-	+
3	Vinyl Chloride	0.100 (0.097)	0.177 (0.170)	ND	+	+
4	Dichlorodifluoromethane	0.100	0.101	ND	-	+
5	Chloroethane	0.129	0.411	ND	-	+
6	Dichloromethane	0.199	0.497	ND	-	+
7	1,1-Dichloroethylene	0.360 (0.356)	0.323 (0.318)	ND	+	+
8	1,1-Dichloroethane	0.459	0.657	ND	-	+
9	trans-Dichloroethylene	0.516 (0.512)	0.448 (0.444)	ND	+	+
10	cis-Dichloroethylene	0.516 (0.512)	0.620 (0.621)	0.710 (0.704)	+	+
11	Chloroform	0.550	0.620	ND	-	+
12	1,2-Dichloroethane	0.591	0.889	0.433	-	+
13	1,1,1-Trichloroethane	0.650	0.680	ND	-	+
14	Carbon Tetrachloride	0.670	0.525	0.426	-	+
15	Bromodichloromethane	0.703	0.796	ND	-	+
16	1,2-Dichloropropane	0.760	1.00	1.00	-	+
17	Trichloroethylene	0.797 (0.796)	0.680 (0.678)	0.646 (0.630)	+	+
18	Benzene	0.813	0.870	0.630	+	-
19	Dibromochloromethane	0.820	0.972	ND	-	+
20	1,1,2-Trichloroethane	0.820	1.08	1.77		+
21	2-Bromo-1-chloropropane (ISTD)	0.860	1.12	1.42	-	+
22	Dichloroiodomethane	0.902	1.04 (1.04)	2.13 (2.16)	+	+
23	Bromoform	0.912	1.12	2.48	-	+
24	1,1,1,2-Tetrachloroethane	0.912	1.12	1.77	-	+
25	Tetrachloroethylene	0.981 (0.983)	0.796 (0.796)	1.16 (1.21)	+	+
26	1,1,2,2-Tetrachloroethane	0.981	1.33	2.99	-	+
27	α,α,α-Trifluorotoluene (ISTD)	1.00	1.00	1.00	+	+
28	Toluene	1.02	1.12	1.21	+	-
29	Chlorobenzene	1.08 (1.08)	1.12 (1.12)	2.37 (2.41)	+	+
30	Ethylbenzene	1.18	1.28	1.91	+	-
31	Bromobenzene	1.23 (1.23)	ND	3.42 (3.50)	+	+
32	Isopropylbenzene	1.31	ND	2.37	+	-
33	m-Xylene	1.41	1.36	2.23	+	-
34	Styrene	1.41	ND	2.86	+	-
35	o-Xylene	1.49	1.41	2.37	+	-
36	p-Xylene	1.49	1.36	2.07	+	-
37	o-Chlorotoluene	1.60 (1.58)	ND	3.23 (3.30)	+	+
38	n-Propylbenzene	1.58	ND	2.78	+	-
39	p-Chlorotoluene	1.71 (1.72)	ND	3.23 (3.30)	+	+
40	m-Dichlorobenzene	1.71 (1.72)	ND	3.88 (3.98)	+	+
41	o-Dichlorobenzene	1.80	ND	5.28 (5.43)	+	+
42	p-Dichlorobenzene	1.83	ND	3.42 (3.50)	+	+

[a] Relative retention time are relative to internal standard α,α,α-trifluorotoluene using the appropriate detector. Where two numbers are given, the first number represents relative retention time for the ElCD.

[b] Compound causes response (+) or does not cause response (-) on indicated detector.

[c] Primary analytical column: 1.8 m by 2-mm I.D. glass packed with 1% SP-1000 on 60/80 Carbopack B, held at 60°C for 10 min, then temperature programmed at 7°C/min for 10 min, then 12°C/min to a final temperature of 200°C.

[d] Halocarbons confirmatory column: 1.8 m by 2-mm I.D. glass packed with n-octane on Porasil C, held at 50°C for 4 min, then temperatureprogrammed at 6°C/min to a final temperature of 140°C.

[e] Aromatics confirmatory column: 1.8 m by 2-mm I.D. glass packed with 5% SP-1200/5% Bentone 34 on 100/120 Supelcoport, held at 60°C for 4 min, then programmed at 3°C/min to 110°C.

[f] Not determined.

quantification of these compounds is not affected. (In fact, of these compounds, only 1,1,1-trichloroethane was observed in any real water sample during this survey.)

More important is the very poor response obtained for 1,2-dibromo-3-chloropropane (DBCP). The insensitivity to this compound is especially disturbing because the chronic exposure concern level (see Section 5) for this compound has been set at 0.05 ppb. The major losses of this compound during analysis appear to lie within the purge/trap system, since the detection limit by direct injection is estimated at 12 ng. This amount would be equivalent to 0.5 ppb in a 25-ml water sample. The poor sensitivity toward this compound is probably caused by a combination of low purging efficiency and losses within the LSC-II. Similar results were obtained on both GC/PID/ElCD systems in operation. The GC/MS employs a manual purge trap system and demonstrates the same poor sensitivity.

After the calibration was completed, quality control Reference Samples were analyzed (see Section 4). If the results of these analyses met the performance criteria, sample analysis was begun.

The calibration factors varied over time with changing detector response and column age. In fact, PID calibration factors were usually recalculated daily because considerable variation was observed. Both ElCD and PID calibration factors were monitored by daily analysis of spiked standards. If the calibration factors failed to give the correct concentrations for the daily standard (error greater than 20%), more calibration analyses were performed and additional quality control Reference Samples were analyzed.

Of the two internal standards used, BCP was detected only by the ElCD, whereas TFT was detected by both the ELCD and PID. When the GC/PID/ElCD system is used, TFT is a more suitable internal standard for both halocarbon and aromatic compounds because the relative retention times (RRTs) calculated relative to this compound better indicate the elution order of all the compounds of interest for all the columns used in this work. Relative retention times calculated with respect to TFT are shown in Table 3 for a number of compounds in addition to those to be quantified in this survey. Relative retention times for the primary chromatographic column are shown in Column A of this table. Also shown are the response for each compound for each detector (+ or -) and the relative retention times of each compound on one or more of the confirmatory columns discussed in Section 4.

Compound Identification and Quantification—All compounds were identified by comparing the retention time of the observed peak with the known retention times obtained from standards within a 1% retention time window. (Relative retention times were used only as an extra check in cases of closely eluting compounds.) The concentration of a compound was determined by applying the appropriate calibration factor to the chromatographic area:

$$\text{Conc (ppb)} = \text{Area} \times R \qquad (1)$$

Both operations (comparison of retention times and calculation of concentration) were performed automatically by external standard calibration factors entered into the integrators. All data were carefully checked for accuracy because slight variations in retention time could sometimes result in an incorrect identification, and poor integration could yield incorrect concentration data. Chromatograms from both detectors were compared for consistency of response for applicable compounds.

Occasional samples contained compounds at concentrations greatly exceeding the range of the calibration data, sometimes causing signal saturation. In such cases additional standards were prepared and analyzed at concentrations near the estimated concentration of the sample. In cases of signal saturation, the sample was reanalyzed using an attenuated detector signal and quantified against a similar standard analyzed under the same conditions.

When unidentified peaks were observed in either PID or ElCD chromatograms, they were reported by relative retention time and relative area (RA). For unknown ElCD peaks, the relative retention times were calculated relative to BCP; PID unknowns were reported relative to TFT. Relative areas (RA) were calculated by assuming that the unknown compound had a response equal to that of the aplicable internal standard:

$$RA = [Area(unknown)/Area(ISTD)] \times Conc(ISTD) \qquad (2)$$

Subsequent analyses of these samples by GC/MS have resulted in identification of most of the unknown compounds observed.

Interferences--Many of the problems of misidentification caused by poor resolution or coelution were solvable by comparing the ElCD and PID chromatograms. However, four potential interference problems remain:

(1) High concentrations of chloroform could mask small quantities of 1,2-dichloroethane. Fortunately, these ground water samples seldom had chloroform concentrations in excess of 40 ppb, where such interference would require raising the detection limit for 1,2-dichloroethane. Any samples containing chloroform at concentrations greater than 40 ppb were reanalyzed using a different chromatographic column (as described in Section 4), and the presence or absence of this compound was determined from the results of the second analysis.

(2) Two of the other trihalomethanes coelute with other compounds: dibromochloromethane with 1,1,2-trichloroethane and bromoform with 1,1,1,2-tetrachloroethane. Because the THMs are so often present in chlorinated waters, confirmatory analyses were not routinely performed to prove the identification. However, the concentrations of the four more common THMs usually follow a pattern of either increasing or decreasing concentration with increase in the number of

bromine atoms per molecule. Any samples that did not follow these trends were reanalyzed using the confirmatory column. Although this approach was definitely subjective, it was not possible to reanalyze all samples containing these two THMs. As noted above, neither 1,1,2-trichloroethane nor 1,1,1,2-tetrachloroethane was observed in any of the actual water samples analyzed in this survey even though most of the samples contained no THMs. One blind sample (see Section 4) containing 1,1,1,2-tetrachloroethane was analyzed. The apparent occurrence of bromoform at a concentration of 18 ppb with no other THMs triggered a second column confirmatory analysis, resulting in correct identification of the tetrachloroethane. However, there is the possibility that these compounds could have remained undetected in THM-containing samples.

(3) A more interesting case of compound misidentification caused by interference occurred when numerous samples with high THM levels appeared to contain small amounts of 1,2-dichloropropane. This compound closely elutes with dibromochloromethane on the confirmatory column, and initially it was thought that the identification was not being confirmed using this column because of interference of this THM at high levels. However, all samples of this type did contain the same unknown peak in the confirmatory column chromatogram. It is suspected that this compound is actually the chlorination product dichloroacetonitrile (DCAN), although only one such sample contained this compound at a concentration sufficient for identification by GC/MS. At the time these analyses were performed, no authentic DCAN standard was available to allow determination of its response.

(4) The other cases of coelution indicated in Table 3 could be resolved by reanalysis of the samples using one or both of the confirmatory columns, as discussed in Section 4.

RESIDUAL CHLORINE

Free and total residual chlorine concentrations were measured for samples from water systems using chlorination. Because of concern about biodegradation of some of the compounds of interest, particularly the aromatics, these measurements were made at the time of purgeables analysis in order to determine whether or not the residual chlorine was still providing protection from this source of sample degradation.

The DPD (N,N-diethyl-p-phenylenediamine) colorimetric method was used for these measurements. This method uses the reaction of HOCl, OCl^-, and chloramines with DPD to form a pink solution. Values for free chlorine are obtained by reaction of DPD with HOCl and/or OCl^- in a buffered solution (pH 6.3-6.5). For total chlorine measurements, KI is added to the sample along with the buffer and DPD. The I^- catalyzes the reaction between the chloramines and DPD, so that the total chlorine value measures the amount of HOCl, OCl^-, and chloramines in the solution.

Stock standards were prepared by weighing 50 to 200 mg KHP and diluting to 100 ml with blank water in a volumetric flask. The stock was stored in an amber glass bottle in the dark when not in use. The standard was replaced when analyses of Reference Standards (Section 4) failed to yield correct results. Working standards were prepared by dilution of an appropriate aliquot of the stock standard with blank water immediately before use.

The TOC oxidizing reagent was a solution of potassium persulfate ($K_2S_2O_8$) (Gold Label, 99.95%-100.05% purity, Fisher Scientific Co., Fairlawn, NJ) and 85% phosphoric acid (H_3PO_4) , reagent grade (Mallinckrodt, Parris, NY); 5 g of potassium persulfate and 3 ml (5 g) of phosphoric acid were diluted to 100 ml with blank water in a volumetric flask. The reagent was stored in an amber glass bottle and replaced every two weeks.

Analytical Procedures

Ten ml of sample was introduced into the sparger, and 0.5 ml of TOC oxidizing agent was added. As the analysis began, the sample was purged with helium. The purgeable components of the sample first passed through a lithium hydroxide scrubber, which removed the inorganic CO_2, then through a pyrolysis/reduction system where the gas stream was joined with a stream of hydrogen. The combined gases passed over a nickel catalyst that converted the purgeable organic carbon to methane, which was detected by flame ionization. The integrated signal from the detector gave a response proportional to the POC concentration in the sample.

The water sample passed through a reaction coil where the nonpurgeable organic carbon was exposed to intense ultraviolet illumination in the presence of the acidified oxidizing reagent. The nonpurgeable organic carbon was thus converted to CO_2, and the sample was transferred to a second sparger where the CO_2 was purged with helium. The CO_2 was then passed through the pyrolysis/reduction system where it was converted to methane and measured by the flame ionization detector. The integrated signal was added to that from the POC measurement, resulting in the concentration of total organic carbon (TOC).

This procedure, performed automatically by the DC-54, was repeated until two sequential analyses gave concentrations within the required level of precision (10% for TOC levels above 300 µg/liter and 20% below that level).

Calibration--The system clean-up and calibration procedure specified in the manufacturer's operation manual (9) were used. The procedure consists of three parts: (1) balancing the totalizer circuit in the totalizer/reaction module, (2) establishing a system blank, and (3) calibrating the system with a carbon standard.

A detailed procedure for balancing the totalizer circuit is given in the manufacturer's operating manual (9). Since it was seldom necessary, the procedure will not be explained here.

The system blank (SB) was established by recirculating a blank water sample through the system until a TOC level of $< 0.005 \pm 0.005$ ppm C was achieved for two consecutive analyses. This is a correction value to be subtracted from

The Hach CN-70 Test Kit (Hach Chemical Company, Ames, Iowa) was used for these analyses. The intensities of the colored solutions were visually compared with a color wheel provided with the kit. Values of free and total chlorine were reported over the range of 0.1 to 3.0 mg/liter (ppm).

TOTAL ORGANIC CARBON

General Procedures

All water samples were analyzed using a standard EPA method (8) and a Dohrmann DC-54 ultralow-level total organic carbon analyzer. The sparger used allowed transfer of the entire sample, including suspended solids, through the UV reaction chamber during the nonpurgeable organic carbon (NPOC) part of the analysis cycle.

This sparger was further modified at SRI to improve the precision obtained in the analyses of some samples. In the early stages of this work, it was noticed that analysis of certain samples yielded data with very poor precision. Initially, it was thought that the lack of precision was caused by suspended solids in the sample, since this phenomenon was never observed with standards or Reference Samples, and not all samples exhibited this behavior. Erratic data were not obtained when the standard glass-fritted sparger was used. However, careful observation of the analysis process revealed that a small amount of sample backed up through the sparger side arm and into the UV reaction chamber when a sample was loaded and the helium purge begun. Lengthening the sparger side-arms by 2.5 in. prevented sample backup and made an immediate improvement in the precision of analyses. It is suspected that the lack of precision was caused by nonpurged carbon dioxide present in that part of the sample that was observed to back up into the reaction chamber, thus escaping the purgeable organic carbon (POC) helium purge. Since both calibration standards and Reference Samples were prepared with nitrogen-purged water having a much lower carbon dioxide concentration, the sample backup was not a problem with these analyses.

Water used for standards and reagents was obtained from a Milli-Q RO system and kept under continuous nitrogen purge until used. Potassium hydrogen phthalate (KHP: $C_8H_5O_4K$) (Aldrich Chemical Co., Inc., Milwaukee, WI) was used as the calibration standard. The concentration of this standard, expressed in mg/liter, parts per million of carbon (ppm C) was calculated as shown below.

$$\text{mg C/liter} = \frac{Wt \times n \times 12}{MW \times V} \times 10^3 = \text{ppm C} \qquad (3)$$

where

Wt = weight of KHP in grams
n = number of carbon atoms per molecule (8 for KHP)
12 = atomic weight of carbon
MW = molecular weight of KHP (204)
V = volume of water in liter.

the results of subsequent analyses. This procedure also decarbonizes the system of accumulated residue.

The system was calibrated daily using KHP standard containing ~1.2 ppm C. Calibration at this concentration resulted in linear response over a concentration range of 0.200 to 12 ppm C.

Calculation of TOC Concentration--The TOC concentration of a sample was determined by correcting the digital readout from the DC-54 using the corrected system.blank (SB) obtained for that day:

$$Conc_{TOC}\ (ppm) = (TOC\ from\ digital\ readout) - SB \qquad (4)$$

SECTION 4

QUALITY ASSURANCE

The following quality assurance protocol was established to monitor the quality of data generated in these analyses.

Reference sample analysis: Four times per month using each instrument.
- Aromatics: one concentration level
- Halocarbons and total organic carbon: two concentration levels

Duplicate analyses: 10% of samples analyzed

Blind sample analyses

Split sample analyses

Confirmatory analyses
1. Second chromatographic column
2. GC/MS

REFERENCE SAMPLES

Concentrates containing standard mixtures of some of the more frequently observed halocarbon and aromatic compounds were provided by TSD as needed. The concentrates were diluted with methanol (1:10 and 1:20 for the halocarbon mixture and 1:10 for the aromatics), and the diluted concentrates were spiked into blank water as needed to provide Reference Samples. Reference Samples for TOC measurements were prepared immediately before use by diluting 0.5 ml of the concentrate into 50 ml or 250 ml of blank water for high and low level measurements, respectively. The remainder of the TOC concentrate was transferred to a crimp-top vial and stored in a refrigerator until needed for the next set of Reference Sample analyses. Once opened, a vial of concentrate was used for about one month, then replaced with a new vial.

Reference Samples were, in general, analyzed weekly using each instrument in use at that time for sample analysis. The contract specified that precision and accuracy (error) measurements be within 40% for purgeable concentrations less than 5 ppb and 20% for concentrations above that level. Precision was defined as the difference between duplicate values, divided by the average of the two (expressed as a percent). This measurement of precision is appropriate for biweekly duplicate measurements. However, since single Reference Samples were analyzed weekly for the purgeables, the precision of the measurements is better expressed by the coefficient of variation (100 times the standard deviation, divided by the mean value). The error was to be calculated with reference to average values obtained from interlaboratory tests. Since none was available, the error was calculated as 100 times the absolute value of the difference between the expected and mean concentration, divided by the expected concentrations. These data, along with the range of values found in these analyses, are summarized in Tables 4 and 5 for halocarbons and aromatics,

TABLE 4. HALOCARBONS REFERENCE SAMPLE ANALYSES--PRIMARY COLUMN

	Low Level[a]					High Level[b]				
	Expected Conc. (ppb)	Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]	Expected Conc. (ppb)	Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]
Chloroform	8.2	6.1 -9.2	7.2	12	-12	34	25-36	31	9	-8.8
1,2-Dichloroethane	3.3	2.4 -3.6	2.9	10	-12	14	9.9-15	13	11	-7.1
1,1,1-Trichloroethane	1.3	0.85-2.0	1.1	22	-15	5.6	3.7-8.0	5.0	20	-11
Carbon tetrachloride	1.5	1.2 -1.8	1.4	10	-6.7	6.2	5.1-7.3	6.4	8	3.2
Bromodichloromethane	1.4	0.96-1.6	1.4	11	0	6.0	5.1-7.5	6.4	9	6.7
Trichloroethylene	2.3	1.7 -2.6	2.0	9	-13	9.1	7.4-10	8.7	6	-4.4
Dibromochloromethane	2.1	1.0 -2.5	1.7	17	-19	8.5	5.3-8.9	7.1	11	-16
Bromoform	1.7	0.59-2.0	1.6	18	-5.9	7.0	5.1-8.2	6.9	10	-1.4
Tetrachloroethylene	1.1	0.82-1.4	1.0	11	-9.1	4.4	3.6-5.4	4.3	8	-2.3

[a] 48 analyses.

[b] 47 analyses.

[c] Coefficient of variation: 100 times the standard deviation divided by the mean value.

[d] Error expressed as 100 times the difference between the expected and mean measured concentrations, divided by the expected concentration.

respectively. For all halocarbon compounds, the errors calculated averaged -11% for the low level and -5% for the high level. While these data demonstrate a slight negative bias, the accuracy and precision requirements were easily met. No bias was observed for the aromatic compounds.

TABLE 5. AROMATICS REFERENCE SAMPLE ANALYSES--PRIMARY COLUMN

	Expected Conc. (ppb)	Concentration Found (ppb)[a]			
		Range	Mean Conc.	CV[b]	% Error[c]
Benzene	8.7	6.9-12	9.5	13	9.2
Toluene	5.3	3.5-6.5	5.1	14	-3.9
Ethylbenzene	5.9	4.3-6.7	5.9	10	0
Total xylenes	7.5	5.0-8.5	7.2	13	-4.0

[a]52 analyses.

[b]Coefficient of variation: 100 times the standard deviation divided by the mean value.

[c]Error expressed as 100 times the difference between the expected and mean measured concentrations, divided by the expected concentration.

Precision and accuracy requirements for TOC Reference Samples were 10% above 300 ppb and 20% below that level. These measurements were made in duplicate, biweekly. The definition of precision specified in the contract was the same as for the purgeables (i.e., the difference divided by the average). This definition is suitable for the biweekly duplicate measurements made, but precision was reported as the coefficient of variation on a monthly basis. The coefficient of variation is also used in Table 6 to express the precision of all TOC measurements made over the course of this study. This table also shows the range of values found and the accuracy of the mean value. TOC Reference Sample analyses demonstrated precision and accuracy (error) well below that required.

No Reference Samples were provided for residual chlorine measurements.

Reference Samples were also analyzed using the confirmatory chromatographic columns and GC/MS. These data are represented in the appropriate sections below.

TABLE 6. TOC REFERENCE SAMPLE ANALYSES

	Expected Conc. (ppm)	Concentration Found (ppm)			
		Range	Mean Conc.	CV[a]	% Error[b]
High level[c]	3.05	2.87-3.11	3.00	2.1	-1.6
Low level[c]	0.610	0.580-0.645	0.606	2.8	-0.66

[a]Coefficient of variation: 100 times the standard deviation divided by the mean value.

[b]Error expressed as 100 times the difference between the expected and mean measured concentrations, divided by the expected concentration.

[c]44 analyses.

DUPLICATE ANALYSES

Approximately 10% of the purgeables analyses were performed in duplicate. Most of these were selected at random (i.e., every tenth sample); however, some of the duplicate purgeables data reported represent analyses that were repeated for specific purposes. The most common reasons were signal saturation for one of the compounds and failure of the integrator to report an area for an off-scale peak. (Nonintegrated on-scale peaks were manually integrated.) Failure of peak recognition, an occasional problem with the HP3380A integrators used for the ElCD chromatograms, presented difficulties mainly with chloroform because only the first eluting peak was affected and the other peaks were seldom off-scale. In such cases duplicate data were reported for the other compounds, and the concentration of the compound in question was reported as "greater than" some value. Occasionally a second bottle of sample was used for the duplicate analysis. This was usually done when the results of a confirmatory analysis, using a different bottle of sample, gave results very different from those obtained in the first analysis. Duplicate analyses were also performed when laboratory contamination was suspected. However, such data were reported only if the suspicion proved false. (Data from proven cases of laboratory contamination were detected from the file.)

Because of the nature of the analysis, all TOC concentrations were determined in duplicate. For these measurements, duplicate data were reported for every tenth sample analyzed.

Duplicate measurements of free and residual chlorine were performed and reported for every tenth sample.

The contract provides that precision between duplicate values for the purgeables analyses by 20% for concentrations above 5 ppb and 40% below that concentration level. Precision requirements for TOC measurements are 10% above 300 ppb and 20% below that level. (Precision is defined as the difference divided by the average, expressed as a percent.) A summary of the precision data obtained is shown in Table 7. The trihalomethanes have been excluded from

TABLE 7. PRECISION OF DUPLICATE ANALYSES

Compound	Concentration ≤5 ppb: Number Duplicate Pairs[a]	Number Meeting Precision Criteria[b]	Range of Precision Values[c]	Mean Precision[c]	Concentration >5 ppb: Number Duplicate Pairs[a]	Number Meeting Precision Criteria[b]	Range of Precision Values[c]	Mean Precision[c]
Vinyl chloride	1	1 (100%)	36	-	1	0	34	--
1,1-Dichloroethylene	6	5 (83%)	4.6-51	29	0	--	--	--
1,1-Dichloroethane	11	10 (91%)	0-53	17	0	--	--	--
1,2-Dichloroethylene	14	13 (92%)	0-43	13	6	4 (67%)	0-22	11
1,2-Dichloroethane	1	1 (100%)	0	--	0	--	--	--
1,1,1-Trichloroethane	12	11 (92%)	0-41	14	2	2 (100%)	5.4-5.7	5.5
Carbon tetrachloride	8	8 (100%)	2.0-38	17	0	--	--	--
1,2-Dichloropropane	2	2 (100%)	0-1.2	0.6	0	--	--	--
Trichloroethylene	8	8 (100%)	0-37	22	8	7 (88%)	2.5-24	13
Tetrachloroethylene	8	8 (100%)	0-27	13	1	1 (100%)	17	--
Chlorobenzene	2	2 (100%)	11-23	17	0	--	--	--
Bromobenzene	1	0 (0%)	67	--	0	--	--	--
Toluene	2	2 (100%)	8-20	14	0	--	--	--
m-Xylene	3	3 (100%)	3.3-35	17	0	--	--	--
o-,p-Xylenes	3	3 (100%)	13-20	17	0	--	--	--
o-Dichlorobenzene	2	2 (100%)	3.8-20	12	0	--	--	--
	Concentration ≤300 ppb				Concentration >300 ppb			
Total organic carbon	11	10 (81%)	0-13	3.6	74	69 (93%)	0-8.7	2.0

[a] Number of times compound found at or above the quantification limit in both analyses, separated into high and low ranges.

[b] Number of times precision between duplicate values met contractual precision criteria: purgeables - 40% for concentration ≤5 ppb and 20% above that level. TOC: 10% ≤300 ppb and 5% above that level.

[c] For each pair, precision calculated as 100 times the absolute value of their difference, divided by their average. The range of the precision values and mean precision value are shown for each parameter.

this summary because duplicate analyses were not always performed on the same day and THM formation did continue in some of these samples. For purgeables, the range, success at meeting precision requirements, and mean precision values are given for each compound for which duplicate data were obtained, divided into concentrations above and below 5 ppb. These data demonstrate that the precision goals were, in general, met for duplicate analyses: the mean precision values for all compounds averaged 16% for concentrations less than 5 ppb and 10% for higher concentrations.

SPLIT SAMPLE ANALYSES

Split samples were real water samples that were analyzed by both TSD and SRI. In most cases samples were selected for split analysis at TSD on the basis of data reported by SRI. The results of these analyses are given in Table 8. Note that detection limits are different for some compounds and that only qualitative data were available at TSD for certain compounds at the beginning of the study. TSD data for purgeables were obtained by separate GC/ElCD and GC/PID analyses. While no formal precision requirements were set for split analyses, these comparative data helped demonstrate the equivalence of data obtained by the two methods.

BLIND SAMPLE ANALYSES

Blind samples were blank water dosed at TSD with known concentrations of analytes and sent to SRI as samples. Only five such samples were analyzed, all early in the contract period. The results of these analyses are shown in Table 9. Since the results of these analyses were satisfactory, shipment of blind samples was discontinued.

CONFIRMATORY ANALYSES

Second Column Confirmatory Analyses

All samples found or suspected to contain pugeable aromatic and halocarbon compounds other than the THMs were reanalyzed using different chromatographic columns that elute the compounds in different orders. In addition, all samples containing chloroform at concentrations greater than 40 ppb were reanalyzed using the confirmatory column because chloroform at this concentration level could mask small quantities of 1,2-dichloroethane. Confirmatory analyses were also performed for samples containing unknown peaks and DCIM. Approximately one-third of the samples were reanalyzed for halocarbons, and 6% for aromatics.

Halocarbons Confirmatory Analyses—A chromatographic column of n-octane on Porasil C was specified for second column halocarbon analyses. The analytical and calibration procedures described for primary analyses were used for second column confirmations. Only electrolytic conductivity detection was specified for these analyses; however, once the PID was installed in the system it became apparent that use of the two detectors allowed confirmation of a greater number of compounds than was possible by ElCD alone.

TABLE 6. COMPARISON OF DATA OBTAINED FOR SPLIT SAMPLE ANALYSES (concentration, ppb)[a]

Sample No.	1,1-Dichloroethene	1,1-Dichloroethane	1,1,1-Trichloroethane	Bis(chloromethyl) ether	Carbon tetrachloride	1,2-Dichloropropane	Trichloroethene	Tetrachloroethene	1,2-Dichloropropene-2	Benzene	Toluene	Ethylbenzene	m-Xylene	o,p-Dichlorobenzene
1			1.3/1.2			0.43/0.41	0.66/0.62							
2			3.4/3.1			3.3/3.3	1.4/1.2							
3			0.30/0.30	0.22/0.43		25/31	0.65/1.0							
4						0.35/0.31								
5													0.32/0.30	
6								0.31/0.44						
7		1.3/2.0		37/33	2.0/1.0			93/84						
8		1.3/0.99		0.73/1.3	1.0/0.97			0.55/0.63	0.60/0.35					
9		0.80/0.33	0.18/0.24		3.3/3.0									
10		0.22/0.15	0.66/0.25		0.37/0.14	0.10/0.18		12/12			1.3/1.3			
11			0.3/0.3											
12		0.20/0.48	0.24/0.13		0.6/0.1			2.0/1.3						
13				0.26/0.37				0.0/0.2						
14				1.4/1.7	0.31/0.18			6.4/5.6	1.3/1.1		1.3/1.3			
15						0.20/0.43								
16				1.7/2.0	1.1/1.1			3.3/3.0	(<0.3)[b]/0.26					
17		0.26/0.26		130/130	0.60/0.30			17/15	70/60			0.24/0.24		
18						11/15								
19				0.17/0.23				2.6/2.7						0.48/0.68
20														
21				0.20/0.26				0.32/0.29	2.0/1.3					
22				0.66/0.54	3.3/2.6			12/11	6.0/6.8					
23											3.0/3.0	0.30/(<0.3)[b]		
24		1.3/1.1	1.2/1.1		0.37/0.06				0.30/0.23					
25			1.3/1.1		3.4/3.6			32/32						0.37/(<0.5)[b]
26											0.94/(<3.0)[b]			
27											1.4/(<3.0)[b]			
28											0.7/3.3			

[a]The first number given was obtained by separate GC/FID or GC/ECD analysis at TRW, and the second by GC/FID/ECD analysis at EMI.
[b]Not reported below quantification limit.

TABLE 9. COMPARISON OF CONCENTRATIONS (ppb) DETERMINED FROM BLIND SAMPLE ANALYSES[a]

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
cis-, trans-Dichloroethylene					
Chloroform	(<0.5)[b]/0.27	61/49		7.5/9.0	1.4/1.5
1,1,1-Trichloroethane		7.7/10		1.7/1.6	
Carbon tetrachloride		1.7/1.2			9.6/12
Bromodichloromethane		3.5/2.2			0.9/1.2
Trichloroethylene				1.7/1.7	
Dibromochloromethane		1.8/1.6			0.77/0.92
Dichloroiodomethane	1.6/1.6				
Bromoform		2.1/1.5			1.1/1.3
1,1,1,2-Tetrachloroethane			2.2/2.3		
Tetrachloroethylene	(<0.5) /0.50	3.9/3.6		1.3/1.4	
Chlorobenzene			5.6/5.0		
Benzene	1.4/1.3	0.97/1.2	1.1/1.1		
Toluene	13/13	6.4/5.2	5.5/5.2		
Ethylbenzene	1.6/1.2	1.5/1.6	0.94/1.0		
m-Xylene	11/11	5.1/4.6	17/21		
p-Dichlorobenzene		4.6[c]/4.7			
Total organic carbon Conc. (ppm)	5.0/4.0	1.15/0.98	NA[d]/2.0	0.30/(<0.2)[b]	2.4/2.3

[a]The first number given was determined from analysis at TSD and the second reported by SRI.

[b]Not reported below quantification limit.

[c]Only dosed concentration available from TSD.

[d]Not reported.

The analytical conditions used are summarized in Table 10. Chromatograms obtained by analysis of a 1 ppb standard mixture of halocarbon compounds and selected aromatics are shown in Figure 4. The circled numbers in the figure correspond to the ID numbers in Tables 2 and 3. Relative retention time data relative to TFT for this column are shown in Column B of Table 3, although this internal standard (ID 27) potentially interferes with a number of the halocarbon compounds of interest and was not normally included in confirmatory halocarbon analyses.

TABLE 10. ANALYTICAL CONDITIONS FOR CONFIRMATORY ANALYSIS OF HALOCARBONS

Sample volume:	25 ml
Internal standards:	50 ng 2-Bromo-1-chloropropane
Purge:	Helium at 40 cm^3/min for 10 min
Desorption:	4 minutes at 180°C
Chromatographic system	
Column:	1.8-m by 2-mm I.D. glass packed with n-octane on Porasil C
Carrier:	Helium at 40 cm^3/min (28 cm^3/min through the LSC-II; 12 cm^3/min directly into injector)
Temperature program:	Initial temperature 50°C for 4 min (during desorption), programmed at 4°C/min to final temperature of 140°C
Analysis time:	30 min

Although this column is useful for confirmatory analyses because of the very different elution order of the halocarbon compounds, there are an unfortunately large number of coelutions in the ElCD chromatograms:

(1) Chloroform and cis-1,2-dichloroethylene
(2) 1,1,1-trichloroethane and trichloroethylene
(3) Bromodichloromethane and tetrachloroethylene
(4) Bromoform, 1,1,1,2-tetrachloroethane, the internal standard BCP, and chlorobenzene.

In cases (1) through (3), the first compound of the pair causes only ElCD response, whereas the second causes a response on both detectors. In the case (4), only chlorobenzene shows significant response on the PID. (Bromoform and 1,1,1,2-tetrachloroethane also coelute on the primary column, so the n-octane column is useless for resolving questions involving this pair of compounds.) Information gained using both detectors has been particularly useful in confirming the presence of cis-1,2-dichloroethylene and tetrachloroethylene since most of the chlorinated waters also contained THMs. Trichloroethylene and 1,1,1-trichloroethane were also frequently observed in the same sample.

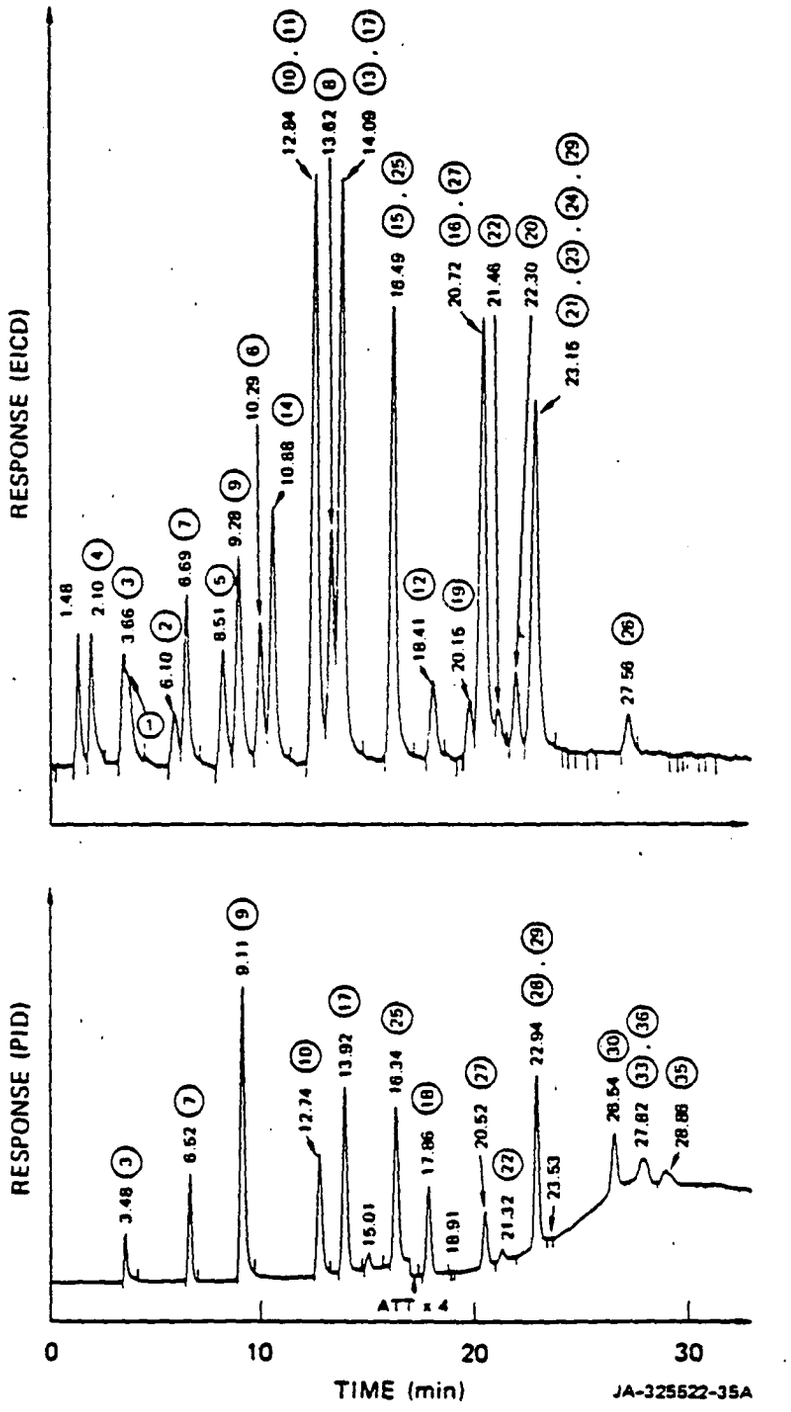


FIGURE 4 CHROMATOGRAMS OBTAINED BY PURGE/TRAP GC/PID/EICD ANALYSIS OF A 1 ppb STANDARD MIXTURE OF HALOCARBON AND AROMATIC COMPOUNDS USING AN n-OCTANE ON PORASIL C COLUMN

Circled numbers refer to ID numbers in Tables 2 and 3.

The availability of the PID chromatogram for these analyses has also been useful for confirming aromatics identifications in certain cases. Benzene and trichloroethylene (ID 18 and 17, respectively), and toluene and tetrachloroethylene (ID 28 and 25) are not resolved on the Bentone column normally used for aromatics confirmatory analyses, but are well resolved on the n-octane column. Use of the PID chromatogram allows confirmation of the aromatics identifications under these conditions.

Procedures similar to those described for the primary analyses were used for compound identification and quantification, except that concentrations were calculated using the response from both detectors for applicable compounds.

For example, if a peak corresponding to the trichloroethylene (A) retention time was observed on the PID chromatogram, the concentration of this compound was calculated using the areas from each chromatogram and the two values were compared. If they differed by more than 40% (100 times their difference divided by their average), it was assumed that 1,1,1-trichloroethane (B) was present. The concentration of the latter compound could then be calculated as follows:

$$Conc_B = [Conc_A(ElCD) - Conc_A(PID)] \frac{R_B(ElCD)}{R_A(ElCD)} \qquad (5)$$

where subscript A refers to the compound showing both PID and ElCD response (trichloroethylene in this example) and subscript B to the coeluting compound having only ElCD response (1,1,1-trichloroethane here); $conc_A$ (PID) and $conc_A$ (ElCD) refer to concentrations of A calculated from the PID and ElCD chromatographic areas, respectively; and R_A and R_B are the calibration factors for compounds A and B calculated for the ElCD.

If the difference in the concentrations of the A compound calculated using both detectors was less than 40%, only the A compound was reported (using the PID calculation), and the other compound was shown as "not reported".

The Reference Samples described for the primary analyses were analyzed using the confirmatory halocarbons system. The calculation method described above was used for quantification of 1,1,1-trichloroethane and trichloroethylene and of bromodichloromethane and tetrachloroethylene. A summary of the results of these analyses is shown in Table 11.

TABLE 11. HALOCARBONS REFERENCE SAMPLE ANALYSES--CONFIRMATORY COLUMN

Halocarbons	Low Level[a] Expected Conc. (ppb)	Low Level[a] Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]	High Level[b] Expected Conc. (ppb)	High Level[b] Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]
Chloroform	8.2	6.9-11	8.0	13	-2.5	34	22-36	33	7	-2.9
1,2-Dichloroethane	3.3	2.1-3.9	2.9	14	-12	14	10-16	13	11	-7.1
1,1,1-Trichloroethane[e]	1.3	0.8-1.4	1.1	14	-15	5.6	2.5-7.3	5.1	23	-8.9
Carbon tetrachloride	1.5	1.1-1.8	1.4	16	-6.7	6.2	4.9-9.4	6.2	18	0
Bromodichloromethane[e]	1.4	1.2-2.4	1.8	21	29	6.0	4.5-10	7.2	22	20
Trichloroethylene[e]	2.3	1.5-2.6	2.2	14	-4.3	9.1	7.6-11	8.6	11	-5.5
Dibromochloromethane	2.1	1.4-2.5	1.8	16	-14	8.5	5.8-8.9	7.7	11	-9.4
Bromoform	1.7	1.2-2.1	1.7	17	0	7.0	5.8-9.4	7.4	10	-5.7
Tetrachloroethylene[e]	1.1	0.82-1.4	1.1	14	0	4.4	4.0-6.1	4.9	12	11

[a] 19 analyses.

[b] 19 analyses.

[c] Coefficient of variation: 100 times the standard deviation divided by the mean value.

[d] Error expressed as 100 times the difference between the expected and mean found concentrations, divided by the expected concentration.

[e] Quantified using response from both PID and ElCD, as described in text.

Aromatics Confirmatory Analyses—Second column confirmations for the aromatic compounds employed a column of 5% SP 1200/5% Bentone 34. Procedures used were similar to those described for primary analyses. The analytical conditions used are shown in Table 12. Although signals from both detectors were monitored during these analyses, only the PID signal was ordinarily required for identification and quantification of the aromatic compounds. Chromatograms obtained by analysis of a 1 ppb standard of the aromatic and selected halocarbon compounds are shown in Figure 5. Circled numbers refer to the ID numbers in Tables 2 and 3. Retention time data relative to TFT for this column are shown in column C of Table 3.

In a few cases this column was used to confirm halocarbon identifications that were not resolvable using the n-octane column. As noted previously, bromoform and 1,1,1,2-tetrachloroethane (ID 23 and 24, respectively) coelute on both the primary and halocarbons confirmatory systems and both showed only ElCD response. They are, however, resolved on the Bentone column.

The procedures described for the primary analyses were used to identify and quantify compounds observed in these analyses.

The Reference Samples described earlier were analyzed using the aromatics confirmatory system. A summary of all such analyses is presented in Table 13.

Comparison of Primary and Second Column Confirmatory Analyses--A measure of the precision between the primary and second column confirmatory analyses is shown in Table 14. For each of the confirmed identifications, precision was calculated as the difference between the two values, divided by their average, expressed as a percent. For all compounds, the mean precision between primary and confirmatory analyses averaged 24% for concentrations below 5 ppb and 17% for higher concentrations.

Gas Chromatography/Mass Spectrometry Confirmatory Analyses

Forty-six samples were individually selected for GC/MS analysis by consultation with the Project Officer. Identification of unknowns was emphasized. Other selected samples contained infrequently observed compounds or were contaminated with a variety of pollutants.

A Finnigan 3200 GC/MS with a 6100 Alpha 16 Data System was used for these analyses. Samples were analyzed in three sets. For the first set of samples, the system was equipped with a semiautomated Tekmar-LSC-I purge/trap analyzer. The LSC-I contributed a high background level of toluene and was replaced with a manual purge/trap system for the remaining two sets of analyses. The manual system consisted of a 6-port Carle valve, a standard purge vessel (identical to those used for the other GC analyses), and a U-shaped glass sorbent trap containing Tenax-GC and coconut charcoal. The trap was wrapped with heating tape and heated by use of a Variac. Analytical conditions are shown in Table 15.

TABLE 12. ANALYTICAL CONDITIONS FOR CONFIRMATORY ANALYSIS OF AROMATICS

Sample volume:	25 ml
Internal standards:	50 ng α,α,α-Trifluorotoluene
Purge:	Helium at 40 cm^3/min for 10 min
Desorption:	4 minutes at 180°C
Chromatographic system	
Column:	1.8-m by 2-mm I.D. glass packed with 5% SP-1200/5% Bentone 34 on Supelcoport (100/120)
Carrier:	Helium at 40 cm^3/min (28 cm^3/min through the LSC-II; 12 cm^3/min directly into injector
Temperature program:	Initial temperature 60°C for 4 min (during desorption), programmed at 3°C/min to final temperature of 110°C
Analysis time:	32 min

TABLE 13. AROMATICS REFERENCE SAMPLE ANALYSES--CONFIRMATORY COLUMN

Compound	Expected Conc. (ppm)	Concentration Found (ppb)[a] Range	Mean Conc.	CV[b]	% Error[c]
Benzene	8.7	8.0-11	9.8	10	13
Toluene	5.3	4.3-6.5	5.6	12	5.7
Ethylbenzene	5.9	5.4-7.0	6.5	8	10
Total xylenes	7.5	7.0-8.8	8.0	9	6.7

[a]11 analyses.

[b]Coefficient of variation: 100 times the standard deviation divided by the mean value.

[c]Error expressed as 100 times the difference between the expected and mean found concentrations, divided by the expected concentration.

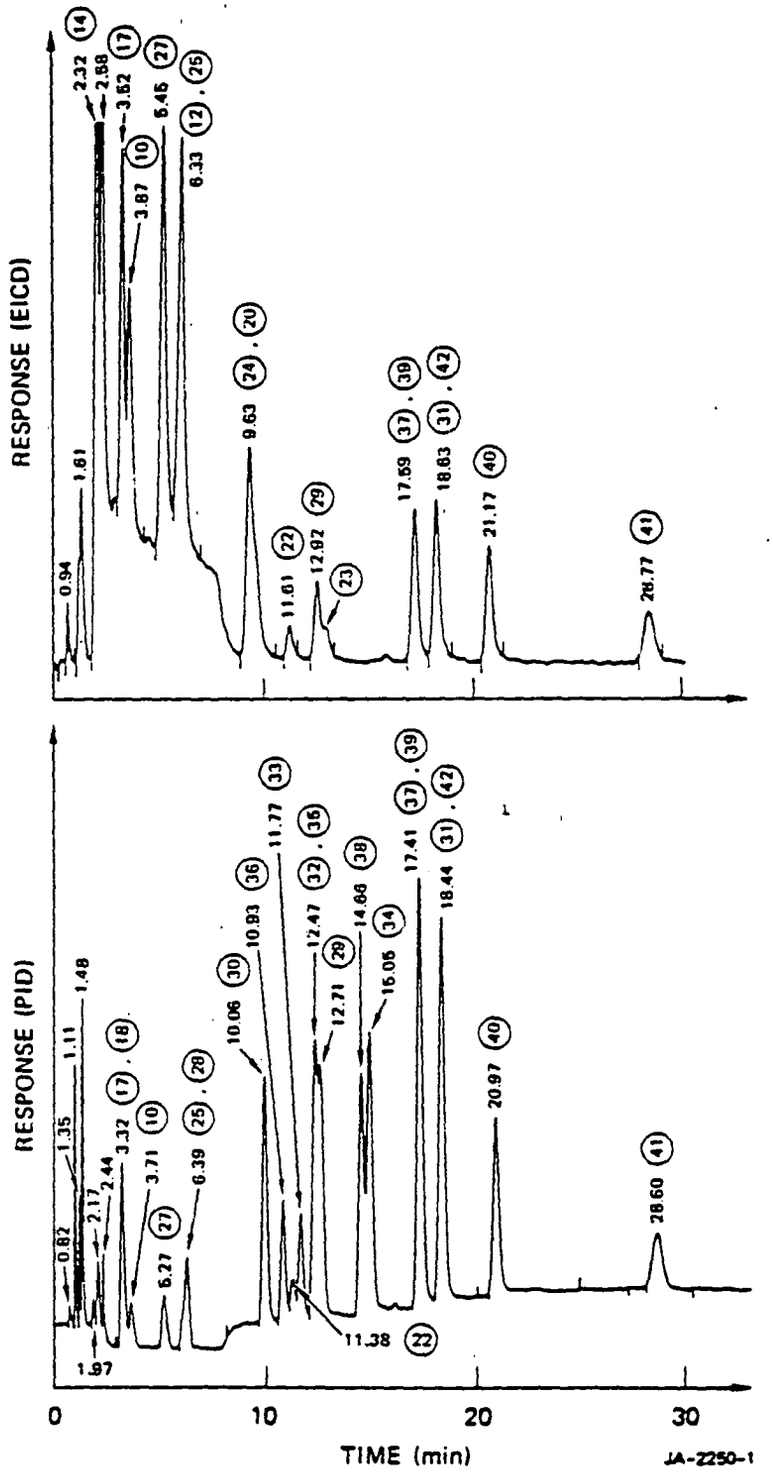


FIGURE 5 CHROMATOGRAMS OBTAINED BY PURGE/TRAP GC/PID/EICD ANALYSIS OF A 1 ppb STANDARD MIXTURE OF AROMATIC AND HALOCARBON COMPOUNDS USING A 5% SP1200/5% BENTONE 34 ON SUPELCOPORT COLUMN

Circled numbers refer to ID numbers in Tables 2 and 3.

33

TABLE 14. PRECISION BETWEEN PRIMARY AND SECOND COLUMN CONFIRMATORY ANALYSES

	Total Number of Confirmed Identifications[a]	Concentration ≤5 ppb			Concentration >5 ppb		
		Number Confirmed Identifications[a]	Range of Precision Values[b]	Mean Precision[b]	Number Confirmed Identifications[a]	Range of Precision Values[b]	Mean Precision[b]
Trichloroethylene	99	74	0-74	16	25	0-44	14
Tetrachloroethylene	78	65	0-70	15	13	9.1-37	19
1,1,1-Trichloroethane	70	63	0-98	21	7	4.7-66	25
1,2-Dichloroethylene (*cis and trans*)	59	47	0-110	23	12	0-38	14
1,1-Dichloroethane	33	33	0-135	24	0	--	--
Carbon tetrachloride	30	27	4.9-53	23	3	0-22	12
1,1-Dichloroethylene	23	22	0-141	34	1	--	12
o-, p-Xylenes	19	19	0-35	11	0	--	--
m-Xylene	17	16	0-57	18	1	--	20
1,2-Dichloroethane	16	15	3.0-48	22	1	--	20
Benzene	14	11	0-63	20	3	8.7-33	24
Toluene	14	12	1.8-45	21	2	--	0
1,2-Dichloropropane	13	12	5.7-71	24	1	--	28
p-Dichlorobenzene	10	10	1.3-80	22	0	--	--
Vinyl chloride	8	7	8.7-45	23	1	--	5.0
Ethylbenzene	7	7	0-76	31	0	--	--
Bromobenzene	6	5	0-42	21	1	--	30
Chlorobenzene	2	2	0-25	13	0	--	--
o-Dichlorobenzene	2	2	38-40	39	0	--	--
1,2-Dibromo-3-chloro-propane	1	0[c]	--	--	1	--	9.5
n-Propylbenzene	1	1	--	70	0	--	--
o-Chlorotoluene	1	1	--	8.0	0	--	--

[a] Number of times the compound was observed at or above the quantification limit in both analyses.

[b] % Precision calculated for each pair of analyses as 100 times the absolute value of their difference, divided by their average value. The range of precision values and the mean precision value are shown for each compound.

[c] Quantification limit for this compound was 5 ppb.

TABLE 15. ANALYTICAL CONDITIONS FOR GC/MS

Sample volume:	25 ml
Internal standards:	250 ng 2-Bromo-1-chloropropane; 87 ng α,α,α-Trifluorotoluene
Purge:	Helium at 40 cm^3/min for 10 min
Desorption:	4 minutes at 200°C
Chromatographic system	
Column:	1.5-m by 2-mm I.D. glass packed with 1% SP-1000 on 60/80 Carbopack B
Carrier:	Helium at 20 cm^3/min
Temperature program:	Initial temperature 60°C for 10 min, programmed at 12°C/min to final temperature of 200°C
Analysis time:	50 min
Mass spectrometer	
Mode:	Electron impact
Electron energy:	70 volts
Seconds/scan:	3
Mass range:	33-300

The system was calibrated by analyzing standard mixtures of halocarbon and aromatic compounds at concentrations from 1 to 7 ppb. Lower level standards were analyzed for most compounds to determine quantification limits. These limits were based on requirements of reasonable area for the primary characteristic ion (usually greater than 500 counts) and on background interference in and completeness of the mass spectrum obtained. Quantification limits were in general 0.3 to 0.5 ppb. Exceptions were 1,1,1,2-tetrachloroethane, bromoform, and dibromochloromethane (1 ppb), 1,2,-dibromo-3-chloropropane (4 ppb), and dichloroiodomethane (5 ppb). Quantification limits and response factors for 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane were not determined because these compounds were never observed in the primary or confirmatory analyses of these samples.

Both external standard and internal standard type response factors were calculated as shown below:

$$RF = \frac{Area(cpd)}{Conc(cpd)} \qquad (6)$$

$$RRF = \frac{Area(cpd)}{Conc(cpd)} \frac{Conc(TFT)}{Area(TFT)} \qquad (7)$$

where RF is the external standard type response factor, RRF is the response factor, relative to TFT, Area(cpd) and conc(cpd) are the area of the primary characteristic ion (from the reconstructed ion current chromatogram) and the concentration of the compound of interest, and Area(TFT) and conc(TFT) are the corresponding parameters for the internal standard α,α,α-trifluorotoluene.

After calibration standards were analyzed, the precision and accuracy obtained by applying both calculation methods were compared. The method giving the best precision and accuracy was used for that batch of samples. Calibration data used for one of the sets of analyses are given in Table 16. For each compound, the table gives the primary ion (m/e) used for quantification, the average external standard type response factors (RF), and the quantification limits.

For each round of analyses, one high and one low level halocarbons Reference Sample and duplicate aromatics Reference Samples were analyzed. The results of these analyses are shown in Table 17.

For each sample, compounds for which standards had been analyzed were identified by comparing the spectrum obtained with that of the standard within a retention window of 20 scans (±30 seconds). The appropriate response factor was then applied to the area obtained to determine the concentration reported. A comparison of the data obtained by GC/MS and GC/PID/ElCD analyses is shown in Table 18. The precision data shown were calculated as the difference between the concentrations found by GC/MS and GC/PID/ElCD primary analysis, divided by the average of the two. The mean precision values found for all compounds averaged 32% for concentrations below 5 ppb and 29% for higher concentrations.

Other "unknown" compounds observed in the primary GC/ElCD/PID analysis of a sample were searched for in the reconstructed ion current chromatogram over the appropriate mass and scan range. If a peak was found, its spectrum was compared against known spectra from the Registry of Mass Spectra Data. The NIH-EPA Chemical Information-Mass Spectral Search system was also used. When possible, authentic samples of the compounds identified were then analyzed to prove the identification.

Two points should be noted with respect to unknown identifications: (1) consistent background contamination of the freon dichlorodifluoromethane prevented confirmation of this compound in samples, and (2) three early-eluting halocarbon compounds (difluoromethane, chloromethane, and chlorodifluoromethane) had the same relative retention time on the primary GC/PID/ElCD system. The relative retention times reported for the GC/PID/ElCD primary analyses were calculatedto include the 10-minute purge time. (This had been done for convenience, since the raw data reports obtained included the 10-minute purge time in the retention time.)

The unknowns identified, along with the sample numbers in which the compounds occurred are listed in Table 19. The relative retention times reported for GC/ElCD/PID analysis of the samples are also shown. For comparison, relative retention times for the survey target compounds, calculated in the same manner, are given in Table 20.

TABLE 16. CALIBRATION DATA AND QUANTIFICATION LIMITS FOR GC/MS SYSTEM

Compound	m/e	RF	Quantification Limit (ppb)
Vinyl chloride	62	2400	0.4
Dichloromethane	84	4010	1
1,1-Dichloroethylene	96	1018	0.4
1,1-Dichloroethane	63	2790	0.4
1,2-Dichloroethylene	96	1480	0.4
Chloroform	83	4290	0.4
1,2-Dichloroethane	62	1460	0.4
1,1,1-Trichloroethane	97	2370	0.4
Carbon tetrachloride	117	3650	0.4
Bromodichloromethane	83	1860	0.4
1,2-Dichloropropane	63	1310	0.5
Trichloroethylene	130	2920	0.4
Dibromochloromethane	129	940	1.0
Dichloroiodiomethane	83	4	5
Bromoform	173	384	1.0
1,1,1,2-Tetrachloroethane	131	ND[a]	1
Tetrachloroethylene	166	3190	0.4
Chlorobenzene	112	4340	0.4
1,2-Dibromo-3-chloropropane	157	75	4
Benzene	78	5970	0.3
Toluene	91	7500	0.3
Ethylbenzene	91	7600	0.3
Bromobenzene	158	ND	0.5
Isopropylbenzene	105	ND	0.5
m-Xylene	91	5820	0.3
Styrene	104	2710	0.5
o-, p-Xylenes	91	5960	0.3
n-Propylbenzene	120	ND	0.5
o-Chlorotoluene	126	6400	0.5
p-Chlorotoluene	126	6800	0.5
m-Dichlorobenzene	147	ND	0.5
o-Dichlorobenzene	146	ND	0.5
p-Dichlorobenzene	146	3830	0.5

[a]Not determined for this set of analyses because compound was not observed in primary GC/PID/ElCD analyses of these samples.

TABLE 17. REFERENCE SAMPLES ANALYSES--GC/MS

Halocarbons	Low Level[a] Expected Conc. (ppb)	Low Level[a] Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]	High Level[b] Expected Conc. (ppb)	High Level[b] Concentration Found (ppb) Range	Mean	CV[c]	% Error[d]
Chloroform	8.2	6.6-8.1	7.5	10	-8.5	34	29-31	30	4	-12
1,2-Dichloroethane	3.3	2.9-3.4	3.1	9	-6.1	14	12-14	13	9	-7.1
1,1,1-Trichloroethane	1.3	1.1-1.2	1.1	5	-15	5.6	4.1-5.3	4.8	13	-14
Carbon tetrachloride	1.5	1.3-1.7	1.5	13	0	6.2	5.5-7	6.1	13	-1.6
Bromodichloromethane	1.4	1.4-1.5	1.4	4	0	6.0	6.7-7.3	6.9	5	15
Trichloroethylene	2.3	1.6-2.2	1.9	16	-17	9.1	8.1-9.6	9.1	10	0
Dibromochloromethane	2.1	1.1-1.5	1.3	16	-38	8.5	6.8-7.7	7.2	6	-15
Bromoform	1.7	1.5-1.9	1.7	10	0	7.0	6.8-9.5	8.0	17	14
Tetrachloroethylene	1.1	1.2-1.3	1.2	5	9.1	4.4	4.2-5.0	4.7	9	6.8
Aromatics[e]										
Benzene	8.7	7.0-9.0	7.9	10	-					
Toluene	5.3	4.1-4.7	4.4	6	-					
Ethylbenzene	5.9	5.5-6.5	5.9	6						
Total Xylenes	7.5	5.9-7.8	6.9	9						

[a] 3 analyses.

[b] 3 analyses.

[c] Coefficient of variation: 100 times the standard deviation divided by the mean value.

[d] % Error calculated as 100 times the difference between the expected and found concentrations, divided by the expected concentration.

[e] 6 analyses, except for toluene (4).

TABLE 18. PRECISION BETWEEN PRIMARY AND GC/MS CONFIRMATORY ANALYSES

Compound	Concentration < 5 ppb			Concentration > 5 ppb		
	Number of pairs[a]	% Precision		Number of Pairs[a]	% Precision	
		Range	Mean		Range	Mean
Vinyl chloride	4	6.9-29	17	1	-	82
1,1-Dichloroethylene	3	8.0-100	43	1	-	8.3
1,1-Dichloroethane	10	<1-66	19	1	-	7.7
cis- or trans-Dichloroethylene				5	9.2-52	21
1.2-Dichroroethane	4	15-32	23	0	-	-
1,1,1-Trichloroethane	11	2.0-70	22	3	15-32	26
Carbon tetrachloride	2	29-92	60	0	-	-
1,2-Dichloropropane	0	-	-	1	-	49
Trichloroethylene	9	<1-85	29	7	<1-55	19
Tetrachloroethylene	6	16-110	55	3	-	-
1,2-Bromo-3-chloropropane	0	-	-	1	-	11
Benzene	3	19-40	30	2	15-57	36
Toluene	2	11-51	31	0	-	-
Ethylbenzene	2	31-54	42	0	-	-
Bromobenzene	4	27-100	49	0	-	-
m-Xylene	2	6.8-13	9.9	0	-	-
o-, p-Xylenes	4	2.2-60	24	0	-	-
p-Dichlorobenzene	2	18-27	22	0	-	-

[a]Number of times compound found at or above the GC/MS quantification limits of both primary and GC/MS analyses.

[b]% Precision calculated for each pair as 100 times the absolute value of their difference divided by their average. The range of %P values and mean value are shown.

TABLE 19. UNKNOWN COMPOUNDS IN SAMPLES IDENTIFIED BY GC/MS ANALYSIS

Identification	Found in Sample No.	RRT[a], Primary GC/PID/ElCD Relative to Internal Standard	
		BCP[b]	TFT[c]
Difluoromethane	314	0.35	-
	698	0.35	-
	700	0.35	-
	894	0.35	-
Chloromethane	265	0.35	-
	676	0.35	-
Chlorodifluoromethane	390	0.35	-
	888	0.35	-
Chlorofluoromethane	700	0.35	-
	888	0.35	-
	894	0.35	-
Chloroethane	770	0.40	-
	888	0.40	-
Dichlorofluoromethane	22	0.44	-
	118	0.44	-
	575	0.44	-
	727	0.44	-
	888	0.44	-
Trichlorofluoromethane	575	0.55	-
	676	0.55	-
	727	0.55	-
1,2-Dichloro-1,1,2-trifluoroethane	888	0.65	-
1,1,2-trichloro-1,2,2-trifluoroethane	377	0.76	-
Dichloroacetonitrile	919	0.92	-
Dichloropropene (any of 3 isomers)	40	1.08	-
Tetrahydrofuran[d]	899	-	0.60
Diethyl ether[d]	888	-	0.65
	894	-	0.65
Cyclohexane[d]	771	-	0.71
Methylcyclohexane[d]	771	-	0.93
4-Methyl-2-pentanone	673	-	0.97

[a]Relative retention times calculated include the 10-min purge time.

[b]RRT reported relative to BCP using ElCD chromatogram.

[c]RRT reported relative to TFT using PID chromatogram.

[d]Identification confirmed by analysis of authentic standard.

TABLE 20. RELATIVE RETENTION TIMES FOR QUANTIFIED COMPOUNDS USING GC/PID/ElCD SYSTEM[a]

ID Number	Compound	RRT[b]	ID Number	Compound	RRT[c]
Electrolytic conductivity detector			Photoionization detector		
3	Vinyl chloride	0.376	18	Benzene	0.862
6	Dichloromethane	0.457	27	α,α,α-Trifluorotoluene (ISTD)	1.000
7	1,1-Dichloroethylene	0.589	28	Toluene	1.023
8	1,1-Dichloroethane	0.670	30	Ethylbenzene	1.132
9,10	cis-, trans-Dichloroethylene	0.717	31	Bromobenzene	1.172
11	Chloroform	0.745	32	Isopropylbenzene	1.231
12	1,2-Dichloroethane	0.779	33	m-Xylene	1.308
13	1,1,1-Trichloroethane	0.827	35,36	o-, p-Xylene	1.367
14	Carbon tetrachloride	0.843	37	o-Chlorotoluene	1.436
15	Bromodichloromethane	0.871	38	n-Proyplbenzene	1.436
16	1,2-Dichloropropane	0.918	39	p-Chlorotoluene	1.553
17	Trichloroethylene	0.947	40	m-Dichlorobenzene	1.553
19	Dibromochloromethane	0.967	41	o-Dichlorobenzene	1.591
20	1,1,2-Trichloroethane	0.967	42	p-Dichlorobenzene	1.616
21	2-Bromo-1-chloropropane (ISTD)	1.000			
22	Dichloroiodomethane	1.010			
23	Bromoform	1.042			
24	1,1,1 2-Tetrachloroethane	1.042			
25	Tetrachloroethylene	1.099			
26	1,1,2,2-Tetrachloroethane	1.099			
29	Chlorobenzene	1.177			
-	1,2-Dibromo-3-chloropropane	1.259			

[a]ID numbers correspond to numbered peaks in Figure 3.

[b]Relative retention times for halocarbon compounds relative to internal standard 2-bromo-1-chloropropane using ElCD. Times calculated include 10-min purge time.

[c]Relative retention times for aromatic compounds relative to internal standard α,α,α-trifluorotoluene using PID. Times calculated include the 10-min purge time.

DATA REPORTING ERRORS

The reported data were monitored for transcription or reporting errors by tracing data for every tenth sample from the original notebook entries through the computer data file. Ninety-seven identification numbers (172 separate analyses) were checked. No significant errors were found.

SECTION 5

REPORTING OF DATA

All sample data, including the results of purgeables primary, duplicate, second column confirmatory, and GC/MS analyses, and TOC and residual chlorine primary and duplicate analyses, were entered directly from SRI into the project data file maintained at the EPA computer facility in Research Triangle Park, North Carolina. The data entry format was established by TSD to accommodate a Texas Instruments Silent 700 terminal. This system proved to be a very efficient method of data transmittal.

Although all samples were analyzed within 30 days of collection, data were entered only after they had been carefully checked and entered into the project notebooks. Delays were as long as four weeks. However, when unusually contaminated samples were encountered, TSD was alerted within 48 hours by telephone. The criteria for phone alert were established after consultation with the Project Officer and were based on EPA guidelines that considered both acute and chronic toxicity factors and potential carcinogenic risks (10). The phone alert criteria used were as follows:

	Observed Conc. (ppb)
1,2-Dibromo-3-chloropropane	5*
Vinyl chloride	10
1,1-Dichloroethylene	10
1,1-Dichloroethane	10
1,2-Dichloropropane	10
Xylenes (total isomers)	10
Carbon tetrachloride	20
Tetrachloroethylene	20
Trichloroethylene	50
1,2-Dichloroethylene	50
Chlorobenzene	50
1,1,1-Trichloroethane	100
Other target compounds (separately)+	20
Combinations of target compounds (total conc)+	50

After the data were received by the Project Officer, all identifications (other than THMs) were verified during the biweekly phone conversations. This review allowed correction of data transmission errors that occasionally occurred. Data were regarded final only after completion of second column confirmatory analyses.

*Detection limit in these analyses.
+Excluding THMs.

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