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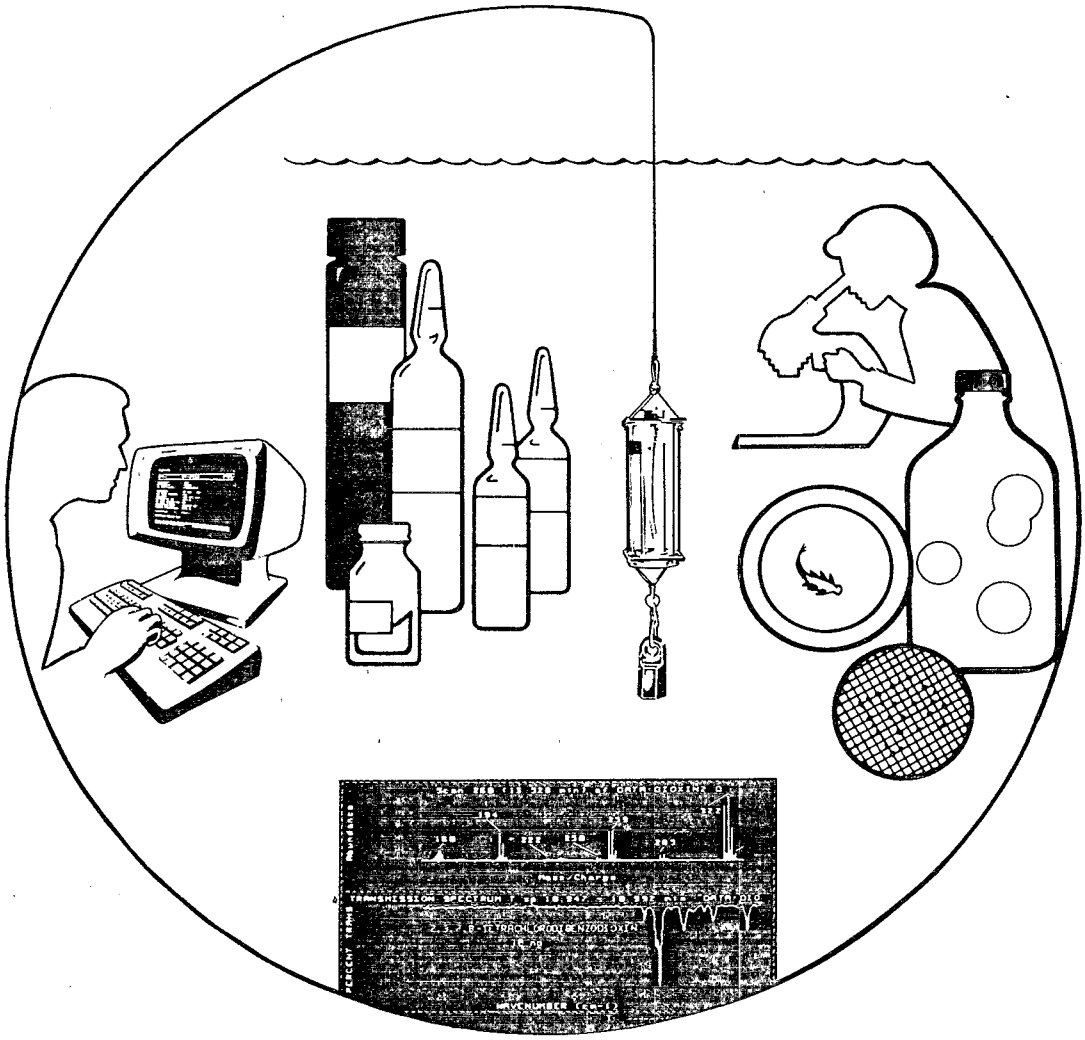
Availability, Adequacy, and Comparability of Testing Procedures for the Analysis of Pollutants Established Under Section 304(h) of the Federal Water Pollution Control Act

Report to Congress



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AVAILABILITY, ADEQUACY, AND COMPARABILITY OF TESTING PROCEDURES FOR THE ANALYSIS OF POLLUTANTS ESTABLISHED UNDER SECTION 304(h) OF THE FEDERAL WATER POLLUTION CONTROL ACT

REPORT TO THE COMMITTEE ON PUBLIC WORKS AND TRANSPORTATION OF THE HOUSE OF REPRESENTATIVES

THE COMMITTEE ON ENVIRONMENT AND PUBLIC WORKS OF THE SENATE

United States
Environmental Protection Agency
Office of Research and Development
Environmental Monitoring Systems Laboratory
Cincinnati, Ohio 45268

NOTICE

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GLOSSARY

Analyte	The constituent or characteristic of a sample which can be measured or identified.
Method	A set of written directions necessary to perform measurements. A method includes the analytical procedure as well as associated requirements such as QA/QC procedures, data reporting, and calibration.
Validate	To verify, using an acceptable scientific process, that a method is based on sound technical principles and has been reduced to practice for routine measurement purposes.
Protocol	A set of definitive directions that includes precise guidance including quality control and data reporting to meet a specific program or regulatory application.
Monitoring	The measurement of chemical, physical, or biological analytes in environmental samples for any Agency purpose.

EXECUTIVE SUMMARY

Congress passed the Water Quality Act of 1987, PL 100-4, on February 4, 1987. Section 518 of the Act directed the United States Environmental Protection Agency (EPA) to study the availability and adequacy of field and laboratory test procedures and methods to support the provisions of the Act. It also requested that the Agency study the comparability of laboratory test procedures among major federal environmental programs.

This study was conducted in three major phases. First, the monitoring requirements and data quality objectives of the Federal Water Pollution Control Act (FWPCA) and other major environmental legislation, such as the Resource Conservation and Recovery Act (RCRA), Superfund Amendments and Reauthorization Act (SARA), Safe Drinking Water Act (SDWA), and the Marine Protection Research and Sanctuaries Act (MPRSA), were reviewed and documented. Second, the test procedures established under the authority of §304(h) and promulgated in 40 CFR 136 were evaluated to determine the availability and adequacy of these test procedures to support FWPCA monitoring and testing programs. Also in the second phase of the study, test procedures established by EPA, and other federal and state programs were compared. The third phase of the study evaluated the adequacy and comparability of quality assurance/quality control programs (QA/QC) to assure the validity of environmental data.

This report was distributed widely for review in the scientific and regulated community. Representatives from EPA headquarters and regional offices and laboratories, as well as other federal and state agencies, participated in a review of this document. In addition, representatives from major trade associations, municipal, commercial and industrial laboratories also reviewed this report.

The major findings and recommendations resulting from this study are summarized below. A more complete discussion of these topics is found in Chapter 1.

Major Findings

1. The test procedures established in 40 CFR 136 under the authority of §304(h) of the FWPCA are adequate for the chemical analysis of priority toxic pollutants for technology-based water pollution controls.

2. The test procedures in 40 CFR 136 are comparable to test procedures established in monitoring programs under SDWA, RCRA and SARA. In fact, the analytical methods established in 40 CFR 136 for toxic pollutants identified in §307(a) of the FWPCA served as the basis for many of the test procedures prepared in support of subsequent legislation under several of these Acts.

3. The test procedures in 40 CFR 136 need to be modified and expanded to respond to the increased emphasis on human health risk assessment and water-quality-based controls and will require significant expansion in the types and numbers of test procedures in 40 CFR 136, additional consideration of test methods for ambient monitoring, and the development of new analytical technology.

4. Improved coordination is needed in the Agency's methods development program to avoid duplication in the development and standardization of test procedures and inconsistencies in quality assurance and quality control guidelines.

5. No Agency guidance exists for certification of laboratories performing analyses under provisions of the FWPCA. Independent laboratory certifications for wastewater analyses are performed by 18 states. Comments received from representatives of the regulated community on the draft of this report strongly supported implementation of a nationwide, federally-administered laboratory certification program.

6. Standardized and validated test procedures are needed for water-related matrices, including domestic sludges,

sediments, drilling muds, and biological tissues to support regulatory and monitoring programs under the FWPCA.

Recommendations

Based on these findings, the Agency should take the following actions:

1. Proceed expeditiously to establish standard test procedures for biomonitoring in 40 CFR 136, and expand the scope of 40 CFR 136 to include tests for additional chemical analytes and for ambient monitoring necessary to support human health risk assessment and water-quality-based controls;

2. Provide standardized and validated test procedures for domestic sludges, sediments, drilling muds, and biological tissues and consider promulgation of these procedures in 40 CFR 136.

3. Consider the establishment of an Environmental Monitoring Management Group to coordinate the development of uniform test procedures and quality assurance/quality control guidelines within the Agency, to provide a long-range program for the development of analytical methods employing new and emerging technology and to explore the feasibility of a uniform, national certification program for laboratories performing test procedures.

PREFACE

Study Mandate

Congress passed the Water Quality Act of 1987, PL 100-4, reauthorizing and amending the Federal Water Pollution Control Act of 1972, PL 92-500, on February 4, 1987. In §518 of the Act, Congress directed the Agency to:

> (a) STUDY - The Administrator shall study the testing procedures for analysis of pollutants established under §304(h) of the Federal Water Pollution Control Act. Such study shall include, but not be limited to, an analysis of the adequacy and standardization of such procedures. In conducting the analysis of the standardization of such procedures, the Administrator shall consider the extent to which such procedures are consistent with comparable procedures established under other Federal Laws.
>
> (b) REPORT - Not later than 1 year after the date of the enactment of this Act, the Administrator shall submit a report on the results of the study conducted under this subsection, together with recommendations for modifying the test procedures referred to in subsection (a) to improve their effectiveness, to the Committee of Public Works and Transportation of the House of Representatives and the Committee on Environment and Public Works of the Senate."

Study Purpose and Scope

The purpose of this study was to determine the availability and adequacy of testing methods to support the testing requirements established under the Federal Water Pollution Control Act (FWPCA). To accomplish this, the major compliance, enforcement and ambient monitoring programs established under the FWPCA were evaluated to determine:

- Chemical and biological testing requirements,
- Data quality objectives,
- Promulgated or recommended tests and methods, and
- Quality assurance/quality control (QA/QC) methods.

The availability and adequacy of the testing methods were examined relative to the needs of the various FWPCA programs. Also, QA/QC methods were evaluated to determine their ability to assure the production of monitoring data needed to support the goals of the Agency's FWPCA programs.

The testing requirements established under other Federal legislatively-mandated environmental programs were also compared. The consistency of these testing requirements and methods was compared with corresponding methods established under FWPCA programs. The following programs were studied: the Safe Drinking Water Act (SDWA) of 1974 as amended in 1986, PL 99-339; the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA or Superfund) as amended by the Superfund Amendments and Reauthorization Act (SARA) of 1986, PL 99-499; the Resource Conservation Recovery Act of 1976 as amended by the Hazardous and Solid Waste Amendments Act of 1984, PL 98-616; as well as programs managed by the U.S. Geological Survey, National Oceanic and Atmospheric Administration, and the U.S. Army Corps of Engineers.

Study Approach

Staff from major program offices in headquarters and regional offices and state agencies were interviewed. Instrument manufacturers were interviewed to determine the status of new technology and availability of new instrumentation. Methods manuals and quality assurance documents were collected and reviewed, and major databases were surveyed to determine the data routinely being generated using these methods. The study was conducted in three phases.

In the first phase, the testing requirements established by the various program offices were catalogued. Common terminology was established when necessary so that the specific suites

of analytes could be compared among corresponding programs. Data quality objectives, when available and well-defined, were also catalogued.

Phase two of the study consisted of assembling available testing methods for the determination of chemical and biological analytes. The testing methods established under §304(h) of the FWPCA, promulgated in 40 CFR 136, were reviewed to determine their availability and adequacy to support all FWPCA testing requirements. Methods established to support other FWPCA monitoring programs, but not promulgated in §304(h) were also reviewed. Testing methods established and promulgated under other regulations were assembled and reviewed to determine the comparability of testing and QA/QC methods.

The third phase of the study was a review of the Agency's FWPCA quality assurance program and the quality control requirements in each testing method to determine the ability of these methods to produce data of sufficient quality to achieve the monitoring objectives established under the various FWPCA programs. The QA/QC methods established under the FWPCA were compared to corresponding methods established by other programs.

This report was distributed widely for review in the scientific and regulated community. Representatives from EPA headquarters and regional offices and laboratories, as well as other federal and state agencies, participated in a review of this document. In addition, representatives from major trade associations, municipal, commercial and industrial laboratories also reviewed this report.

ACKNOWLEDGMENT

The information in this report was prepared with the assistance of Enseco, Inc. under Contract No. 68-01-3410. To prepare this report, published regulations, manuals, and data bases of the U. S. Environmental Protection Agency were reviewed. Interviews were conducted with State water pollution staff, Federal agency personnel, research foundations, and representatives of a variety of national organizations. Preliminary findings were identified and presented to a workgroup at the Environmental Monitoring Systems Laboratory, Cincinnati, for comments and revision. A draft of this report was widely distributed to representatives of the regulating and regulated communities. The information in this final report reflects an attempt to present a balanced and representative analysis of current information on availability and adequacy of test procedures for measuring pollutants under the provisions of the Federal Water Pollution Control Act.

CHAPTER ONE
STUDY FINDINGS AND RECOMMENDATIONS

Introduction

Latest figures from the Department of Commerce estimated that in 1985, manufacturing establishments in the United States expended $2.8 and $11.7 billion in capital improvements and operating costs, respectively, for pollution abatement (1-1). Since the study only included environmental programs at manufacturing facilities, Resource Conservation and Recovery Act (RCRA) and Superfund activities occurring off-site and federal and state Superfund activities were not considered. Therefore, the total expenditure in the United States for pollution control is significantly larger. Considering the additional requirements established recently under the Federal Water Pollution Control Act (FWPCA), Safe Drinking Water Act (SDWA), RCRA, and Comprehensive Environmental Response Compensation and Liability Act (CERCLA), these annual expenditures are projected to increase in the future. Approximately 7-10% of the total expenditure for pollution control is used for planning and conducting studies and analyzing the data from environmental programs (1-2). Of this total monitoring expenditure, one-third to one-half is used for laboratory testing (1-3), which amounts to about a billion dollars. The adequacy and accuracy of these laboratory tests are critical to establishing efficient and cost-effective pollution control programs.

Over the last decade, there has been explosive growth in the requirements to collect environmental monitoring data. Until 1976, the majority of chemical monitoring was performed for a few conventional analytes (e.g., minerals, demand analyses, nutrients, and oil/grease) in ambient waters and industrial and municipal effluents. Biomonitoring consisted of effluent toxicity tests and field surveys of phytoplankton, zooplankton, macroinvertebrates and fish in both stressed and natural ecosystems. As a result of a 1976 consent decree (Natural Resources Defense Council, Inc. et al. v. Train, 8 ERC 2120 (D.D.C. 1976)), and the 1977 Clean Water Act Amendments to the FWPCA, there was a dramatic shift in emphasis to the control of and monitoring for priority toxic pollutants. In addition, EPA and state agencies broadened their monitoring programs from a focus principally on the analyses of chemical constituents of surface waters and wastewaters to the analyses of biological toxicity, as well as sediments and biological tissues. The Agency realized that technology-based controls and chemical monitoring alone would not achieve the goals of the FWPCA, and in 1984 adopted toxicity testing as a key component of its toxics control strategy (1-4).

Over the same time period, new monitoring programs were established by EPA under the SDWA, the RCRA, Superfund, Toxic Substances Control Act (TSCA), Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), and by other federal and state agencies with emphasis on control of and monitoring for toxic pollutants. Including all environmental monitoring programs, the number of chemical and biological analytes has increased more than ten-fold in the last decade and may increase by another order of magnitude in the next decade.

In addition to the significant growth in the size and complexity of testing requirements,

there is the need to measure environmental pollutants at lower concentration levels. In the early 1970's, measurement of conventional pollutants was required at the part per million level. In the late 1970's and the early 1980's, some toxic priority pollutants were regulated to the part per billion level. Future monitoring in some cases may require the measurement of some toxic chemicals to the part per trillion level.

While the complexity of the chemical and biological testing requirements has increased, the scrutiny of the results has increased in equal measure. In the early 1970's and before, the vast majority of testing was required to support ambient air and water monitoring studies in which testing methods and QA/QC were rarely an issue. Today, due to the much greater emphasis on pollution control and the costs associated with waste treatment, laboratory methods and data quality are carefully scrutinized as a matter of routine.

Testing methods promulgated in 40 CFR 136 under the provisions of §304(h) have grown in number, complexity, and degree of validation correspondingly with the monitoring requirements of the FWPCA. When introduced in 1973, 40 CFR 136 contained approved methods for 71 analytes. Including the proposal for additional testing methods in September, 1987, 40 CFR 136 now contains 262 analytes and over 500 test methods. Additional biological parameters and test methods are soon to be proposed to support the toxicity testing requirements established under the toxics control strategy.

This report responds to the request by the Congress for a review of the test procedures established under §304(h) of the FWPCA. The methods for priority toxic pollutants developed in response to §307(a) of the 1977 Clean Water Act Amendments to the FWPCA were examined in detail to evaluate the availability and adequacy of the FWPCA methods and to compare these methods to similar methods established under other environmental legislation. The report identifies current method needs for the support of FWPCA regulations and monitoring requirements, describes steps EPA will take to manage the development and standardization of methods, and identifies areas where EPA could further standardize test procedures and QA/QC practices over time.

The findings and recommendations presented in this chapter were based on information obtained as described in the Study Approach. The subsequent chapters of this report present detailed information relating to these findings as summarized below:

Issue	Discussion
Availability and Adequacy of §304(h) Methods (Findings 1-9)	Chapter 4
Comparability of §304(h) Methods (Findings 10-14)	Chapter 5
Quality Control / Quality Assurance (Findings 4, 13, and 14)	Chapter 6
Emerging Technologies	Chapter 7

Availability and Adequacy of §304(h) Testing Methods

1) **Finding: Testing methods established to date under §304(h) of the FWPCA are substantially adequate to meet the chemical testing requirements of the Industrial Pretreatment and National Pollutant Discharge Elimination System (NPDES) programs to monitor compliance for priority pollutants.** The Agency has made significant progress in defining method performance for the Agency methods for priority toxic pollutants promulgated in 40 CFR 136 and incorporating these data into QC performance criteria. The results of additional validation studies are being incorporated into 40 CFR 136 methods as they become available. However, such studies are recognized to be costly and time consuming.

   Recommendation: The Agency should establish sound, realistic priorities and a joint OW/ORD action plan for incorporating method validation data into promulgated methods and

establishing additional performance criteria for other EPA chemical methods promulgated in 40 CFR 136. Other additional appropriate test methods which have been validated and contain method performance statistics should be promulgated under 40 CFR 136.

2) **Finding: The methods in 40 CFR 136 are not completely adequate to fully support the implementation of controls for pollutants beyond the priority pollutants, including effluent toxicity, or for certain pollutants requiring low detection levels.** The primary reason for this is that the methods standardization and promulgation process under Part 136 has lagged behind the development and availability of adequate methods for these areas. The Agency is taking action to correct the problem by incorporating toxicity test procedures in 40 CFR 136 to support biomonitoring programs, as the biological test methods in 40 CFR 136 are presently limited to five microbiological indicator tests. It is necessary, however, to measure some priority toxic pollutants at detection levels below the capability of some of the currently promulgated methods. In addition, the implementation of some water quality-based controls requires analyses of specific chemical pollutants which are not currently included in 40 CFR 136. Finally, the adequacy of point source controls will be judged in part based on ambient measurements.

A review of the data in EPA's STORET environmental data base shows that many state agencies routinely monitor for more analytes than are found on the list of §307(a) toxic pollutants. In the future, methods will be required to measure an expanded list of toxic chemicals and new, additional methods will be needed to screen for toxic inorganic and organic pollutants that are not on current Agency target compound lists. As biomonitoring is used to identify toxic discharges and stream segments with water quality problems, toxicity reduction evaluation (TRE) programs need to be performed to identify the source of the toxicity. Numerous TRE studies have shown that the causative chemical is often not a toxic pollutant established under §307.

Recommendation: The action plan should establish a schedule for promulgating biomonitoring methods as soon as possible. In addition, OW and ORD should agree on ways to improve the process for developing and standardizing test procedures. The process should set priorities for expanding the applicability of existing §304(h) chemical and biological test methods for FWPCA compliance and, where appropriate, to ambient monitoring programs by modifying existing methods and adding new methods. New chemical methods need to be developed and standardized over time in a priority sequence to measure an expanded list of toxic pollutants and to measure at concentration levels to support water quality-based controls. Existing methods to measure inorganic and organic chemicals will need to be modified to achieve better sensitivity. Many chemicals beyond the priority toxic pollutant list, such as water-soluble polar organics, are also toxic but are not measurable using the methods currently approved in 40 CFR 136. Therefore, the plan should set priorities for research efforts to develop liquid chromatography methods with mass spectrometry detection. Similarly, if measurements for the analysis of toxic metals are to be performed at the concentration levels of water quality standards, efforts to develop inductively coupled plasma/mass spectrometry detection techniques should be considered. The pace of development, documentation and standardization of biomonitoring methods needs to be accelerated to support the toxics program initiatives which will rely heavily on such methods to complement chemical monitoring.

3) **Finding: For each chemical analyte in 40 CFR 136, there are typically multiple analytical methods approved for use, and these methods often have different (or unstated) detection limits, precision,**

and accuracy. As the data quality needs of each FWPCA monitoring program become more demanding, there will be a need to differentiate the use of multiple methods promulgated for each test analyte. For some of the methods approved in 40 CFR 136, one or more of the principal descriptors of method capability (detection limits, precision and accuracy) is not published in the method or in readily-accessible background documents. In addition, a survey of the use of §304(h) methods showed that over a hundred of the test methods are apparently not being used by government, commercial, and industrial laboratories.

Recommendation: The action plan should consider the differing data quality needs of the National Pollutant Discharge Elimination System, Industrial Pretreatment, and other FWPCA monitoring programs so that the correct testing can be identified for differing monitoring applications. The action plan should then determine the degree to which detection limits, precision, and accuracy achieved with each test method approved in 40 CFR 136 should be established and documented in the method. The Agency should consider deleting any test methods that are causing confusion or detrimental program results. The Agency should continue close coordination with other methods standardization groups such as Standard Methods, American Society for Testing and Materials, Association for Official Analytical Chemists and the U.S. Geological Survey.

4) **Finding: The Agency's current mandatory quality assurance program under the FWPCA is not intended to fully document the quality of enforcement, compliance and ambient monitoring data produced by government, commercial and industrial laboratories.** Specific laboratory quality control requirements and criteria have been incorporated into 15 test methods for priority toxic pollutants promulgated in 40 CFR 136. The Discharge Monitoring Report-Quality Assurance (DMR-QA) annual performance evaluation (PE) study, which includes data from over 7000 major NPDES dischargers, is used most effectively by the Office of Water Enforcement in improving the quality of data being generated by the regulated community. However, due to budget restrictions, the study collects data for only 29 chemical and no biological analytes out of 262 promulgated at 40 CFR 136. EPA has not established a formal laboratory certification program to validate the capability of laboratories performing monitoring for NPDES permittees.

Recommendation: The Agency should develop quality control data requirements for all test methods in Part 136 which are used in the NPDES and industrial pretreatment programs as well as for laboratories performing ambient monitoring. These data would enable the Agency to verify that the required QC methods were followed and to evaluate the quality of data produced. The Agency should study the feasibility of a laboratory certification program incorporating such performance evaluation studies for all laboratories performing testing required by the FWPCA.

5) **Finding: Not all analytical methods for sediments and biological tissues for ambient monitoring under the FWPCA toxics control program have been standardized and validated.** Furthermore, since 40 CFR 136 analytical methods and equivalency procedures are not provided for ambient monitoring, there is no assurance that comparable data are being obtained from various programs, such as state monitoring programs. An examination of the data in STORET shows that data are collected and stored for every state resulting from monitoring of surface waters, bottom sediments and biological tissues. As these media are the primary receptors of toxic pollutants, the analysis of bottom sediments and biological tissues is becoming increasingly important in the determination of the extent of historical contamination and the effectiveness of current environmental controls.

Recommendation: The action plan should set priorities for research to develop, standardize and validate methods for the analysis of toxic pollutants in bottom sediments and biological tissues, and should consider ambient toxics monitoring and effluent toxicity methods for promulgation in 40 CFR 136. Existing §304(h) technology and methods can be applied to the analyses of sediments and biological tissues with the inclusion of appropriate sample extraction and cleanup and quality control methods.

6) **Finding: EPA is developing rulemaking providing guidelines for disposal of sewage sludge and will be conducting a national sewage sludge survey.** Analytical methods for the analysis of pollutants in sludge are available for five categories of pollutants (organics, pesticides/ herbicides, dioxins/ furans, metals, and classicals) and are in various stages of standardization. To date, methods for analysis of metals and classicals in sludge have been fully standardized and published. Methods for the other categories are now undergoing intra- and inter-laboratory studies.

Recommendation: The joint OW/ORD work plan to be developed should provide a schedule for completing the standardization of analytical methods for sewage sludge for promulgation in 40 CFR 136.

7) **Finding: There is a significant difference between §404 dredge spoil material monitoring requirements established by various Corps of Engineers (COE) district offices and the bottom sediment monitoring programs of state agencies.** Methods developed to support the §404 program under the FWPCA and §301 under the Marine Protection, Research and Sanctuaries Act (MPRSA), while developed jointly by the EPA and COE have not been incorporated into 40 CFR 136. A spot check of several COE district office programs indicates that while districts rely to some extent on the methods developed by the COE Waterways Experiment Station, each COE district office is free to specify different testing methods. As a result, valid comparisons of sediment data from EPA, COE and state programs can be difficult.

Recommendation: The EPA and COE should coordinate incorporation of sediment methods into 40 CFR 136 to insure that they meet the §404 program requirements. This would ensure that monitoring data generated from analyses of sediments required under EPA and COE programs and by state agencies are comparable.

8) **Finding: Extensive additional development, standardization and validation of biological monitoring methods needs to be performed to support the FWPCA toxics control and field monitoring programs.** The Agency will soon propose to amend 40 CFR 136 to include various biomonitoring methods required to support the NPDES permit program and related programs. These toxicity test methods (e.g., acute and chronic) have been standardized and subjected to single and multiple laboratory evaluations. Still other important toxicity test methods and many of the important biological field monitoring methods are still under development or require further standardization and validation. Biological test methods, particularly field and laboratory methods requiring the culturing of test organisms, are difficult to standardize. Rigid methods cannot address the specifics of each field and laboratory situation.

Recommendation: The OW/ORD action plan should prioritize FWPCA biomonitoring program needs so that the method development and standardization efforts can focus on the most important needs first. As recommended by the EPA Science Advisory Board, additional studies of the basic biology of designated test species or indicator organisms should be undertaken. The plan should also establish QA/QC program guidance and provide QA support for biomonitoring laboratories and augment training programs on the use of biological

test methods. EPA should evaluate the feasibility of a laboratory evaluation or certification program similar to the EPA program for evaluating and certifying drinking water chemistry and microbiology laboratories.

9) **Finding: The continuing growth in monitoring programs and methods requires a responsive mechanism for adding or changing methods promulgated under §304(h).** It typically takes several years from proposal to final rule to add new testing technologies to 40 CFR 136. Because of the continued development of new and better technology by laboratory research and instrument manufacturers, the methods promulgated for priority toxic organic pollutants in 1984 substituted performance criteria for detailed specifications in non-critical areas of the method that were undergoing rapid development.

With the rapid advances of technology and improvements in test methods, it is also clear that many new approaches are emerging that may produce data that are equivalent to or better than data produced by the methods currently approved in 40 CFR 136. The current method equivalency program in 40 CFR 136 effectively controls the use of new methods proposed by monitoring laboratories for the measurement of analytes which are currently promulgated. However, as biomonitoring and chemical methods are added to measure a broader range of sample matrices and analytes at lower levels, it may be difficult to apply the current statistical protocols of the existing method equivalency protocol. Requirements for method equivalency may need to be altered for biological methods.

Recommendation: The action plan should set a realistic schedule for defining explicit performance criteria in each §304(h) method so that minor improvements in technology and methods can be validated by the analyst by collection of data to meet these criteria. This would considerably speed the adoption of minor improvements and technology and yet control changes to the standardized analytical methods. In addition, the Agency should reevaluate its current statistical protocols for evaluating method equivalency to allow for the approval of methods which considerably expand the capability or improve the quality of data of existing §304(h) methods.

Comparability of FWPCA Monitoring Requirements and Testing Methods with Other Federal and State Programs

10) **Finding: An evaluation of the monitoring programs established under the authority of major environmental laws, demonstrates that the analytical methods are sometimes unnecessarily different, as they relate to similar sample matrices, target analytes, and data quality objectives.** Monitoring programs established under FWPCA, SDWA, RCRA, Superfund, TSCA and FIFRA are increasingly concerned with the same sample media. Different program objectives have resulted in differences in the specific monitoring requirements and lists of analytes. This has resulted in parallel programs for developing and standardizing analytical methods and has led to confusion for those performing the required monitoring. The past attempts by the Agency to streamline analytical methods used by different programs have not been successful.

Recommendation: The Agency should establish a workgroup to compile and evaluate monitoring requirements including target analytes and the data quality objectives in each Agency program. Eventually, representatives of other federal agencies such as Department of the Interior-U.S. Geological Survey, Department of Commerce-National Oceanic and Atmospheric Administration and the Department of Defense- Corps of Engineers as well as state agencies could be included. The goal would be to integrate, when

appropriate, the monitoring requirements, target analytes and data quality objectives, as well as clarifying needed distinctions among programs. Significant efforts are ongoing in each program office to rank the importance of chemicals according to toxicity, production/use, physical properties, bioaccumulation in the environment, carcinogenicity, and several other factors.

Program offices could combine their ranking systems into one common system where possible. A master list of chemicals could then be developed, reviewed, and prioritized. While measurement of every chemical on this list would not be required in every sample matrix by every Agency program, the list would contain chemicals which are common to all program offices. The Industrial Technology Division presently maintains such a list to track substances that are on the major regulatory lists from all of the program offices. This "List of Lists" could serve as a basis for the list to be studied by the work group. The work group could meet on an infrequent basis to refine and, if necessary, reprioritize the target substances and biological monitoring analytes as well as review the data quality objectives for each of the Agency's monitoring programs. The end result would be a master list of chemical and biological monitoring analytes and sample matrices for the whole or subset of this master list of chemicals, the required detection levels by chemical or by sample matrix, and the precision and accuracy goals to support each Agency monitoring program. This effort would precede the selection of methods from among those currently available and the development of new testing methods by the combined task group.

11) **Finding: Nomenclature for toxic chemicals and definitions of common method performance criteria are not standardized.** This compromises the Agency's ability to develop consistent monitoring requirements and methods.

Recommendation: The Agency should adopt standardized nomenclature including the use of Chemical Abstract Service (CAS) numbers to assure that each target chemical is unambiguously identified. Furthermore, insofar as practical, the Agency should adopt common statements of method performance criteria and expressions of data quality objectives throughout all offices and monitoring programs.

12) **Finding: Duplication of methods and methods manuals by Agency program offices and other federal and state agencies has resulted in confusion in the regulated community.** Almost all of the chemical methods promulgated or recommended for EPA programs, as well as those of other federal and state agencies, rely on the technology standardized for the measurement of toxic pollutants under the FWPCA. There are some legitimate differences among programs since not all monitoring requirements are developed from the same criteria. However, a careful review of selected high-use methods shows that differences are often superficial and unnecessary, and that some program offices have adopted out-of-date 40 CFR 136 methods or made changes which degraded rather than improved the methods.

As monitoring programs become driven by criteria developed to protect human health and aquatic life, the requirements for the analyses of a particular matrix such as water, sediment, biological tissue, and air samples may be the same whether established under FWPCA, SDWA, RCRA or Superfund programs. The apparent duplicative efforts involved in developing separate methods manuals to accomplish the same purpose seem to be difficult to justify. At the same time, gaps remain in the availability and adequacy of methods required to control many other toxic pollutants.

Recommendation: An Environmental Methods Management Group should be formed to coordinate common analytical methods and methods manuals throughout the Agency. A first objective should be the establishment of a computerized catalogue of the availability,

applicability, and degree of standardization of methods currently in use in the Agency. Experts who would coordinate the exchange of information, should be identified as focal points in each major scientific or technical area.

Methods used in special environmental monitoring studies performed or funded by federal and state agencies should be included where possible in the method tabulations. This data base could be tied into other existing data bases in the scientific community. Then, any investigator with the responsibility for developing an environmental monitoring program could search this data base to determine the availability and adequacy of methods to support the subject study. This would tend to eliminate duplicative efforts among investigators.

A second objective of the Group would be to annually review and coordinate all Agency methods development and validation activities to assure that the Agency's resources are efficiently directed towards solving the methods development and validation problems of greatest priority. Again, interagency coordination at the federal level should follow to minimize replicative efforts on the part of the other federal agencies who are performing environmental monitoring.

The Group could also consider over the long term the feasibility of the development of a common methods manual for all programs. Although this would be a difficult task and require a long-term commitment, a single manual is technically feasible because the majority of methods in use today employ common technology. Such a methods manual would consist of a description, in detail, of the technology, specific directions as to how each method must be modified to achieve the required detection limits, and precision and accuracy on each sample matrix type. The exact group of chemicals and sample matrices for which a method has been standardized and validated should be listed in the method. However, there are numerous questions of manageability and usefulness that need to be addressed.

13) **Finding: Although the EPA has a national quality assurance program which provides a range of QA supports and guidance, the mandatory quality assurance programs and specific quality control methods established within the Agency's operating programs and in other federal and state programs are often inconsistent, sometimes inadequate, and not always cost-effective.** There are literally dozens of different federal and state laboratory evaluation programs and different QA requirements that must be met by commercial and industrial environmental laboratories operating interstate. The majority of the program requirements are based on sound rationale but responses to these separate and uncoordinated federal and state regulatory programs are costly, repetitive and do not necessarily improve data quality.

    Environmental data generated in one state may be scrutinized in detail, while the data can go nearly unchecked and uncontrolled in a neighboring state. In addition to being an inequitable burden both on the laboratories and those funding the work, this diversity of quality assurance makes data comparisons difficult.

    Recommendation: The Administrator should establish a task force of the Environmental Methods Management Group to coordinate the development of uniform QA/QC requirements within methods, and a tiered structure of minimal QA/QC requirements across all Agency monitoring programs. The Administrator should consider discussions with other federal agencies toward developing uniform methods and quality assurance requirements across all federal environmental programs.

14) **Finding: Because of the increased reliance upon complex laboratory measurements performed under carefully controlled conditions, EPA**

should determine whether there is a need for a uniform laboratory certification program for the FWPCA programs. The Agency has a formal program of certification of drinking water laboratories. The Agency also has two water laboratory approval programs based largely on study performance: 1) the Discharge Monitoring Report - Quality Assurance (DMR-QA) studies for major dischargers under the National Pollutant Discharge Elimination System (NPDES) who must perform satisfactorily on a group of basic analytes, once per year, and 2) the Water Pollution (WP) Studies conducted semiannually for all wastewater and ambient monitoring laboratories. In the non-water areas, performance evaluation (PE) studies are conducted quarterly for the Resource Conservation Recovery Act (RCRA) and Comprehensive Environmental Response Compensation and Liability Act/Superfund Amendments and Reauthorization Act of 1986 (CERCLA/SARA) laboratories.

These five program areas for laboratory evaluation/approval in the EPA are compounded by the state studies conducted by most primary states in three or more of these areas. Consequently, any laboratory operating interstate may be required to operate according to varying but overlapping QA/QC requirements and performance requirements for a number of state and federal programs.

Recommendation: A task force should be created, which consists of representatives from ORD and EPA program offices, and other federal and state agencies and interested parties to evaluate the feasibility of a nationally coordinated environmental laboratory certification program. The task force should consider whether criteria should be developed requiring routine review of QC documentation of laboratories performing environmental analyses.

Chapter One References

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3. Carter, M.J., 1987. Confidential Market Analysis.
4. U.S. Environmental Protection Agency, 1984. Development of water quality-based permit limitations for toxic pollutants. 49 Federal Register: 9016, March 9, 1984.

CHAPTER TWO
DETERMINATION OF TESTING REQUIREMENTS ESTABLISHED UNDER MAJOR ENVIRONMENTAL PROGRAMS

As the first part of this study, a detailed assessment was performed to determine the monitoring requirements and data quality objectives established under major environmental legislation. Specifically, an assessment was performed to: 1) determine the chemical and biological measurements that are required by various Federal Water Pollution Control Act (FWPCA) programs; 2) assess the monitoring requirements established under other environmental legislation; and 3) determine the relationship of the monitoring requirements among the various regulatory programs.

Testing Requirements Established Under the FWPCA

Congress enacted the Federal Water Pollution Control Act Amendments in 1972 (PL 92-500), replacing several previously enacted but uncoordinated water pollution control acts, such as the Water Quality Act of 1965, Clean Water Restoration Act of 1966, the Water Quality Improvement Act of 1970, all of which were amendments to the original Federal Water Pollution Control Acts of 1948 and 1956 (2-1). The 1972 FWPCA is the basic water pollution control statute for most of EPA's current water regulations and programs requiring monitoring. The FWPCA was amended in 1977 (PL 95-217), in 1978 (PL 95-576), and again recently with the Water Quality Act of 1987 (PL 100-4).

The broad goals of the FWPCA are to: (1) achieve adequate water quality to protect fish, shellfish and wildlife and for recreational purposes (fishable, swimmable standard); and (2) eliminate the discharge of pollutants in toxic amounts to the Nation's waters. The FWPCA established a comprehensive regulatory program to be carried out by the Environmental Protection Agency (EPA) and the states. The basic elements of the program, relative to monitoring, include the following:

- A system of technology-based effluent limits establishing base-level or minimum treatment which must be achieved by direct industrial dischargers (existing and new sources) and publicly-owned treatment works (POTW's), and a complementary system of pretreatment requirements applicable to discharges to POTW's.
- A program for imposing more stringent limits where such limits are necessary for achieving water quality standards or objectives.
- A permit program (the National Pollutant Discharge Elimination System - NPDES) requiring dischargers to disclose the volume and nature of their discharges; authorizing EPA to specify the limitations to be imposed on such discharges; imposing on permittees an obligation to monitor and report as to their compliance or non-compliance with the permit limits; and authorizing EPA enforcement in the event of non- compliance.
- Specific provisions for accidental discharges of toxic chemicals (e.g., accidental oil spills).
- Extensive environmental monitoring programs, such as outlined in Section 106(e), were required to identify problems and judge the effectiveness of the water pollution control program.

A detailed review of the FWPCA and associated EPA regulations is beyond the scope of this study. However, a brief synopsis of the major programs that require monitoring is useful to understanding the need for standardized monitoring methods for all programs so that data can be easily and meaningfully compared. Figure 2-1 outlines the overall scheme for controlling wastewater discharges under the FWPCA.

Technology-Based Limits

The first of the four major FWPCA regulatory mechanisms is the system of technology-based limits which must be adopted pursuant to §§301, 304, and 307. Consistent with "the goal of eliminating toxic substances in toxic amounts", these technology-based standards are to be achieved regardless of whether uncontrolled discharges would have an impact on water quality. There are three basic types of technology-based limits:

(1) §301(b) establishes limits for Direct Industrial Dischargers on an industry-by-industry basis that are of the following types:

- Best Practicable Technology (BPT) is defined as the average of the best existing performance by well-operated plants within each industrial category. BPT emphasizes end-of-pipe treatment for toxic chemicals rather than in-plant control measures and considers cost versus benefits.
- Best Conventional Pollutant Control Technology (BCT) is designed to limit "conventional" pollutants (e.g., biochemical oxygen demand, suspended solids, fecal coliform bacteria, and pH).
- Effluent Limits for Nonconventional, Nontoxic Pollutants control the remaining pollutants (e.g., chlorine, phenol).
- New Source Direct Discharges are controlled differently than those discharges in operation at the passage of the act. EPA is compelled to look at plant operations, various alternative production processes or other aspects of the operation in order to reduce discharges, regardless of cost or availability of technology.
- Best Available Economically Achievable Control Technology (BAT) is the most stringent of the technology-based limitations. Rather than using the average of the best technology most widely used within an industry category (BPT), BAT is based on the best technology in existence regardless of its usage. This limit typically forces adoption of better technology by industry as the technology develops through time.

(2) Limits for Publicly Owned Treatment Works (POTW's). POTW's are also required to obtain NPDES discharge permits and achieve technology-based effluent limitations, but the standards are different than for industrial facilities. Secondary treatment and eventually Best Practicable Waste Treatment Technology (BPWTT) are required, although the emphasis has largely been on conventional pollutants.

(3) Pretreatment Limits for Indirect Discharges. Industrial facilities that discharge into publicly owned treatment works, and thus are not subject to standards applicable to direct discharges, are subject to categorical pretreatment standards under §307(b). Under the pretreatment regulations, the release of certain pollutants is prohibited, such as those that could interfere with the operation of the POTW, or pass through the treatment system without a reduction in concentration. To date, EPA has identified six pollutants under the NRDC, et al., Consent Decree (Paragraph 4(c)) that should be prohibited from discharge to POTW's. (2-2). Treatment requirements were also adopted, industry-by-industry, for treating wastes, particularly toxics. In the 1987 amendments to the FWPCA, the EPA was mandated to study the adequacy of pretreatment technology for toxics in POTW discharges(§519).

The approximately 100,000 manufacturing facilities discharging into the 1500 POTW's with

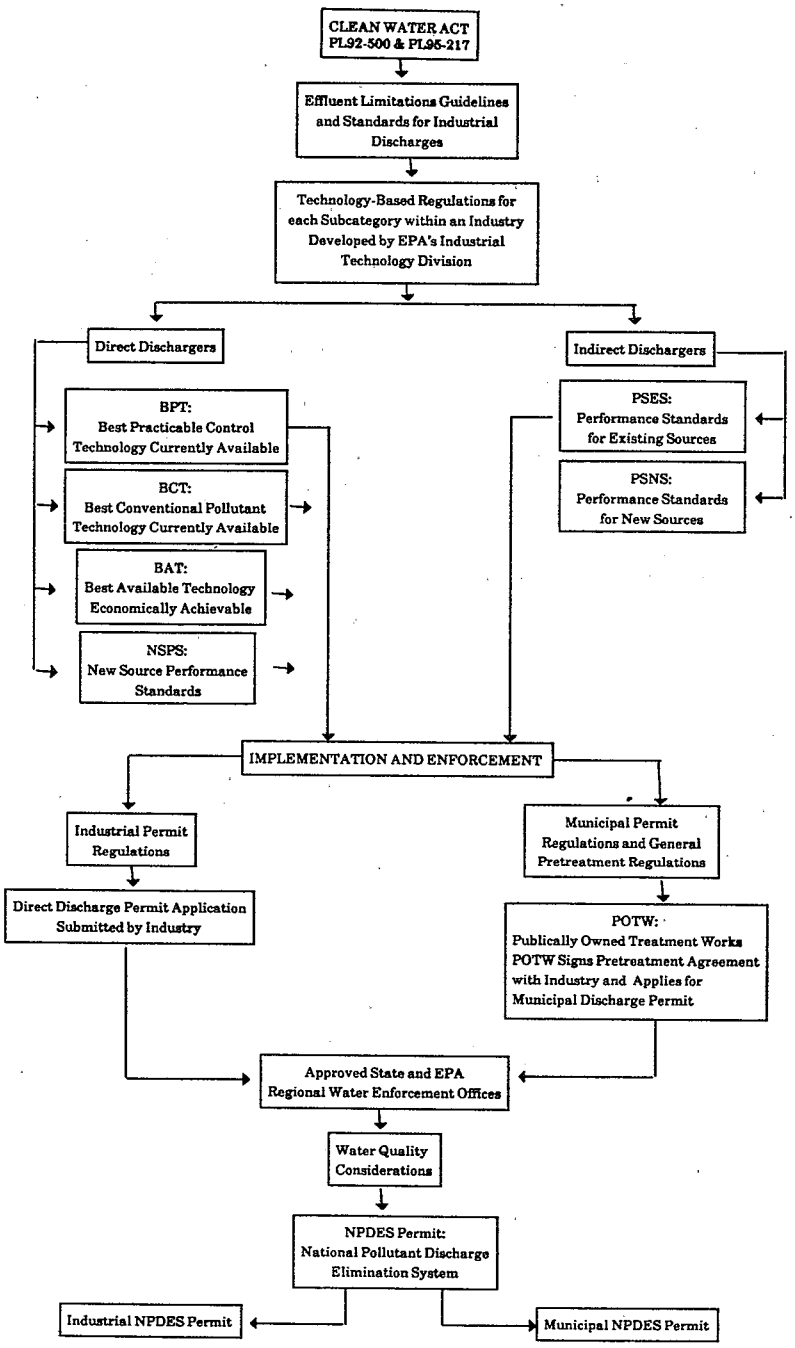

Figure II-1. Control of industrial wastewater discharges in the United States.

approved industrial pretreatment programs are required to monitor for the chemicals established by the Agency. These chemicals are listed in Table II-1. (A complete description of Table II-1 begins on page 2-23.) While no data base exists today to indicate which chemicals are being monitored, a data base is in the process of being established to track the monitoring being performed in this program. It is very likely where POTW's effluents are determined to be toxic by biomonitoring, that additional monitoring in the industrial pretreatment program will be required.

Water-Quality-Based Limits

The technology-based limits discussed above are independent of the quality of the receiving water. If these limits are considered inadequate to achieve "fishable, swimmable" water quality, the FWPCA mandates more stringent limits. The States have a key role in this process. As a result of the FWPCA and the Water Quality Act of 1987, each state must establish water quality standards (WQS) based on water quality criteria (WQC) published by EPA. The state water quality standards established to date are summarized in Table II-1.

EPA has developed or is in the process of developing water quality criteria under §304 (a) for the priority toxic pollutants to protect humans, animals, and aquatic organisms. These criteria are used to establish the WQS in most cases, although a state may adopt a different site-specific standard based on EPA methodological guidance. In addition to numeric standards, all states have adopted narrative standards (i.e., "no toxic pollutants may be discharged in toxic amounts") which may be implemented by numerical methods such as biomonitoring.

Ambient monitoring (water quality and biomonitoring) is principally done by state agencies (2-3,4,5) under §106(e), EPA, and several other federal agencies, such as the U.S. Geological Survey, U.S. Forest Service, and U.S. Fish and Wildlife Service, to determine the presence of conventional and toxic pollutants in ambient surface waters. The data collected are used to identify problems, to help develop controls, and to judge the effectiveness of the controls. States are required to develop maximum daily pollutant loads for stream segments that consider the WQS. Effluent limitations are then set to ensure attainment of the WQS.

As each state monitors its waters, methods are required to measure the chemicals at detection levels low enough to determine compliance with the water quality standards. Water quality criteria and state standards established to date indicate that improvements in the detection levels of some methods established under §304(h) would be required to support future ambient monitoring requirements. However, §304(h) methods are not currently required to be used to perform any ambient monitoring required under the FWPCA.

There is an increasing emphasis by state agencies on monitoring stream and lake sediments and fish or shellfish tissue to determine the impact of historical discharges of toxic pollutants and the effectiveness of current controls. Data entered into STORET indicate that data are being collected in every state on these sample matrices. There is no comprehensive information, however, on the adequacy of the methods that state agencies are currently using, or the comparability of data supplied by the various states.

The NPDES Permit Program

The primary regulatory mechanism for controlling pollution is the National Pollutant Discharge Elimination System (NPDES). Under the NPDES program, any person who wishes to discharge pollutants into the waters of the United States from any point source must first apply for and obtain a permit. EPA is the responsible agency for issuing permits unless a state has an approved permit program (39 do as of January 1988). Each state without an approved program is still required to certify that the permitted discharge will meet with applicable state laws and standards. The permit, when issued, sets effluent limitations and other control requirements, schedules of compliance, and monitoring requirements. Currently, there

TABLE II-1: CHEMICAL ANALYTES REQUIRED FOR MONITORING IN WATER OR WITH WATER QUALITY STANDARDS

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
ACENAPHTHENE*	10	10	24	520	1	NS	TABLE II			APPENDIX IX	CLP
ACENAPHTHYLENE*	10	10	23		1	NS	TABLE II			APPENDIX IX	CLP
ACETONE*			4					APPENDIX C		APPENDIX IX	CLP
ACETOPHENONE										APPENDIX IX	
ACETONITRILE										APPENDIX IX	
2-ACETYLAMINOFLUORENE										APPENDIX IX	
ACROLEIN*	8	10	33	21	1	NS	TABLE II			APPENDIX IX	HSL
ACRYLONITRILE*	8	10	37	0.058	1	3	TABLE II			APPENDIX IX	HSL
ALKALINITY*	8		92	20000	16	10000					
ALUMINUM*	8		176		2	100	TABLE IV		DWPL	APPENDIX VIII	CLP
ALDRIN*	6	10	27	0.000074	16	1	TABLE II			APPENDIX IX	CLP/HSL
ALLYL CHLORIDE							TABLE V			APPENDIX IX	
4-AMINOBIPHENYL										APPENDIX IX	
AMMONIA*	17		2850	NAR	24	20			DWPL		HSL
ANILINE			5				TABLE V			APPENDIX IX	HSL
ANTHRACENE*	13	10	24				TABLE II			APPENDIX IX	CLP
ANTIMONY*	8		69	146	1	NS	TABLE III		CON	APPENDIX IX	CLP
ARAMITE										APPENDIX IX	
AROCLOR 1016*	8	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1221*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1232*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1242*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1248*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1254*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
AROCLOR 1260*	10	10	162	0.000079	16	0.1	TABLE II		CON	APPENDIX IX	CLP/HSL
ARSENIC*	10		517	0.0022	22		TABLE III		50	APPENDIX IX	CLP/HSL
ASBESTOS			14	30KF/L			TABLE V				
BARIUM*	2	10	96	1000	8	NS	TABLE IV		1000	APPENDIX IX	CLP
BERYLLIUM*	4	10	74	0.0068	8	NS	TABLE III		CON	APPENDIX IX	CLP/HSL
BENZO(A)ANTHRACENE*	8	10	21				TABLE II			APPENDIX IX	CLP/HSL
BENZENE*	13	10	131	0.66	1	0.7	TABLE II		5	APPENDIX IX	CLP/HSL
BENZIDINE*	6	10	23	0.00012	6	NS	TABLE II			APPENDIX VIII	HSL
BENZOIC ACID*								APPENDIX C			CLP/HSL
BENZO(B)FLUORANTHENE*	10	10	19				TABLE II			APPENDIX IX	CLP/HSL
BENZO(K)FLUORANTHENE*	10	10	20				TABLE II			APPENDIX IX	CLP
BENZO(GHI)PERYLENE*	8	10	20				TABLE II			APPENDIX IX	CLP

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
BENZO(A)PYRENE*	13	10	40				TABLE II			APPENDIX IX	CLP/HSL
BENZYL ALCOHOL										APPENDIX IX	CLP
alpha-BHC*	8	10	18	0.0092	1	0.7	TABLE II			APPENDIX IX	CLP/HSL
beta-BHC*	8	10	15	0.0163	1	0.3	TABLE II			APPENDIX IX	CLP/HSL
delta-BHC*	6	10	15	0.08	12	NS	TABLE II			APPENDIX IX	CLP/HSL
gamma-BHC*	8	10	15	0.0123	1	NS	TABLE II			APPENDIX IX	CLP/HSL
BIPHENYL*								APPENDIX C			
BIS(2-CHLOROETHOXY)METHANE*	6	10	19				TABLE II			APPENDIX IX	CLP
BIS(2-CHLOROETHYL)ETHER*	8	10	18	0.03			TABLE II			APPENDIX IX	CLP/HSL
BIS(2-CHLOROMETHYL)ETHER*	2	10	4	3.76E-9						APPENDIX VIII	HSL
BIS(2-CHLOROISOPROPYL)ETHER*	6	10	17	34.7			TABLE II			APPENDIX IX	CLP
BIS(2-ETHYLHEXYL)PHTHALATE*	15	10	67	15000			TABLE II			APPENDIX IX	CLP/HSL
BOD*	46	10	6765								
BORON*			134	750	11	NS	TABLE III		DWPL		
BROMIDE*			3				TABLE III				
BROMOBENZENE									ALL		
BROMOCHLOROMETHANE									ALL		
BROMODICHLOROMETHANE*	8	10	48				TABLE II		100**	APPENDIX IX	CLP/HSL
BROMOFORM*	6	10	32				TABLE II		100**	APPENDIX IX	CLP/HSL
BROMOMETHANE*	10	10	23				TABLE II		ALL	APPENDIX IX	CLP/HSL
4-BROMOPHENYLPHENYLETHER*	6	10	16				TABLE II			APPENDIX IX	CLP
n-BUTYLBENZENE		10							DISC		
sec-BUTYLBENZENE		10							DISC		
tert-BUTYLBENZENE		10							DISC		
BUTYLBENZYLPHTHALATE*	15	10					TABLE II			APPENDIX IX	CLP
CADMIUM*	17		1060	10	22	NS	TABLE III		10	APPENDIX IX	CLP/HSL
CARBAZOLE								PAR 4(C)			
CARBON DISULFIDE*			2				TABLE V			APPENDIX IX	CLP/HSL
CARBON TETRACHLORIDE*	10	10	65	0.4	1	3	TABLE II		5	APPENDIX IX	CLP/HSL
CHLORDANE*	6	10	38	0.00046	12	.055	TABLE II		CON	APPENDIX IX	CLP/HSL
CHLORINE*				7.5							
CHLORINE, TOTAL RESIDUAL*	6		2723		12	NS	TABLE IV				
P-CHLOROANILINE										APPENDIX IX	CLP
CHLOROBENZENE*	10	10	51	488			TABLE II		ALL	APPENDIX IX	CLP/HSL
CHLOROBENZILATE										APPENDIX IX	
P-CHLORO-M-CRESOL*	12	10	15	30			TABLE II			APPENDIX IX	CLP/HSL

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
CHLOROETHANE*	8	10	30				TABLE II		ALL	APPENDIX IX	CLP/HSL
CHLOROFORM*	19	10	147	0.19	1	NS	TABLE II		100**	APPENDIX IX	CLP/HSL
CHLOROMETHANE*	8	10	38				TABLE II		ALL	APPENDIX IX	CLP/HSL
2-CHLORONAPHTHALENE*	6	10	16				TABLE II			APPENDIX IX	CLP
2-CHLOROPHENOL*	12	10	25	2000	1	NS	TABLE II			APPENDIX IX	CLP
4-CHLOROPHENYLPHENYLETHER*	6	10	17		1	NS	TABLE II			APPENDIX IX	CLP
CHLOROPRENE										APPENDIX IX	
o-CHLOROTOLUENE									ALL		
p-CHLOROTOLUENE									ALL		
CHLORPYRIFOS				0.0056			TABLE V				
CHROMIUM*	36		2948	50	24	NS	TABLE III		50	APPENDIX IX	CLP/HSL
CHRYSENE*	12	10	22				TABLE II			APPENDIX IX	CLP/HSL
COBALT*	6		25		2	NS	TABLE IV			APPENDIX IX	CLP
COD	27		1536								
COLOR			338	NAR	38	NS	TABLE IV		15CU(S)		
COPPER*	26		2166	2.9	20	5000	TABLE III		1000S	APPENDIX IX	CLP/HSL
m-CRESOL*							TABLE V			APPENDIX IX	CLP
o-CRESOL*							TABLE V			APPENDIX IX	CLP/HSL
p-CRESOL*							TABLE V			APPENDIX IX	CLP
CYANIDE*	21		1111	1	23	10	TABLE III		CON	APPENDIX IX	CLP/HSL
p-CYMENE*								APPENDIX C			
2,4-D*			12	100	11	NS	TABLE V		100	APPENDIX IX	
4,4'-DDD*	6	10	18	0.06			TABLE II			APPENDIX IX	CLP/HSL
4,4'-DDE*	6	10	18	14			TABLE II			APPENDIX IX	CLP/HSL
4,4'-DDT*	6	10	18	0.000024	16	50	TABLE II			APPENDIX IX	CLP/HSL
DACONIL			3								
DACTHAL			3								
n-DECANE*								APPENDIX C			
DEMETON				0.1	4	NS					
DIALLATE										APPENDIX IX	
DIBENZ(A,H)ANTHRACENE*	8	10	20				TABLE II			APPENDIX IX	CLP/HSL
DIBENZOFURAN*			3					PAR 4(C)		APPENDIX IX	CLP
DIBENZOTHIOPHENE*								APPENDIX C			
DIBROMOCHLOROMETHANE*	6	10	13				TABLE II		100**	APPENDIX IX	CLP/HSL
1,2-DIBROMO-3-CHLOROPROPANE									VUL	APPENDIX IX	
1,2-DIBROMOETHANE			2				TABLE V		VUL	APPENDIX IX	

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
DI-N-BUTYL PHTHALATE*	15	10	44	35000			TABLE II			APPENDIX IX	CLP/HSL
o-DICHLOROBENZENE*	10	10	46		1	10	TABLE II		ALL	APPENDIX IX	CLP/HSL
m-DICHLOROBENZENE*	8	10	31		1	20	TABLE II		ALL	APPENDIX IX	CLP/HSL
p-DICHLOROBENZENE*	10	10	35		1	0.3	TABLE II			APPENDIX IX	CLP/HSL
3,3'-DICHLOROBENZIDINE*	6	10	17	.01	1	NS	TABLE II			APPENDIX IX	CLP/HSL
trans-1,4-DICHLORO-2-BUTENE										APPENDIX IX	
DICHLORODIFLUOROMETHANE*			9						DISC	APPENDIX IX	HSL
1,1-DICHLOROETHANE*	12	10	35				TABLE II		ALL	APPENDIX IX	CLP/HSL
1,2-DICHLOROETHANE*	12	10	73	0.94	1	1	TABLE II		5	APPENDIX IX	CLP/HSL
1,1-DICHLOROETHYLENE*	12	10	40	0.033	1	70	TABLE II		7	APPENDIX IX	CLP/HSL
cis-1,2-DICHLOROETHYLENE			2		1	NS	TABLE II		ALL		
trans-1,2-DICHLOROETHYLENE*	6	10	40		1	NS	TABLE II		ALL	APPENDIX IX	CLP/HSL
2,4-DICHLOROPHENOL*	13	10	34	365	1	NS	TABLE II			APPENDIX IX	CLP/HSL
2,6-DICHLOROPHENOL				0.2						APPENDIX IX	
1,2-DICHLOROPROPANE*	6	10	33				TABLE II		ALL	APPENDIX IX	CLP/HSL
1,3-DICHLOROPROPANE									ALL		
2,2-DICHLOROPROPANE									ALL		
1,1-DICHLOROPROPENE									ALL		
cis-1,3-DICHLOROPROPENE*	6	10	14				TABLE II		ALL	APPENDIX IX	CLP
trans-1,3-DICHLOROPROPENE*	6	10	13				TABLE II		ALL	APPENDIX IX	CLP
DIELDRIN*	6	10	20	0.000071	16	1	TABLE II			APPENDIX IX	CLP/HSL
DIETHYL ETHER*								APPENDIX C			
DIETHYL PHTHALATE*	10	10	29	35000			TABLE II			APPENDIX IX	CLP/HSL
DIMETHOATE					1	0.14				APPENDIX IX	
p-(DIMETHYLAMINO)AZOBENZENE										APPENDIX IX	
7,12-DIMETHYLBENZ(A)ANTHRACENE										APPENDIX IX	
3,3'-DIMETHYLBENZIDINE										APPENDIX IX	
alpha,alpha-DIMETHYLPHENETHYLAMINE										APPENDIX IX	
2,4-DIMETHYLPHENOL*	10	10	27	2120	1	0.4	TABLE II			APPENDIX IX	CLP/HSL
DIMETHYL PHTHALATE*	10	10	26	313000			TABLE II			APPENDIX IX	CLP/HSL
m-DINITROBENZENE		10					TABLE V			APPENDIX IX	
4,6-DINITRO-O-CRESOL*	6	10	21	13.4			TABLE II			APPENDIX IX	CLP/HSL
2,4-DINITROPHENOL*	10	10	21				TABLE II			APPENDIX IX	CLP/HSL
2,4-DINITROTOLUENE*	8	10	17	0.11			TABLE II		DWPL	APPENDIX IX	CLP/HSL
2,6-DINITROTOLUENE*	8	10	18				TABLE II			APPENDIX IX	CLP/HSL
DINOSEB										APPENDIX IX	
DI-N-OCTYL PHTHALATE*	6	10	25				TABLE II			APPENDIX IX	CLP
1,4-DIOXANE*								PAR 4(C)		APPENDIX IX	HSL

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
DIPHENYLAMINE*								APPENDIX C		APPENDIX IX	
DIPHENYL ETHER*								APPENDIX C			
DISULFOTON							TABLE V			APPENDIX IX	
1,2-DIPHENYLHYDRAZINE*	8	10	17	0.042			TABLE II	APPENDIX C		APPENDIX VIII	HSL
n-DOCOSANE*								APPENDIX C			
n-DODECANE*								APPENDIX C			
n-EICOSANE*								APPENDIX C			
ENDOSULFAN I*	8	10	17	0.0087			TABLE II			APPENDIX IX	CLP
ENDOSULFAN II*	8	10	17	0.0087			TABLE II			APPENDIX IX	CLP
ENDOSULFAN SULFATE*	6	10	17				TABLE II			APPENDIX IX	CLP
ENDRIN*	10	10	38	0.0023	18	NS	TABLE II		0.2	APPENDIX IX	CLP/HSL
ENDRIN ALDEHYDE*	8	10	15				TABLE II			APPENDIX IX	CLP/HSL
ETHYLBENZENE*	12	10	71	430			TABLE II		ALL	APPENDIX IX	CLP/HSL
ETHYL METHACRYLATE										APPENDIX IX	
ETHYL METHANESULFONATE										APPENDIX IX	
FAMPHUR										APPENDIX IX	
FLUORANTHENE*	10	10	25	42	1	NS	TABLE II			APPENDIX IX	CLP/HSL
FLUORENE*	12	10	23				TABLE II			APPENDIX IX	CLP
FLUORIDE*	15		321		18	1000	TABLE IV		2000S		
GOLD*	2		3								
GROSS ALPHA*			4		11				CON		
GROSS BETA*			3		16	1000PCI/L			CON		
GUTHION				0.01	8	NS	TABLE V				
GLYPHOSATE			1						CON		
HEPTACHLOR*	8	10	16	0.00028	12	0.02	TABLE II		CON	APPENDIX IX	CLP/HSL
HEPTACHLOR EPOXIDE*	6	10	15		4	0.02	TABLE II		CON	APPENDIX IX	CLP/HSL
HEXACHLOROBENZENE*	8	10	27	0.72			TABLE II			APPENDIX IX	CLP/HSL
HEXACHLOROBUTADIENE*	6	10	20	0.45	2	NS	TABLE II		DISC	APPENDIX IX	CLP/HSL
HEXACHLOROCYCLOPENTADIENE*	8	10	19	5.2	3	NS	TABLE II		CON	APPENDIX IX	CLP
HEXACHLORODIBENZO-P-DIOXINS										APPENDIX IX	
HEXACHLORODIBENZOFURANS										APPENDIX IX	
HEXACHLOROETHANE*	6	10	16	1.9	1	NS	TABLE II			APPENDIX IX	CLP/HSL
HEXACHLOROPHENE										APPENDIX IX	
HEXACHLOROPROPENE										APPENDIX IX	
n-HEXACOSANE*								APPENDIX C			
n-HEXADECANE*								APPENDIX C			
HEXANOIC ACID*								APPENDIX C			

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
2-HEXANONE*			1							APPENDIX IX	CLP
INDENO(1,2,3-CD)PYRENE*	8	10					TABLE II			APPENDIX IX	CLP/HSL
INDIUM	2										
IODOMETHANE										APPENDIX IX	
IRON	12		874	300	15	1000	TABLE IV		300S	GWM	CLP
ISOBUTYL ALCOHOL										APPENDIX IX	
ISODRIN										APPENDIX IX	
ISOPHORONE*	12	10	26	5200			TABLE II		DWPL	APPENDIX IX	CLP/HSL
ISOPROPYLBENZENE									DISC		
p-ISOPROPYLTOLUENE									DISC		
ISOSAFROLE										APPENDIX IX	
KEPONE							TABLE V			APPENDIX IX	
LEAD*	27		1368	50	22	NS	TABLE III		50S	APPENDIX IX	CLP/HSL
MAGNESIUM			34		1	NS	TABLE IV				CLP
MALATHION			1	0.1	7	160	TABLE V				
MANGANESE	4		157	50	7	150			50S	GWM	CLP
MERCURY*	12		862	0.012	17	NS	TABLE III		2	APPENDIX IX	CLP/HSL
METHACRYLONITRILE										APPENDIX IX	
METHAPYRILENE										APPENDIX IX	
METHOXYCHLOR*			1	0.03	12	NS	TABLE V		100	APPENDIX IX	CLP
3-METHYLCHOLANTHRENE										APPENDIX IX	
METHYLENE BROMIDE									ALL	APPENDIX IX	
METHYLENE CHLORIDE*	17	10	132				TABLE II			APPENDIX IX	CLP/HSL
METHYL ETHYL KETONE*			1					APPENDIX C		APPENDIX IX	CLP/HSL
METHYL METHACRYLATE							TABLE V			APPENDIX IX	
METHYL METHANESULFONATE										APPENDIX IX	
2-METHYLNAPHTHALENE										APPENDIX IX	CLP
METHYL PARATHION							TABLE V			APPENDIX IX	
METHYL ISOBUTYL KETONE*										APPENDIX IX	CLP/HSL
MIREX			3	0.001	7	NS					
MOLYBDENUM*	4		45				TABLE IV		DWPL		CLP
NAPHTHALENE*	15		64	620	1	NS	TABLE II		DISC	APPENDIX IX	CLP/HSL
1,4-NAPHTHOQUINONE										APPENDIX IX	
1-NAPHTHYLAMINE										APPENDIX IX	
2-NAPTHYLAMINE								APPENDIX C		APPENDIX IX	
NICKEL*	17		1126	7.1	10	NS	TABLE III		CON	APPENDIX IX	CLP/HSL

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
NITRATE-NITRITE	2		287	10000	5	NS	TABLE IV		10000		
o-NITROANILINE							TABLE V			APPENDIX IX	CLP
m-NITROANILINE							TABLE V			APPENDIX IX	CLP
p-NITROANILINE							TABLE V			APPENDIX IX	CLP
NITROBENZENE*	6	10	18	6680	1	NS	TABLE II			APPENDIX IX	CLP/HSL
NITROGEN, TOTAL ORGANIC	2		79				TABLE IV				
o-NITROPHENOL*	10	10	16							APPENDIX IX	CLP
p-NITROPHENOL*	13	10	18							APPENDIX IX	CLP
4-NITROQUINOLINE 1-OXIDE										APPENDIX IX	
N-NITROSODI-N-BUTYLAMINE*				0.0064						APPENDIX IX	
N-NITROSODIETHYLAMINE				0.0008						APPENDIX IX	
N-NITROSODIMETHYLAMINE*	6	10	18	0.0014			TABLE II			APPENDIX IX	
N-NITROSODIPHENYLAMINE*	8	10	21	4.9			TABLE II			APPENDIX IX	CLP/HSL
N-NITROSODIPROPYLAMINE*	8	10	17				TABLE II			APPENDIX IX	CLP/HSL
N-NITROSOMETHYLETHYLAMINE										APPENDIX IX	
N-NITROSOMORPHOLINE										APPENDIX IX	
N-NITROSOPIPERIDINE										APPENDIX IX	
N-NITROSOPYRROLIDINE				0.016						APPENDIX IX	
5-NITTRO-O-TOLUIDINE										APPENDIX IX	
n-OCTACOSANE*								APPENDIX C			
n-OCTADECANE*								APPENDIX C			
OIL AND GREASE*	46		3508	NAR	56	NS	TABLE IV				
OXIRANE											HSL
PALLADIUM*	2		1								
PARAQUAT			4								
PARATHION				0.013	8	30	TABLE V			APPENDIX IX	
PENTACHLOROBENZENE				74						APPENDIX IX	
PENTACHLORODIBENZO-P-DIOXINS										APPENDIX IX	
PENTACHLORODIBENZOFURANS										APPENDIX IX	
PENTACHLOROETHANE*				281			TABLE II			APPENDIX IX	CLP
PENTACHLORONITROBENZENE										APPENDIX IX	
PENTACHLOROPHENOL*	19	10	45	3.2	2	30	TABLE II		CON	APPENDIX IX	CLP/HSL
PH*	85		9660	NAR	56	NS			6.5-8.5S	GWM	
PHENACETIN										APPENDIX IX	
PHENANTHRENE*	17	10	28				TABLE II			APPENDIX IX	CLP/HSL

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
PHENOL*	13	10	271	2560	23	1	TABLE II			APPENDIX IX	CLP/HSL
PHENOLICS*	17		739							G/M	
p-PHENYLENEDIAMINE										APPENDIX IX	
PHORATE										APPENDIX IX	
PHOSPHORUS*	8		1275	0.1	18	NS	TABLE IIV				
2-PICOLINE								APPENDIX C		APPENDIX IX	
PLATINUM*	2		1								
PRONAMIDE										APPENDIX IX	
PROPIONITRILE										APPENDIX IX	
n-PROPYLBENZENE									DISC		
PYRENE*	10	10	24				TABLE II			APPENDIX IX	CLP
PYRIDINE			1							APPENDIX IX	
RADIUM*											
RADIUM 226*	2		34		10	NS					
SAFROLE										APPENDIX IX	
SELENIUM*	6		267	10	19	NS	TABLE III		10	APPENDIX IX	CLP/HSL
SILVER*	13		432	0.12	18	NS	TABLE III		50	APPENDIX IX	CLP/HSL
STYRENE*			12				TABLE V	APPENDIX C	ALL	APPENDIX IX	CLP
SULFATE*			222		21	NS	TABLE IV		250S		
SULFIDE*	8		334	2	2	NS	TABLE IV			APPENDIX IX	
SULFITE*			13				TABLE IV				
SULFOTEPP										APPENDIX IX	
SURFACTANTS*	2		200								
2,4,5-T*			12				TABLE V		DWPL	APPENDIX IX	
2,4,5-TP*				10	12	NS	TABLE V		10	APPENDIX IX	
TANTALUM	2										
alpha-TERPINEOL*								APPENDIX C			
TETRACHLORODIBENZO-P-DIOXINS										APPENDIX IX	
TETRACHLORODIBENZOFURANS										APPENDIX IX	
2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN*	6	10	20	1.3E-08					CON	APPENDIX IX	CLP/HSL
1,2,4,5-TETRACHLOROBENZENE			2	38						APPENDIX IX	
1,1,1,2-TETRACHLOROETHANE									ALL	APPENDIX IX	
1,1,2,2-TETRACHLOROETHANE*	12	10	33	0.17	1	40	TABLE II		ALL	APPENDIX IX	CLP/HSL
TETRACHLOROETHYLENE*	21	10	89	0.8			TABLE II		ALL	APPENDIX IX	CLP/HSL
2,3,4,6-TETRACHLOROPHENOL			1	1.0						APPENDIX IX	
n-TETRACOSANE*								APPENDIX C			
n-TETRADECANE*								APPENDIX C			

TABLE II-1 (Cont.)

ANALYTE	EFFLUENT GUIDELINES AND PRETREATMENT STANDARDS FREQUENCY,%	LIMITS,UG/L	NPDES MONITORING REQUIREMENT	WATER QUALITY CRITERIA UG/L	WATER QUALITY STANDARDS NUMBER	UG/L	NPDES PERMIT 122.21	OTHER CWA LISTS	SDWA LISTS	RCRA LISTS	CERCLA LISTS
THALLIUM*	2		27	13	2	NS	TABLE III		CON	APPENDIX IX	CLP/HSL
THIONAZIN										APPENDIX IX	
TIN*			54				TABLE III			APPENDIX IX	CLP
TITANIUM*	2		12				TABLE III				
TOC*	2		1146							GWM	
TOLUENE*	19	10	147	5000	1	100	TABLE II		ALL	APPENDIX IX	CLP/HSL
o-TOLUIDINE										APPENDIX IX	
TOXAPHENE*	8	10	46	0.0002	13	NS	TABLE II		5	APPENDIX IX	CLP/HSL
n-TRIACONTANE*								APPENDIX C			
1,2,3-TRICHLOROBENZENE*								PAR 4(C)	DISC		
1,2,4-TRICHLOROBENZENE*	10	10	35				TABLE II		DISC	APPENDIX IX	CLP/HSL
1,1,1-TRICHLOROETHANE*	17	10	92	18400	1	200	TABLE II		200	APPENDIX IX	CLP/HSL
1,1,2-TRICHLOROETHANE*	8	10	33	0.6	1	NS	TABLE II			APPENDIX IX	CLP/HSL
TRICHLOROETHYLENE*	15	10	107	2.7	1	5	TABLE II		5	APPENDIX IX	CLP/HSL
TRICHLOROFLUOROMETHANE*			26						DISC	APPENDIX IX	HSL
2,3,6-TRICHLOROPHENOL*								PAR 4(C)			
2,4,5-TRICHLOROPHENOL*				2600				PAR 4(C)		APPENDIX IX	CLP
2,4,6-TRICHLOROPHENOL*	17	10	67	1.2			TABLE II			APPENDIX IX	CLP/HSL
1,2,3-TRICHLOROPROPANE									ALL	APPENDIX IX	
o,o,o-TRIETHYL PHOSPHOROTHIOATE										APPENDIX IX	
1,2,4-TRIMETHYLBENZENE									DISC		
1,3,5-TRIMETHYLBENZENE									DISC		
sym-TRINITROBENZENE										APPENDIX IX	
TSS*	2		9751	NAR							
TUNGSTEN	2		2								
VANADIUM*			58				TABLE V		DWPL	APPENDIX IX	CLP
VINYL ACETATE*			5				TABLE V			APPENDIX IX	CLP
VINYL CHLORIDE*	8	10	49	2			TABLE II		2	APPENDIX IX	CLP/HSL
p-XYLENE							TABLE V		ALL	APPENDIX IX	CLP/HSL
o-XYLENE							TABLE V		ALL	APPENDIX IX	CLP/HSL
m-XYLENE							TABLE V		ALL	APPENDIX IX	CLP/HSL
ZINC*	29		1930	47	19	NS	TABLE III		5000S	APPENDIX IX	CLP/HSL

NOTES: *APPROVED 304(H) METHOD FOR THIS PARAMETER
** LIMIT IS FOR TOTAL TRIHALOMETHANES
NS NOT STATED IN SOURCES REVIEWED

are approximately 65,000 major and minor NPDES permits established for industrial and municipal dischargers.

Extensive monitoring requirements were promulgated along with the establishment of the NPDES program as a result of the 1972 amendments to the FWPCA. From that time until 1977, the vast majority of effluent monitoring was for conventional and nonconventional contaminants. As a result of a 1976 consent decree (Natural Resource Defense Council, et al., v. Train, 8 ERC 2120 (D.D.C. 1976)), as well as amendments to the FWPCA in 1977, there has been an increased emphasis on the control of and extensive monitoring for toxic pollutants. The list of 129 priority pollutants established under Section 307(a), which was subsequently reduced to 126, was designed to be a good indicator of the extent of discharge of toxic pollutants. The monitoring analytes established by the effluent guideline process for 51 industrial categories are shown in Table II-1.

However, as the NRDC, the Agency and Congress recognized, the list of priority pollutants was not believed to be an all inclusive list of toxic pollutants which could be possibly discharged by industrial facilities and publicly owned treatment works (POTW's). The purpose of a study performed by the Agency as a result of paragraph 4(C) in the NRDC consent decree was to determine if additional non-priority pollutant chemicals were being discharged (2-6). In that study, EPA collected and analyzed approximately 40,000 samples, taken from 40 POTW's and facilities in 43 different industries. Of 433 chemicals positively identified in the study, 48 were priority pollutants and 385 were not.

Monitoring requirements established in all major NPDES permits were reviewed in July, 1986. At that time, an average of 10 and 12 analytes were required to be monitored in municipal and industrial permits, respectively. These monitoring requirements were established as a result of the effluent guideline process as well as monitoring of the NPDES permitted effluents for priority pollutants in the permit application process. Based on the 4(C) study, there are additional toxic chemicals being discharged for which monitoring requirements may be necessary in the future.

The major initiative underway to control the discharge of toxic pollutants will rely heavily on whole effluent toxicity permit limits to identify effluents where the current chemical-by-chemical monitoring requirements have been inadequate to identify toxic discharges. Dischargers suspected of discharging toxic pollutants will be required to perform toxicity testing. When toxicity is found, a toxicity reduction evaluation (TRE) program may be required. Part of the TRE study is to determine the chemicals that are causing toxicity. In many of the studies performed to date by the EPA Regions and states, the toxic agent was not a priority toxic pollutant. It is anticipated as a result of the biomonitoring program, that the list of toxic chemicals for which monitoring will be required will extend beyond the list of toxic priority chemicals established under §307. Therefore, reliable methods will be required to measure the presence of a much broader suite of toxic chemicals and also to detect pollutants that are not on a target list.

The specific monitoring requirements in an NPDES permit are therefore critical to achieving this goal. Specific requirements are governed by §122.16 and §§122.20-122.25 of the NPDES regulations, such as the requirements for maintaining and installing monitoring equipment, monitoring methods and frequencies, and test methodologies. The NPDES regulations leave some aspects of monitoring requirements to the discretion of the permit writer. In these cases, the permit writer relies on policy documents, technical support documents, and other permits to develop specific permit monitoring requirements.

Additional FWPCA Programs That Require Monitoring

Section 403 of the FWPCA establishes the Ocean Discharge Criteria Program. Regulations developed under this section give guidance to §402 permit writers for discharges into the ocean

or territorial waters. Under this program, methods for predicting the impact of discharges to the environment were developed, including toxicity test methods and biomonitoring requirements.

Section 404 of the FWPCA governs the issuance of permits by the Corps of Engineers (COE) for disposal of dredged or fill material into navigable waters. In December, 1980, the COE and EPA proposed chemical and biological methods for predicting the impact of dredged material and for monitoring these activities in the field. Testing protocols jointly developed by the EPA and COE have not been incorporated into §304(h). Monitoring requirements for each dredge and fill permit are established by the individual district COE offices. To date, a limited suite of chemical and biological monitoring analytes are usually required. Judging by the data in STORET, there is a significant difference in monitoring being performed on sediments analyzed by state agencies to determine the extent of sediment contamination and the list of analytes commonly specified by COE to control the discharge of pollutants through dredge and fill activities.

Section 405 of the FWPCA governs the disposal of sewage sludge in addition to §402 of the act. Regulations for governing the issuance of permits under §§405 and 402 are to include specifications on criteria, requirements, and methods. As a result of the domestic sewage sludge study, initially chemical monitoring will be required of POTW sludges for 32 chemicals. This list will be expanded within two years by an additional 20 to 30 chemicals. While methods established in 40 CFR 136 under the authority of §304(h) do not currently apply to sludge monitoring, methods will be promulgated in the sludge regulations with the intent of incorporating these methods into 40 CFR 136. The EPA has until 1988 to finalize the regulations under Section 405 that deal specifically with toxic materials (including pathogens) in sewage sludges.

Required FWPCA Monitoring and §304(h) Methods

In summary, the implementation of the FWPCA requires many sample analyses to be performed in support of various monitoring programs. Methods are generally available for each of these programs, although not all of these methods have been standarized and promulgated under 40 CFR 136. In addition, usage of the methods authorized under §304(h) and codified in 40 CFR 136 has been required only for the analysis of process waters and treated effluents under the National Pollutant Discharge Elimination System (NPDES) and industrial pretreatment programs. The use of §304(h) methods is not required for ambient surface water monitoring. In addition, the use of methods in 40 CFR 136 is not required for the analysis of sediments and biological tissues, which are increasingly being tested because they are commonly regarded as the ultimate receptors of toxic pollutants.

While few biological testing methods have been included in 40 CFR 136 to date, methods will soon be proposed for acute and chronic toxicity testing to support the water quality based approach to permit writing being implemented by the Agency. Also not included under §304(h) are the chemical and biological testing methods used to test dredge and fill material required to be analyzed under §404. The Army Corps of Engineers, with concurrence of the EPA, has published but not promulgated separate testing methodology for these purposes

The end result is that there are numerous monitoring programs required by various sections of the FWPCA that use methods that have not been promulgated in to CFR 136 or subjected to a comparable standardization process.

Testing Requirements Established by Other Related Environmental Legislation

With the recognition of the problems associated with toxics, various recent environmental legislation has focused on controlling the release of basically the same suite of toxic chemicals in the same

environmental media. For example, concern over contamination of groundwater with volatile organic chemicals is addressed in four major pieces of environmental legislation. The consequence of this widespread concern for toxics has resulted in the promulgation of monitoring requirements by other programs which are similar to and yet different from FWPCA requirements. For example, primary drinking water standards can be applied to assess the impact of an effluent discharge into a surface water used for a drinking water supply. The major pieces of environmental legislation which have monitoring requirements which directly overlap those under the FWPCA are:

- CERCLA, the Comprehensive Environmental Response, Compensa-tion, and Liability Act (Superfund)
- SDWA, the Safe Drinking Water Act
- RCRA, the Resource Conservation and Recovery Act
- MPRSA, the Marine Protection, Research and Sanctuaries Act

Monitoring requirements under these four acts as recently amended, combined with requirements under FWPCA, form the basis for most of the monitoring of waters, soils, wastes, and biological tissues. The basic monitoring requirements of each of these Acts as they relate to FWPCA programs are briefly summarized below. The recent amendments to these Acts have consistently directed the Agency to expand the monitoring requirements to include more toxic chemicals. While many of these changes will not be finalized for years, it is obvious that the trend is towards the development of larger lists of monitoring analytes. The Agency does not have the resources and the regulated community does not have the capability to support totally different monitoring requirements and methods for each regulatory program.

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)

From the onset, the focus of the CERCLA monitoring program was to collect data for toxic chemicals from Superfund sites. It was imperative that the data be consistent and legally defensible. The CERCLA program therefore established a target list of analytes patterned after the toxic priority pollutant list. The initial list consisted of the priority pollutants plus additional organic compounds and metals which could be measured using essentially the §304(h) test procedures for priority pollutants. Over the years, the list has been revised to delete compounds for which the analytical protocols have been deemed to be inappropriate based on method performance data.

The current target list of analytes includes 127 organic compounds (including 2,3,7,8-TCDD), 23 metals and cyanide. The majority of analytical efforts at Superfund sites involve the analysis of waste, soil, and water samples for these 151 target analytes using rigid protocols established by the Contract Laboratory Program (CLP). Recognizing that a target list does not always detect every compound that may be of concern, the program has specified methods to tentatively identify and estimate the concentration of additional organic chemicals that may be present. Among the requirements of the Superfund Amendments and Reauthorization Act (SARA) is a mandate to prepare an initial list of at least 100 hazardous substances commonly found at Superfund sites. This list was published April 17, 1987 (52 FR 12866). SARA has mandated that this list will ultimately grow to 275 chemicals. While most of the substances contained in this initial list are target analytes in the CLP monitoring program, additional substances were listed that may be the focus of future monitoring requirements.

Two additional significant changes made by SARA are the requirement to perform health assessments at all National Priority List (NPL) sites, and the provision of applicable, relevant, and appropriate regulations (ARAR's). To properly perform the health and biological effects studies, animal and plant tissue as well as air samples will require analysis. The CLP list of analytes will have to be expanded considerably and the analytical methods will have to be modified to achieve lower detection limits to test compliance with all ARAR's.

Safe Drinking Water Act (SDWA)

The SDWA authorizes the Agency to set national primary drinking water regulations (NPDWR's) for public water suppliers. Public water suppliers are required to perform routine monitoring to demonstrate compliance with the regulations. The 1986 amendments to the SDWA specified 83 contaminants that must be regulated by July 1989. The first phase of regulation (52 FR 25690) was promulgated on July 8, 1987.

The current NPDWR's contain substances that have regulated limits termed maximum contaminant levels (MCL's) as well as substances that do not have regulated limits, but for which monitoring is required (unregulated contaminants). Including the contaminants for which regulations were promulgated on July 8, 1987, MCL's have been established in 40 CFR 141 for 33 contaminants:

- 11 inorganics and metals.
- 6 chlorinated hydrocarbon pesticides and herbicides.
- 12 volatile organic chemicals, including trihalomethanes.
- 3 radiological analytes.
- 1 microbiological analyte

Monitoring requirements have also been established for 51 unregulated volatile organic chemicals. These unregulated contaminants have been separated into three lists for monitoring purposes. The 34 contaminants listed in 40 CFR Part 141.40(c) must be measured by all water suppliers. Measurement of the two chemicals listed in 40 CFR Part 141.40(f) is required only by those suppliers vulnerable to contamination by these chemicals. Monitoring for the 15 chemicals listed in 40 CFR Part 141.40(i) would be at a state's discretion.

By July 19, 1989, NPDWR's must be established for 83 contaminants referenced in the Act. This list of 83 contaminants includes volatile organic chemicals, inorganics and metals, synthetic organic chemicals, microbiological contaminants, and radionuclides. In addition to the list of 83 contaminants, the Agency must compile a priority list of contaminants and develop NPDWR's for contaminants on this list. The Agency has developed a candidate list of priority chemicals which include:

- 7 contaminants removed from the original list of 83 contaminants,
- 24 disinfectants and disinfection by-products,
- 17 substances from the SARA §110 Priority List,
- 45 pesticides registered under FIFRA, and
- 18 volatile organic chemicals.

In addition to the NPDWR's, the Agency has also specified secondary drinking water standards. These standards relate to aesthetic qualities of water (e.g., taste, odor and color). The standards are not enforceable limits, but rather guidance values. Secondary standards have been established for twelve contaminants.

Resource Conservation and Recovery Act (RCRA)

The Subtitle C RCRA program, designed to manage hazardous wastes from "cradle to grave", has implemented a series of complex monitoring requirements which extend into other programs. The primary focus of many of these requirements pertains to preventing or remediating groundwater contamination The RCRA program has promulgated various monitoring requirements relating to this issue, including analyses to determine if a waste is hazardous, what waste treatment must be used, and the extent of contamination at a waste site. While it is beyond the scope of this study to define all of the RCRA monitoring requirements, certain requirements directly overlap FWPCA monitoring requirements.

For example, the concern over contaminants that could migrate from a land disposal site into the surrounding environment has resulted in the development of a leaching method to simulate this disposal scenario (Extraction Method Toxicity). Wastes which have specific "hazardous constituents" above specified levels in the leachate are defined as hazardous wastes

and must be managed to specified standards. The Agency is in the process of expanding the list of contaminants that must be measured in leachates to determine if the waste is hazardous and changing the test method to allow for the measurement of toxic organic chemicals (Toxicity Characteristic Leaching Method).

In a related area, a company can petition the Agency to delist a waste from a specific facility that is classified (listed) as a hazardous waste. This delisting petition involves demonstrating that the waste does not contain "hazardous constituents" at concentrations that would result in groundwater contamination above specified health criteria.

Groundwater monitoring is required at hazardous waste disposal facilities These requirements have two separate goals. The first goal is associated with demonstrating that contamination is not occurring and is termed detection monitoring. Under detection monitoring, facilities with interim status (40 CFR 265) must monitor for indicators of groundwater contamination and analytes which have primary and secondary standards promulgated under SDWA. Detection monitoring at facilities with Part B permits (40 CFR 264) is established in the permit.

If contamination is suspected, facilities must demonstrate that hazardous constituents are not present. A list of hazardous constituents was developed by the Agency to assess whether a waste should be designated (listed) as hazardous. This list was promulgated as Appendix VIII to 40 CFR 261 and contains approximately 375 compounds, salts, classes of compounds, mixtures, and other "constituents" which were shown in studies to have toxic, carcinogenic, mutagenic, or teratogenic effects. The Agency may also require that biological testing be performed to determine the extent and type of damage possible with a waste. A suite of test procedures has been developed for site assessment.

Thus, many of the RCRA programs have been oriented towards measurement of the constituents contained in Appendix VIII. Because of the nature of the Appendix VIII list, the development of a well-defined, measurable monitoring list is impossible. For example, it was shown that methods to measure all constituents contained in this list are currently not available. Therefore, the Agency developed a related list for groundwater monitoring. This list, promulgated in Appendix IX to 40 CFR 264, contains all Appendix VIII constituents that can be measured in water along with compounds measured at Superfund sites using CLP protocols which were not listed in Appendix VIII.

Marine Protection, Research, and Sanctuaries Act (MPRSA)

The Marine Protection, Research, and Sanctuaries Act (PL 92-532) of 1972 requires monitoring in several sections of the Act to determine if dumping of industrial wastes, sewage, or dredged and fill material adversely impacts the quality of the marine and estuarine environment, human health, and the economic potential of the ocean. Title I discusses the Ocean Dumping Permits Program requirements which are to be administered by the EPA (§102) and the Corps of Engineers (§103).

For permits, monitoring and surveillance of dumping is required (§104(a)(5)) using both chemical and biological methods. Furthermore, under Title II (Ocean Dumping Research Program), "the development and assessment of scientific techniques to define and quantify the degradation of the marine environment" are specifically mandated in order to conduct the research program. Monitoring programs are to include but not be limited to bottom oxygen concentrations; contaminant levels in biota, sediments, and the water column; diseases in fish and shellfish; and changes in types and abundance of indicator species (§202(2)(C)). The Act specifically requires cooperation between EPA, the Corps of Engineers, and the Department of Commerce in these programs.

Evolution of Testing Requirements

The Agency views "monitoring" in its broadest sense, incorporating much more than the act of extracting and analyzing water samples or measuring biological impacts. The monitoring process begins with the

identification of information needs and ends with the actual use of monitoring results in decision making. A comprehensive monitoring strategy must address the entire process, identifying the actions to be taken with respect to each step to ensure effective support for program objectives.

The purpose of monitoring in the Office of Water is to develop information to help State and EPA managers perform their regulatory and programmatic functions for protection of surface water quality and associated aquatic resources. These activities are carried out by a variety of programmatic offices in EPA.

Trends in Monitoring Strategy

To determine the scope and magnitude of the monitoring effort performed under the FWPCA, the data in the STORET system were reviewed. Over 2000 agencies or offices of different agencies have submitted data to STORET. There are over 650,000 monitoring stations across the U.S. and 106,000,000 pieces of data within STORET. Table II-2 shows the type of agencies which have submitted data to STORET and Table II-3 shows the type of data which have been entered in STORET. Only a small fraction of the biomonitoring data collected by most federal and state programs (e. g., ecological data) for ambient monitoring have been entered into STORET (2-5) because the system was not originally designed to accommodate the hierachical structure of these data. However, a new biological data management system (BIOS) has been developed by the Agency to handle these data. Based on analysis of the data submitted, the following trends in monitoring strategy were detected.

Since the enactment of the 1972 Amendments to FWPCA, the strategy for water quality monitoring in the Office of Water has changed considerably. In developing the system of limitations required by the 1972 Amendments to FWPCA, EPA focused in the early 1970's on developing a chemical database indicative of water quality. Discharges were regulated principally for gross or "conventional" measures of pollution. Conventional pollutants included biochemical oxygen demand (BOD), dissolved oxygen (DO), suspended and dissolved solids, bacteria, nutrients, pH, and temperature. This surrogate approach, while appropriate for the control of pollutants of greatest concern at that time, failed to account for other pollutants (e.g., organics, pesticides, metals) that presented the risk of toxicity to aquatic life and humans.

Table II-2 Agencies Submitting Data to STORET

Sewage Treatment Districts
Army Arsenals
Bureau of Reclamation
EPA Headquarters
Corps of Engineers
Universities (Public and Private)
Fish & Wildlife Service
NOAA
Private Contractors
Electric Power Research Institute
EPA Regional Offices
U.S. Geological Survey
U. S. Air Force
Bureau of Sport Fisheries & Wildlife
U. S. Forest Service
Various State Agencies (all 50 states)
Bureau of Land Management
Cities
Department of Energy
County Agencies
Water and Power Resources
River Basin Commissions
Federal Highway Administration
EPA Research Laboratories
Tennessee Valley Authority
Office of Surface Mining
EPA National Enforcement Center
EPA and Canada Cooperative

This situation precipitated litigation (2-6) that resulted in a Consent Decree (Natural Resources Defense Council, Inc., et al. v. Train, 8 ERC 2120 (D.D.C. 1976)), mandating identification of the "priority pollutants." EPA identified 65 priority pollutants (129 specific chemicals, later reduced to 126 chemicals) of concern to 21 industrial categories. There are now 51 major industrial categories which include over 700 subcategories and greater than 70% of all industries (2-7). The Consent Decree,

Table II-3 Type of Data Submitted to STORET

1	Conventional and priority pollutants in effluents (discharge permit. compliance monitoring)
2	Effluent toxicity to aquatic organisms (discharge permit compliance monitoring)
3	Chemical data for acid mine drainage
4	Ambient surface water hydrological, chemical, priority pollutant, and biological integrity data from Federal and state surface water monitoring programs (§106[e] Basic Monitoring Program)
5	Priority pollutants in freshwater fish tissue and sediments (§106[e] Basic Water Monitoring Program)
6	Nutrients, pH, and alkalinity of lakes (Clean Lakes Program)
7	Pesticides and toxic chemicals in marine mussels (Mussel Watch Program)
8	Dioxin data (National Dioxin Study)
9	Chemical and biological integrity data from the Chesapeake Bay and other major bays (National pprogram)
10	Water quality, priority pollutants, and biological integrity data from the Great Lakes
11	Toxic chemicals in leachate and ground water beneath landfills
12	Priority pollutants in ground water supplies
13	Contaminants in drinking water

slightly modified, was adopted into the language of the 1977 Amendments to FWPCA.

During the period, 1976-1984, the EPA emphasized a chemical-by-chemical approach to monitoring activities and developed effluent guidelines and pretreatment standards. This resulted in a significant increase in the total number of chemical measurements made on each sample. During this time, the number of chemicals routinely measured increased by over an order of magnitude. Methods for chemical analyses were greatly improved due to the introduction of new analytical technology for the priority pollutants.

Intensive surveys were performed on surface waters, and numerous studies were completed on bioaccumulation, toxicity, acid deposition, and ecosystem surveys. As with the monitoring programs developed under RCRA and Superfund, additional sample matrices became of concern. For all programs, the number of sample matrices of concern has increased three to four-fold from a focus almost exclusively on air and surface water samples to a much larger and difficult to analyze suite of sample matrices. These new matrices include 43 uncontaminated and contaminated soil, sediment, waste, sludge, groundwater, marine water, drinking water, and tissue (human, fish, and plant) samples.

Using the chemical-by-chemical approach, the Agency kept significant amounts of toxic compounds out of surface waters during the 1970's. However, by 1984, it became apparent that a chemical-by-chemical approach, by itself, could not adequately protect all surface waters for the following reasons:

- existing lists of target analytes do not contain all chemicals which are toxic,
- many toxic compounds at toxic levels cannot be measured by available methods,
- toxicological data are not available to support the development of water quality criteria for the thousands of compounds which are toxic,
- chemical specific approaches cannot account for possible interactions among pollutants that may occur in complex effluents (2-8), and
- complete chemical analyses are prohibitively extensive.

As a result of this recognition, EPA adopted a national policy in 1984 (2- 9) to include toxicity in the development of water quality-based permit limitations. This approach is consistent with the original intent of Congress and authorized in the FWPCA (§§301 & 303) and is necessary to implement State derived water quality standards (2-10) and determine stream segment wasteload allocations.

The term "toxic pollutants" is defined in the FWPCA as,

> those pollutants, or combination of pollutants, including disease-causing agents, which after discharge and upon exposure, ingestion, inhalation or assimilation into any organisms, either directly from the environment or indirectly by ingestion through food chains, will, on the basis of information available to the Administrator,

cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring (2-11).

The key phrase from the FWPCA, "toxic pollutants in toxic amounts" (2-12), when adopted as a national policy, required a very significant change in monitoring strategy. Particularly, this has resulted in increased ambient monitoring to identify water quality-limited bodies of water and to develop appropriate source and nonpoint source pollution controls.

As health-based criteria are used to establish monitoring standards, there will be a need to detect lower and lower levels of pollutants. During the 1960's, it was necessary to detect conventional pollutants at the parts per million level. During the 1970's, it was necessary to measure toxic pollutants at the part per billion level, and in the 1980's and ongoing, it will be necessary to measure some toxic chemicals at the part per trillion level to determine compliance with health-based standards.

A toxics orientation has begun to pervade all FWPCA related regulations and has caused a greater emphasis to be placed on biomonitoring techniques. This approach, reflected in the third round of NPDES permits, has resulted in the increased use of whole effluent toxicity testing in establishing permit limitations. This approach is being applied to major and selected minor industrial and municipal dischargers on a case-by-case basis.

The Domestic Sewage Study and effluent testing of POTW's in a number of states has demonstrated that municipal dischargers could have significant toxicity due to the presence of toxic chemicals that are not covered by existing pretreatment standards. The toxics control strategy has resulted in the need for significant improvements in chemical monitoring methods, including lower detection limits and new analytical tests. Additional emphasis has been placed on monitoring at the ecosystem level, including numerous fate and biological effects studies. As the Agency continues to shift monitoring concern from emphasis on conventional analytes to a focus principally on toxic pollutants, the number of analytes will likely grow another order of magnitude in the next decade.

Future Monitoring Needs

To determine priorities for future monitoring, and to address continuing concerns that EPA HQ had not been providing sufficient program direction and technical guidance to the states and regions on surface water monitoring, the Office of Water initiated a major study of the Agency's surface water monitoring activities in December 1985. The study, *Surface Water Monitoring: A Framework for Change*, was completed in September 1987. The study identified numerous deficiencies in past approaches to monitoring and recommended that EPA and states:

- develop guidance on designing scientifically sound, cost-effective assessment programs that make use of new and emerging approaches such as ecoregions, volunteer monitoring, and biological monitoring methods to complement traditional water chemistry techniques;
- accelerate the development and application of promising biological monitoring techniques and evaluate the role that biological methods should play in monitoring programs;
- analyze the feasibility of requiring NPDES permittees to conduct ambient monitoring;
- improve their ability to document progress in water pollution control;
- centrally coordinate EPA activities to integrate water-related data; and
- make existing monitoring data more accessible and useful to water qualities managers.

EPA's Office of Water has begun a number of projects to implement recommendations made in the study and to fulfill new

requirements resulting from the Water Quality Act of 1987. These efforts include:

- a guidance document on volunteer monitoring directed to state program administrators;
- the preparation of profiles of state monitoring programs assessing current state monitoring and assessment activities and resources available to states;
- a study of monitoring objectives and approaches analyzing the usefulness and status of existing and emerging monitoring and assessment methods;
- a study of assessment criteria and methodologies;
- the development of monitoring program guidance to improve the scope and effectiveness of state monitoring and assessment programs;
- the development of "Rapid Bioassessment Protocols," which provide field methods for conducting qualitative biological assessments using fish and macroinvertebrates;
- a national policy on the role of ecological risk assessment in the water program;
- development of the "Waterbody System," a data system which provides a waterbody-specific format for storing 305(b) water quality assessment information;
- the "Water Quality Data Systems Steering Committee," which was established to provide management direction for water quality data systems.

A ground water monitoring strategy was developed in 1985 which provided a cross agency analysis of the need for and use of ground water monitoring data. Within this approach, individual program monitoring strategies such as RCRA, Superfund, and Pesticides focus on their program's specific interrelationships between programs and the overall direction of the Agency's ground water monitoring effort.

Amendments to the Safe Drinking Water Act (SDWA), passed in June, 1986, call for a major expansion in the scope and authorities of the Public Water Supply (PWS) and Underground Injection Control (UIC) programs. These SDWA revisions require EPA to promulgate drinking water standards for at least 83 new contaminants on a three year schedule and to develop a priority list of at least 25 more contaminants for future regulation every three years. The Office of Drinking Water must initiate a monitoring program to include unregulated contaminants and start developing new ground-water monitoring methods for governing waste disposal injection wells.

To add further complexity to the monitoring requirements previously discussed, the number of EPA programs with their own requirements and distinct technical methods has also increased significantly over the last decade. Until the early 1970's, all monitoring was conducted or required by the air and water program offices. As a result of different program emphasis, there was no overlap in monitoring requirements or methods in the air and water programs. Since then, major monitoring programs and requirements have been established by the Superfund, RCRA, TCSA, FIFRA and Drinking Water offices. Each program office, operating under separate legislative mandates, has established distinct monitoring requirements and methods. While the number of programs with monitoring requirements has increased three to four-fold, the actual complexity and scope of monitoring requirements has increased more than fifteen-fold due principally to the complexity of the RCRA and Superfund programs. A significant future need will be to achieve consistency between these various programs.

Another aspect of the significant changes in monitoring requirements during the last decade, is the tremendous increase in scrutiny that data generated today receive compared to during the 1970's. During the early 1970's and before, most data were collected to provide trend information on the effectiveness of environmental controls. Data were not routinely used in enforcement actions or in litigation. As a result, the technical methods did not have to be as well defined or as carefully followed. Now, data routinely undergo legal scrutiny and as a result, the methods must

be documented more completely and the methods followed more carefully by a laboratory. Better QA/QC methods are needed to demonstrate adherence to testing protocols.

As more responsibility to collect environmental data was transferred from state and federal agencies to the private sector, the number and size of commercial and industrial laboratories increased three to five-fold during the past decade. The task of these laboratories is much greater than ever before as they typically receive requests to analyze virtually any sample for any analyte required by any regulation using a wide array of methods, instrumental techniques, and quality control methods. Therefore, for the Agency to ensure the integrity of the database used to make important monitoring, cleanup, and enforcement decisions, it must be able to rely on the data determined by the testing methods established by the Agency. Again, this suggests that a strong QA/QC program is necessary. Subsequent sections address the issue of the availability and adequacy of testing methodology and the comparability of FWPCA testing and QA/QC methods with those established by other major EPA programs as well as other federal and state agencies.

Inventory of Chemical Testing Requirements

The chemicals that must be measured to support various monitoring programs constitute a diverse and extensive list of organic compounds, metals, anions and radiological analytes. To assess the adequacy of the test methods, the analytes to be measured must first be defined.

The previous sections of this chapter described in general terms the monitoring requirements under FWPCA, CERCLA, SDWA, RCRA and MPRSA. This section of the report contains an inventory of chemical analytes that can be considered to represent a core list of current, and to some degree, future monitoring analytes. This list, presented in Table II-1, contains all analytes that could be readily identified as: 1) analytes required for monitoring under FWPCA programs; and 2) analytes required for monitoring under other Agency programs.

Due to the dynamic and evolving nature of monitoring requirements for chemical analytes, it is almost impossible to completely define all analytes that must be measured in a given program. The table prepared for this section contains a comprehensive listing of chemical analytes that are used later in this report as the basis for the assessment of the adequacy and availability of test methods. It is likely that analytes will be added to or deleted from the lists used to compile Table II-1 before this report is completed.

New monitoring requirements which may be implemented in the next two to three years were determined by reviewing regulations that are in a preliminary, developmental, stage. These analytes were not included in the core list, but are discussed in the latter part of this section.

The information presented in Table II-1 was obtained from a review of the following:

- Point source effluent guideline and industrial pretreatment standards promulgated in 40 CFR 400-454
- NPDES permit discharge monitoring requirements as recorded in the Permit Compliance System (PCS)
- Health-based water quality criteria
- State promulgated water quality standards
- NPDES permit application requirements
- STORET
- Other FWPCA programs
- SDWA requirements
- RCRA requirements
- CERCLA requirements

While the table prepared from the review of the monitoring programs is an attempt to present an inclusive list of FWPCA monitoring requirements, it should be noted that one significant factor, nomenclature, complicated this review Most organic compounds have two or more names that are commonly used. (Table II-

4). In addition, groups of isomers (e.g., xylenes, dinitrotoluenes) are sometimes specified in the requirements. Another example of a problem is the designation of classes of compounds, e.g., chloroalkyl ethers. Current methods are available for measuring specific compounds, not isomeric groups and classes.

Table II-4 Examples of Organic Compound Names Used Interchangeably

Acetone	=	2-Propanone
Bromomethane	=	Methyl bromide
2-Butanone	=	Methyl ethyl ketone
Chloromethane	=	Methyl chloride
Methylene chloride	=	Dichloromethane
4-Methyl-2-pentanone	=	Methyl isobutyl ketone
Tetrachloroethene	=	Tetrachloroethylene
Trichloroethene	=	Trichloroethylene
Methyl phenol	=	Cresol
1,2-Dibromoethane	=	Ethylene dibromide
1,2-Dichloroethane	=	Ethylenedichloride
Lindane	=	gamma-BHC

An example of this problem is documented in the development of the "priority pollutant" list The original toxic pollutant list specified in the 1976 NRDC Consent Decree contained 65 entries (classes of compounds, metabolites, etc.) which were transformed into the 129 priority pollutants for monitoring purposes. This transformation of a regulatory list to a practical list for monitoring purposes has not been performed for some of the lists under development.

To minimize problems associated with nomenclature, the approach used for this assessment was as follows:

- A name for each analyte was selected based on common usage considering citations in both analytical methods and regulations.
- Isomer groups were segregated into the individual compounds.
- Where possible, the individual compounds associated with a class were listed. Where this was not possible because the category was too broad (e.g., PNA's), the information was deleted in the primary table and presented separately.

The list of analytes in Table II-1 is presented from an analytical chemist's perspective. Furthermore, an attempt was made to consolidate the information as much as possible. Thus, each analyte is listed once, using a name that is recognizable by an analytical chemist. Due to the confusion regarding nomenclature, some analytes may not be listed by the name appearing in some specific program. For example, ethylene dibromide, a contaminant listed under SDWA, is shown in the table as 1,2-dibromoethane.

Based on the review of the information described above, a total of 323 analytes were identified. These analytes and the detailed information obtained on each, are presented. This table contains an alphabetical listing of chemical analytes and an inventory of information contained under major headings as summarized below:

- Effluent Guidelines and Standards.
- NPDES Monitoring Requirements.
- Water Quality Criteria.
- Water Quality Standards.
- NPDES Permits.
- Other FWPCA Lists.
- SDWA Requirements.
- RCRA Requirements.
- CERCLA Requirements.

An asterisk by a analyte indicates that an approved method has been promulgated in §304(h). Alternate names and Chemical Abstracts Registry names for these compounds are available in literature (2-13,14,15). The analyte list does not include the pesticides listed under the remanded regulation in 40 CFR 455 unless they were also required for monitoring in

some other area. Due to their complex nature, these analytes have been considered separately.

Effluent Guideline and Industrial Pretreatment Standards

The Agency has promulgated effluent guidelines and industrial pretreatment standards for 51 point source industrial categories (2-21,33 & 35). These effluent guidelines and standards were reviewed to determine the specific chemical analytes for which standards have been promulgated.

Each point source category represents a broad industrial category such as "inorganic chemicals." This category is then divided into subparts (e.g., aluminum chloride, calcium carbide, sodium fluoride, etc.). Effluent guidelines and standards are established for each subpart. For the purposes of this study, the information contained in each subpart was consolidated to determine what analytes are measured in each category.

This information was then used to assess the frequency distribution of the analytes. Two numbers appear in Table II-1 under the heading "Effluent Guidelines and Pretreatment Standards." The first number represents the frequency for which the analyte has an established standard, calculated by dividing the number of times the analyte appeared by the major industrial categories.

The effluent guidelines and standards have numeric discharge limitations for each regulated analyte. Although most of these guidelines and standards are promulgated as mass discharges of a pollutant per unit of manufacturing production or raw material use, concentrations based on the minimum pollutant discharge limitations can be calculated. These values represent the most stringent requirements that would be expected to be achieved by an analytical method related to technology-based controls. The second number in this column is this limit, expressed as g/L.

As indicated previously, the pesticide manufacturing effluent guidelines were not included. Pesticides which are monitored for other reasons are contained in the analyte list.

NPDES Monitoring Requirements

A survey of four regions (II, III, V, IX) was performed to determine NPDES permit monitoring requirements. This survey was designed to 1) identify the chemical analytes which were specified in the permits and 2) quantify the frequency at which these analytes were specified.

The values presented in the table represent the number of times the analyte is cited in permits in these four regions. Many analytes listed in NPDES permits were not included in this table due to the problem of correctly identifying the analyte. Examples of this problem included analytes such as "pesticides, general", "mercaptans", "combined metals sum", "chlorinated organic compounds" and "resin acids".

In addition, the determination of the detection frequency was also complicated by the nomenclature. Multiple entries were frequently listed for the same analyte e.g., "ethyl benzene" and "ethylbenzene". In a review of permits in one region, the following names were listed: lindane, benzene hexachloride, hexachlorocyclohexane, delta benzene hexachloride, G-BHC-Delta(sic). These names all refer to one or more of the BHC pesticide isomers. Up to 15 different citations were noted for BOD.

Because of these complicating factors, the information contained in Table II-1 should be used only to provide an estimation of the monitoring requirements. However, it appears that methods have been promulgated for most analytes for which monitoring is required. However, there is still a significant number of analytes for which no methods have been promulgated. For example, Table II-5 lists 35 analytes that were identified in this review that did not appear as monitoring analytes in any other area reviewed and that do not have §304(h) methods. Standard nomenclature should be a significant priority for the NPDES permit program.

Water Quality Criteria

Ambient water quality criteria, which are based on the results of toxicity tests and other biological data, have been developed for many analytes (2-36,37). These criteria provide guidance to the states, relating to: 1) human and non-human acute and chronic toxicity of analytes; and 2) carcinogenic and organoleptic properties. For non-carcinogens, the criteria represent estimate concentrations which prevent adverse health effects. For carcinogens, the criteria represent levels of incremental cancer risk. The "criteria" are therefore designed to represent a concentration for a given constituent that, when not exceeded, will provide an adequate degree of safety.

The science of establishing health-based criteria is not fully developed. However, the numbers that have been established in the water quality criteria documents are increasingly being cited in regulations or used as a basis for developing state water quality standards. Thus, these criteria are important from the perspective of evaluating the adequacy of a testing method.

Numeric values in µg/L are shown for the specific compounds for which water quality criteria have been developed. The value shown is the lowest value as provided in the Water Quality Criteria Summary dated September 2, 1986, incorporating both the aquatic toxicity and human health criteria. Also, water quality criteria have been established for classes of compounds, e.g., chloroalkyl ethers. These values were not included.

Water Quality Standards.

Water quality criteria are used to establish water quality standards. Water quality standards are established by the states to protect water uses (2-17,19-27,31 & 35). Standards are established based on water use (e.g., aquatic life protection, recreational, agricultural, drinking water supply, etc.). Both narrative and numeric standards have been established. Narrative standards are general statements concerning important environmental conditions. Numeric standards are the concentration levels that will be protective of the designated use. Numeric standards have been established for both conventional analytes and toxics. Of the 57 states and territories, 39 have adopted at least one numeric standard for toxics.

Two sets of numbers are shown under the general heading Water Quality Standards. The first number is the number of states and territories that have established a numeric

Table II-5 Parameters Identified in Four EPA Regions that are Required to be Measured and that do not have a §304(h) Method

Parameters	Frequency*
Benzisothiazole	1
Carbaryl	1
Carbofuran	1
Chlorendic Acid	1
Diazinon	1
Dichlorobenzyltrifluoride	2
Difolalan	1
Ferricyanide	1
Ferrocyanide	1
Formaldehyde	13
Glyphosate	1
Hydrazine	13
Iodide	1
Iodine 129	4
Isothiazolone	1
Lithium	2
Palladium	1
Phthalic Acid	1
Polonium 210	9
RDX	15
Samarium	2
Sevin	2
Sodium Nitrite	1
Strontium 90	1
Sulfur dioxide	3
Tellerium	1
Tetrahydrofuran	2
Thiocyanate	1
Thiosulfate	1
Triethanolamine	1
Trifluralin	1
Trinitrotoluene	25
Tritium	3
Urea	3
Zirconium	1

*Number of times the parameter was listed.

standard for the analyte indicated. The second number is the lowest concentration that has been established by any state. As in the previous areas, water quality standards have been established for generic categories ("pesticides", "biocides", "petroleum"). Furthermore, different names are used for what are presumably the same analytes, e.g., phenols, phenolics, and phenolic compounds.

As with the water quality criteria, the numeric standards are an important indicator as to the adequacy of a test method. The values shown in Table II-1 indicate the best performance required of a method, not necessarily what would be required for most uses.

Other FWPCA Lists

Although many of the water programs are well established, there are many other programs which are in the process of being developed. While many of these programs are oriented toward establishing monitoring requirements which are in many ways similar to the existing requirement, e.g., development of effluent guidelines for additional point source categories, some programs are involved in defining new requirements.

For example, the program to develop regulations to implement recommendations of the Domestic Sewage Study is considering the analytes monitored under RCRA. In reviewing the monitoring requirements under consideration, two groups of analytes were noted that are currently being used in the development of baseline data. These two groups were the "Appendix C" and "Paragraph 4(c)" analytes, both derived from the 1976 Settlement Agreement (2-16).

The Appendix C list is a list of 26 organic compounds derived from a list of classes of compounds, contained in Appendix C of the Settlement Agreement. The Paragraph 4(c) analytes were derived from an intensive study of other toxics which were identified in industrial effluents pursuant to requirements specified in the Settlement Agreement.

SDWA Requirements

As described previously, 40 CFR 141 has specified 33 NPDWR's (national primary drinking water regulations) and monitoring requirements for 52 volatile organic compounds. In addition, 12 contaminants are subject to maximum contamination levels in 40 CFR 143 as secondary standards (SMCL's). For those contaminants that have regulated levels (NPDWR's) or secondary standards (SMCL's), the level of concern is shown in concentration units of µg/L. The SMCL levels are further noted by the post script "S". The 52 volatile organic compounds designated as unregulated contaminants were categorized into three groups. Each group of contaminants has different monitoring requirements. The classification of a specific contaminant into one of these three groups is shown in Table II-1 with the following codes:

- ALL - Contaminants required to be measured by all water supply systems
- VUL - Contaminants required to be measured by vulnerable systems
- DISC - Contaminants required to be measured at the state's discretion

In addition, analytes which are under consideration for development of NPDWR's are shown with the following designations:

- CON - Contained in the list of 83 contaminants, including the proposed changes, as noticed in the July 8, 1987 Federal Register
- DWPL - Draft contained in Drinking Water Priority List for 1988

Table II-1 does not contain all of the analytes in these two lists due to the general problems described previously, which were associated with defining a list for monitoring purposes.

RCRA Monitoring Requirements

The RCRA program has developed a number of monitoring requirements associated with the multitude of issues surrounding the

management of hazardous waste. Among these requirements are groundwater monitoring requirements for the group of hazardous constituents contained in Appendix IX to 40 CFR 264. The 250 analytes contained in Appendix IX include virtually all of the analytes contained in the other RCRA programs. Because of the comprehensive and easily definable nature of the Appendix IX list, all analytes contained in Appendix IX are shown in Table II-1 as part of the core list.

Other analytes contained in the core list which are referenced in FWPCA programs are noted with the following conventions:

- GWM - Routine detection monitoring analytes specified in 40 CFR 265
- OTC - Analytes contained in the proposed organic toxicity characteristic (51 FR 21648)
- Appendix VIII - Analytes contained in Appendix VIII that were deleted in the development of Appendix IX due to concerns.over the adequacy of the test methods.

CERCLA Lists

As discussed previously, 151 analytes are monitored at Superfund sites by laboratories under contract to the Agency. These analytes are designated by the term CLP under the CERCLA Lists column of Table II-1, indicating that the analytes are measured in the Contract Lab Program.

The list of analytes in the CLP was based on the priority pollutant list. Since the inception of the program in 1980, 11 analytes have been deleted based on the performance of the method. These analytes are listed below:

In addition to the CLP analytes listed in the CERCLA column in Table II-1 are those analytes contained in the priority list of 100 hazardous substances listed in the April 17, 1987 Federal Register, designated by the term HSL.

Bis(2-chloromethyl) ether	Acrolein
Aniline	Acrylonitrile
Benzidine	2-Chloroethyl vinyl ether
1,2-Diphenylhydrazine	Trichlorofluoromethane
Dichlorodifluoromethane	Endrin aldehyde
Tin	N-Nitrosodimethylamine

Of the 11 analytes indicated by the term HSL that are not CLP analytes, 7 were originally contained in the CLP analyte list but were subsequently deleted based on poor method performance data. Note that some of those compounds are still listed as priority pollutants.

Additional Analytes

As stated previously, Table II-1 presents a core list of analytes for which monitoring is readily defined.Tables II-6 through II-14 contain lists of substances for which monitoring requirements are not fully defined. However, substances contained in these lists may be added to the existing requirements. A brief description of these lists is summarized below.

Table II-6: Water Quality Criteria

This list contains substances that have established water quality criteria, but could not be defined from a laboratory perspective.

Table II-7: SDWA List

The amended SDWA specified the development of NPDWR's for a list of 83 contaminants. This list, shown in Table II-7 contains substances that could not be clearly defined, i.e., adipates, viruses. Furthermore, monitoring requirements for many of the analytes on this list have not been established.

Table II-8: Table V of 40 CFR 122, Appendix D

This list contains substances which "must be identified if expected to be present" in industrial

Table II-6 Poorly Defined Water Quality Criteria Parameters

Parameters	Comment
BHC	All isomers listed separately
Chloroalkyl ethers	Class
Chlorinated benzenes	Class
Chlorinated ethanes	Class
Chlorinated ethenes	Class
Chlorinated naphthalenes	Class
Chlorophenols	Class
Chlorophenoxy herbicides	Class
Diamine toluene	Class

discharges. Some of these analytes are contained in NPDES permits. Others are poorly defined.

Table II-9: Appendix VIII to 40 CFR 261

The list contains many poorly defined and unmeasurable analytes.

Table II-10: Michigan List

The State of Michigan petitioned the Agency to expand the Appendix VIII list by the addition of 120 substances.

Table II-11: Sludge Monitoring List

This table contains a list of analytes to be measured in the POTW sludge monitoring program.

Table II-12: Pesticide Chemicals

On December 15, 1986, the Agency remanded 40 CFR 455, the effluent limitations guidelines, pretreatment standards, and new source performance standards, for the pesticide chemicals category. This action deleted a list of 61 pesticides, and 14 methods developed to measure these pesticides. The pesticides and methods that were effected by this action are shown in Table II-12.

Table II-13: Hazardous Substances

Under 40 CFR 116, 299 inorganic salts and organic compounds are listed in Table 116.4A as hazardous substances. In 40 CFR 117, reportable quantities have been established for each substance, ranging from 1 to 5,000 pounds. This regulation set forth the quantity that requires reporting of a discharge to EPA.

This table contains a list of analytes to be promulgated to be measured in the POTW sludge monitoring program.

Table II-14: STORET Analytes

STORET is a database established by the Agency which contains environmental data submitted by various groups. A survey of the data submitted by California revealed a number of analytes for which data are being generated and for which §304(h) methods do not exist. Examples of those analytes are included in Table II-14. A review of data submitted by nine other states showed that many additional analytes are being measured for which there are no §304(h) methods.

Table II-15: SDWA Priority List

The SDWA requires EPA to compile a priority list of contaminants by 1988. To meet this goal, the EPA has defined seven groups of contaminants which are being considered in the development of the first priority list (52 FR 25720). These seven groups and substances contained in these groups are shown in Table II-15. These substances will form the basis for adding additional contaminants to drinking water monitoring requirements.

Inventory of Biological Testing Requirements

The biological analytes that must be measured in support of various monitoring programs constitute a diverse and largely nonspecific list that is applicable to various media (drinking water, ambient waters, groundwater, wastewater, leachates, sludge, and soils). Overall, FWPCA analytes can be divided into two broad groups: 1) human health

Table II-7 Drinking Water Analytes and Tests

Volatile Organic Chemicals	Organics
Trichloroethylene	Endrin
Tetrachloroethylene	Lindane
Carbon tetrachloride	Methoxychlor
1,1,1-Trichloroethane	Toxaphene
1,2-Dichloroethane	2,4-D
Vinyl chloride	2,4,5-TP
Methylene chloride	Aldicarb
Benzene	Chlordane
Chlorobenzene	Dalapon
Dichlorobenzene(s)	Diquat
Trichlorobenzene(s)	Endothall
1,1-Dichloroethylene	Glyphosate
trans-1,2-Dichloroethylene	Carbofuran
cis-1,2-Dichloroethylene	Alachlor
Microbiology and Turbidity	Epichlorohydrin
Total coliforms	Toluene
Turbidity	Adipates
Giardia lamblia	2,3,7,8-TCDD (Dioxin)
Viruses	1,1,2-Trichloroethane
Standard plate count	Vydate
Legionella	Simazine
Inorganics	Polynuclear aromatic hydrocarbons (PAHs)
Arsenic	Polychlorinated biphenyls
Barium	Atrazine
Cadmium	Phthalates
Chromium	Acrylamide
Lead	Dibromochloropropane (DBCP)
Mercury	1,2-Dichloropropane
Nitrate	Pentachlorophenol
Selenium	Picloram
Silver	Dinoseb
Fluoride	Ethylene dibromide
Aluminum	Dibromomethane
Antimony	Xylene
Molybdenum	Hexachlorocyclopentadiene
Asbestos	**Radionuclides**
Sulfate	Radium 226 and 228
Copper	Beta particle and photon radioactivity
Vanadium	Uranium
Sodium	Gross alpha particle activity
Nickel	Radon
Zinc	
Thallium	
Beryllium	
Cyanide	

related, and 2) ecosystem related. Unlike the inventory of chemical analytes previously discussed, the various sections of the FWPCA and related statutes, and the regulations promulgated under these statutes, seldom specify the biological characteristics or properties to be monitored within these two broad types. Biological monitoring requirements are generally described in broad terms such as "biological integrity," which depends on the diversity, stability, and productivity of indigenous populations of fish and aquatic life. There are thousands of species of common estuarine, marine, and freshwater organisms. Much is known about the environmental requirements and pollution tolerance of the common species, but no list of essential or indicator species has been promulgated for the various saline and freshwater habitats.

The success of the Agency's pollution abatement and control program must be based on the absence of toxicity in point and non-point sources, and the maintenance of the biological integrity of communities of organisms in receiving waters.To provide support for the implementation of the FWPCA, and to determine if the mandated goal of "swimmable, fishable waters" has been achieved, the Agency has developed biological field and laboratory methods for waters, wastewaters, sludges, and sediments, which: 1) detect and quantify disease-causing agents (human pathogens); 2) measure the toxicity of pure compounds, effluents, and surface waters; 3) determine the bioaccumulation of toxic pollutants (toxic substances in tissues); and 4) determine the integrated effects of all toxic pollutants on the biological integrity (diversity, stability, and productivity) of communities of fish and aquatic life.

Microbiological analytes related to human health include disease-causing agents (pathogens) such as viruses, bacteria, protozoa, and parasites, and nonpathogens that are indicators of the presence of pathogens or fecal materials. The microbiological analytes required or recommended under the FWPCA and SDWA are listed in Table II-16, and methods to determine mammalian toxicity and mutagenicity are listed in Table II-17.

Table II-8 Table V of 40 CFR 122, Appendix D

Acetaldehyde	Isopropanolamine
Allyl alcohol	Kelthane
Allyl chloride	Kepone
Amyl acetate	Malathion
Aniline	Mercaptodimethur
Benzonitrile	Methoxychlor
Benzyl chloride	Methyl mercaptan
Butyl acetate	Methyl methacrylate
Butylamine	Methyl parathion
Captan	Mevinphos
Carbaryl	Mexacarbate
Carbofuran	Monoethyl amine
Carbon disulfide	Monomethyl amine
Chlorpyrifos	Naled
Coumaphos	Napthenic acid
Cresol	Nitrotoluene
Crotonaldehyde	Parathion
Cyclohexane	Phenolsulfonate
2,4-D (2,4-Dichloropheynoxy acetic acid)	Phosgene
Diazinon	Propargite
Dicamba	Propylene oxide
Dichlobenil	Pyrethrins
Dichlone	Quinoline
2,2-Dichloropropionic acid	Resorcinol
Dichlorvos	Strontium
Diethylamine	Strychnine
Dimethylamine	Styrene
Dinitrobenzene	2,4,5-T(2,4,5-Trichlorophenoxy acetic acid)
Diquat	TDE(Tetrachlorodiphenylethane)
Disulfoton	2,4,5-TP (2-(2,4,5-Trichlorophenoxy) propanoic acid)
Diuron	Trichlorofan
Dodecylbenzenesulfonate	
Epichlorohydrin	Triethanolamine
Ethion	Triethylamine
Ethylene diamine	Trimethylamine
Ethylene dibromide	Uranium
Formaldehyde	Vanadium
Furfural	Vinyl acetate
Guthion	Xylene
Isoprene	Xylenol
	Zirconium

Table II-9 Appendix VIII to 40 CFR Part 261

75058	Acetonitrile
98862	Ethanone, 1-phenyl
53963	Acetamide, N-9H-fluoren-2-yl
75365	Acetyl chloride
591082	Acetamide, N-(aminothioxymethyl)-
107028	2-Propenal
79061	2-Propenamide
107131	2-Propenenitrile
1402682	Aflatoxins
116063	Propanal, 2-methyl-2-(methylthio)-, O-[(methylamino)
309002	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-
107186	2-Propen-1-o1
107051	1-Propene, 3-chloro-
20859738	Aluminum phosphide (AlP)
92671	[1,1'-Biphenyl]-4-amine
2763964	3(2H)-Isoxazolone, 5-(aminomethyl)-
504245	4-Pyridinamine
61825	1H-1,2,4-Triazol-3-amine
7803556	Vanadic acid, ammonium salt of
62533	Benzenamine
7440360	Antimony
140578	Sulfurous acid, 2-chloroethyl-, 2-[4-(1,1-dimethylethyl)
7440382	Arsenic
7778394	Arsenic acid (AsH3O4)
1303282	Arsenic oxide (As2O5)
1327533	Arsenic oxide (As203)
492808	Benzamine, 4,4'carbonimidoylbis[N,N-dimethyl-
115026	L-Serine, diazoacetate (ester)
7440393	Barium
542621	Barium cyanide
225514	Benz(c)acridine
56553	Benzo(a)anthracene
98873	Benzene, (dichloromethyl)-
71432	Benzene
98055	Arsonic acid, phenyl-
92875	Benzidine
205992	Benzo(b)fluoranthene
205823	Benzo(j)fluoranthene
50328	Benzo(a)pyrene
106514	2,5-Cyclohexadiene-1,4-dione
98077	Benzene, (trichloromethyl)-
100447	Benzene, (chloromethyl)-
7440417	Beryllium
111911	bis(2-Chloroethoxy)methane
111444	bis(2-Chloroethyl) ether
108601	bis(2-Chloroisopropyl) ether
542881	Bis(chloromethyl)ether
117817	bis(2-Ethylhexyl) phthalate
598312	2-Propanone, 1-bromo
75252	Tribromomethane
101553	4-Bromophenyl phenyl ether
357573	Strychnidin-10-one, 2,3-dimethoxy

(Continued)

Table II-9 (Continued)

85687	Butyl benzyl phthalate
75605	Arsenic acid, dimethyl
7440439	Cadmium
13765190	Chromic acid, calcium salt
592018	Calcium cyanide
75150	Carbon disulfide
353504	Carbonic difluoride
56235	Tetrachloromethane
75876	Acetaldehyde, trichloro
305033	Benzenebutanoic acid, 4-[bis(2-chloroethyl)amino-
57749	4,7-Methano-1H-indene 1,2,4,5,6,7,8,8-octachloro-2,3,3a,
1_064	Chlorinated benzenes, NOS
1_065	Chlorinated ethane, NOS
1_066	Chlorinated fluorocarbons, NOS
1_067	Chlorinated naphthalene, NOS
1_068	Chlorinated phenol, NOS
494031	2-Naphthaleneamine, N,N-bis(2-chloroethyl)
107200	Acetaldehyde, chloro-
1_070	Chloroalkylethers, NOS
106478	Benzenamine, 4-chloro-
108907	Chlorobenzene
510156	Benzeneacetic acid, 4-chloro-alpha-(4-chlorophenyl)-
59507	4-Chloro-3-methylphenol
106898	1-Chloro-2,3-epoxypropane
110758	2-Chloroethylvinyl ether
67663	Chloroform
107302	Chloromethyl methyl ether
91587	2-Chloronaphthalene
95578	2-Chlorophenol
5344821	1-(o-Chlorophenyl)thiourea
126998	2-Chloro-1,3-butadiene
542767	Propanenitrile, 3-chloro
7440473	Chromium
218019	Chrysene
6358538	2-Naphthalenol, 1-[(2,5-dimethoxyphenyl)azo]-
8007452	Coal tars
544923	Copper cyanide (CuCN)
8001589	Creosote
106445	p-Cresol
95487	o-Cresol
108394	m-Cresol
1319773	Phenol, methyl
4170303	2-Butenal
57125	Cyanides (soluble salts and complexes) NOS
460195	Ethanedinitrile
506683	Cyanogen bromide
506774	Cyanogen chloride
14901087	beta-D-Glucopyranoside, (methyl-ONN-azoxy)methyl
131895	Phenol, 2-cyclohexyl-4,6-dinitro-
50180	2H-1,3,2-Oxazaphosphorin-2-amine, N,N-bis(2-chloroethyl)
94757	2,4-Dichlorophenoxyacetic acid, salts and esters
20830813	5,12-Naphthacenedione, 8-acetyl-10-[(3-amino-2,3,6-tri

(Continued)

Table II-9 (Continued)

72548	4,4'-DDD
72559	4,4'-DDE
50293	4,4'-DDT
2303164	Carbamothioic acid, bis(1-methylethyl)-S-(2,3-dichloro
226368	Dibenz(a,h)acridine
224420	Dibenz(a,j)acridine
53703	Dibenzo(a,h)anthracene
194592	7H-Dibenzo(c,g)carbazole
192654	Naphtho[1,2,3,4-def]chrysene
189640	Dibenzo[b,def]chrysene
189559	Benzo(rst)pentaphene
96128	Propane, 1,2-dibromo-3-chloro-
84742	1,2-Benzenedicarboxylic acid, dibutyl ester
95501	1,2-Dichlorobenzene
541731	1,3-Dichlorobenzene
106467	1,4-Dichlorobenzene
25321226	Dichlorobenzenes
91941	3,3'-Dichlorobenzidine
110576	trans-1,4-Dichloro-2-butene
764410	2-Butene, 1,4-dichloro (mixture of cis and trans)
75718	Dichlorodifluoromethane
156605	trans-1,2-Dichloroethene
25323302	Dichloroethylene, NOS
75354	1,1-Dichloroethene
120832	2,4-Dichlorophenol
87650	2,6-Dichlorophenol
696286	Arsonous dichloride, phenyl-
142289	1,3-Dichloropropane
26638197	Dichloropropane, NOS
96231	1,3-Dichloro-2-propanol
26545733	Dichloropropanol, NOS
26952238	Dichloropropene, NOS
10061015	cis-1,3-Dichloropropene
10061026	trans-1,3-Dichloropropene
542756	1,3-Dichloropropene
60571	2,7:3,6-Dimethanonaphth(2,3-b)oxirene, 3,4,5,6,9,9-hexa
1464535	1,2:3,4-Diepoxybutane
692422	Arsine, diethyl
123911	1,4-Dioxane
1615801	Hydrazine, 1,2-diethyl-
3288582	O,O-Diethyl S-methyl ester of phosphorodithioic acid
311455	Phosphoric acid, diethyl-4-nitrophenyl ester
84662	Diethyl phthalate
297972	O,O-Diethyl-O-(2-pyrazinyl)phosphorothioate
56531	Phenol, 4,4'-(1,2-diethyl-1,2-ethenediyl)bis, (E)-
94586	1,3-Benzodioxole, 5-propyl
329657	3.4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
55914	Diisopropylfluorophosphate
60515	Phosphorodithioic acid, O,O-dimethyl s-[2-(methylamino)-
119904	1,1'-Biphenyl-4,4'-diamine, 3,3'-dimethoxy
60117	Benzenamine, N,N-dimethyl-4-(pehnylazo)-
57976	7,12-Dimethylbenz(a)anthracene

(Continued)

Table II-9 (Continued)

119937	[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dimethyl-
79447	Carbamic chloride, dimethyl-
57147	Hydrazine, 1,1-dimethyl
540738	Hydrazine, 1,2-dimethyl
122098	Benzeneethanamine, alpha, alpha-dimethyl-
105679	2,4-Dimethylphenol
131113	1,2-Benzenedicarboxylic acid, dimethyl ester
77781	Sulfuric acid, dimethyl ester
100254	1,4-Dinitrobenzene
25154545	Dinitrobenzene, NOS
534521	Phenol, 2-methyl-4,6-dinitro-
51285	2,4-Dinitrophenol
121142	2,4-Dinitrotoluene
606202	2,6-Dinitrotoluene
88857	Phenol, 2-(1-methylpropyl)-4,6-dinitro-
117840	Di-n-octyl phthalate
122394	Diphenylamine
122667	1,2-Diphenylhydrazine
621647	Di-n-propylnitrosamine
298044	Phosphorodithioic acid, O,O-diethyl S-[2-(ethylthio)
541537	2,4-Dithiobiuret
959988	Endosulfan-I
33213659	Endosulfan-II
115297	6,9-Methano-2,4,3-benzodioxathiepen, 6,7,8,9,10,10-
145733	7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid,
53494705	Endrin ketone
72208	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-
51796	Carbamic acid, ethyl ester
107120	Ethyl cyanide
142596	Ethylenebisdithiocarbamic acid, -sodium salt
111546	Carbamodithioic acid, 1,2-ethanediylbis-, salts and
106934	1,2-Dibromoethane
107062	1,2-Dichloroethane
110805	2-Ethoxyethanol
151564	Aziridine
75218	Ethylene oxide
96457	Ethylenethiourea
75343	1,1-Dichloroethane
97632	Ethyl methacrylate
62500	Methanesulfonic acid, ethyl ester
52857	Phosphorothioic acid, O,O-dimethyl O-[p-[(dimethylamino)
206440	Fluoranthene
7782414	Fluorine
640197	Acetamide, 2-fluoro
62748	Fluoroacetic acid, sodium salt
50000	Formaldehyde
765344	Oxiranecarboxyaldehyde
1_193	Halomethane, NOS
76448	4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-da,4,7,
1024573	2,5-Methano-2H-indeno[1,2b]oxirène, 2,3,4,5,6,7,7-hepta
118741	Hexachlorobenzene
87683	Hexachlorobutadiene

(Continued)

Table II-9 (Continued)

77474	1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-
1_200	Hexachlorodibenzo-p-dioxins
1_201	Hexachlorodibenzofurans
67721	Hexachloroethane
70304	Hexachlorophene
1888717	Hexachloropropene
757584	Tetraphosphoric acid, hexaethyl ester
302012	Hydrazine
74908	Hydrocyanic acid
7664393	Hydrofluoric acid
7783064	Hydrogen sulfide
193395	Indeno(1,2,3-cd)pyrene
9004664	Iron dextran
78831	Isobutyl alcohol
465736	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,
120581	1,3-Benzodioxole, 5-(1-propenyl)-
143500	1,3,4-Metheno-2H-cyclobuta(cd)pentalen-2-one, 1,1a,3,3a,
303344	2-Butenoic acid, 2-methyl- 7-[(2,3-dihydroxy-2-(1-
7439921	Lead
301042	Acetic acid, lead (2+) salt
7446277	Phosphoric acid, lead (2+) salt
1335326	Lead, bis(acetato-O)tetrahydroxytri-
58899	Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1-alpha, 2-alpha,
108316	Maleic anhydride
123331	3,6-Pyridazinedione, 1,2-dihydro-
109773	Propanedinitrile
148823	L-Phenylalanine, 4-[bis(2-chloroethyl)amino]-
628864	Fulminic acid, mercury (2+) salt
7439976	Mercury
126987	2-Propenenitrile, 2-methyl-
91805	1,2-Ethanediamine, N,N-dimethyl-N'-2pyridinyl-N'-(2-
16752775	Ethanimidothioic acid, N-[[(methylamino)carbonyl]oxy]-,
72435	Benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-
74839	Bromomethane
74873	Chloromethane
79221	Carbonchloridic acid, methyl ester
71556	1,1,1-Trichloroethane
56495	Benz[j]aceanthrylene, 1,2-dihydro-3-methyl-
101144	4,4'-Methylenebis(2-chloroaniline)
74953	Dibromomethane
75092	Methylene chloride
78933	2-Butanone
1338234	2-Butanone peroxide
60344	Hydrazine, methyl-
74884	Iodomethane
624839	Isocyanic acid, methyl ester
75865	Propanenitrile, 2-hydroxy-2-methyl-
80626	Methyl methacrylate
66273	Methyl methanesulfonate
298000	Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl)
56042	4(1H)-Pyrimidinone, 2,3-dihydro-6-methyl-2-thioxo-
50077	6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-

(Continued)

Table II-9 (Continued)

70257	Guanidine, N-methyl-N'nitro-N-Nitroso-
505602	Ethane, 1,1'-thiobis[2-chloro-
91203	Naphthalene
130154	1,4-Naphthoquinone
134327	1-Naphthylamine
91598	beta-Naphthylamine
86884	Thiourea, 1-naphthalenyl-
7440020	Nickel
13463393	Nickel carbonyl [Ni(CO)4], (T-4)-
557197	Nickel cyanide
54115	Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)-, and salts
10102439	Nitrogen oxide (NO)
100016	p-Nitroaniline
98953	Nitrobenzene
10102440	Nitrogen oxide (NO2)
51752	Ethanamine, 2-chloro-N-(2-chloroethyl)-N-methyl-
302705	Ethanamine, 2-chloro-N-(2-chloroethyl)-N-methyl, N-oxide
126852	Ethanamine, 2-chloro-N-(2-chloroethyl-N-methyl-
55630	1,2,3-Propanetriol, trinitrate
100027	4-Nitrophenol
79469	Propane, 2-nitro-
56575	Quinoline, 4-nitro-1-oxide-
35576911	Nitrosamine, NOS
924163	N-Nitrosodi-n-butylamine
1116547	Ethanol, 2,2'-nitrosoimino)bis-
55185	N-Nitrosodiethylamine
62759	N-Nitrosodimethylamine
759739	Urea, N-ethyl-N-nitroso-
10595956	N-Nitrosomethylethylamine
684935	Urea, N-methyl-N-nitroso-
615532	Carbamic acid, methylnitroso-, ethyl ester
4549400	Vinylamine, N-methyl-N-nitroso-
59892	N-Nitrosomorpholine
16543558	N-Nitrosonornicotine
100754	N-Nitrosopiperidine
930552	N-Nitrosopyrrolidine
13256229	Glycine, N-methyl-N-nitroso-
99558	5-Nitro-o-toluidine
152169	Diphosphoramide, octamethyl-
20816120	Osmium oxide (OsO4), (T-4)-
123637	1,3,5-Trioxane, 2,4,5-trimethyl-
56382	Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl)
608935	Pentachlorobenzene
1_289	Pentachlorodibenzo-p-dioxins
1_290	Pentachlorodibenzofurans
76017	Ethane, pentachloro-
82688	Pentachloronitrobenzene
87865	Pentachlorophenol
62442	Acetamide, N-(4-ethoxyphenyl)-
108952	Phenol
25265763	Benzenediamine
62384	Mercury, (acetato-O)phenyl-

(Continued)

Table II-9 (Continued)

103855	Thiourea, phenyl-
75445	Carbonic dichloride
7803512	Phosphine
298022	Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)
1__303	Phthalic acid esters, NOS
85449	1,3-Isobenzofurandione
109068	2-Picoline
12674112	PCB-1016
11104282	PCB-1221
11141165	PCB-1232
53469219	PCB-1242
12672296	PCB-1248
11097691	PCB-1254
11096825	PCB-1260
1336363	Polychlorinated biphenyl, NOS
151508	Potassium cyanide
506616	Potassium silver cyanide
23950585	Benzamide, 3,5-dichloro-N-(1,1-dimethyl-2-propynyl)-
1120714	1,2-Oxathiolane, 2,2-dioxide
107108	n-Propylamine
107197	2-Propyn-1-ol
78875	1,2-Dichloropropane
75558	2-Methylaziridine
51525	4(1H)-Pyrimidinone, 2,3-dihydro-6-propyl-2-thioxo-
110861	Pyridine
50555	Yohimban-16-carboxylic acid, 11,17-Dimethoxy-18-[(3,4,5-
108463	Resorcinol
81072	1,2-Benzisothiazol-3(2H)-one, 1,1-dioxide and salts
94597	Safrole
7783008	Selenious acid (H2SeO3)
7782492	Selenium
7446346	Selenium sulfide
630104	Selenourea
7440224	Silver
506649	Silver cyanide (AgCN)
93721	Propanoic acid, 2-(2,4,5-trichlorophenoxy)-
143339	Sodium cyanide (NaCN)
18883664	D-Glucopyranose, 2-deoxy-2-(3-methyl-3-nitrosoureido)-
1314961	Strontium sulfide (SrS)
57249	Strychnine and salts
1746016	Dibenzo[b,e][1,4]dioxin, 2,3,7,8-tetrachloro-
95943	1,2,4,5-Tetrachlorobenzene
1__331	Tetrachlorodibenzo-p-dioxins
1__332	Tetrachlorodibenzofurans
25322207	Tetrachloroethane, NOS
630206	1,1,1,2-Tetrachloroethane
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethene
58902	2,3,4,6-Tetrachlorophenol
3689245	Thiopyrophosphoric acid ([(HO)2P(S)]2O), tetraethyl
78002	Plumbane, tetraethyl-
107493	Tetraethylpyrophosphate

(Continued)

Table II-9 (Continued)

509148	Methane, tetranitro-
7440280	Thallium
1314325	Thallium (III) oxide
563688	Acetic acid, thallium (1 +) salt
6533739	Thallium (I) carbonate
7791120	Thallium (I) chloride
10102451	Nitric acid, thallium (1 +) salt
12039520	Thallium selenide
10031591	Sulfuric acid, thallium salt
62555	Ethanethioamide
39196184	2-Butanone, 3,3-dimethyl-1-(methylthio)-, O-[(methyl
74931	Methanethiol
108985	Benzenethiol
79196	Hydrazinecarbothioamide
62566	Thiourea
137268	Thioperoxydicarbonic diamide, tetramethyl
108883	Toluene
25376458	Benzenediamine, ar-methyl-
95807	1,3-Benzenediamine, 4-methyl-
823405	1,3-Benzenediamine, 2-methyl-
496720	1,2-Benzenediamine, 4-methyl-
584849	Benzene, 2,4-diisocyanato-1-methyl-
106490	Benzenamine, 4-methyl-
636215	Benzenamine, 2-methyl-, hydrochloride
8001352	Toxaphene
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethene
75707	Trichloromethanethiol
75694	Trichlorofluoromethane
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
93765	2,4,5-Trichlorophenoxyacetic acid
25735299	Trichloropropane, NOS
96184	1,2,3-Trichloropropane
126681	O,O,O-Triethylphosphorothioate
99354	sym-Trinitrobenzene
52244	Tris(1-aziridinyl)phosphine sulfide
126727	Tris(2,3-dibromopropyl)phosphate
72571	2,7-Naphthalendisulfonic acid, 3,3'-[(3,3'dimethyl[1,1'-
66751	2,4(1H,3H)-Pyrimidinedione, 5-[bis(2-chloroethyl)amino]-
2056259	Undecamethylenediamine, N,N'-bis(2-chlorobenzyl),-
1314621	Vanadium oxide (V205)
75014	Vinyl chloride
81812	2-H-1-Benzopyran-2-one, 4-hydroxy-3-(3-oxo-1-phenyl
557211	Zinc cyanide
1314847	Zinc phosphide (Zn3P2)

Table II-10 Michigan List

602879	Acenaphthene, 5-nitro
531828	Acetamide N-(4-(5-nitro-2-furyl)-thiazolyl)
3546109	Acetic acid, (4-[bis(2-chloroethyl)amino]phenyl)-
50760	Actinomycin D
132321	3-Amino-9-ethyl carbazole
569642	Ammonium, (4-(p-(dimethylamino)-alpha-phenylbenzyli
838880	Aniline, 4,4'-methylenebis (2-methyl)-
60093	Aniline, p-(phenylazo)-
139651	Aniline, 4,4'-thiodi-
137177	Aniline, 2,4,5-trimethyl-
90040	o-Anisidine
134292	o-Anisidine hydrochloride
120718	o-Anisidine, 5-methyl
99592	o-Anisidine, 5-nitro
117793	Anthraquinone, 2-amino
82280	Anthraquinone, 1-amino-2-methyl
129157	Anthraquinone, 2-methyl-1-nitro
1332214	Asbestos
50066	Barbituric acid, 5-ethyl-5-phenyl
142041	Benzenamine hydrochloride
120627	Benzene, 1,2-(methylenedioxy)-4-(2-(octylsulfinyl)
531862	Benzidine sulfate
17804352	Benzimidazolecarbamic acid, 1-(butylcarba
1689845	Benzonitrile, 3,5-dibromo-4-hydroxy-
83794	(1)-Benzopyrano(3,4-b)furo(2,3-h)(1)benzopyran-6(6aH)
92933	Biphenyl, 4-nitro
1910425	4,4'-Bipyridinium, 1,1'-dimethyl-, dichloride
126998	2-Chloro-1,3-butadiene
3817116	1-Butanol, 4-(butylnitrosoamino)-
95067	Carbamic acid, diethyldithio-, 2-chloroallyl ester
1563662	Carbamic acid, methyl-, 2,3-dihydro-2,2-dimethyl-7-
315184	Carbamic acid, methyl-, 4-dimethylamino-3,5-xylyl ester
22781233	Carbamic acid, methyl-, 2,3-(dimethylmethylenedioxy)
63252	Carbamic acid, methyl-, 1-naphthyl ester
101279	Carbamic acid, m-chloro, 4-chloro-2-butynyl ester
7782505	Chlorine
7440484	Cobalt
7646799	Cobalt (II) chloride
56724	Coumarin, 3-chloro-7-hydroxy-4-methyl-, O-ester with O,
7700176	Crotonic acid, 3-hydroxy, alpha-methylbenzyl ester, di
7786347	Crotonic acid, 3-hydroxy-, methyl ester, dimethyl phos
2425061	4-Cyclohexene-1,2-dicarboximide N-((1,1,2,2-tetrachloro
133062	4-Cyclohexene-1,2-dicarboximide N-(trichloromethyl)thio-
156105	Diphenylamine, 4-nitroso-
107073	Ethanol, 2-chloro-
1836755	Ether, 2,4-dichlorophenyl p-nitrophenyl-
3570750	Formic acid, 2-(4-(5-nitro-2-furyl)-2-thiazolyl)
66819	Glutarimide, 3-[2-(3,5-dimethyl-2-oxocyclohexyl)-2-

(Continued)

Table II-10 (Continued)

1024573	2,5-Methano-2H-indeno[1,2b]oxirene, 2,3,4,5,6,7,7-hepta
57410	Hydantoin, 5,5-diphenyl-
630933	Hydantoin, 5,5-diphenyl-monosodium salt
123319	Hydroquinone
1072522	N-(2-hydroxyethyl)ethyleneimine
135206	Hydroxylamine, N-nitroso-N-phenyl-, ammonium salt
7778543	Hypochlorous acid, calcium salt
7681529	Hypochlorous acid, sodium salt
61574	2-Imidazolidinone, 1-(5-nitro-2-thiazolyl)-
54853	Isonicotinic acid hydrazide
463514	Ketene
7439932	Lithium
2385855	1,3,4-Metheno-1H-cyclobuta[cd]pentalene, 1,1a,2,2,3,3a,
2243621	1,5-Naphthalenediamine
117806	1,4-Naphthoquinone, 2,3-dichloro-
72333	17-alpha-19-Norpregna-1,3,5(10)-trien-20-yn-17-ol, 3-
57578	2-Oxetanone
101804	4,4'-Oxydianiline
5131602	m-Phenylenediamine, 4-chloro-
95830	o-Phenylenediamine, 4-chloro-
39156417	m-Phenylenediamine, 4-methoxy-, sulfate
52686	Phosphoric acid, (2,2,2-trichloro-1-hydroxyethyl)-,
21609905	Phosphorothioic acid, phenyl, O-(4-bromo-2,5-dichloro
2104645	Phosphorothioic acid, phenyl-, O-ethyl O-(p-nitro
4104147	Phosphoramidothioic acid, acetamidoyl, O,O-bis(p-
470906	Phosphoric acid, 2-chloro-1-(2,4-dichlorophenyl)vinyl di
961115	Phosphoric acid, 2-chloro-1-(2,4,5-trichlorophenyl)
300765	Phosphoric acid, 1,2-dibromo-2,2-dichloroethyl di
62737	Phosphoric acid, 2,2-dichlorovinyl dimethyl ester
13171216	Phosphoric acid, dimethyl ester, ester with 2-chloro-N-
141662	Phosphoric acid, dimethyl ester, ester with (E)-3-
6923224	Phosphoric acid, dimethyl ester, ester with (E)-3-
512561	Phosphoric acid, trimethyl ester
78308	Phosphoric acid, tri-o-tolyl ester
680319	Phosphoric triamide, hexamethyl-
786196	Phosphorodithioic acid, s(((p-chlorophenyl)thio)
13071799	Phosphorodithioic acid, O,O-diethyl-S-(((1,1-dimethyl
2642719	Phosphorodithioic acid, O,O-diethyl ester, S-ester with
86500	Phosphorodithioic acid, O,O-dimethyl ester, S-ester with
732116	Phosphorodithioic acid, O,O-dimethyl ester, S-ester with
78342	Phosphorodithioic acid, S,S'-p-dioxane-2,3-dryl O,O,O',
563122	Phosphorodithioic acid, S,S'-methylene O,O,O',O'-tetra
8065483	Phosphorodithioic acid, O,O-diethyl O-(2-(ethylthio)
333415	Phosphorodithioic acid, O,O-diethyl O-(2-isopropyl-6-
115902	Phosphorodithioic acid, O,O-diethyl O-(p-(methylsul
2921882	Phosphorodithioic acid, O,O-diethyl O-(3,5,6-trichloro-
55389	Phosphorodithioic acid, O,O-dimethyl-, O-(4-methylthio)-
301122	Phosphorodithioic acid, S-(2-(ethylsulfinyl)ethyl) O,

(Continued)

Table II-10 (Continued)

59536651	Polybrominated biphenyls, NOS
107051	1-Propene, 3-chloro-
78977	Propionitrile, 2-hydroxy-
6959484	Pyridine, 3-chloromethyl-, hydrochloride
136403	Pyridine, 2,6-diamino-3-(phenylazo)-, monohydrochloride
315220	(2,3,4-gh)Pyrrolizine-2,6(3H)dione, (4,5,8,10,12,13,13a,
1420048	Salicylanilide, 2',5-dichloro-4'-nitro, compound with 2-
57567	Semicarbazide
100425	Styrene
121755	Succinic acid, mercapto-, diethyl ester, S-ester with O,
64675	Sulfuric acid, diethyl ester
95807	1,3-Benzenediamine, 4-methyl-
95534	o-Toluidine
95794	o-Toluidine, 5-chloro-
33245395	p-Toluidine, N-(2-chloroethyl)-2,6-dinitro-N-propyl-
97563	o-Toluidine, 4-(o-tolylazo)-
1582098	p-Toluidine, alpha, alpha, alpha-trifluoro-2,6-dinitro-
7203909	Triazene, 3,3-dimethyl-1-(p-chlorophenyl)-
101053	s-Triazine, 2,4-dichloro-6-(o-chloroanilino)-
51525	4(1H)-Pyrimidinone, 2,3-dihydro-6-propyl-2-thioxo-
139946	Urea, 1-ethyl-3-(5-nitro-2-thiazolyl)-
137304	Zinc bis(dimethyldithiocarbamato)-
39300453	Crotonic acid, 2-(1-methylheptyl)-4,6-dinitro

Table II-11 Sludge Monitoring List

Aldrin/Dieldrin	LA, I, CD
Arsenic	I
Benzene	LA, LF
Benzidine	OD
Benzo(a)pyrene	LA, LF, I, OD
Beryllium	I
Bis(2-ethylhexyl)phthalate	LF, I, OD
Cadmium	LA, LF, I, OD
Carbon tetrachloride	I
Chlordane	LA, LF, I, OD
Chloroform	I
Chromium	LA, I
Copper	LA, LF
DDT/DDD/DDE	LA, LF, OD
N,N-dimethyl nitrosamine	LA, LF
Heptachlor	OD
Hexachlorobenzene	LA
Hexachlorobutadiene	LA
Lead	LA, LF, I
Lindane	LA, LF
Mercury	LA, LF, I, OD
Molybdenum	LA
Nickel	LA, LF, I
PCBs	LA, LF, I, OD
Selenium	LA
Toxaphene	LA, LF, I, OD
Trichloroethylene	LF
Vinyl chloride	I
Zinc	LA

Key: LA refers to land application and distribution and marketing
KF refers to landfilling I refers to incineration
OD refers to ocean dumping

Table II-12 Pesticide Chemicals

Alachlor	Glyphosate
AOP	Hexazinon
Benfluralin	Isopropalin
Benomyl	KN Methyl
Bentazon	Mancozeb
Bolstar	Maneb
Bromacil	Mephosfolan
Busan 40	Metham
Busan 85	Methomyl
Butachlor	Metribuzin
Carbam-S	Mevinphos
Carbendazim	Nabam
Carbofuran	Naled
Chlorbenzilate	Niacide
Chloropyrifos	Oxamyl
Chloropyrifos methyl	Phorate
Coumaphos	Profluralin
Cyanazine	Propachlor
2,4-DB	Ronnel
2,4-DB isobutyl ester	Simetryne
2,4-DB isooctyl ester	Stirophos
DBCP	Terbacil
DEET	Terbufos
Dichlorvos	Terbutryne
Dinoseb	Triadimephon
Ethalfluralin	Trichloronate
Etridiazole	Tricyclazole
Fensulfothion	ZAC
Fenthion	Zineb
Ferbam	Ziram
Fluometuron	

Source:40 CFR 455 (Remanded)

Table II-13 Hazardous Substances

Common name	CAS No.	Synonyms	Isomers	CAS No.
Acetaldehyde	75070	Ethanal, ethyl aldehyde, acetic aldehyde		
Acetic acid	64197	Glacial acetic acid, vinegar acid		
Acetic anhydride	108247	Acetic oxide, acetyl oxide		
Acetone cyanohydrin	75865	2-methyllactonitrile, alpha-hydroxyisobutyronitrile.		
Acetyl bromide	506967			
Acetyl chloride	79367			
Acrolein	107028	2-propenal, acrylic aldehyde, acrylaldehyde, acraldehyde.		
Acrylonitrile	107131	Cyanoethylene, Fumigrain, Ventox, propenenitrile, vinyl cyanide.		
Adipic acid	124049	Hexanedioic acid		
Aldrin	309002	Octalene, HHDN		
Allyl alcohol	107186	2-propen-1-ol, 1-propenol-3, vinyl carbinol		
Allyl chloride	107051	3-chloropropene, 3-chloropropylene, Chlorallylene.		
Aluminum sulfate	10043013	Alum		
Ammonia	7664417			
Ammonium acetate	631618	Acetic acid ammonium, salt		
Ammonium benzoate	1863634			
Ammonium bicarbonate	1066337	Acid ammonium carbonate, ammonium hydrogen carbonate.		
Ammonium bichromate	7789095			
Ammonium bifluoride	1341497	Acid ammonium fluoride, ammonium hydrogen fluoride.		
Ammonium bisulfite	10192300			
Ammonium carbamate	1111780	Ammonium aminoformate		
Ammonium carbonate	506876			
Ammonium chloride	12125029	Ammonium muriate, sal ammoniac, salmiac, Amchlor.		
Ammonium chromate	7788989			
Ammonium citrate dibasic	3012655	Diammonium citrate, citric acid diammonium salt.		
Ammonium fluoborate	13826830	Ammonium fluoroborate, ammonium borofluoride.		
Ammonium fluoride	12125018	Neutral ammonium fluoride		
Ammonium hydroxide	1336216			
Ammonium oxalate	6009707			
	5972736			
	14258492			
Ammonium silicofluoride	16919190	Ammonium fluosilicate		
Ammonium sulfamate	7773060	Ammate, AMS, ammonium amidosulfate		
Ammonium sulfide	12135761			
Ammonium sulfite	10196040			
	10192300			
Ammonium tartrate	3164292	Tartaric acid ammonium salt		
	14307438			
Ammonium thiocyanate	1762954	Ammonium rhodanide, ammonium sulfocyanate, ammonium sulfocyanide.		
Ammonium thiosulfate	7783188	Ammonium hyposulfite		
Amly acetate	628637	Amylacetic ester	iso-	123922
		Pear oil	sec-	626380
		Banana oil	tert-	625161
Aniline	62533	Aniline oil, phenylamine, aminobenzene, aminophen, kyanol.		
Antimony pentachloride	7647189			
Antimony potassium tartrate	28300745	Tartar emetic, tartrated antimony, tartarized antimony, potassium antimonyltartrate.		
Antimony tribromide	7789619			
Antimony trichloride	10025919	Butter of antimony		
Antimony trifluoride	7783564	Antimony fluoride		
Antimony trioxide	1309644	Diantimony trioxide, flowers of antimony		
Arsenic disulfide	1303328	Red arsenic sulfide		
Arsenic pentoxide	1303282	Arsenic acid anhydride, arsenic oxide		
Arsenic trichloride	7784341	Arsenic chloride, arsenious chloride, arsenous chloride, butter of arsenic.		
Arsenic trioxide	1327533	Arsenious acid, arsenious oxide, white arsenic.		
Arsenic trisulfide	1303339	Arsenious sulfide, yellow arsenic sulfide		
Barium cyanide	542621			
Benzene	71432	Cyclohexatriene, benzol		

Table II-13 (Continued)

Common name	CAS No.	Synonyms	Isomers	CAS No.
Benzoic acid	65850	Benzenecarboxylic acid, phenylformic acid, dracylic acid.		
Benzonitrile	100470	Phenyl cyanide, cyanobenzene		
Benzoyl chloride	98884	Benzenecarbonyl chloride		
Benzyl chloride	100447			
Beryllium chloride	7787475			
Beryllium fluoride	7787497			
Beryllium nitrate	7787555			
	13597994			
Butyl acetate	123864	Acetic acid butyl ester	iso-	110190
			sec-	105464
			tert-	540885
Butylamine	109739	1-aminobutane	iso-	78819
			sec-	513495
			sec-	13952846
			tert-	75649
n/butyl phthalate	84742	1.2-benzenedicarboxylic acid, dibutyl ester, dibutyl phthalate.		
Butyric acid	107926	Butanoic acid, ethylacetic acid	iso-	79312
Cadmium acetate	543908			
Cadmium bromide	7789426			
Cadmium chloride	10108642			
Calcium arsenate	7778441	Tricalcium orthoarsenate		
Calcium arsenite	52740166			
Calcium carbide	75207	Carbide, acetylenogen		
Calcium chromate	13765190	Calcium chrome yellow, geblin, yellow ultramarine.		
Calcium cyanide	592018			
Calcium dodecylbenzenesulfonate	26264062			
Calcium hypochlorite	7778543			
Captan	133062	Orthocide-406, SR-406, Vancide-89		
Carbaryl	63252	Sevin		
Carbofuran	1563662	Furadan		
Carbon disulfide	75150	Carbon bisulfide, dithiocarbonic anhydride		
Carbon tetrachloride	56235	Tetrachloromethane Perchloromethane		
Chlordane	57749	Toxichlor, chlordan		
Chlorine	75003			
Chlorobenzene	108907	Monochlorobenzene, benzene chloride		
Chloroform	67663	Trichloromethane		
Chlorpyrifos	2921882	Dursban		
Chlorosulfonic acid	7790945	Sulfuric chlorohydrin		
Chromic acetate	1066304			
Chromic acid	11115745	Chromic anhydride, chromium trioxide		
Chromic sulfate	10101538			
Chromous chloride	10049055			
Cobaltous bromide	7789437	Cobalt bromide		
Coabaltous formate	544183	Cobalt formate		
Cobaltous sulfamate	14017415	Cobalt sulfamate		
Coumaphos	56724	Co-Ral		
Cresol	1319773	Cresylic acid	m-	108394
		Hydroxytoluene	o-	95487
			p-	106445
Crotonaldehyde	4170303	2-butenal propylene aldelhyde		
Cupric acetate	142712	Copper acetate, crystalized verdigris		
Cupric acetoarsenite	12002038	Copper acetoarsenite, copper acetate arsenite, Paris green.		
Cupric chloride	7447394	Copper chloride		
Cupric nitrate	3251238	Copper nitrate		
Cupric oxalate	5893663	Copper oxalate		
Cupric sulfate	7758987	Copper sulfate		
Cupric sulfate, ammoniated	10380297	Ammoniated copper sulfate		
Cupric tartrate	815827	Copper tartrate		
Cyanogen chloride	506774			
Cyclohexane	110827	Hexahydrobenzene, hexamethylene, hexanaphthene.		
2,4-D acid	94757	2,4-dichlorophenoxyacetic acid		
2,4-D ester	94111	2,4-dichlorophenoxyacetic acid ester		
	94791			
	94804			
	1320189			
	1928387			
	1928616			
	1929733			
	2971382			
	25168267			
	53467111			

Table II-13 (Continued)

Common name	CAS No.	Synonyms	Isomers	CAS No.
DDT	50293	p,p'-DDT		
Diazinon	333415	Dipofene, Diazitol, Basudin, Spectracide		
Dicamba	1918009	2-methoxy-3,6-dichlorobenzoic acid		
Dichlobenil	1194656	2,6-dichlorobenzonitrile, 2,6-DBN		
Dichlone	117806	Phygon, dichloronaphthoquinone		
Dichlorobenzene	25321226	Di-chloricide	Ortho	95501
		Paramoth (Para)	Para	106467
Dichloropropane	26638197	Propylene dichloride	1,1	78999
			1,2	78875
			1,3	142289
Dichloropropene	26952238		1,3	542756
			2,3	78886
Dichloropropene-dichloropropane (mixture).	8003198	D-D mixture Vidden D		
2,2-Dichloropropionic acid	75990	Dalapon		
Dichlorvos	62737	2,2-dichlorovinyl dimethyl phosphate, Vapona.		
Dieldrin	60571	Alvit		
Diethylamine	109897			
Dimethylamine	124403			
Dinitrobenzene (mixed)	25154545	Dinitrobenzol	m-	99650
			o-	528290
			p-	100254
Dinitrophenol	51285	Aldifen	(2,5-)	329715
			(2,4-)	
			(2,6-)	573568
Dinitrotoluene	25321146	DNT	2,4	121142
			2,6	606202
			3,4	610399
Diquat	85007	Aquacide		
	2764729	Dextrone, Reglone, Diquat dibromide		
Disulfoton	298044	Di-syston		
Diuron	330541	DCMU, DMU		
Dodecylbenzenesulfonic acid	27176870			
Endosulfan	115297	Thiodan		
Endrin	72208	Mendrin, Compound 269		
Epichlorohydrin	106898	-chloropropylene oxide		
Ethion	563122	Nialate, ethyl methylene, phosphorodithioate.		
Ethylbenzene	100414	Phenylethane		
Ethylenediamine	107153	1,2-diaminoethane		
Ethylenediamine-tetraacetic acid (EDTA).	60004	Edetic acid, Havidote, (ethylenedinitrilo)-tetraacetic acid.		
Ethylene dibromide	106934	1,2-dibromoethane acetylene dibromide sym-dibromoethylene.		
Ethylene dichloride	107062	1,2-dichloroethane sym-bichloroethane		
Ferric ammonium citrate	1185575	Ammonium ferric citrate		
Ferric ammonium oxalate	2944674	Ammonium ferric oxalate		
	55488874			
Ferric chloride	7705080	Flores martis, iron trichloride		
Ferric fluoride	7783508			
Ferric nitrate	10421484	Iron nitrate		
Ferric sulfate	10028225	Ferr[illegible]rsulfate, ferric sesquisulfate, ferric [illegible]fate.		
Ferrous ammonium sulfate	10045893	Mohr's salt, iron ammonium sulfate		
Ferrous chloride	7758943	Iron chloride, iron dichloride, iron protochloride.		
Ferrous sulfate	7720787	Green vitriol		
	7782630	Iron vitriol, iron sulfate, iron protosulfate		
Formaldehyde	50000	Methyl aldehyde, methanal, formalin		
Formic acid	64186	Methanoic acid		
Fumaric acid	110178	Trans-butenedioic acid, trans-1,2-ethylenedicarboxylic acid, boletic acid, allomaleic acid.		
Furfural	98011	2-furaldehyde, pyromucic aldehyde		
Guthion	86500	Gusathion, azinphos-methyl		
Heptachlor	76448	Velsicol-104, Drinox, Heptagran		
Hexachlorocyclopentadiene	77474	Perchlorocyclopentadiene		
Hydrochloric acid	7647010	Hydrogen chloride, muriatic acid		
Hydrofluoric acid	7664393	Fluohydric acid		
Hydrogen cyanide	74908	Hydrocyanic acid		
Hydrogen sulfide	7783064	Hydrosulfuric acid sulfur hydride		
Isoprene	78795	2-methyl-1,3-butadiene		

Table II-13 (Continued)

Common name	CAS No.	Synonyms	Isomers	CAS No.
Isopropanolamine dodecylbenzenesulfonate.	42504461			
Kelthane	115322	Di(p-chlorophenyl)-trichloromethylcarbinol, DTMC, dicofol.		
Kepone	143500	Chlordecone 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd)pentalen-2-one.		
Lead acetate	301042	Sugar of lead		
Lead arsenate	7784409			
	7645252			
	10102484			
Lead chloride	7758954			
Lead fluoborate	13814965	Lead fluoroborate		
Lead fluoride	7783462	Lead difluoride, plumbous fluoride		
Lead iodide	10101630			
Lead nitrate	10099748			
Lead stearate	7428480	Stearic acid lead salt		
	1072351			
	52652592			
Lead sulfate	7446142			
Lead sulfide	1314870	Galena		
Lead thiocyanate	592870	Lead sulfocyanate		
Lindane	58899	Gamma-BHC, gamma-benzene hexachloride.		
Lithium chromate	14307358			
Malathion	121755	Phospothion		
Maleic acid	110167	Cis-butenedioic acid, cis-1,2-ethylenedicarboxylic acid, toxilic acid.		
Maleic anhydride	108316	2,5-furandione, cis-butenedioic anhydride, toxilic anhydride.		
Mercaptodimethur	203657	Mesurol		
Mercuric cyanide	592041	Mercury cyanide		
Mercuric nitrate	10045940	Mercury nitrate, mercury pernitrate		
Mercuric sulfate	7783359	Mercury sulfate, mercury persulfate		
Mercuric thiocyanate	592858	Mercury thiocyanate, mercuric sulfocyanate, mercuric sulfocyanide.		
Mercurous nitrate	7782867			
	10415755	Mercury protonitrate		
Methoxychlor	72435	DMDT, methoxy-DDT		
Methyl mercaptan	74931	Methanethiol, mercaptomethane, methyl sulfhydrate, thiomethyl alcohol.		
Methyl methacrylate	80626	Methacrylic acid methyl ester, methyl-2-methyl-2-propenoate.		
Methyl parathion	298000	Nitrox-80		
Mevinphos	7786347	Phosdrin		
Mexacarbate	315184	Zectran		
Monoethylamine	75047	Ethylamine, aminoethane		
Monomethylamine	74895	Methylamine, aminomethane		
Naled	300765	Dibrom		
Naphthalene	91203	White tar, tar camphor, naphthalin		
Naphthenic acid	1338245	Cyclohexanecarboxylic acid, hexahydrobenzoic acid.		
Nickel ammonium sulfate	15699180	Ammonium nickel sulfate		
Nickel chloride	37211055	Nickelous chloride		
	7718549			
Nickel hydroxide	12054487	Nickelous hydroxide		
Nickel nitrate	14216752			
Nickel sulfate	7786814	Nickelous sulfate		
Nitric acid	7697372	Aqua fortis		
Nitrobenzene	98953	Nitrobenzol, oil of mirbane		
Nitrogen dioxide	10102440	Nitrogen tetraoxide		
Nitrophenol (mixed)	25154556	Mononitrophenol	m-	554847
			o-	88755
			p-	100027
Nitrotoluene	1321126		Ortho	88722
			Meta	99081
			Para	99990
Paraformaldehyde	30525894	Paraform, Formagene, Triformol, polymerized formaldehyde, polyoxymethylene.		
Parathion	56382	DNTP, Niran		
Pentachlorophenol	87865	PCP, Penta		
Phenol	108952	Carbolic acid, phenyl hydroxide, hydroxybenzene, oxybenzene.		

Table II-13 (Continued)

Common name	CAS No.	Synonyms	Isomers	CAS No.
Phosgene	75445	Diphosgene, carbonyl chloride, chloroformyl chloride.		
Phosphoric acid	7664382	Orthophosphoric acid		
Phosphorus	7723140	Black phosphorus, red phosphorus, white phosphorus, yellow phosphorus.		
Phosphorus oxychloride	10025873	Phosphoryl chloride, phosphorus chloride		
Phosphorus pentasulfide	1314803	Phosphoric sulfide, thiophosphoric anhydride, phosphorus persulfide.		
Phosphorus trichloride	7719122	Phosphorous chloride		
Polychorinated biphenyls	1336363	PCB, Aroclor, polychlorinated diphenyls		
Potassium arsenate	7784410			
Potassium arsenite	10124502	Potassium metaarsenite		
Potassium bichromate	7778509	Potassium dichromate		
Potassium chromate	7789006			
Potassium cyanide	151508			
Potassium hydroxide	1310583	Potassium hydrate, caustic potash, potassa		
Potassium permanganate	7722647	Chameleon mineral		
Propargite	2312358	Omite		
Propionic acid	79094	Propanoic acid, methylacetic acid, ethylformic acid.		
Propionic anhydride	123626	Propanoic anhydride, methylacetic anhydride.		
Propylene oxide	75569	Propene oxide		
Pyrethrins	121299	Pyrethrin I		
	121211	Pyrethrin II		
Quinoline	91225	1-benzazine, benzo(b)pyridine, leuocoline, chinoleine, leucol.		
Resorcinol	108463	Resorcin, 1,3-benzenediol, meta-dihydroxybenzene.		
Selenium oxide	7446084	Selenium dioxide		
Silver nitrate	7761888	Nitric acid silver (1 –) salt lunar caustic		
Sodium	7440235	Natrium		
Sodium arsenate	7631892	Disodium arsenate		
Sodium arsenite	7784465	Sodium metaarsenite		
Sodium bichromate	10588019	Sodium dichromate		
Sodium bifluoride	1333831			
Sodium bisulfite	7631905	Sodium acid sulfite, sodium hydrogen sulfite.		
Sodium chromate	7775113			
Sodium cyanide	143339			
Sodium dodecylbenzene-sulfonate	25155300			
Sodium fluoride	7681494	Villiaumite		
Sodium hydrosulfide	16721805	Sodium hydrogen sulfide		
Sodium hydroxide	1310732	Caustic soda, soda lye, sodium hydrate		
Sodium hypochlorite	7681529	Bleach		
	10022705			
Sodium methylate	124414	Sodium methoxide		
Sodium nitrite	7632000			
Sodium phosphate, dibasic	7558794			
	10039324			
	10140655			
Sodium phosphate, tribasic	7785844			
	7601549			
	10101890			
	10361894			
	7758294			
	10124568			
Sodium selenite	10102188			
	7782823			
Strontium chromate	7789062			
Strychnine	57249			
Styrene	100425	Vinylbenzene, phenylethylene, styrol, styrolene, cinnamene, cinnamol.		
Sulfuric acid	7664939	Oil of vitriol, oleum		
Sulfur monochloride	12771083	Sulfur chloride		
2,4,5-T acid	93765	2,4,5-trichlorophenoxyacetic acid		
2,4,5-T amines	6369966	Acetic acid (2,4,5-trichlorophenoxy)-compound with N,N-dimethylmethanamine (1:1).		
	6369977	Acetic acid (2,4,5-trichlorophenoxy)-compound with N-methylmethanamine (1:1).		
	1319728	Acetic acid (2,4,5-trichlorophenoxy)-compound with 1-amino-2-propanol (1:1).		
	3813147	Acetic acid (2,4,5-trichlorophenoxy)-compound with 2,2'2"-nitrilotris [ethanol] (1:1).		

Table II-13 (Continued)

Common name	CAS No	Synonyms	Isomers	CAS No.
2,4,5-T esters	2545597	2,4,5-trichlorophenoxyacetic esters		
	93798			
	61792072			
	1928478			
	25168154			
2,4,5-T salts	13560991	Acetic acid (2,4,5-trichlorophenoxy)-sodium salt.		
TDE	72548	DDD		
2,4,5-TP acid	93721	Propanoic acid 2-(2,4,5-trichlorophenoxy)		
2,4,5-TP esters	32534955	Propanoic acid, 2-(2,4,5-trichlorophenoxy)-, isooctyl ester.		
Tetraethyl lead	78002	Lead tetraethyl, TEL		
Tetraethyl pyrophosphate	107493	TEPP		
Thallium sulfate	10031591			
	7446186			
Toluene	108883	Toluol, methylbenzene, phenylmethane, Methacide.		
Toxaphene	8001352	Camphechlor		
Trichlorfon	52686	Dipterex		
		Dylox		
Trichlorethylene	79016	Ethylene trichloride		
Trichlorophenol	25167822	Collunosol, Dowicide 2 or 2S, Omal, Phenachlor.	(2,3,4-)	15950660
			(2,3,5-)	933788
			(2,3,6-)	933755
			(2,4,5-)	95954
			(2,4,6-)	88062
			(3,4,5-)	609198
Triethanolamine dodecylbenzenesulfonate.	27323417			
Triethylamine	121448			
Trimethylamine	75503	TMA		
Uranyl acetate	541093			
Uranyl nitrate	10102064			
	36478769			
Vanadium pentoxide	1314621	Vanadic anhydride, vanadic acid anhydride		
Vanadyl sulfate	27774136	Vanadic sulfate, vanadium sulfate		
Vinyl acetate	108054	Acetic acid ethylene ether		
Vinylidene chloride	75354	1,1-dichlorethylene		
		1,1-dichloroethene		
Xylene (mixed)	1330207	Dimethylbenzene	m-	108383
		Xylol	o-	95476
			p-	106423
Xylenol	1300716	Dimethylphenol, hydroxydimethylbenzene		
Zinc acetate	557346			
Zinc ammonium chloride	14639975			
	14639986			
	52628258			
Zinc borate	1332076			
Zinc bromide	7699458			
Zinc carbonate	3486359			
Zinc chloride	7646857	Butter of zinc		
Zinc cyanide	557211			
Zinc fluoride	7783495			
Zinc formate	557415			
Zinc hydrosulfite	7779864			
Zinc nitrate	7779886			
Zinc phenolsulfonate	127822	Zinc sulfocarbolate		
Zinc phosphide	1314847			
Zinc silicofluoride	16871719	Zinc fluosilicate		
Zinc sulfate	7733020	White vitriol, zinc vitriol, white copperas		
Zirconium nitrate	13746899			
Zirconium potassium fluoride	16923958			
Zirconium sulfate	14644612	Disulfatozirconic acid		
Zirconium tetrachloride	10026116			

Table II-14 Examples of Parameters in STORET but not §304(h)

Atrazine
Bidrin
Caffeine
Cesium
Diethenylether
Disyston
Dursban
Fenthion
Gallium
Germanium
Kelthane
Lanthanium
Methyl myristate
Methyl palmitate
Perthane
Phorate
Phosdrin
Propazin
Ronnel
Rubidium
Simazine
Zirconium

Ecosystem-related measurements include toxicity of wastes, wastewaters, surface waters, and sediments to aquatic life, and the properties of indigenous communities in receiving waters. Toxicity tests applicable to biomonitoring include tests for acute and chronic toxicity to fish, invertebrates, and other aquatic life, and mutagenicity are listed in Tables II-17 and II-18.

Measurements of the biological integrity of communities of aquatic organisms involve detailed studies of the free living organisms such as the native aquatic bacteria, microscopic plants and animals, the flowering aquatic plants (aquatic weeds), invertebrates, and fish. The biological integrity of aquatic ecosystems is related to questions such as:

- Are the expected kinds (species) of organisms present in the expected numbers and diversity, carrying out life functions, such as growth and. reproduction, at normal rates, free of disease and other pollution-related effects?
- Are the organisms free of toxic substances?
- Is suitable habitat available?

To answer these questions the organisms present in aquatic ecosystems must be identified to species, and estimates must be made of the abundance (standing crop), diversity, and the condition of the organisms. Some of the basic biological measurements that are made in monitoring the biological integrity of surface waters are listed in Table II-19. A comprehensive guidance manual for field studies on biological integrity was prepared by the Agency (2-40).

Specific analytes included in the SDWA and FWPCA regulations are listed in Table II-20. Table II-21 lists the microbiological standards and criteria under the SDWA and FWPCA. EPA has published a list of recommended species for use in tests for the acute toxicity of effluents under the NPDES permits program (2-16), and recommends the use of only three species for chronic toxicity tests (2-17). The recommended species for effluent acute and chronic toxicity tests are tabulated in Table II-22.

The biological analytes that are typically required in the NPDES permit regulations and technical support documents are "acute or chronic toxicity". Yet, listing acute or chronic toxicity without reference to the species which are required or recommended by EPA and the states for performing acute or chronic toxicity testing is incomplete. It must be understood, however, that listing "recommended" species does not mean that all species must be tested or that another species which are uniquely important to a specific body of water could not also be required. These species are recommended because of their wide distribution throughout the Nation's waters, sensitivity to pollutants, or ease of culturing in the lab.

The point to be made is that the degree of specificity that is present in listing chemical analytes, even with the problems with nomenclature previously discussed, is far greater than the degree of specificity for biological analytes. Because of the need for tailoring monitoring requirements to the specific body of water being protected or investigated, it is not probable that the specificity in biological analytes will ever reach the level demonstrated for chemical analytes. Although this lack of specificity would appear to

Table II-15 SDWA Priority List

Disinfectants and Disinfection By-Products	Substance on the SARA 110 Priority List (From the First Two Priority Subgroups) Not Otherwise Required to be Regulated by the SDWA	NPS Design-Analytes List, With Substance Already Scheduled for Regulation, or Otherwise Covered in This Notice, Deleted (Continued)	Monitoring Contaminants Proposed for Inclusion on the First DWPL
A. Disinfectants	Dieldrin/Aldrin	Acifluorifen	Chloroform
Chlorine	Chloroform	Ametryn	Bromodichloromethane
Hypochlorite ion	Heptachlor/	Baygon	Bromoform
Chlorine dioxide	Heptachlorepoxide	Bentazon	1,1,1,2-Tetrachloroethane
Chlorite	N-nitrosodiphenylamine	Broacilm	Ethylbenzene
Chlorate	N-nitrosodimethylamine	Butylate	1,3-Dichloropropane
Chloramine	4,4'-DDE,DDT,DDD	Carbaryl	Bromobenzene
Ammonia	Chloroethane	Carboxin	Chloromethane
Ozone	Bromodichloromethane	Carboxin sulfoxide	Styrene
B. Trihalomethanes	Isophorone	Chloramben	Bromomethane
Chloroform	1,1,2,2-Tetrachloroethane	Chlorothalonil	1,2,3-Trichloropropane
Bromoform	3,3'-Dichlorobenzidine	Cyanazine	1,1,2,2-Tetrachloroethane
Bromodichloromethane	Benzidine	Cycloate	Chloroethane
Dibromochloromethane	Phenol	DCPA	2,2-Dichloropropane
Dichloroiodomethane	Bis(2-chloroethyl)ether	DCPA acid metabolites	o-Chlorotoluene
C. Halonitriles	2,4-Dinitrotoluene	Diazanon	p-Chlorotoluene
Bromochloroacetonitrile	Bis(chloromethyl)ether	Dicamba	1,1-Dichloropropene
Dichloroacetonitrile	N-nitrosodi-n-propylamine	1,3-Dichloropropene	1,1-Dichloroethane
Dibromoacetonitrile		3,5-Dichlorobenzoic acid	
D. Halogenated Acids		Diphenamid	
Alcohols, Aldehydes, and Ketones		Disulfoton and sulfone	
Monochloroacetic acid		Diuron	
Dichloroacetic acid		ETU	
Trichloroacetic acid		Fenamiphos sulfone	
Chloralhydrate		Fenamiphos sulfoxide	
2,4-dichlorophenol		Fluormeturon	
E. Others		Hexazinone	
Chloropicrin		Hexachlorobenzene	
Cyanogen chloride		Hydroxydicamba	
3-chloro-4-dichloromethyl)-5-hydroxy-2(5H)furanone (MX)		Methomyl	
		Methyl paraoxon	
		Metolachlor	
		Metribuzin	
		Metribuzin DA, DADK, DK	
		Prometon	
		Prometryn	
		Pronamide	
		Pronamide metabolite	
		Propachlor	
		Propazine	
		Propham	
		Tebuthiuron	
		Terbacil	
		Trifluralin	
		2,4,5-T	

Table II-16 Human Pathogens, Parasites, and Indicator Organisms(1)

Analytes	Source of Methods
I. Microbiological	
A. Viruses	
1. Non-pathogens (indicators of pathogens)	
Coliphage	2
2.Pathogens	
Adenovirus (30 + types)	2
Coxsackievirus A (24 types)	1
Coxsackievirus B (6 types)	1
Echovirus (34 types)	1
Gastroenteritis type Norwalk (2 types)	2
Hepatitis type A (1 type)	2
Norwalk (Gastroenteritis type)	2
Agents (2 types)	
Poliovirus (3 types)	1
Reovirus (3 types)	2
Rotavirus (4 types)	2
B. Bacteria	
1. Non-pathogens (indicators of pathogens)	
Clostridium perfringers	5
Fecal coliforms	3,4
Fecal streptococci	3,4
Staphylococci (coagulase positive)	3
2. Pathogens	
Aeromonas hydrophila	5
Clostridium botulinum	5
Enteropathogenic E. coli	3
Legionella	2
Leptospira	3
Mycobacteria	5
Pseudomonas aeruginosa	3
Salmonella	4
Shigella	3
Vibrio cholerae	3
Vibrio parahemolyticus	5
C. Protozoa	
Balantinium coli	5
Cryptosporidium	2
Entamoeba histolytica	5
Giardia lamblia	6
D. Worms, worm larvae, and eggs	
Nematodes	3
Ascaris ova	5
Taenia ova	5
Trichuris ova	5

(1) Code for Sources of Methods

1.Berg, G., R. S. Safferman, D. R. Dahling, D. Berman, and C. J. Hurst.1984.USEPA Manual of Methods for Virology..Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.EPA 600/4-84-013.

2. Methods remaining to be developed

Table II-16 (Notes, Continued)

3. APHA.1985.Standard Methods for the Examination of Water and.Wastewater, 16th ed. Amer. Publ. Hlth. Assoc., Washington, DC.

4. Bordner, R. H. and J. A. Winter. 1978. Microbiological Methods for.Monitoring the Environment, Water and Wastes. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/8-78-017.

5. Methods are available in EPA reports and/or open literature.

6. Methods currently being developed.

Table II-17 Toxicity Tests

Analytes	Source of Methods
1. Toxicity to algae, invertebrates, and fish	1,2,3
2. Microbial Mutagenicity (Ames Test)	4
3. Mammalian toxicity/mutagenicity (using cell cultures)	5
4. Microbial toxicity (Toxicity to bacteria providing assimilative capacity in surface waters)	5

1. Peltier, W.H., and C.I. Weber. 1985. Methods for Measuring the Acute Toxicity of Effluent to Freshwater and Marine Organisms. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio EPA-600/4-85-013.
2. Horning, W. B., and C. I. Weber. 1985. Short-Term Methods for Estimating the Chronic Toxicity of Effluents to Freshwater Organisms. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/4-85-014.
3. Weber, C. I., W. B. Horning, D. J. Klemm, T. W. Neiheisel, P. A. Lewis, E. L. Robinson, D. McMullen. 1987. Short-Term Methods for Estimating the Chronic Toxicity of Effluents to Marine and Estuarine Organisms. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/4-87-028.
4. FR 50(165):34592; FR 51(131):24897.
5. Williams, L. R., and J. E. Preston. 1982. Interim Procedures for Conducting the Salmonella/Microsomal Mutagenicity Assay (Ames Test). U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. EPA 600/4-82-068.
6. EPA methods remaining to be developed. Some methods are available in the open literature.

Table II-18 Use of Captive Organisms in Bioaccumulation and Toxicity Tests (1)

Type of Test	Organism					
	Phyto-plankton	Zoo-plankton	Peri-phyton	Macro-phyton	Macro-invert	Fish
IN SITU TESTS						
1. Bioaccumulation						
Toxic Metals	X	X	X	X	X	X
Pesticides (organics)	X	X	X	X	X	X
Flesh Tainting					X	X
2. Toxicity Tests						
Acute Toxicity					X	X
Histopathology					X	X
Histochemistry			X	X	X	X
Cholinesterase					X	X
IN-PLANT TESTS (EFFLUENTS)						
1. Bioaccumulation						
Toxic metals	X	X	X	X	X	X
Pesticides (organics)	X	X	X	X	X	X
Flesh tainting					X	X
2. Toxicity tests						
Acute toxicity	X	X			X	X
Low-level responses (behavioral responses)					X	X
Histpathology					X	X
3. Biostimulatory tests						
Algal growth response	X		X			
LABORATORY TESTS						
1. Bioaccumulation						
Toxic Metals	X	X	X	X	X	X
Pesticides (organics).	X	X	X	X	X	X
2. Toxicity tests						
Acute toxicity	X	X			X	X
Chronic toxicity	X	X	X	X	X	X
Histopathology					X	X
Low-level responses (behavioral responses)					X	X
3. Biostimulatory tests	X		X			

(1) From 2-5

Table II-19 Properties of Indigenous Communities of Aquatic Organisms Used in Determining the Biological Integrity of Surface Waters (1)

Parameters	Biological Community					
	Phyto-plankton	Zoo-plankton	Peri-phyton	Macro-phyton	Macro-invert	Fish
STANDING CROP						
1. Count	X	X	X	X	X	X
2. Volume	X	X	X		X	
3. Wet weight	X	X	X	X	X	X
4. Dry weight	X	X	X	X	X	
5. Ashfree weight	X	X	X	X	X	
6. DNA content	X					
7. ATP content	X	X	X			
8. Chlorophyll a content	X		X	X		
TAXONOMIC COMPOSITION						
1. Species identification	X	X	X	X	X	X
Indicator species	X	X	X	X	X	X
Numbers within species	X	X	X	X	X	X
Total number of species	X	X	X	X	X	X
Diversity index	X	X	X	X	X	X
2. Pigment composition						
Biomass/Chlorophyll a	X		X			
Chloro a/Chloro b	X		X			
Chloro a/Chloro c	X		X			
Pheophytin content	X		X			
3. Nitrogen fixation	X		X			
METABOLIC ACTIVITY/CONDITION						
1. Primary Productivity						
Carbon-14 uptake	X		X	X		
Oxygen evolution	X		X	X		
2. Respiration rate						
Plankton oxygen uptake	X	X				
Electron Transport	X	X				
Benthic oxygen uptake			X	X	X	
3. Nitrogen fixation	X		X			
4. Chemical composition	X		X			
Macronutrient content	X		X	X		
Enzyme content						
Cholinesterase					X	X
Phosphatase	X		X	X		
Nitrate reductase	X		X			
Toxic chemical content	X	X	X	X	X	X
5. Flesh tainting					X	X
6. Histopathology					X	X
7. Condition factor	X	X	X	X	X	X

(1) From 2-5

Table II-20 List of Required or Recommended Microbiological Analytes Under FWPCA and SDWA

Species or parameter	Test Temperature	Test Time Period
Safe Drinking Water Act		
(1)Total coliforms	35C	24-48 hrs
(2)Fecal coliforms	44.5	24 hrs
(3)Fecal Streptococci	35	48 hrs
(4) Heterotrophic plate count	35	48-72 hrs
(5) *Salmonella* spp	various	various
(6) Enterovirus	36.5.	2 hrs
(7) Cryptosporidium (to be developed)	28	7 days
(8) *Giardia lamblia*	-	-
(9) Legionella (to be developed)	-	-

diminish the usefulness of biological analytes, biological monitoring that is not focused on a specific biological component of an ecosystem, increases the chances of detecting unpredictable but often significant consequences of man's activities.

As evidenced by Table II-23, a significant part of the biomonitoring program under the FWPCA is required by the NPDES permit program. Other than FWPCA and SDWA requirements for microbiological monitoring in municipal, industrial effluents, and public water supplies, this program requires the most frequent monitoring across the broadest area. Biomonitoring under the NPDES program has been evolving, as previously described in this chapter, due to an increased emphasis on the control of toxics to protect human health and the integrity of biological systems.

In an effort to obtain "ground truth" data, the various regional offices of the EPA and the appropriate State agencies were surveyed in 1986, (2-15). Regions and States were asked the number of NPDES permits they administered,

Table II-21 Water Quality Standards for Microbiological Parameters

Water or Wastewater	Microbiological Standards Coliforms/100 ml Total	Fecal	Reference Source
Potable Water	<5	-	PL 93-523
Chlorinated Effluents	-	200-400	PL 92-500
2" Treatment Wastes	-	200-400	40 CFR Part 133
Selected Industrial Wastes	-	200-400	PL 92-500
Leather and Tanning	-	400	40 CFR Part 425
Feed Lots	-	400	40 CFR Part 412
Meat Products	-	400	40 CFR Part 432
Beet Sugar	-	400	40 CFR Part 409
Canned Fruits and Vegetables	-	400	40 CFR Part 407
Textiles	-	400	40 CFR Part 410
Effluents from Marine Sanitation Devices- Type I	-	1000	40 CFR Part 140 and Amendments
Effluents from Marine.Sanitation Devices- Type I I	-	200	40 CFR Part 140 and Amendments

Table II-22 Water Quality Criteria for Microbiological Parameters

Water or Wastewater	Statistical Measure	Microbiological Standards			Reference Source
		Enterococci	Coliforms/100 ml		
			Total	Fecal	
Public Water Supply	log X		20,000	2,000	A
Recreational Water:					
Freshwater	geometric mean of >5 samples/30 days	33		126	A,B
Marine Waters	geometric mean of >5 samples/30 days	35			A,B
Shellfish-Raising Waters	Daily Median			14	A,C
	Highest 10% of Daily Values			43	

A Quality Criteria for Water, EPA 1986. Office of Water Regulations and Standards, Washington, DC 20460 EPA 440/5-86-001.

B EPA, 1986. Ambient Water Quality Criteria for Bacteria - 1986 Office of Water Regulations and Standards, EPA, Washington, DC EPA 440/5-84-002.

C National Shellfish Sanitation Program Manual of Operation. U.S. Dept of HEW, 1965. Public Health Service Publ. No 33. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

the number of permits with a biological toxicity testing requirement, the number of permits with expressed toxicity limits and with requirements for toxicity reduction evaluations. Regional and State programs were discussed, including the use of biological testing such as acute and chronic bioassay techniques, instream biotic assessments, analysis of aquatic organisms for bioaccumulation, as well as the use of biological investigative techniques. The results of the survey must be characterized as extremely diverse due to the different stages each Region or State had reached in the evolution of their program. Responses ranged from "no current program" through "an emerging program" to a "developing program."

To date, few states have a formal written policy or strategy on the use of biological testing in their NPDES program. However, many states have developed preliminary policies or were developing a policy. Biological testing methods were generally either effluent (end-of-pipe) testing or determining the biological integrity of receiving waters. Permits requiring effluent testing were the most prevalent. Required toxicity tests were typically static or flow-through tests of undiluted or diluted wastewater for 96 hours or less (acute testing) or up to 7 days (chronic testing). These state or federal programs required methods appropriate for ambient or environmental damage assessment from toxic pollutants, including:

- studies and assessments related to macroinvertebrates, fish, algae, periphyton, protozoa,
- primary productivity,
- sediment bioassays and analyses,
- fish flesh tainting,
- fish and mussel flesh analyses for bioaccumulated compounds,
- toxicity to caged organism, and

- fish avoidance reactions (behavioral bioassays).

Table II-24 summerizes the statistics for the regions and states. Several figures, which are noteworthy, resulted from this study:

- 1,802 NPDES permits or 24 percent of the number of major permits required biological toxicity testing.
- 1,417 industrial permits required effluent biological toxicity testing; this is 79 percent of permits requiring testing and 38 percent of the number of major industrial permits.
- 385 municipal permits required effluent biological toxicity testing; this is 21 percent of permits requiring testing and 11 percent of the number of major municipal permits.
- 37 States required industries to conduct bioassays.
- 27 States required municipalities to conduct bioassays.

A brief review of the responses found that the following species or test methods were being specifically required or used:

- Water flea (Daphnia spp.).
- Fathead minnow (*Pimephales promelas*).
- Silversides (*Menidia* sp).
- Mysid shrimp (*Mysidopsis bahia*).
- *Ceriodaphnia* sp.
- Ames test (screening only).
- Killifish.
- Threespine stickle back (*Gasterosteus aculeatus*).
- Golden shiner.
- Rainbow trout.
- Lobster (American).
- Algae (*Selenastrum* sp.).
- Sheepshead minnow.
- Salmonid fish.
- Amphipods (*Gammarus* sp. *Hyallela* sp.).
- Mayfly (*Hexagenia* sp.).
- Oyster larvae (*Crassostrea virginica, C.gigas*).
- Microtox test method (Photobacterium phosphoreum).

Based on the information in Table II-24, the Regions with significant biomonitoring requirements were Regions II, IV, V, VI, and IX. The biomonitoring requirements of Regions II, V, VI, IX were investigated further by examining the specific analytes being required for all current NPDES permits issued within the region. As of July, 1987, due to the lag period between the implementation of the toxic monitoring policy by the Regional offices and the States and the initial filing of data with the Regional offices (DMR Reports), few Regional offices were requiring toxicity data as reported in the STORET files. The number of times that biological toxicity testing requirements were cited in permits is presented below:

Region II	
Bioassay (not otherwise specified).	149
LC50, Fathead Minnow, flow through	1
LC50, Fathead Minnow, static	8
LC50, Mysid shrimp, static	3
LC50, Sheepshead minnow, static	3
Toxicity, Concentration	1
Toxicity, Final concentration	3
Region IV	
Bioassay	364
Toxicity Limits	141
Region V	
Bioassay (not otherwise specified)	1
Toxicity, Concentration	2
Region VI	
Bioassay (not otherwise specified)	334
Toxicity, concentration	2
Region IX	
Bioassay	47
Toxicity, Final concentration	50

It is believed that the number of NPDES permits requiring toxicity testing will significantly increase when "round three" permits begin to be cited in the STORET files. For instance, Region VI reports that the number of permits with bioassay requirements will increase from 334 to 980. It should be recognized that general permits (e.g., offshore oil and gas operations) will significantly increase the amount of bioassay data being generated but will not increase the tabulated number of permits requiring bioassay data proportionally

because general permits are reported as one permit.

The only other biological analyte required in NPDES permits relates to microbiological analytes. Again, for Regions II, V, VI, and IX, the following number of NPDES permits required microbiological monitoring:

Region II	
Coliform, fecal	904
Coliform, total	180
Region V	
Coliform, fecal	689
Coliform, fecal, MF, M-FC	158
Coliform, fecal, MPN + MF	80
Coliform, total	1
Region VI	
Coliform, fecal	593
Coliform, total	1
Region IX	
Coliform, fecal	55
Coliform, total	231

No listings were found within these four regions for any other biological analytes for effluent testing. It should be emphasized that there are some apparent differences between the Regional offices in coding NPDES permit requirements for entry into the national Permit Compliance System (PCS) Program. This will cause the same confusion that was evident with the chemical analytes where numerous names were used for reporting the same analyte. Clearly, compared to the extensive lists of chemical analytes being specifically required, biological analytes required for effluent testing constitute a small percentage. However, the total biological monitoring effort is significant because numerous field studies of biological integrity are conducted in support of the issuance of permits (to determine wasteload allocations), to determine ambient conditions, and to determine compliance. Very few of these data could be entered into the PCS because biological data management software were not available.

Table II-23 List of recommended or required species for acute or chronic toxicity testing under NPDES permits program.

Species or parameter		Test Temper -ature (°C)	Life Stage
Acute Toxicity			
Freshwater			
Vertebrates			
Cold Water			
Brook trout	*Salvelinus fontinalis*	12	30-90 days
Coho salmon	*Oncorhynchus kisutch*	12	30-90 days
Rainbow trout	*Salmo gairdneri*	12	30-90 days
Warm Water			
Bluegill	*Lepomis macrochirus*	20	1 -90 days
Channel catfish	*Ictalurus punctatus*	20	1 -90 days
Fathead minnow	*Pimephales promelas*	20	1 -90 days
Invertebrates			
Cold Water			
Stonefiles	*Pteronarcys* spp.	12	Larvae
Crayfish	*Pacifastacus leniusculus*	12	Juvèniles
Mayfiles	*Baetis* spp. or *Ephemerella* spp.	12	Nymphs
Warm Water			
Amphipods	*Hyalella*, spp.,	20	Juveniles
	Gammarus lacustris, G. fasciatus or	20	Juveniles
	G. pseudolimnaeus	20	Juveniles
Cladocera	*Daphnia magna* or *D. pulex,*	20	1 - 24 h
	Ceriodaphnia spp.	20	1 - 24 h
Crayfish	*Orconectes* spp.,	20	Juveniles
	Cambarus spp.,	20	Juveniles
	Procambarus spp.,	20	Juveniles
Mayflies	*Hexagenia limbata* or *H. bilineata*	20	Nymphs
Midges	*Chironomus* spp.	20	Larvae
Marine and Estuarine			
Vertebrates			
Cold Water			
English sole	*Parophrys vetulus*	12	1-90 days
Sanddab	*Citharichthys stigmaeus*	12	1-90 days
Winter flounder	*Pseudophleuronectes americanus*	12	Postmetamorph
Warm Water			
Flounder	*Paralichthys dentatus,*	20	1-90 days
	P. lethostigma		1-90 days
Longnose killfish	*Fundulus similis*	20	1-90 days
Mummichog	*Fundulus heteroclitus*	20	1-90 days
			(Continued)

Table II-23 (Continued)

Species or parameter		Test Temperature (°C)	Life Stage
Pinfish	*Lagodon rhomboides*	20	1-90 days
Sheepshead minnow	*Cyprinodon variegatus*	20	1-90 days
Silverside	*Menidia* spp.	20	1-90 days
Spot	*Leiostomus xanthurus*	20	1-90 days
Threespine stickleback	*Gasterosteus aculeatus*	20	1-90 days
Invertebrates			
Cold Water			
Dungeness crab	*Cancer magister*	12	Juvenile
Oceanic shrimp	*Pandalus jordani*	12	Juvenile
Green sea urchin	*Strongylocentrotus droebachiensis*	12	Gametes/embryo
Purple sea urchin	*S. purpuratus*	12	Gametes/embryo
San dollar	*Dendraster excentricus*	12	Gametes/embryo
Warm Water			
Blue crab	*Callinectes sapidus*	20	Juvenile
Mysid	*Mysidopsis* spp. *Neomysis* spp.	20	1-5 days 1-5 days
Grass shrimp	*Palaemonetes* spp.	20	1-10 days
Penaid shrimp	*Penaeus setiferus*, *P. duorarum*, *P. aztecus*	20	Post larval Post larval Post larval
Sand shrimp	*Crangon* spp.	20	Post larval
Pacific oyster	*Crassostrea gigas*	20	Post larval
American oyster	*Crassostrea virginica*	20	Embryo/larval
Chronic Toxicity			
Freshwater			
Fathead minnow	*(Pimephales promelas)*	25	Larvae/embryo
Cladocera	*(Ceriodaphnia dubia)*	25	Neonate/adult
Alga	*(Selenastrum capricornutum)*	24	

The following notes refer to the acute toxicity tests:

a. To avoid unnecessary logistical problems in trying to maintain different test temperatures for each test organism, it would be sufficient to use one temperature (12°C) for cold water organisms and one temperature (20°C) for warm water organisms.

b. The optimum life stage is not known for all test organisms.

c. Mayes et al., 1983, found no significant difference in the sensitivity of fish ranging in age from 10 to 100 days, in tests with nine toxicants.

d. *Daphnia* pulex is recommended over *D. magna* because it is more widely distributed in the United States, test results are less sensitive to feeding during tests, and it is not as easily trapped on the surface film.

Table II-24. Summary of NPDES Permits Requiring Biological Toxicity Testing and States with Biological Testing Programs. 2-18.

States	NPDES Permits							State Program		
	Major Industrial	Industrial with Bioassays [1]	With Toxicity Limits	Major Municipal	Municipal with Bioassays [1]	With Toxicity Limits	Biotic Assessments Required	Static Bioassays	Flow-through/ Chronic Bioassays	Biotic Assessment Locations
Alabama	82	25	25	85	0	0	0	Few	10	7
Alaska	308	2	0	19	0	0	0	0	0	0
Arizona*	23	0	0	19	0	0	0	0	0	0
Arkansas	56	34	0	59	0	0	0	12	0	40
California	98	440	440	148	110	110	0	Some	Some	0
Colorado	70	0	0	70	8	0	0	2	2	3
Connecticut	130	1	1	68	0	0	0	100	10	6
Delaware	21	5	0	15	1	0	0	0	0	2
D.C.	0	0	0	1	1	0	0	0	0	0
Florida	122	35	35	125	10	10	0	0	0	0
Georgia	60	25	0	120	1	0	0	Many	12	20
Hawaii	19	2	0	11	1	0	3	0	0	0
Idaho	42	3	0	28	2	0	0	0	0	0
Illinois	104	4	0	175	1	1	0	25	10	30
Indiana	88	6	0	94	0	0	0	15	0	5
Iowa*	34	0	0	62	0	0	0	0	0	2
Kansas*	14	0	0	32	0	0	0	Few	0	4
Kentucky	205	17	1	56	3	2	0	50	0	12
Louisiana	145	100	0	75	0	0	6	0	0	0
Maine	56	10	8	68	8	5	0	0	0	0
Maryland	52	13	0	35	20	0	0	Few	Few	0
Massachusetts	57	10	8	68	8	5	0	0	0	0
Michigan*	122	3	0	95	2	0	0	30	5	50
Minnesota	28	2	0	50	0	0	0	75	2	0
Mississippi	39	20	4	45	0	0	0	15	0	1
Missouri*	70	0	0	70	0	0	2	0	16	200
Montana*	6	2	0	17	0	0	0	10	2	8
Nebraska*	26	0	0	44	0	0	0	0	0	6
Nevada	3	0	0	10	1	1	1	0	0	0
New Hampshire	57	10	8	69	9	5	0	0	0	0
New Jersey	200	118	118	160	111	111	0	5	5	Few
New Mexico	16	5	0	21	0	0	0	0	0	8
New York	166	10	0	266	10	0	0	0	10	5
North Carolina	94	30	30	121	24	24	0	150	12	50
North Dakota*	7	0	0	15	0	0	0	0	0	0
Ohio*	150	1	0	155	0	0	0	75	10	20
Oklahoma	36	22	0	59	0	0	0	0	0	0
Oregon	23	15	2	36	0	0	1	4	30	15
Pennsylvania*	171	0	0	225	0	0	0	0	0	35

(Continued)

*States with a principally pollutant specific approach for toxics..
[1]Numbers may represent major and minor permits.

Table II-24. (Continued)

States	NPDES Permits							State Program		
	Major Industrial	Industrial with Bioassays[1]	With Toxicity Limits	Major Municipal	Municipal with Bioassays[1]	With Toxicity Limits	Biotic Assessments Required	Static Bioassays	Flow-through/ Chronic Bioassays	Biotic Assessment Locations
Rhode Island	16	12	0	19	12	0	0	0	0	0
South Carolina	80	55	5	115	5	0	40	100	10	15
South Dakota	4	0	0	29	1	0	0	0	0	16
Tennessee	86	12	5	75	2	0	0	Many	12	12
Texas	234	133	0	241	0	0	0	0	0	0
Utah	19	0	0	39	14	0	0	0	0	0
Vermont*	8	0	0	31	0	0	0	0	0	0
Virginia	100	120	0	25	25	0	20	36	2	Few
Washington	45	40	30	45	3	0	0	0	6	0
West Virginia	75	39	39	34	0	0	0	100	0	60
Wisconsin	62	36	0	88	0	0	0	0	0	450
Wyoming	30	0	0	20	2	0	0	0	0	0
Totals	3759	1417	759	3652	385	274	73	-	-	-
No. of States	-	-	-	-	-	-		23	20	29

*States with a principally pollutant specific approach for toxics..
[1]Numbers may represent major and minor permits.

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CHAPTER THREE
CRITERIA FOR DETERMINATION OF ADEQUACY OF TESTING METHODS

The adequacy of a method is based on its performance characteristics relative to the data requirements. Obviously, a method that is adequate in one situation could be inadequate in another. For example, a method developed to measure a pollutant at a concentration of 10 mg/L is adequate for measuring an industrial discharge with an effluent limitation of 100 mg/L but is inadequate for measuring the same pollutant in ambient water at a water quality criteria concentration of 0.1 mg/L.

A thorough understanding of a method's performance characteristics is therefore essential in assessing its adequacy for a given need. In addition, a method developed for monitoring purposes should be based on sound scientific principles and be practical for routine use. The development and standardization of a method to this level of use is a multistep process termed validation. The validation process verifies that the method is capable of reliably producing results of a known quality.

Because of time restrictions and the need to provide monitoring methods to the regulated community, methods are often published without performing the level of validation required to identify and remedy any weaknesses of the method. The performance characteristics and the degree of standardization of a method are therefore the controlling criteria for the determination of adequacy relative to a specific need.

For any given combination of analytes and samples, an array of test methods may be available. These methods typically have been developed by different laboratories and achieved very different levels of documentation and standardization. The methods will not necessarily provide equivalent results in terms of detection limits, precision or bias. However, based on the data quality objectives of the user, each may be adequate. The determination of adequacy of a specific method is therefore dependent on the specific monitoring needs.

A method that has completed an initial validation phase may be suitable for research or limited monitoring applications. However, when methods which have not been fully validated are promulgated or required for routine monitoring use, the Agency may expose itself to criticism from the regulated community. Resources and time are not available to fully validate all methods nor is this required as a pre-condition of program use under the FWPCA. There should be an appropriate balance, depending on the data quality objectives, between the level of effort expended in standardizing a method and the return gained in the confidence and respect of the community of laboratories who must use these methods.

This chapter defines criteria for judging the adequacy of a method, first by defining performance characteristics and then by discussing the validation and standardization process.

This chapter has been divided into two sections. The first part discusses the criteria for chemical procedures and the second part

addresses the criteria for biological methods. Where there is overlap between the two sections, the overlapping discussion has been placed in the first section.

Method Performance Characteristics

There are many characteristics of a method that can be used to evaluate its performance. In most cases, no single method will contain all of the desirable characteristics. The selection of a method is therefore based on evaluating which characteristics are important for a given need. For the purposes of this report, certain characteristics which are directly applicable to establishing the adequacy of a method were identified. This section provides a brief description of these characteristics, summarizing information presented elsewhere (3-1 to 3-9).

Detection Limits

The definition and determination of detection limits are a controversial subject of debate in the scientific and regulatory community. This controversy exists in two areas. First, what is the most appropriate and meaningful measure of the limit of detection? Second, how should a protocol be designed to collect the information that will result in establishing realistic and useful detection limits? A number of terms have been defined relating to detection limits (3-9, 3-10). These terms and their definitions are shown in Table III-1. Within the EPA, Superfund focuses on sample quantification limits, the Federal Water Pollution Control Act (FWPCA), on method detection limits, and the Safe Drinking Water Act (SDWA) and the Resource Conservation and Recovery Act (RCRA) on practical quantitation limit. Limits of detection and limit of quantitation have also been established by the American Chemical Society with funding and staff participation from the EPA. The PQL is an interlaboratory concept while LOQ is specific to an individual laboratory. The Agency developed the PQL concept to define a measurement concentration that is time and laboratory independent for laboratory purposes. The detection limit terms defined in Table III-1 have a quantifiable relationship. A method should contain an experimentally determined, clearly identified and defined detection limit for each analyte and matrix for which the method is applicable.

The detection limit should be related to results obtained during routine analyses of environmental samples, since many times detection limits are used to establish regulatory limits. The American Chemical Society states that "quantitative interpretation, decision making and regulatory actions should be limited to data at or above the limit of quantification" (3-9). The Agency's PQL concept is based not only on quantitation but also on precision and accuracy, normal operating conditions of a laboratory, and the fundamental need (in compliance monitoring) to have a sufficient number of laboratories available to conduct the analyses. The PQLs do not actually represent the results of normal laboratory procedures but are a model of what normal laboratory procedures might achieve. The Agency should establish one common definition of and means for determining a quantitation limit for a method and all applications of that method.

Precision

Precision is a measure of agreement among individual measurements of the same property, under prescribed similar conditions (3-11, 3-12). For analytical methods, precision may be specified as either "intralaboratory" (within laboratory) or "interlaboratory" (between laboratories) precision. Intralaboratory precision estimates represent the agreement expected when a single laboratory uses the method to make repeated measurements of the same sample. Interlaboratory precision refers to the agreement expected when two or more laboratories analyze the same sample with the same method. Intralaboratory precision is more commonly reported in methods because it is easier to obtain, but interlaboratory precision assessments may be more appropriate for regulatory applications and should be included in the methods.

Table III-1 Examples of Detection Limit Definitions

Instrument Detection Limit (IDL)	The smallest signal above background noise that an instrument can detect at a 99% confidence level.
Method Detection Limit (MDL)	The minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.
Limit of Detection (LOD)	The lowest concentration level that can be determined to be statistically different from a blank, numerically defined as 3 times the standard deviation of seven replicate measurements.
Limit of Quantitation (LOQ)	The level above which quantitative results may be obtained with a specified degree of confidence, numerically defined as 10 times the standard deviation of seven replicate measurements. It is specific to an individual laboratory.
Practical Quantitation Limit (PQL)	The PQL is analogous to the LOQ It is an interlaboratory concept and is numerically estimated at 5 to 10 times the MDL. PQLs are derived from laboratory performance, under ideal circumstances, of the best laboratories and not all laboratories. PQLs provide routine performance goals that many laboratories must strive to achieve.

Precision estimates should ideally represent the entire measurement process, including sampling, preparation, analysis, calibration, and any other components of the method. For water programs however, precision estimates contained in a method are usually used to describe only the laboratory performance component rather than the entire measurement process.

Accuracy

Accuracy is a measure of the closeness of an individual measurement to the true concentration. It includes both precision and bias. It is determined by analyzing a sample containing a known native or spiked concentration of the target pollutant. Accuracy is usually expressed either as a percent recovery (R) or as a percent bias (R-100). As with precision, the accuracy estimate in a method for water-based matrices usually applies to the laboratory performance portion of the measurement system rather than to the entire measurement process.

Interferences

Because of the complexity of environmental samples, most analytical methods are subject to interferences. Interferences that are not accounted for can cause analytical results to be biased. Interferences can be classified into three categories: 1) interferences that can be eliminated by exercising an option within the method; 2) interferences which are numerically related to another analyte which can be corrected for arithmetically; and 3) interferences that cannot be eliminated. The best way to eliminate an interference is to remove the interfering substance. Techniques include: 1) chemical techniques, such as the addition of reagents that will precipitate, complex or chemically alter the interfering substance; 2) separation techniques such as liquid-liquid partition or column partition to remove the interfering substance; and 3) physical techniques such as distillation, filtration, or purging which can isolate either the analyte of interest or the interfering substance.

However, despite these techniques, many interferences cannot be eliminated. This problem often limits the usefulness of methods since the response from the interfering substances may overwhelm any response due to trace levels of the target analytes. For example, large quantities of petroleum hydrocarbons may prevent the determination of the trace quantities of chlorinated volatile organic chemicals in a sample analyzed by gas chromatography/mass spectrometry. Alternate methods may be used to minimize the effects of the interference. In the example stated above, the use of a chlorine specific gas chro-

matography detector may resolve the interference problem.

In any event, each method should contain a discussion of known interferences and provide procedures for handling each. Where modifications beyond the scope of the method have been required to address interferences, the specific detection limits, accuracy and precision data obtained using these modifications should be reported with the sample results.

Applicability

A method developed for regulatory use should represent state-of-the-art technology that has been demonstrated to be practical for routine use. Frequently, in the process of developing technology to this level for a specific need, (e.g., routine monitoring for benzene in water at the ppb level) the major problems associated with implementing the technology in other areas (e.g., monitoring benzene in wastes) have also been solved. Thus, small modifications of a method can result in the application of a method developed for a specific sample matrix to an entirely different program and sample matrix.

This aspect of analytical method development presents two fundamental issues:

- The method development and performance data collection process only defines the quality of the data for the matrix and analytes originally tested, and
- Changes in the method for a new matrix or the inclusion of additional analytes will require the performance testing of the "new" method for the new analytes and sample types.

Therefore, it is important that a method contain information regarding its applicability. If a method is stated to be applicable to a variety of matrices (waters, soils, wastes, etc.) then the method must provide the following:

- Operational details of how to modify procedural steps to accommodate the different matrices,
- Method performance data (detection limit, precision and accuracy statements, holding times, etc.) for each matrix for which the method is stated to be applicable, and
- Performance criteria to meet if the method is used for other applications.

Once the data quality objectives of a particular need are defined, then it can be determined if a method is adequate for its intended use.

Dynamic Range

In general, methods can only be used to measure analytes over a specified concentration range, defined as the linear dynamic range. The linear dynamic range is limited at the lower level by the detection limit and above the detection limit by the linearity of the measurement process. This range is usually defined by the performance characteristics of the instrument detector, although other factors such as integration software, mass loading on column, etc., can sometimes limit this range.

In most cases, samples containing high concentrations of the target analytes can be diluted to extend the range. However, a broad dynamic range is desirable to minimize reanalyses of samples containing target analytes in concentrations exceeding the linear range. A method should provide information pertaining to the linear dynamic range. This information must be verified by each laboratory using working calibration standards over the range of interest. A method should also describe what operational steps should be performed when target analytes are present at concentrations exceeding this range.

Analytes

Many methods, especially methods for organic compounds and metals can be used to simultaneously measure many analytes of similar chemical properties. The increasing emphasis on an ever expanding list of toxic pollutants combined with the need for analytical methods to meet program demands has resulted in a tendency to add analytes to existing methods. It is often technically feasible, and

from a practical viewpoint desirable, to add analytes to existing methods.

Even though the underlying principle of a method may be appropriate for the inclusion of additional analytes, the method must be tested to demonstrate that the method reliably measures the additional analytes. Test methods should list all analytes for which the method can be used. Performance data should be contained in the method for each analyte listed. Unfortunately, many analytes are listed in proposed or final regulations without any supporting performance data. In addition, uniform criteria to define adequate performance have not been defined by the Agency. If known, the classes of chemicals for which each multianalyte method is technically applicable should be stated. This would aid in the selection of test methodology for special applications.

Reporting

In order to ensure that all appropriate quality control procedures were followed in the analysis process, specific documentation of QC results should be required to be provided with the analytical results. Results should be expressed so that their meaning is not distorted by the reporting process. Therefore, uniform units should be used throughout the report for chemically related analytes. The reports should also make clear which results, if any, have been corrected for blank and recovery measurements. Detection limits should carefully be adjusted if necessary as a result of the need to dilute samples.

Analysis Time/Capacity/Cost

The often overriding method characteristics which constrain the final selection of a method are the analysis time and cost. In addition, factors such as the availability of laboratories and/or instrumentation to perform the method can constrain the selection process. Clearly, these factors should not be used as a rationale for the collection of data inappropriate for the intended use.

However, the advantages of methods which can be performed by more laboratories, in shorter times at lower costs can outweigh the need for more expensive techniques which provided data of only slightly better quality. The key factor in this decision is to recognize the limitations of data acquired by alternate, less expensive techniques and ensure that these limitations do not conflict with the program needs. There currently are many methods in 40 CFR 136 which have different cost/quality tradeoffs. However, no criteria have been established to allow a laboratory to make an intelligent choice of the appropriate methods.

Method Validation and Standardization

The previous section described how the performance characteristics of a method were important criteria for defining adequacy. This section describes how the degree of validation and standardization of a method is also an important criteria. A fully validated and standardized method is a method that has been ruggedized by a systematic process and is applicable for its intended use. Ideally, only those methods that have been fully validated and standardized should be used for Agency needs. However, due to resource and time constraints, it is not always possible to fully validate and standardize every method for every application required by the Agency. The degree of validation and standardization required for a given method depends to some extent on the intended use of the data. For example, methods which will be used extensively for regulatory purposes or where significant decisions must be based on the quality of the analytical data normally require more extensive validation and standardization than methods developed to collect preliminary baseline data.

The validation process includes: 1) the selection of a method that is capable of producing measurements of the type and quality needed for a particular application and is a cost-effective approach to the analytical requirement; and 2) the verification that the method selected is based on sound technical principals and that it has been reduced to practice for practical purposes (3-13). This level of validation ensures that the method has been generally validated. General validation consists of testing, evaluating and characterizing the method to the extent necessary to demonstrate

that the method achieves a specified performance. This process establishes quantitative measures of performance under typical conditions of use. A method that is generally validated cannot unequivocally be assumed to be valid for every specific use (3-6). As shown in Figure III-1, there are three levels of validation and standardization. The first level represents the initial documentation and development of a method that must be performed for any method that is to be used for Agency purposes. A method validated to this level can be considered to be minimally validated.

Methods that have been minimally validated may be adequate for some program needs. For example, the extensive validation process may not be justified for a method with limited application, such as a method appropriate only for a single discharger, (e.g., for a specific pesticide produced by only one manufacturer). The costs and time required to fully validate and standardize a method beyond this minimal level must therefore be balanced against factors such as the degree of use of the method and the importance of the data for decision making. The use of a method that is only minimally validated should be carefully evaluated based on the circumstances. The user of the method should understand the potential limitations of the usefulness of the data. Where possible, and in all cases for methods that will have extensive regulatory use, a method should be fully validated and standardized. This increased level of validation verifies that the method is suitable for its intended use.

A method that is fully developed and standardized can be used as the basic framework for specific needs. Depending on the program needs, the method may require additional validation specific for each intended use of the data. For example, a procedure that has been generally validated for water may require additional validation to document its performance at regulatory levels. A method that has been generally validated can also be used as the basis for expansion of the method into new areas, such as additional matrices or analytes. These three levels of validation and standardization, and the components of each level, are shown in Figure 3-1, and are discussed in more detail in the subsequent sections.

Initial Demonstration of Method Performance (Minimal Validation)

As described previously, a user's particular need may sometimes outweigh the advantages of using a fully validated and standardized method. There is, however, a minimum level of validation that should be expected of any method used to generate environmental measurement data. This level of validation is associated with the initial testing of the method. This initial phase is required to:

- Document the operational details of the method,
- Provide single laboratory performance data, and
- Ensure that the method can be used by at least one other laboratory.

The process used to achieve this minimal level of validation includes the following activities:

- Definition of the requirements,
- Selection and basic method development,
- Collection of basic performance data,
- Confirmation testing, and
- Interim method description.

The initial method selection process should be based on the measurement need. This process should identify the analytes of interest, define the matrices to be measured and specify the required performance of the method. Existing methods are then reviewed to identify candidate methods which are potentially adequate to meet the requirements. If no existing method can be adapted, a new method must be developed.

The next step in this initial development process is to test the method in the laboratory to collect basic operational information. The analysis of reference materials, blanks and typical sample matrices are performed to generate the appropriate data. These laboratory

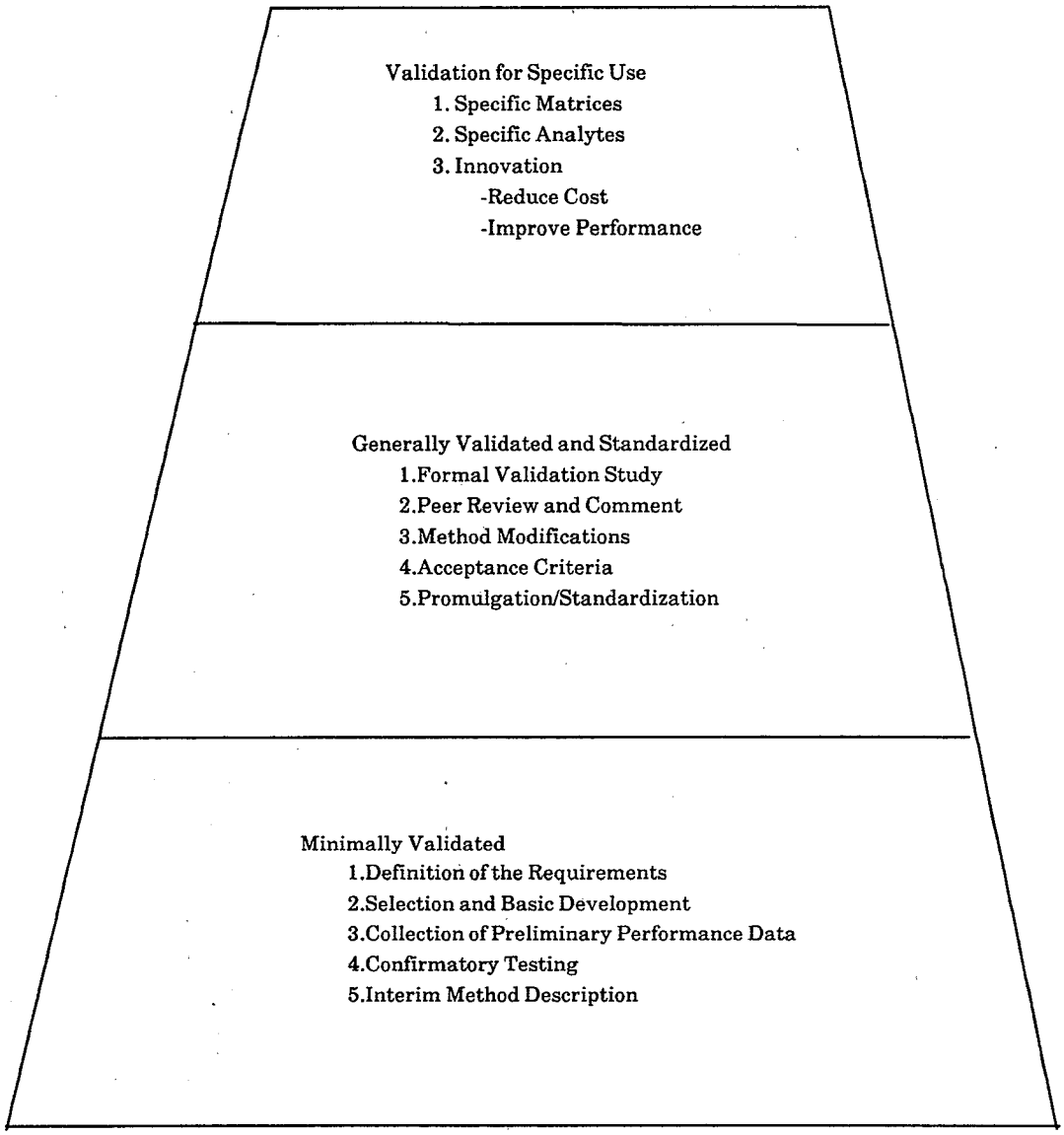

Figure III-1. Hierarchy of analytical methods.

tests should, at a minimum, provide other users of the method information related to:

- Operative variables, (e.g., GC retention times, key mass spectral ion fragment),
- Routinely achievable detection limits,
- Useful dynamic range, and
- Typical spike recoveries in sample types of interest.

Although not required, it is prudent at this point to disseminate information about the method to the technical community, either by presentations at scientific conferences or through an informal distribution of the method. By allowing the technical community the

opportunity to experiment with the method, improvements can be incorporated.

Once a method has been developed by the researcher, limited confirmatory testing to verify the previous work should be performed. The primary purpose of confirmatory testing is to provide independent confirmation of the method performance, i.e., whether or not at least one other competent laboratory can follow the method and obtain similar detection limits, precision and bias.

Following completion of the confirmatory testing, an interim method description can be written. The method should be sufficiently characterized by this time that any changes to the method resulting from further development work would be minor in nature. A method that has been developed to this level can be considered to be adequate for at least some needs. For example, a method at this level may be adequate as an interim method for collecting baseline data for a program with urgent needs.

The adequacy of methods which have not been developed to this minimum level cannot be defined. It is highly likely that methods used for a specific program which do not have this level of development and standardization will be subjected to close scrutiny and challenge by the regulated community. In addition, changes to the method which will occur as a method becomes better developed may later render the initial data unusable.

General Validation and Standardization

A method which has been minimally validated as described above is capable of generating adequate data for many needs. However, some program needs require methods which have tighter controls and have been more thoroughly tested and developed. Examples of this type of need are methods which will be used by thousands in response to National Pollutant Discharge Elimination System (NPDES) monitoring requirements.

Methods that have been minimally validated have been used in discharge regulations promulgated by EPA's Industrial Technology Division (ITD). In order to fulfill its mandate under the FWPCA and CWA to regulate substances that may be a threat to human health or the environment, ITD had applied specialized methods to site and industrial subcategory specific discharges. Some examples are:

(1) A method for determination of diesel oil in drilling muds and drill cuttings. This method was initially validated in a single commercial laboratory under contract to EPA, then further validated and applied by the Offshore Oil and Gas industry in a study of the use of diesel oil to free stuck drill bits in drilling operations.

(2) Methods determination of chlorinated dioxins and furans for the National Dioxin Study. These methods were developed by, and validated in, EPA's individual research laboratories. In order to meet Congressional deadlines, time constraints precluded full validation.

Fully validated and standardized methods incorporate the following features which may not be found in minimally developed methods:

- Formal performance testing
- Peer review and comment
- Method modifications
- Development of acceptance criteria
- QA/QC Requirements
- Promulgation
- Ongoing assessment

Formal Testing

Formal testing is a process which uses established well designed methods to collect performance data. A formal well-designed performance study generally results in a substantially better characterization of method performance as compared to the initial development work described previously. This testing can occur as a collaborative study or alternatively as an ongoing process whereby performance data are collected during routine use of the method.

Many of the 40 CFR 136 methods have undergone formal collaborative interlaboratory studies. (See Chapter 6). These studies involved the testing of the method over a wide concentration range and on a variety of sample matrices using many laboratories. Where monitoring activities have been initiated before completion of a collaborative study, data to support method performance have been obtained by collecting ongoing quality control data from laboratories using the method on a routine basis. For example, information has been collected for representative analytes from contract laboratories using specified analytical protocols under the Superfund Contract Laboratory Program. In both cases, data collected from formal testing programs are statistically evaluated to establish acceptance criteria for routine use. In addition, minor changes which are deemed appropriate based on either the results from the study or input from study participants are incorporated.

Peer Review and Comment

As required in Section 101(e) of the FWPCA, the EPA "is required to invite and consider written comments on proposed and interim regulations from any interested or affected persons or organizations" (40 CFR 25.10). This policy is based on a number of objectives involving public participation. Nowhere is this policy more important than in the development of analytical methods. By presenting the information at an early stage and encouraging the involvement of the technical community, many potential problems are resolved, thus minimizing wasted analytical efforts.

It should be noted that once a validated method has been proposed for use it gains a much higher degree of acceptability. This factor is due to the fact that the method is generally available and many users confuse proposal by the Agency with promulgation. For this reason, it is important to only propose test methods which have been minimally validated and standardized. A proposed method should be capable of being used routinely.

For example, the "600 Series" methods proposed in 1979 were sound methods that had not been fully validated at the time of proposal. Before finalization, thousands of samples were analyzed using these methods. The methods gained wide acceptance and were generally recognized to provide adequate data. The actual performance data collected during this period as well as the practical experience gained in the use of the methods led to improvements in the methods when they were finally promulgated. Revisions were made in the methods to give analysts more flexibility to practice professional judgment as long as specified performance criteria were achieved.

Promulgation/General Acceptance

The use of fully validated and standardized methods offer advantages over methods which are minimally validated. These advantages include factors such as:

- Improved comparability of data,
- Increased availability of a standard reference,
- Higher degree of legal acceptability, and
- Increased assurance of data quality.

Methods which have not been fully developed and documented are subject to change or interpretation by the analysts using the methods. In addition, modifications to the method may be operational changes. These changes may result in data which are not directly comparable either over a long period of time or between different laboratories. A fully developed validated and standardized method helps to resolve these issues.

The wide distribution of a validated method enables all users to ensure that the same method was followed. Thus, to the extent defined by the method, data generated by all laboratories using the method can theoretically be comparable. A method that has been fully validated contains data pertaining to the critical method performance characteristics. Thus, the user has assurance that data generated by the method will be of a known, defined quality.

As a method gains widespread use, it may evolve to where the users may decide that it should be formally standardized by consensus by

a standards organization. A method used by the Agency for regulatory purposes may require formal promulgation. In both cases, methods which are developed to this level generally gain widespread acceptance. Guidelines for the format of standardized methods have been established by EPA, ASTM, AOAC, ACS, USGS and other organizations.

The prototype format developed by EMSL-Cincinnati is regarded as an acceptable model for the format of a method. In this system, each method should be referenced by a unique number and should contain the following elements:

- Title
  - Legal or regulatory criteria, if appropriate
  - Originating organization
- Scope and Application
  - Matrices
  - Analytes
- Summary of Method
- Definitions
- Interferences
- Safety Precautions
- Apparatus and Equipment
- Sample Collection, Preservation and Storage
- Reagents
- Calibration
- Method
- Quality Control
- Calculations
- Performance Data
  - Precision
  - Bias
  - Detection Limits
  - Dynamic Range
- Reporting Requirements

Ongoing Assessment

It is essential to continuously assess the performance of the method on an ongoing basis. For example, data collected over a long period of time on performance evaluation samples has been used to assess the relative detection limits, precision and accuracy of methods. Such information can be used to determine if a method can provide adequate data for a specific use and can also be used to assess whether the method requires additional modification.

Validation for a Specific Use

In developing a method for a specific need, the best starting point is a method that has been generally validated. A generally validated method will have the important operational details documented. For example, the only change required to make an instrumental method developed for a water matrix applicable to a solid matrix may be changing the sample preparation step. Similarly, a method developed to measure one compound can be demonstrated to measure a related compound.

A generally validated method thus provides a reference base for the development of new methods. The performance characteristics (detection limit, precision, etc.) of the developed method can be used to assess the performance of the new method.

A generally validated method has an additional advantage. It serves as the yardstick by which alternative methods can be measured. As technology improves, modifications to the existing method may be warranted. The impact of these modifications can be evaluated with respect to the performance of the existing method to determine if the modifications are really an improvement. For example, the methods in 40 CFR 136 have formed the basis of methods developed for other needs.

Criteria for Determination of Adequacy of Biological Methods

The generation of scientifically accurate and valid biological measurements for environmental pollutants requires approximately the same criteria for assessing

the adequacy of a method as previously described for chemical analyses. The same performance characteristics and development states of the method must be known in order to make an assessment of adequacy, and those sections will not be repeated.

However, there are several differences which are important. Instrument specific characteristics such as detection limits and dynamic range are good examples. These characteristics, which measure the capacity, ability, or efficiency of the analytical instrument being used to make the chemical measurement, are not usually appropriate concepts for all biological measurements unless instrumentation is required. Biological methods may or may not be dependent on instrumental efficiency depending on the amount of instrumentation required to perform the test method. For instance, a field survey of the number and types of aquatic weeds along a stream bank can be accomplished without any instrumentation. In this case, the detection limit of the method is based on the visual acuity and knowledge of the observer, not a limit imposed by instrumentation. In the case of chlorophyll measurements, involving the use of an ultraviolet/visible spectrophotometer or flowmeter, instrument characteristics would be important.

Biological Detection Limits

The "health" of the test organism or biological system being monitored is a unique attribute without a complimentary attribute for analytical methods. The health of a toxicity test organism has a profound effect on the quality of the data, and must therefore be considered a key criterion for assessing adequacy. Biological system health is primarily relevant to biological field assessments.

The health of test organisms and biological systems cannot be "calibrated" before the experiment in the same way as analytical instrumentation. A single living organism is far more complex than the most sophisticated analytical instrumentation ever conceived. Organisms can adapt to their environment, hybridize, mutate, or go dormant during the measurement time period. There are no knobs to turn to adjust for these factors to achieve consistent performance during a test method. For these reasons, the biological procedure must include biological standards (e.g., standard reference toxicants) in order to ensure data integrity.

Precision

The precision of toxicity measurements is similar to that of finely tuned instruments operating at detection limits. The users of biological methods must account for the inherent variability in response. Typically for toxicity test methods, this means using replicate exposures at each concentration and running parallel tests with each sample or batch of test organisms using a standardized toxicant so that the "health" or sensitivity of the test organisms can be independently measured. It also means that the natural variability in sensitivity will have to be accounted for. More importantly, this variability must also be accounted for when permit limits, criteria, or standards are set.

In aquatic toxicity tests, most EPA methods require that a control or series of controls be run concurrently with the test series and that the survivorship in the controls must be 80-90% or greater in order for the test results to be acceptable. Chronic tests have minimal performance requirements also. As an additional check, the results from the standard toxicant test with the same batch of test organisms should be similar to previously generated data (cusum graph). In a sense, using requirements such as these two examples are means of calibrating the method. As with chemical methods, variability is an essential criterion for assessing the adequacy of a test method. The mechanism within each method for making this assessment is the quality assurance/quality control (QA/QC) section.

Precision statements, detection limits, dynamic range, and the inherent biological variability are intricately related. For instance, single laboratory precision for an acute toxicity test can be determined by performing multiple standard toxicant tests with the same batch of test organisms. Precision can be described by a mean, standard deviation, and relative standard

deviation (percent coefficient of variation, or CV) of the point estimates from replicated tests. However, with chronic tests, the results are reported in terms of the No-Observed-Effect-Concentration (NOEC) or the Lowest-Observed-Effect-Concentration (LOEC). These concentration levels, essentially the detection limits of the test organisms or population, would clearly be a function of the concentration series and the health of the test organism or test population including such factors as age, physiological condition, and quality of diet. For these situations, precision can only be described by listing the NOEC-LOEC interval for each test rather than calculating a statistic. When all tests of the toxicant yield the same NOEC-LOEC intervals, maximum precision has been attained, yet the "true" NOEC could fall anywhere within the interval, NOEC± (NOEC-LOEC). This means that the dynamic range could be changing both within and between replicate runs with the test method.

Applicability

As with the chemical method characteristics, applicability of the biological method is a key criterion for assessing the method's adequacy. For biological methods, a key component of applicability is whether special conditions in the lab or a unique lab location (e.g., coastal area) are required to perform the test. For instance, those organisms that require large amounts of high quality, flowing natural seawater, natural freshwater, or tidal fluctuations obviously cannot be used because they would require a highly specialized lab or location that may be difficult or impossible to recreate at all labs across the country. For the test method to be applicable, particularly for widespread NPDES biomonitoring, biological test methods must be adaptable to a wide variety of labs. The availability of labs that can realistically perform the test methods with reproducible results should be a key criterion in determining applicability of a method. Similarly, the choice of a test species must also be based on available culturing techniques or widespread, constant sources of test organisms to ensure timely testing. The test organism should not be overly susceptible to disease or stress, require unique water quality requirements, or exhibit unpredictable population characteristics (e.g., sudden mortalities). The key criterion for determining applicability is the ease with which the test can be performed on a routine basis.

For field assessment methods, the necessary element for determining applicability is the degree of flexibility allowed in the method for each unique field assessment. Field assessment methods must be specific enough to ensure consistency between replicate measurements of the same ecosystem, but flexible enough to allow for tailoring of the method to each unique ecosystem.

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CHAPTER FOUR
AVAILABILITY AND ADEQUACY OF METHODS TO SUPPORT TESTING REQUIRED UNDER THE FEDERAL WATER POLLUTION CONTROL ACT (FWPCA)

While methods are promulgated in 40 CFR 136 under the authority of §304(h) to support the National Pollution Discharge Elimination System (NPDES) and industrial pretreatment programs, the broader potential applicability of these methods to all FWPCA programs is addressed in this chapter. First, the history and status of the §304(h) and method equivalency programs are reviewed. Subsequently, the availability and adequacy of methodology to support all FWPCA programs are reviewed.

Test methods for FWPCA monitoring needs are promulgated in 40 CFR 136. Over 500 specific test methods have been approved for the determination of 252 biological, inorganic chemical, non-pesticide organic chemical, pesticide organic chemical and radiological analytes. For most analytes, an array of methods are available to meet the specific capability and needs of the user. Some methods require extensive and/or expensive instrumentation (e.g., GC/MS) and can only be performed by well-equipped laboratories. Other methods are within the capability of smaller laboratories and may be appropriate for a specific monitoring need.

The philosophy behind the promulgation of the §304(h) methods is to provide standardized methods that are as near to state-of-the-art as possible that are also practical for routine use.

Overview of §304(h) Program

Authority

Standardized analytical test methods are promulgated under the authority of §§301, 304(h), 307 and 501(a) of the FWPCA Amendments of 1972 as amended by the Clean Water Act (CWA) of 1977. Section 304(h) requires the Administrator to promulgate "guidelines establishing test methods for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to §401 of the FWPCA or permit application pursuant to §402 of the FWPCA." Section 501(a) authorizes the Administrator "to prescribe such regulations as are necessary to carry out his function under the Act."

The Administrator has also made these test methods applicable to monitoring and reporting of NPDES permits (40 CFR 122, 122.21, 122.41, 122.44 and 123.25), and implementation of the pretreatment standards issued pursuant to 307 of the FWPCA (40 CFR 403, 403.10 and 403.12).

History and Background

On October 16, 1973, the Agency established test methods for 71 analytes in 40 CFR 136 (38 FR 28758). The analytes were grouped as follows:

- General analytical methods, 15 analytes
- Metals, 28 analytes
- Nutrients, anions and organics, 17 analytes
- Physical and biological analytes, 6 analytes
- Radiological analytes, 5 analytes

The methods which were approved were for the most part cited in three compilations of methods.

- *Annual Book of Standards, Part 23, Water*, 1972, American Society for Testing and Materials (ASTM),
- *Methods for Chemical Analysis of Water and Wastes*, 1971, EPA, and
- *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, 13th Edition.

Since 1973, 40 CFR 136 has been amended 13 times. Most of these amendments have pertained to approval of equivalent alternate test methods. Two significant amendments, one in 1976 and one in 1984, that greatly expanded the scope of 40 CFR 136 are discussed below.

On December 1, 1976, forty-four additional analytes were added (40 FR 52780). The analytes were still listed in one table, grouped into categories which were little changed from the 1973 rule. However, this amendment increased significantly the number of approved methods and added, among other things, methods developed by the U.S. Geological Survey. In addition, criteria for sample preservation and sample holding times were established.

Probably the most significant amendment was finalized on October 26, 1984. This amendment established:

- New test methods (including quality control requirements) for the analysis of toxic organic pollutants;
- A new test based upon inductively coupled plasma optical emission spectroscopy for the analysis of metals;
- Mandatory container materials, preservatives, and holding times; and
- Definition of the method performance characteristic "method detection limit".

The list of analytes and approved methods (Table I of 40 CFR 136) was restructured into five tables and additional analytes were added as summarized below:

- Table 1A - Biological Test Methods, 5 analytes
- Table 1B - Inorganic Test Methods, 75 analytes
- Table 1C - Non-Pesticide Organic Compound Methods, 97 analytes
- Table 1D - Pesticide Methods, 70 analytes
- Table 1E - Radiological Analytes, 5 analytes

The mandatory containers, preservation techniques and holding times were summarized in a separate table.

This amendment resulted in the addition of 12 GC or HPLC methods and five GC/MS methods. The full texts of these methods were printed as Appendix A to Part 136. The full text of the ICP method was printed in Appendix C. The definition of and procedure for the determination of the method detection limit (MDL) was set forth in Appendix B.

As a result of a settlement agreement between EPA and Virginia Electric Power Company, EPA proposed on September 3, 1987, to incorporate results of method standardization studies for the inductively coupled plasma and flame and furnace atomic absorption test methods into 40 CFR 136. Among other things, the Agency also proposed that the public be given the opportunity to comment on nationwide approval of alternate test methods.

Future Actions

Below are brief descriptions of activities currently being addressed by the §304(h) workgroup. On October 26, 1984, the Agency proposed to add 32 additional organic analytes to

Table 1C. A draft Federal Register notice is in review to finalize this proposed amendment.

A Federal Register notice has been drafted to amend Table 1A, "List of Approved Biological Test Methods," to propose methods for measuring the toxicity of pollutants in effluents, drilling muds, and receiving waters, including short-term methods for estimating the acute and chronic toxicity to freshwater and marine organisms. Methods will also be proposed for measuring mutagenicity, and monitoring for viruses in wastewaters and sludges. Citations to microbiological methods are also scheduled to be updated.

A Federal Register notice has been prepared to conclude the rulemaking published October 26, 1984. This final rule under the FWPCA will promulgate control limits for analytical methods, delete several outmoded analytical methods, approve the use of certain analytical methods, e.g., 1624 and 1625 for 32 pollutants, and update references.

The 304(h) EPA workgroup also intends to propose an array of pesticide methods, as well as update method citations for current pesticide analytes in 40 CFR 136 to withdraw out-dated methods (e.g. thin layer chromatography) as proposed in October, and to add approximately 61 more pesticide analytes to Table 1D of Part 136.

The Process of Incorporating Standard Analytical Test Procedures into 40 CFR 136

Briefly presented are the various steps that a new test procedure goes through prior to promulgation in 40 CFR 136 under the authority of 304(h) of the FWPCA.

A standing group of the Agency, called the Steering Committee, has been established with representation from each EPA Assistant Administrator and the General Counsel. This committee is the primary mechanism for coordinating and integrating the Agency's regulatory development activities. Its key functions are to approve Start Action Requests (SAR) (A SAR initiates work on a rule or related action) and charter workgroups, monitor the progress of staff-level workgroups, especially regarding cross-media or inter-office problem-solving, and ensure, when appropriate, that significant issues are resolved or elevated to top management.

The primary purpose of a workgroup is to develop regulatory actions and supporting materials. The workgroup's first task is to prepare a SAR. For major and significant rules, the workgroup takes the responsibility of preparing a Development Plan (DP) to present to the Steering Committee for review. The DP sets forth the framework for developing proposed major or significant Agency rules. Its purpose is to explain the need for the action, identify regulatory goals and objectives; present the major regulatory issues and alternatives; and identify any policies, decision criteria or other factors that will influence regulatory choices; and present the work plan for developing the regulation. The workgroup's chairperson also prepares periodic workgroup reports for the Steering Committee.

Prior to presenting a FR notice to the Administrator or other approving official for sign-off, the notice undergoes a formal review by senior management (usually Assistant and Regional Administrators and the General Counsel). This is called Red Border Review.

Concurrent with the Red Border Review process, since information requirements are generally included in a §304(h) rule, e.g., reporting, monitoring or record-keeping, an Information Collection Request (ICR) must be prepared and submitted to the Office of Management and Budget (OMB) for their clearance. This is required under the Paperwork Reduction Act. Information requirements in final rules are not valid and enforceable until OMB clears the corresponding ICR.

Upon final sign-off by the Administrator or other approving official, the proposed notice is published in the Federal Register.

Methods Equivalency Program

Once test methods are promulgated, a flexible control system in §304(h) allows improved methods to be adopted by the laboratory community. As part of this program, data

comparability must be assured. Section 136.4 of the amended regulations published December 1, 1976, established the Methods Equivalency Program (4-1). The regulations allow for two levels of approval of alternate test methods. Limited use may be granted to an individual National Pollution Discharge Elimination System (NPDES) permit holder, or commercial, state or U. S. Environmental Protection Agency (USEPA) Regional Laboratory. Nationwide approvals may be initiated by any person or organization, but are primarily intended for instrument or analytical system manufacturers. On September 3, 1987, EPA proposed that the public be given the opportunity to comment on test methods before they are given nationwide approval.

The Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) has the responsibility for nationwide coordination of a methods equivalency program to determine the technical acceptability of proposed alternate test methods under the provisions of the FWPCA, and to make recommendations to the appropriate regional director for final approval or denial of the proposed method.

Objectives

The provision for approval of alternate analytical techniques is based on two principles. First, it was realized that for some dischargers, effluent characteristics or other circumstances would preclude the use of approved test methods. For these dischargers, it was the Agency's dual objective to allow some flexibility for analytical methods while maintaining control over method modifications. These goals are realized through the mechanism of the limited-use approval of alternate test methods. Secondly, the Agency recognized that it must be continuously informed of advances in analytical technology as they relate to present and future compliance monitoring requirements. Toward that end, a mechanism was established by which manufacturers of innovative analytical equipment or instrumentation would gain nationwide approval that would enable any entity regulated by the FWPCA to routinely use the method for reportable measurements.

Description of Program

Applications for limited-use approval of alternate test methods are evaluated on a case-by-case basis for methods which, in the opinion of the applicant are required because of unique waste characteristics which would preclude the use of approved test methods. Many requests for limited-use approval are initiated because the proposed is more accurate or precise than approved methods. In states which have been approved by EPA to administer the NPDES program, such applications are submitted to the state permitting authority. Each application includes a detailed method description, appropriate literature, performance comparability data, quality control data, and precision and accuracy data. Minimum comparability data requirements for limited approvals includes data from analyses of three grab samples from each permitted discharge. Each sample must be analyzed eight times; four each by the approved and proposed methods. This results in 24 data points for each contaminant for which approval is sought. All requirements for sampling, preservation and storage must be carefully followed.

In non-primacy states, the applications are directed to the EPA Regional Administrator or designee, usually the Regional Quality Assurance Officer (QAO). The QAO provides a copy of the application to the Director, EMSL-Cincinnati, who, through the Equivalency Program coordinates internal and external technical reviews of the application. For these reviews, technical experts at EMSL-Cincinnati or, in the case of methods for radioactivity, the Environmental Monitoring Systems Laboratory - Las Vegas provide supporting technical expertise. Statistical support is obtained through the Computer Services and Systems Division at the Andrew W. Breidenbach Environmental Research Center, Cincinnati.

One intent of the nationwide approval process is to provide a mechanism for instrument manufacturers to seek approval of their instruments. However, any applicant may request nationwide approval of an alternate test method. Requests are submitted to the Director, EMSL-Cincinnati, and must contain the same

type of information required for limited-use approvals, except that more data is collected to establish comparability. Nationwide NPDES approval of alternate test methods is based on comparability data from analyses of five representative wastewater types. For each industry or discharge type specified by EMSL-Cincinnati, the applicant must collect six samples and analyze each eight times; four each by the approved and proposed methods.

Completed applications including comparability data are subjected to rigorous internal and external review by the same staff as used for limited NPDES approvals described above. Statistical evaluation is performed by contractor personnel using a package of proven statistical tests known as the Equivalency Data Analysis and Storage System (EDASS). Based on review comments and the results of statistical testing of the data, the Director, EMSL- Cincinnati recommends approval or denial of the request. If approval is indicated, the entire application package, including supporting information, and technical and statistical reviews are submitted to the Chairman of the §304(h) workgroup with a request that the proposed method be considered for incorporation into 40 CFR 136 as an approved test method.

Summary of Equivalency Applications

Since its beginning in 1977, the Methods Equivalency Program has been highly visible and widely utilized. To date, over 600 requests for approval of alternate test methods have been processed for the NPDES compliance monitoring program. Approximately 500 of those applications were requests for limited-use approval; the remaining were for nationwide approval. Method variances have been requested for all of the approved methods, both biological and chemical (organic and inorganic). For inorganic analytes, the most common inquiries have been for approval of rapid methods such as test kits and automated techniques and for elimination of labor-intensive steps such as digestions or distillations when, in the opinion of the applicant, those steps are not necessary to achieve acceptable analytical results.

Applications for approval to modify methods for organic analytes, the 600-series methods, comprise approximately 10% of the total number of applications. Variances most often sought for the organic methods involve substitution of capillary chromatographic columns for the prescribed packed columns and for modifications in extraction and concentration methods. These variances are frequently justified on the basis of decreased sample processing time and the resultant savings in resources.

The desire by the regulated community and the Agency for sensitive, rapid, reliable, and inexpensive test methods is evident when examining the types of analytical techniques for which EMSL-Cincinnati has recommended nationwide approval. Most recent among them are the inductively-coupled argon plasma (ICP) and direct current plasma (DCP) optical emission spectrometric methods. ICP is widely used and represents state-of-the-art analysis for up to 30 metals simultaneously. The DCP method has similar capabilities and is also expected to be well accepted and result in considerable savings, especially for larger laboratories. Electrode methods for chloride and fluoride and test kit methods for numerous inorganics are now approved for general use, as are flow injection versions of the currently approved continuous flow (Technicon and others) methods. Other refinements of previously approved methods have also been approved. Examples of these include automatic hydride generation accessories to replace the manual method for selenium and arsenic and a scaled-down test procedure for chemical oxygen demand, the micro-COD.

Innovative methodology that shows great potential for compliance monitoring programs is currently being studied and is expected to be submitted for nationwide approval. One technique involves digestion of effluent samples using closed vessel microwave heating. This method would decrease digestion time by up to 80% of that currently required by hotplate digestion methods. Applications are also expected from manufacturers of ion chromatographic instruments capable of simplified analyses of multiple inorganic anions in the same sample. When these new principles

can be used with the Agency's compliance programs, they can result in improved data quality and impressive savings of resources and time. Thus it is to the advantage of the entire regulated community to expeditiously approve methods based on these concepts. These new techniques are discussed in more detail in Chapter Seven.

Availability and Adequacy of §304(h) Methods for Measuring Chemical Analytes

Over 500 test methods covering 247 chemical analytes have been promulgated in 40 CFR 136. Approximately one third of these methods have been developed or standardized by EMSL-Cincinnati. The remaining methods, developed by other organizations, are primarily cited for inorganic analytes. In fact, only three non-EPA methods, ASTM D3086 and "Standard Methods" methods 509A and 509B have been promulgated for the determination of specific organic chemicals.

In addition to the methods promulgated under §304(h), EMSL-Cincinnati has developed and standardized many other methods to support water program needs. Examples of these methods include:

- the extended 600 series methods for pesticides, some of which were promulgated in 40 CFR 455 before this part was remanded
- the 500 series methods, for measuring organics under SDWA

Many of these methods are used routinely by the regulated community. For example, method 614, developed for the measurement of organophosphorus pesticides is frequently used in studies associated with determining these analytes, although it has not been promulgated in 40 CFR 136. This test procedure formed the basis for method 8140, contained in the methods manual of the Office of Solid Waste, SW-846. Thus, some methods which are commonly used for environmental measurements have not been promulgated in 40 CFR 136, due to the boundaries currently imposed on the §304(h) process, i.e., if a method is not required for the NPDES or industrial pretreatment programs, the method has not been promulgated under §304(h).

This section assesses the availability and adequacy of the §304(h) methods to meet FWPCA monitoring requirements. This assessment has grouped the §304(h) methods into four major groups.

- EPA methods promulgated in 40 CFR 136
- Other methods promulgated in 40 CFR 136
- EMSL-Cincinnati methods that have been developed and standardized, but not promulgated in 40 CFR 136
- EMSL-Cincinnati methods that are under development

Methods for the Measurement of Analytes Listed in Table II-1

Table II-1 listed 323 chemical analytes that must be mentioned under various Agency programs. Of these, 91 are contained in monitoring requirements and analytical methods associated only with the Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of 1980 or Safe Drinking Water Act regulations. These analytes are listed in Table IV-1. Due to consolidation in the Agency programs, these analytes may be required to be measured to support some FWPCA programs in the future. No 40 CFR 136 methods specifically address these analytes. However, many of these analytes could be measured in water samples using approved §304(h) methods, if the need developed. For example, many volatile organic chemicals contained in Appendix IX to 40 CFR 264 can be measured using the technology promulgated in 40 CFR 136 for volatile organics. Of the 91 analytes listed in Table IV-1, 32 are clearly measurable using either the EPA 500 series methods or the methods in the Superfund Contract Laboratory Program. With the exception of oxirane (ethylene oxide), the remaining analytes are all contained in the RCRA Appendix IX list. Ongoing efforts within the Agency are directed towards generating method performance data for these compounds

in water samples. Based on the preliminary results from these evaluations, it is reasonable to expect that existing 304(h) methods could be extended to the measurement of these analytes.

Furthermore, standardized methods are available for the measurement of SDWA and CERCLA analytes in water samples. For example, standardized methods have been established for all of the SDWA volatile organic contaminants shown in Table IV-1. These methods (502.1, 502.2, 503.1, 504, 524.1 and 524.2) have been standardized to the degree that they could be promulgated in 40 CFR 136 if required.

Of the remaining 232 analytes which are directly associated with the FWPCA needs stated in Chapter 2, 173 have test methods promulgated in 40 CFR 136 and 59 do not.

However, as shown in Table IV-2, of these 59 analytes, 32 have methods that have been proposed for promulgation in 40 CFR 136 and methods have been validated by EMSL-Cincinnati for another 7 analytes. In addition to the analytes in Table IV-2, Table II-5 listed 30 analytes that were shown as examples of the analytes contained in NPDES permits with no methods available in 40 CFR 136. Methods for some of these analytes have been developed by EMSL- Cincinnati. Finally, Table II-12 listed 61 pesticides that were remanded in 40 CFR 455. As shown in the table, methods are available for these analytes although these methods currently are not promulgated in 40 CFR 136.

In summary, methods are available in some degree of standardization and validation for the 232 analytes identified in Chapter 2. Methods for many of these compounds have been promulgated in 40 CFR 136 or proposed for promulgation. Methods for the remaining analytes need to be proposed by USEPA.

In order to assess the adequacy of the §304(h) methods, three aspects were reviewed:

- The development status of both §304(h) methods and non-304(h) methods developed by EMSL-Cincinnati;
- Method performance characteristics contained in each method, as defined in Chapter Three;
- Actual method performance data.

These three aspects of the methods are summarized below.

Development Status and Performance Characteristics

Over the past 10 years, the definition of an adequate method has changed. Methods promulgated in the 1970's were adequate for the needs at that time, and in many cases are still suitable for specific needs. However, the increased concern over toxics and the increased scrutiny that analytical data routinely undergo has required a reexamination of the adequacy of some methods.

For example, methods that were developed in the 1970's for pesticides reflected the state-of-the-art at that time. Furthermore, these methods did not contain all of the elements (e.g., quality control requirements) that are now recognized as essential elements for any method. Since then, technology has improved and the Agency has recognized the need to incorporate additional requirements into methods. One result of this ongoing and evolving process is that those methods that have not been incorporated into 40 CFR 136 (e.g., method 524.2) contain method elements (e.g., capillary column technology and demonstration of method detection limits) that would be desirable to incorporate into the existing promulgated methods.

A second result of this process is that some promulgated methods are probably now obsolete. For example, in October, 1984, the Agency proposed (49 FR 43437) to withdraw approval for "Standard Methods" 509A and ASTM D-3086 promulgated for the measurement of pesticides. Compared to the EPA method, Method 608, these methods do not contain adequate QC requirements and do not stipulate control limits for analytical performance. A review of the development status of the §304(h) methods developed by EPA indicates that with the exception of certain older

Table IV-1. Chemical Parameters Listed in Table II-1 with no CWA Monitoring Requirements

PARAMETER	SDWA LISTS	RCRA LISTS	CERCLA LISTS
ACETOPHENONE		APPENDIX IX	
ACETONITRILE		APPENDIX IX	
2-ACETYLAMINO-FLUORENE		APPENDIX IX	
ALLYL CHLORIDE		APPENDIX IX	
4-AMINOBIPHENYL		APPENDIX IX	
ARAMITE		APPENDIX IX	
BENZYL ALCOHOL		APPENDIX IX	CLP
BROMOBENZENE	ALL		
BROMOCHLORO-METHANE	ALL		
n-BUTYLBENZENE	DISC		
sec-BUTYLBENZENE	DISC		
tert-BUTYLBENZENE	DISC		
p-CHLOROANILINE		APPENDIX IX	CLP
CHLOROBENZILATE		APPENDIX IX	
CHLOROPRENE		APPENDIX IX	
o-CHLOROTOLUENE	ALL		
p-CHLOROTOLUENE	ALL		
m-CRESOL*		APPENDIX IX	CLP
o-CRESOL*		APPENDIX IX	CLP/HSL
p-CRESOL*		APPENDIX IX	CLP
DIALLATE		APPENDIX IX	
1,2-DIBROMO-3-CHLOROPROPANE	VUL	APPENDIX IX	
trans-1,4-DICHLORO-2-BUTENE		APPENDIX IX	
1,3-DICHLOROPROPANE	ALL		
2,2-DICHLOROPROPANE	ALL		
1,1-DICHLOROPROPENE	ALL		
p-(DIMETHYLAMINO) AZOBENZENE		APPENDIX IX	
7,12-DIMETHYLBENZ(A) ANTHRACENE		APPENDIX IX	
3,3'-DIMETHYL-BENZIDINE		APPENDIX IX	
alpha,alpha-DIMETHYL-PHENETHYLAMINE		APPENDIX IX	
m-DINITROBENZENE		APPENDIX IX	
DINOSEB		APPENDIX IX	
DISULFOTON		APPENDIX IX	
ETHYL METHACRYLATE		APPENDIX IX	
ETHYL METHANE-SULFONATE		APPENDIX IX	
FAMPHUR		APPENDIX IX	
HEXACHLORODIBENZO-P-DIOXINS		APPENDIX IX	
HEXACHLORODIBENZO-FURANS		APPENDIX IX	
HEXACHLOROPHENE		APPENDIX IX	
HEXACHLOROPROPENE		APPENDIX IX	
IODOMETHANE		APPENDIX IX	
ISOBUTYL ALCOHOL		APPENDIX IX	
ISODRIN		APPENDIX IX	

(Continued)

TableIV-1. (Continued)

PARAMETER	SDWA LISTS	RCRA LISTS	CERCLA LISTS
ISOPROPYLBENZENE	DISC		
p-ISOPROPYLTOLUENE	DISC		
ISOSAFROLE		APPENDIX IX	
KEPONE		APPENDIX IX	
METHACRYLONITRILE		APPENDIX IX	
METHAPYRILENE		APPENDIX IX	
3-METHYL-CHOLANTHRENE		APPENDIX IX	CLP
METHYLENE BROMIDE		APPENDIX IX	
METHYL METHACRYLATE		APPENDIX IX	
METHYL METHANESULFONATE		APPENDIX IX	
2-METHYL-NAPHTHALENE		APPENDIX IX	
METHYL PARATHION		APPENDIX IX	CLP
METHYL ISOBUTYL KETONE*		APPENDIX IX	CLP/HSL
1,4-NAPHTHOQUINONE		APPENDIX IX	
1-NAPHTHYLAMINE		APPENDIX IX	
o-NITROANILINE			CLP
m-NITROANILINE			CLP
p-NITROANILINE		APPENDIX IX	CLP
4-NITROQUINOLINE 1-OXIDE		APPENDIX IX	CLP/HSL
N-NITROSOMETHYL-ETHYLAMINE		APPENDIX IX	
N-NITROSO-MORPHOLINE		APPENDIX IX	
N-NITROSOPIPERIDINE		APPENDIX IX	
5-NIITRO-O-TOLUIDINE		APPENDIX IX	
OXIRANE			HSL
PENTACHLORO-DIBENZO-P-DIOXINS		APPENDIX IX	
PENTACHLORO-DIBENZOFURANS		APPENDIX IX	
PHENACETIN		APPENDIX IX	
p-PHENYLENEDIAMINE		APPENDIX IX	
PHORATE		APPENDIX IX	
PRONAMIDE		APPENDIX IX	
PROPIONITRILE		APPENDIX IX	

(Continued)

Table IV-1. (Continued)

PARAMETER	SDWA LISTS	RCRA LISTS	CERCLA LISTS
n-PROPYLBENZENE	DISC		
SAFROLE		APPENDIX IX	
SULFOTEPP		APPENDIX IX	
TETRACHLORO-DIBENZO-P-DIOXINS		APPENDIX IX	
TETRACHLORODI-BENZOFURANS		APPENDIX IX	
1,1,1,2-TETRACHLORO-ETHANE	ALL	APPENDIX IX	
THIONAZIN		APPENDIX IX	
o-TOLUIDINE		APPENDIX IX	
1,2,3-TRICHLORO-PROPANE	ALL	APPENDIX IX	
o,o,o-TRIETHYL PHOS-PHOROTHIOATE		APPENDIX IX	
1,2,4-TRIMETHYL-BENZENE	DISC		
1,3,5-TRIMETHYL-BENZENE	DISC		
sym-TRINITROBENZENE		APPENDIX IX	
p-XYLENE	ALL	APPENDIX IX	CLP/HSL
o-XYLENE	ALL	APPENDIX IX	CLP/HSL
m-XYLENE	ALL	APPENDIX IX	CLP/HSL

methods, the methods are highly developed and standardized. The methods typically contain the method performance data discussed in Chapter Three and have been thoroughly tested. The two exceptions to this general assessment are 1) many of the methods for inorganic analytes published in "Methods for Chemical Analysis of Water and Wastes (MCAWW), 1983"; and 2) methods for organic analytes published in "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater, 1978."

Most of the inorganics methods in MCAWW are consensus methods. The methods have been subjected to extensive use over several decades and as shown later in this chapter, their method performance is known and adequate. By comparison, the methods provided in the 1978 manual for organics have for the most part been superseded by the 600 Series methods.

The Agency has proposed to withdraw the obsolete methods for the pesticides listed in Table 1D of 40 CFR 136, that have a corresponding 600 series method. The Agency has not proposed to delete the obsolete pesticides methods in Table 1D for the analytes that do not have a 600 series counterpart. These obsolete methods, for the remaining 49 pesticides, do not meet the minimum requirements specified in Chapter Three and should also be withdrawn. It will be necessary to replace these methods in 40 CFR 136.

As stated previously, with the exception of obsolete organic methods that have been proposed for withdrawal, non-EPA methods are approved only for biological, inorganic and radiological analytes. Three hundred thirty-five non-EPA methods for inorganic analytes are approved in 40 CFR 136,Table 1B. As described in more detail in Chapter Five, these methods are not as fully developed and standardized as the EPA methods. Essential method elements such as detection limits, performance criteria and QC requirements are typically not included

TableIV-2 Chemical Parameters Required for CWA Monitoring with No 304(h) Methods

PARAMETER	OTHER PROCEDURES	
	CLP	EMSL
ACETONE*	X	1624
ANILINE		
ASBESTOS		
BENZOIC ACID*	X	1625
BIPHENYL*		1625
BIS(2-CHLOROMETHYL)ETHER		
CARBAZOLE*		1625
CARBON DISULFIDE	X	
CHLORPYRIFOS		622
p-CYMENE*		1624
DACONIL		
DACTHAL		
n-DECANE*		1625
DEMETON		614
DIBENZOFURAN*	X	1625
DIBENZOTHIOPHENE*		1625
1,2-DIBROMOETHANE		504
cis-1,2-DICHLOROETHYLENE		
2,6-DICHLOROPHENOL		
DIETHYL ETHER*		1624
DIMETHOATE		
1,4-DIOXANE*		1624
DIPHENYLAMINE*		1624
DIPHENYL ETHER*		1625
1,2-DIPHENYLHYDRAZINE*		1625
n-DOCOSANE*		1625
n-DODECANE*		1625
n-EICOSANE*		1625
GUTHION		
GLYPHOSATE		140A
n-HEXACOSANE*		1625
n-HEXADECANE*		1625
HEXANOIC ACID*		1625
2-HEXANONE	X	
INDIUM		
METHYL ETHYL KETONE*	X	1624
MIREX		617
2-NAPTHYLAMINE*		1625
N-NITROSODIETHYLAMINE		
N-NITROSODIBUTYLAMINE		
N-NITROSOPYROLIDINE		
n-OCTACOSANE*		1625
n-OCTADECANE*		1625
PARAQUAT		
PENTACHLOROBENZENE		
2-PICOLINE*		1625
PYRIDINE		
STYRENE*	X	1624
TANTALUM		

TableIV-2: (Continued)

PARAMETER	OTHER PROCEDURES	
	CLP	EMSL
alpha-TERPINEOL*		1624
1,2,4,5-TETRACHLOROBENZENE		
2,3,4,6-TETRACHLOROPHENOL		
n-TETRACOSANE*		1625
n-TETRADECANE*		1625
n-TRIACONTANE*		1625
1,2,3-TRICHLOROBENZENE*		1625
2,3,6-TRICHLOROPHENOL*		1625
2,4,5-TRICHLOROPHENOL*	X	1625
TUNGSTEN		

in these methods. EPA methods have been approved for all analytes in 40 CFR 136.

Based on results of the Water Supply (WS), Water Pollution (WP) and Discharge Monitoring Report-Quality Assurance (DMR-QA) performance evaluation studies, many of the inorganic methods are used by less than one percent of the participating laboratories and should be proposed for deletion from 40 CFR 136. For example, over 4500 results for cadmium are contained in the SDWA Performance Evaluation Study for Water Supplies (WS) data base. Over 90% of these results are from laboratories using EPA methods 213.1 and 213.2. Most of the remaining results are from laboratories using "Standard Methods" AA methods. Four results are from laboratories using ASTM methods. No results are contained in the data base from the "Standard Methods" colorimetric method, or from any United States Geological Survey (USGS), American National Standards Institute (ANSI) or Association of Official Analytical Chemists (AOAC) method. The cost of maintaining these methods may not be justified as long as there are other acceptable methods available.

Many other EMSL-Cincinnati methods have been standardized to the extent that they can be considered to be appropriate for various FWPCA needs. These methods have been through the steps defined as the initial demonstration of method performance in Figure 3-1, but have not been promulgated in 40 CFR 136. These methods are listed in Table IV-3.

Table IV-3 Test Procedures Developed by EMSL-Cincinnati not Promulgated in 40 CFR 136

A. INORGANIC PROCEDURES	
Method 200.1	Determination of Acid Soluble Metals
Method 200.11	Determination of Metals in Fish Tissue by Inductively Coupled Plasma - Atomic Emission Spectrometry
Method 300.0*	The Determination of Inorganic Anions in Water by Ion Chromatography
B. NON-PESTICIDE ORGANIC PROCEDURES	
Method 502.1*	Volatile Halogenated Organic Compounds in Water by Purge and Trap Gas Chromatography
Method 502.2*	Volatile Organic Compounds In Water By Purge and Trap Capillary Column Gas Chromatography With Photo-ionization and Electrolytic Conductivity Detectors in Series
Method 503.1*	Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography
Method 504*	1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) in Water by Microextraction and Gas Chromatography
Method 524.1*	Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry
Method 524.2*	Volatile Organic Compounds in Water by Purge and Trap Capillary

	Column Gas Chromatography/Mass Spectrometry

C. PESTICIDE PROCEDURES

Method 505	Analysis of Organohalide Pesticides and Aroclors in Drinking Water by Microextraction and Gas Chromatography
Method 515	Determination of Chlorinated Herbicides in Drinking Water
Method 608.1	The Determination of Organochlorine Pesticides in Industrial and Municipal Wastewater
Method 608.2	Analysis of Certain Organochlorine Pesticides in Wastewater by Gas Chromatography
Method 614	The Determination of Organophosphorous Pesticides in Industrial and Municipal Wastewater
Method 614.1	Analysis of Organo-phosphorous Pesticides in Wastewater by Gas Chromatography
Method 615	Determination of Phenoxy Acid Herbicides in Industrial & Municipal Wastewater
Method 617	The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater
Method 618	Determination of Volatile Pesticides in Municipal and Industrial Wastewaters by Gas Chromatography
Method 619	The Determination of Triazine Pesticides in Industrial and Municipal Wastewater
Method 622	The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater
Method 622.1	Thiophosphate Pesticides
Method 627	The Determination of Dinitroaniline Pesticides in Industrial and Municipal Wastewater
Method 630	The Determination of Dithiocarbamate Pesticides in Industrial and Municipal Wastewater
Method 630.1	The Determination of Dithiocarbamates Pesticides in Wastewater as Carbon Disulfide by Gas Chromatography
Method 632	The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater
Method 632.1	Analysis of Carbamate and Amide Pesticides in Wastewater by Liquid Chromatography
Method 633	The Determination of Organonitro Pesticides in Industrial and Municipal Wastewater
Method 633.1	Neutral Nitrogen-Containing Pesticides
Method 634	Determination of Thiocarbamate Pesticides in Industrial and Municipal Wastewaters by Gas Chromatography
Method 645	Analysis of Certain Amine Pesticides and Lethane in Wastewater by Gas Chromatography
Method 646	Analysis of Dinitro Aromatic Pesticides in Wastewater by Gas Chromatography
Method 680	Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry
Method 1**	Determination of Nitrogen- and Phosphorus- Containing Pesticides in Groundwater by Gas Chromatography with a Nitrogen-Phosphorus Detector
Method 2**	Determination of Chlorinated Pesticides in Ground water by Gas Chromatography with an Electron Capture Detector
Method 3**	Determination of Chlorinated Acids in Groundwater by Gas Chromatography with an Electron Capture Detector
Method 4**	Determination of Pesticides in Ground Water by High Performance Liquid Chromatography with an Ultraviolet Detector
Method 5**	Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Ground water by Direct Aqueous Injection High Performance Liquid Chromatograph (HPLC) with Post Column Derivation
Method 6**	Determination of Ethylene Thiourea (ETU) in Ground water by Gas Chromatography with a Nitrogen-Phosphorus Detector

* Procedure has been approved for SDWA use
** National Pesticide Survey Methods

Method Performance Data

The data obtained through EMSL-Cincinnati's WS, WP and DMR-QA performance evaluation sample studies, although limited to a purge water matrix, can be used to establish certain performance characteristics of methods used by environmental monitoring laboratories. In addition, the performance of alternate methods for a specific analyte can be compared with one another, and can be used to compare method performance for a specific pollutant with the regulatory levels which have been established for that pollutant. Since the ultimate objective of the Agency's analytical methods review is to support the Agency's regulatory or enforcement activities, the precision, mean recovery, and detection limits of the methods for each regulated pollutant should be sufficient to ensure that the resulting data will be of adequate, known quality and legally defensible.

The FWPCA WP performance evaluation studies and SDWA WS performance evaluation studies are described in Chapter Six. The two programs consist of sending prepared sample concentrates with specified analytes at unknown concentrations, to governmental, industrial and commercial laboratories. These laboratories analyze the samples and report the results back to EMSL- Cincinnati. The data from the WP and WS studies have been used by EPA to establish the precision, mean recovery, and to a limited degree practical quantitation limits for a number of the 40 CFR 136 methods and SDWA methods, by typical users.

Precision and mean recovery are expressed in the form of linear regression equations which represent overall, interlaboratory values for standard deviation of a single measurement of each analyte (precision) and the expected recovery of that analyte using a specified analytical method. This is the same form of regression analysis used to construct the control limits promulgated in the methods for organic chemicals in Appendix A of 40 CFR 136. Since participants can select any methods approved for an analyte when multiple methods are available for the analyte, analysis of the WS and WP data bases result in regression equations which in some instances can be used to compare the performance of two analytical methods.

The total number of analytes and corresponding methods found in the WS and WP data bases are shown in Tables IV-4 through IV-6, grouped following 40 CFR 136 as inorganics, non-pesticide organics, and pesticides. These lists exclude any analyte or method that had insufficient data (statistical elements for at least two true values and seven or more reported values for at least one of those true values) to develop regression equations for mean recovery and precision.

In this report, the regression equations for precision and mean recovery of specific methods developed from the WS and WP studies are compared with the equations used to specify the QA/QC control limits for the promulgated methods, where such equations are available. This comparison of the control limits equations to the actual performance gives a good indication of how closely the QA/QC methods are being followed and how realistically achievable they are. Where the WS and WP studies had data for the same analyte and the same analytical method, the regression equations used in this and subsequent comparisons were based on the combined WS and WP data.

The regression equations for precision and mean recovery can be used effectively to evaluate how well the analytical methods support regulatory goals. This is done by using the equations for a specific method and constituent to calculate the expected precision and mean recovery of measurements at the applicable regulatory limit. This has been done in tabular form as shown by the examples in Table IV-7 through IV-10. These four tables present method performance data for arsenic (Table IV-7), barium (Table IV-8), 1,1,1-trichloroethane (Table IV-9), and aldrin (Table IV-10). The tables for all chemicals and analytical methods which were compared in this way are included in the Appendix to this report. Only those methods for which there were sufficient performance evaluation data in the WS and WP data bases to develop precision and mean recovery regression equations were compared. For some methods

and chemicals, there are insufficient data to develop reliable regression equations.

In Tables IV-7 through IV-10, method performance is shown for each analytical method which is applicable. The range of analyte concentrations under the term "database range" shown in the table represents the extremes of the true values for the test solutions sent to the participating laboratories. Extrapolation of the regression equations for precision and mean recovery outside these ranges results in precision and mean recovery estimates which are inherently more uncertain than estimates within the range. In this evaluation, however, extrapolation was done if the concentration of interest was within one order of magnitude of the low or high ends of this concentration range.

Three regression equations derived from the WS and WP data are shown: mean recovery in units of mass per unit of sample volume (for example, micrograms per liter, milligrams per liter); mean recovery expressed as a percentage of the true concentration in the check sample; and precision, expressed as mass per unit of sample volume. The precision equation calculates the standard deviation of the analytical measurements about the true value of the sample concentration. It can be used directly to calculate the range of expected measurements at any desired concentration level by simply multiplying by the number of standard deviations from the true concentration for a desired probability level. For example, the 95 percent probability level is 1.96 standard deviations from the mean recovery. Thus, the range of measurements which could be expected to occur 95 percent of the time for a specified true concentration (or regulatory limit) may be estimated by multiplying the precision estimated from the applicable regression equation by 1.96 and adding or subtracting the resulting value from the mean recovery of the true concentration.

For evaluation of the performance of the analytical methods in relation to regulatory requirements, four water-based regulatory levels are used as shown in the example in Table IV-7 through IV-10. These regulatory levels are as follows:

- SDWA maximum contaminant levels (MCLs)
- FWPCA industrial effluent limitations guidelines (ELG)
- FWPCA industrial categorical pretreatment standards (PS)
- FWPCA 303 water quality criteria (Gold Book).

The SDWA MCLs as used in these comparisons are promulgated or proposed primary and secondary MCLs wherever possible. For some water quality constituents, there are no current promulgated drinking water standards, so criteria which were previously developed by EPA (Quality Criteria for Water, July 1976, EPA) were used for drinking water. For certain organic chemicals, EPA has proposed recommended maximum contaminant levels (RMCLs, now called maximum contaminant level goals-MCLG) and these have been used as the basis of comparison with the analytical methods performance. If the RMCLs or MCLGs are zero, which is the case for chemicals suspected or known to be carcinogenic, and there is no proposed MCL, then adjusted acceptable daily intakes (AADI) were used if available. The categorical industrial effluent limitations guidelines (ELG) and pretreatment standards (PS) establish maximum allowable discharges of conventional, nonconventional, and toxic pollutants to receiving waters and publicly owned treatment works (POTWs), respectively. These ELG and PS serve as the basis for permit limits for specific plants unless water quality-based standards, which are more stringent, are used to derive the permit limits. The permittee must self-monitor its discharge, using approved analytical methods, to document to the regulatory agencies that the permit limits are being achieved. The regulatory agencies may also collect samples of a discharger's effluent and analyze them to determine compliance with the permit.

Most of these guidelines and standards are promulgated as mass discharges of a pollutant per unit of manufacturing production or raw

Table IV-4 List of Analytes and Methods with Regression Equations in Combined WS and WP Studies

INORGANICS

5-DAY BOD			
METHOD	11	R24 - 405.1	WINKLER (AZIDE MODIFICATION)
METHOD	22	R53 - 507.1	WINKLER (AZIDE MODIFICATION)
METHOD	52	R34 - 33.019	ELECTRODE
ALUMINUM			
METHOD	13	R19 - 200.7	INDUCTIVELY COUPLED PLASMA (ICP)
METHOD	14	R24 - 202.1	ATOMIC ABSORPTION (AA)
METHOD	15	R24 - 202.2	AA; FURNACE
METHOD	23	R53 - 303C	AA
METHOD	24	R53 - 304	AA; FURNACE
AMMONIA-NITROGEN			
METHOD	14	R24 - 350.2	TITRATION
METHOD	15	R24 - 350.3	ELECTRODE
METHOD	16	R24 - 350.1	AUTOMATED PHENATE
METHOD	17	R24 - 350.2	NESSLERIZATION
METHOD	24	R53 - 417B	NESSLERIZATION
METHOD	25	R53 - 417D	TITRATION
METHOD	26	R53 - 417G	AUTOMATED PHENATE
METHOD	27	R53 - 417E	ELECTRODE
ANTIMONY			
METHOD	13	R24 - 204.1	AA
METHOD	14	R24 - 204.2	AA; FURNACE
METHOD	15	R19 - 200.7	ICP
METHOD	21	R53 - 303A	AA
METHOD	22	R53 - 304	AA; FURNACE
ARSENIC			
METHOD	14	R19 - 200.7	ICP
METHOD	15	R24 - 206.2	AA; FURNACE
METHOD	16	R24 - 206.3	AA; GASEOUS HYDRIDE
METHOD	17	R24 - 206.4	SILVER DIETHYLDITHIOCARBAMATE
METHOD	24	R3 - 404A AFTER B(4)	SILVER DIETHYLDITHIOCARBAMATE
METHOD	25	R3 - 301A-VII	AA; GASEOUS HYDRIDE
METHOD	26	R53 - 303E	AA; GASEOUS HYDRIDE
METHOD	27	R53 - 304	AA; FURNACE
METHOD	32	R25 - D2972-78B	AA; GASEOUS HYDRIDE
BARIUM			
METHOD	14	R24 - 208.1	AA
METHOD	15	R24 - 208.2	AA; FURNACE
METHOD	22	R3 - 301A-IV	AA
BERYLLIUM			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 210.1	AA
METHOD	15	R24 - 210.2	AA; FURNACE
METHOD	23	R53 - 303C	AA

Table IV-4 (Continued)

INORGANICS

CADMIUM			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 213.1	AA
METHOD	15	R24 - 213.2	AA; FURNACE
METHOD	23	R3 - 301A-II	AA
METHOD	25	R3 - 301A-III	AA
METHOD	26	R53 - 303A	AA
METHOD	28	R53 - 304	AA; FURNACE
CALCIUM			
METHOD	12	R19 - 200.7	ICP
METHOD	13	R24 - 215.1	AA
METHOD	14	R24 - 215.2	EDTA
METHOD	21	R3 - 301A	AA
METHOD	22	R3 - 306C	EDTA
METHOD	23	R53 - 303A	AA
METHOD	24	R53 - 311C	EDTA
CHLORIDE			
METHOD	13	R24 - 325.3	MERCURIC NITRATE
METHOD	14	R24 - 325.1	AUTOMATED FERRICYANIDE
METHOD	15	R24 - 325.2	AUTOMATED FERRICYANIDE
METHOD	24	R53 - 407A	SILVER NITRATE
METHOD	25	R53 - 407B	MERCURIC NITRATE
CHROMIUM			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 218.1	AA
METHOD	15	R24 - 218.2	AA; FURNACE
METHOD	24	R3 - 301A-II	AA
METHOD	26	R3 - 301A-III	AA
METHOD	27	R53 - 303A	AA
METHOD	29	R53 - 304	AA; FURNACE
COBALT			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 219.1	AA
METHOD	15	R24 - 219.2	AA; FURNACE
METHOD	22	R53 - 303A	AA
METHOD	24	R53 - 304	AA; FURNACE
COD			
METHOD	12	R24 - 410.1	DICHROMATE REFLUX
METHOD	13	R24 - 410.2	DICHROMATE REFLUX
METHOD	14	R24 - 410.3	DICHROMATE REFLUX
METHOD	15	R24 - 410.4	SPECTROPHOTOMETRIC
METHOD	22	R53 - 508A	DICHROMATE REFLUX
METHOD	54	R41 - 8000	SPECTROPHOTOMETRIC
METHOD	55	R42 - P. 1	SPECTROPHOTOMETRIC

Table IV-4 (Continued)

INORGANICS

COPPER			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 220.1	AA
METHOD	15	R24 - 220.2	AA; FURNACE
METHOD	23	R53 - 303A	AA
METHOD	25	R53 - 304	AA; FURNACE
METHOD	54	R41 - 8506	BICINCHONINATE
CORROSIVITY			
METHOD	21	R3 - 203	LANGELIER INDEX
FLUORIDE			
METHOD	14	R24 - 340.1	SPADNS
METHOD	15	R24 - 340.2	MANUAL ELECTRODE
METHOD	16	R24 - 340.3	AUTOMATED COMPLEXONE
METHOD	24	R3 - 414B	ELECTRODE
METHOD	25	R3 - 414A AND C	SPADNS
METHOD	27	R53 - 413B	MANUAL ELECTRODE
METHOD	28	R53 - 413C	SPANDS
METHOD	44	R52 - I-4327-84	AUTOMATED ELECTRODE
METHOD	52	R28 - 380-75WE	ELECTRODE
IRON			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 236.1	AA
METHOD	15	R24 - 236.2	AA; FURNACE
METHOD	23	R53 - 303A	AA
METHOD	26	R53 - 315B	PHENANTHROLINE
METHOD	53	R44 - 8008	PHENANTHROLINE
KJELDAHL-NITROGEN			
METHOD	14	R24 - 351.3	NESSLERIZATION
METHOD	15	R24 - 351.4	POTENTIOMETRIC
METHOD	16	R24 - 351.2	SEMI-AUTOMATED BLOCK DIGESTION
METHOD	17	R24 - 351.3	TITRATION
METHOD	18	R24 - 351.3	ELECTRODE
METHOD	19	R24 - 351.1	AUTOMATED PHENATE
METHOD	23	R53 - 420A + 417D	TITRATION
METHOD	24	R53 - 420A + 417E	NESSLERIZATION
METHOD	25	R53 - 420A + 417E	ELECTRODE
METHOD	27	R53 - 420B + 417B	NESSLERIZATION
LEAD			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 239.1	AA
METHOD	15	R24 - 239.2	AA; FURNACE
METHOD	23	R3 - 301A-II	AA
METHOD	25	R3 - 301A-III	AA
METHOD	26	R53 - 303A	AA
METHOD	28	R53 - 304	AA; FURNACE

Table IV-4 (Continued)

INORGANICS

MAGNESIUM			
METHOD	12	R19 - 200.7	ICP
METHOD	13	R24 - 242.1	AA
METHOD	23	R53 - 303A	AA
METHOD	24	R53 - 318B	GRAVIMETRIC
MANGANESE			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 243.1	AA
METHOD	15	R24 - 243.2	AA; FURNACE
METHOD	24	R53 - 303A	AA
METHOD	27	R53 - 319B	PERSULFATE
METHOD	54	R41 - 8034	PERIODATA (PP. 2-113 AND 2-117)
MERCURY			
METHOD	13	R24 - 245.1	MANUAL COLD VAPOR
METHOD	14	R24 - 245.2	AUTOMATED COLD VAPOR
METHOD	21	R3 - 301A-VI	MANUAL COLD VAPOR
METHOD	22	R53 - 303F	MANUAL COLD VAPOR
MOLYBDENUM			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 246.1	AA
METHOD	15	R24 - 246.2	AA; FURNACE
METHOD	21	R53 - 303C	AA
NICKEL			
METHOD	13	R19 - 200.7	ICP
METHOD	14	R24 - 249.1	AA
METHOD	15	R53 - 249.2	AA; FURNACE
METHOD	23	R53 - 303A	AA
METHOD	25	R53 - 304	AA; FURNACE
NITRATE-NITROGEN			
METHOD	15	R24 - 352.1	BRUCINE SULFATE
METHOD	16	R24 - 353.1	AUTOMATED HYDRAZINE REDUCTION
METHOD	17	R24 - 353.2	AUTOMATED CADMIUM REDUCTION
METHOD	18	R24 - 353.3	CADMIUM REDUCTION
METHOD	19	R24 - 300.0	ION CHROMATOGRAPHIC (SUPPRESSED)
METHOD	26	R3 - 419C	CADMIUM REDUCTION
METHOD	27	R3 - 419D	BRUCINE SULFATE
METHOD	27	R3 - 419D	BRUCINE SULFATE
METHOD	28	R3 - 605	AUTOMATED CADMIUM REDUCTION
METHOD	29	R53 - 418C	CADMIUM REDUCTION
METHOD	54	R37 - 93MM-79	ELECTRODE
METHOD	70	R53 - 418F	AUTOMATED CADMIUM REDUCTION
NON-FILTERABLE RESIDUE			
METHOD	12	R24 - 160.2	GLASS FIBER 103 TO 105 C
METHOD	23	R53 - 209C	GALSS FIBER 103 TO 105 C

Table IV-4 (Continued)

INORGANICS

OIL AND GREASE		
METHOD 12	R24 - 413.1	TRICLOOROTRIFLUOROETHANE GRIMTRC
METHOD 22	R53 - 503A	TRICLOOROTRIFLUOROETHANE GRIMTRC
ORTHOPHOSPHATE		
METHOD 13	R24 - 365.1	AUTOMATED ASCORBIC ACID REDUCTION
METHOD 14	R24 - 365.2	MANUAL ASCORBIC ACID REDUCTION
METHOD 15	R24 - 365.3	MANUAL TWO REAGENT
METHOD 24	R53 - 424F	MANUAL ASCORBIC ACID REDUCTION
PH-UNITS		
METHOD 12	R24 - 150.1	ELECTRODE
METHOD 21	R3 - 424	ELECTRODE
METHOD 22	R53 - 423	ELECTRODE
POTASSIUM		
METHOD 12	R19 - 200.7	ICP
METHOD 13	R24 - 258.1	AA
METHOD 23	R53 - 303A	AA
METHOD 24	R53 - 322B	FLAME PHOTOMETRIC
RESIDUAL FREE CHLORINE		
METHOD 24	R3 - 409F	DPD COLORIMETRIC
METHOD 25	R3 - 409E	DPD TITRAMETRIC
SELENIUM		
METHOD 12	R19 - 200.7	ICP
METHOD 13	R24 - 270.2	AA; FURNACE
METHOD 14	R24 - 270.3	AA; GASEOUS HYDRIDE
METHOD 22	R3 - 301A-VII	AA
METHOD 23	R53 - 304	AA; FURNACE
METHOD 24	R53 - 303E	AA; GASEOUS HYDRIDE
METHOD 31	R25 - D3859-79	AA; GASEOUS HYDRIDE
SILVER		
METHOD 13	R19 - 200.7	ICP
METHOD 14	R24 - 272.1	AA
METHOD 15	R24 - 272.2	AA; FURNACE
METHOD 24	R3 - 301A-II	AA
METHOD 26	R53 - 303A	AA
METHOD 28	R53 - 304	AA; FURNACE
SODIUM		
METHOD 12	R19 - 200.7	ICP
METHOD 13	R24 - 273.1	AA
METHOD 21	R3 - 320A	FLAME PHOTOMETRIC
METHOD 22	R53 - 303A	AA
METHOD 23	R53 - 325B	FLAME PHOTOMETRIC

Table IV-4 (Continued)

INORGANICS

SPECIFIC CONDUCTIVITY		
METHOD 12	R24 - 120.1	WHEATSTONE BRIDGE
METHOD 22	R53 - 205	WHEATSTONE BRIDGE
SULFATE		
METHOD 14	R24 - 375.3	GRAVIMETRIC
METHOD 15	R24 - 375.4	TURBIDIMETRIC
METHOD 16	R24 - 375.1	AUTOMATED COLORIMETER(BAR.CHLORANILATE)
METHOD 23	R53 - 426A	GRAVIMETRIC
METHOD 24	R53 - 426B	GRAVIMETRIC
METHOD 25	R33 - 246C	TURBIDIMETRIC
THALLIUM		
METHOD 13	R19 - 200.7	ICP
METHOD 14	R24 - 279.1	AA
METHOD 15	R24 - 279.2	AA; FURNACE
METHOD 21	R53 - 303A	AA
TITANIUM		
METHOD 13	R24 - 283,1	AA
METHOD 14	R24 - 283.2	AA; FURNACE
METHOD 21	R53 - 303C	AA
TOC		
METHOD 12	R24 - 415.1	COMBUSTION OR OXIDATION
METHOD 22	R53 - 505	COMBUSTION OR OXIDATION
METHOD 41	R9 - P. 41	COMBUSTION/INFRARED
TOTAL ALKALINITY		
METHOD 13	R24 - 310.1	MANUAL TITRATION
METHOD 14	R24 - 310.2	AUTOMATED TITRATION
METHOD 21	R3 - 403	MANUAL TITRATION
METHOD 22	R53 - 403	MANUAL TITRATION
TOTAL CYANIDE		
METHOD 13	R24 - 335.2	MANUAL SPECTROPHOTOMETRIC
METHOD 14	R24 - 335.3	AUTOMATED SPECTROPHOTOMETRIC
METHOD 23	R53 - 412C	TITRIMETRIC
METHOD 24	R53 - 412D	MANUAL SPECTROPHOTOMETRIC
TOTAL FILTERABLE RESIDUE		
METHOD 12	R24 - 160.1	GLASS FIBER FILTRATION, 180 C
METHOD 21	R3 - 208B	GLASS FIBER FILTRATION, 180 C
METHOD 22	R53 - 209B	GLASS FIBER FILTRATION, 180 C

Table IV-4 (Continued)

INORGANICS

TOTAL HARDNESS		
METHOD 14	R24 - 130.1	AUTOMATED COLORIMETRIC
METHOD 15	R24 - 130.2	EDTA
METHOD 16	R24 - 215.1 + 242.1	AA (SUM OF CA AND MG AS CORBONATE)
METHOD 22	R53 - 314B	EDTA
METHOD 23	R53 - 303A	AA (SUM OF CA AMD MG AS CARBONATE)
TOTAL PHENOLICS		
METHOD 11	R24 - 420.1	MANUAL 4-AAP WITH DISTILLATION
METHOD 12	R24 - 420.2	AUTOMATED 4-AAP WITH DISTILLATION
METHOD 21	R3 - 510A + 510B	MANUAL 4-AAP WITH DIST.+CHLOROFORM EXTR.
METHOD 22	R3 - 510A + 510C	MANUAL 4-AAP WITH DISTILLATION
METHOD 31	R25 - D1783-80A	MANUAL 4-AAP WITH DIST.+CHLOROFORM EXTR
TOTAL PHOSPHORUS		
METHOD 13	R24 - 365.2	MANUAL ASCORBIC ACID REDUCTION
METHOD 14	R24 - 365.3	MAN. ASC. ACID RED. (2 REAGENTS)
METHOD 15	R24 - 365.1	AUTOMATED ASCORBIC ACID RED.
METHOD 16	R24 - 365.4	SEMI-AUTO. BLOCK DIGESTION
METHOD 24	R53 - 424F	MANUAL ASCORBIC ACID REDUCTION
TOTAL RESIDUAL CHLORINE		
METHOD 11	R24 - 330.1	TITRIMETRIC - AMPEROMETRIC
METHOD 12	R24 - 330.2	STARCH AND PRINT
METHOD 13	R24 - 330.3	IODOMETRIC
METHOD 14	R24 - 330.4	DPD-FAS
METHOD 15	R24 - 330.5	SPECTROPHOTOMETRIC, DPD
METHOD 21	R53 - 408A	IODOMETRIC
METHOD 22	R53 - 408B	STARCH AND POINT
METHOD 23	R53 - 408C	TITRIMETRIC - AMPEROMETRIC
METHOD 24	R53 - 408D	DPD - FAS
METHOD 25	R53 - 408E	SPECTROPHOTOMETRIC, DPD
TURBIDITY		
METHOD 12	R24 - 180.1	NEPHELOMETRIC
METHOD 22	R3 - 214A	NEPHELOMETRIC
VANADIUM		
METHOD 13	R19 - 200.7	ICP
METHOD 14	R24 - 286.1	AA
METHOD 15	R24 - 286.2	AA; FURNACE
METHOD 23	R53 - 303C	AA
METHOD 24	R53 - 304	AA; FURNACE
ZINC		
METHOD 13	R19 - 200.7	ICP
METHOD 14	R24 - 289.1	AA
METHOD 15	R24 - 289.2	AA; FURNACE
METHOD 23	R53 - 303A	AA

Table IV-5 List of Analytes and Methods with Regression Equations in Combined WS and WP Studies

ORGANICS

1,1,1-TRICHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	13	R54 - 624	GC/MS
METHOD	14	R54 - 601	GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD	16	R55 - 524.2	PURGE AND TRAP, CAP. COLUMN GC/MS
METHOD	17	R56 - 502.2	PURGE AND TRAP, CAP. COLUMN GC
1,1,1,2-TETRACHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,1,2,2-TETRACHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,1,2-TRICHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,1-DICHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,1-DICHLOROETHENE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD	16	R55 - 524.2	PURGE AND TRAP, CAP. COLUMN GC/MS
METHOD	17	R56 - 502.2	PURGE AND TRAP, CAP. COLUMN GC
1,1-DICHLOROPROPANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,2-DICHLOROETHANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	13	R54 - 624	GC/MS
METHOD	14	R54 - 601	GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD	16	R55 - 524.2	PURGE AND TRAP, CAP. COLUMN GC/MS
METHOD	17	R56 - 502.2	PURGE AND TRAP, CAP. COLUMN GC
1,2,3-TRICHLOROPROPANE			
METHOD	11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD	15	R55 - 524.1	PURGE AND TRAP, GC/MS

Table IV-5 (Continued)

ORGANICS

1,2-DICHLOROBENZENE		
METHOD 11	R54 - 601	GC
METHOD 12	R54 - 602	GC
METHOD 14	R54 - 624	GC/MS
METHOD 15	R54 - 625	GC/MS
1,3-DICHLOROBENZENE		
METHOD 11	R54 - 601	GC
METHOD 12	R54 - 602	GC
METHOD 14	R54 - 624	GC/MS
METHOD 15	R54 - 625	GC/MS
1,3-DICHLOROPROPANE		
METHOD 11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 15	R55 - 524.1	PURGE AND TRAP, GC/MS
1,4-DICHLOROBENZENE		
METHOD 11	R54 - 601	GC
METHOD 12	R54 - 602	GC
METHOD 15	R54 - 625	GC/MS
2,2-DICHLOROPROPANE		
METHOD 11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 15	R55 - 524.1	PURGE AND TRAP, GC/MS
BENZENE		
METHOD 11	R54 - 602	GC
METHOD 12	R54 - 624	GC/MS
BROMODICHLOROMETHANE		
METHOD 11	R30 - 501.1	PURGE AND TRAP, HALIDE GC
METHOD 12	R31 - 501.2	LIQUID/LIQUID, ECGC
METHOD 13	R54 - 624	GC/MS
METHOD 14	R54 - 601	GC
METHOD 18	R39 - 501.3	PURGE AND TRAP, SELECTED ION GC/MS
METHOD 19	R48 - 524	PURGE AND TRAP, GC/MS
BROMOFORM		
METHOD 11	R30 - 501.1	PURGE AND TRAP, HALIDE GC
METHOD 11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 12	R31 - 501.2	LIQUID/LIQUID, ECGC
METHOD 13	R54 - 624	GC/MS
METHOD 14	R54 - 601	GC
METHOD 15	R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD 18	R39 - 501.3	PURGE AND TRAP, SELECTED ION GC/MS
METHOD 19	R48 - 524	PURGE AND TRAP, GC/MS

Table IV-5 (Continued)

ORGANICS

CARBONTETRACHLORIDE		
METHOD 13	R54 - 624	GC/MS
METHOD 14	R54 - 601	GC
CHLOROBENZENE		
METHOD 11	R54 - 601	GC
METHOD 12	R54 - 602	GC
METHOD 13	R54 - 624	GC/MS
CHLOROFORM		
METHOD 11	R30 - 501.1	PURGE AND TRAP, HALIDE GC
METHOD 12	R31 - 501.2	LIQUID/LIQUID, ECGC
METHOD 18	R39 - 501.3	PURGE AND TRAP, SELECTED ION GC/MS
METHOD 19	R48 - 524	PURGE AND TRAP, GC/MS
DIBROMOCHLOROMETHANE		
METHOD 11	R30 - 501.1	PURGE AND TRAP, HALIDE GC
METHOD 12	R31 - 501.2	LIQUID/LIQUID, ECGC
METHOD 13	R54 - 624	GC/MS
METHOD 14	R54 - 601	GC
METHOD 18	R39 - 501.3	PURGE AND TRAP, SELECTED ION GC/MS
METHOD 19	R48 - 524	PURGE AND TRAP, GC/MS
DIBROMOMETHANE		
METHOD 11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 15	R55 - 524.1	PURGE AND TRAP, GC/MS
ETHYLBENZENE		
METHOD 11	R54 - 602	GC
METHOD 12	R54 - 624	GC/MS
METHYLENE CHLORIDE		
METHOD 11	R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 13	R54 - 624	GC/MS
METHOD 14	R54 - 601	GC
METHOD 15	R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD 16	R55 - 524.2	PURGE AND TRAP, CAP. COLUMN GC/MS
METHOD 17	R56 - 502.2	PURGE AND TRAP, CAP. COLUMN GC
PCB-AROCLOR 1016/1242		
METHOD 16	R54 - 608	GC
METHOD 18	R46 - P. 43	GC
PCB-AROCLOR 1232		
METHOD 16	R54 - 608	GC
METHOD 18	R46 - P. 43	GC

Table IV-5 (Continued)

ORGANICS	
PCB-AROCLOR 1248	
METHOD 16 R54 - 608	GC
METHOD 18 R46 - P. 43	GC
PCB-AROCLOR 1254	
METHOD 16 R54 - 608	GC
METHOD 18 R46 - P. 43	GC
PCB-AROCLOR 1260	
METHOD 16 R54 - 608	GC
METHOD 18 R46 - P. 43	GC
TETRACHLOROETHENE	
METHOD 13 R54 - 624	GC/MS
METHOD 14 R54 - 601	GC
TOLUENE	
METHOD 11 R54 - 602	GC
METHOD 12 R54 - 624	GC/MS
TOTAL TRIHALOMETHANE	
METHOD 11 R30 - 501.1	PURGE AND TRAP, HALIDE GC
METHOD 12 R31 - 501.2	LIQUID/LIQUID, ECGC
METHOD 18 R39 - 501.3	PURGE AND TRAP, SELECTED ION GC/MS
METHOD 19 R48 - 524	PURGE AND TRAP, GC/MS
TRICHLOROETHENE	
METHOD 11 R55 - 502.1	PURGE AND TRAP, HALIDE GC
METHOD 13 R54 - 624	GC/MS
METHOD 14 R54 - 601	GC
METHOD 15 R55 - 524.1	PURGE AND TRAP, GC/MS
METHOD 16 R55 - 524.2	PURGE AND TRAP, CAP. COLUMN GC/MS
METHOD 17 R56 - 502.2	PURGE AND TRAP, CAP. COLUMN GC

Table IV-6 List of Analytes and Methods with Regression Equations in Combined WS and WP Studies

PESTICIDES

2,4,5-TP (SILVEX)			
METHOD	12	R29 - P. 20	DERIVATIZATION-GC
METHOD	21	R3 - 509B	DERIVATIZATION-GC
METHOD	32	R25 - D3478-79	DERIVATIZATION-GC
2,4-D			
METHOD	12	R29 -P. 20	DERIVATIZATION-GC
METHOD	21	R3 -509B	DERIVATIZATION-GC
METHOD	32	R25 - D3478-79	DERIVATIZATION-GC
ALDRIN			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
CHLORDANE			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
DDD			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
DDE			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
DDT			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
DIELDRIN			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC
ENDRIN			
METHOD	14	R29 - P. 1	GC
METHOD	22	R3 - 509A	GC
HEPTACHLOR			
METHOD	16	R54 - 608	GC
METHOD	18	R46 - P. 7	GC
METHOD	23	R33 - 509A	GC

Table IV-6 (Continued)

PESTICIDES		
HEPTACHLOR EPOXIDE		
METHOD 16	R54 - 608	GC
METHOD 18	R46 - P. 7	GC
METHOD 23	R33 - 509A	GC
LINDANE		
METHOD 14	R29 - P. 1	GC
METHOD 22	R3 - 509Ai	GC
METHOXYCHLOR		
METHOD 14	R29 - P. 1	GC
METHOD 22	R3 - 509A	GC
METHOD 32	R25 - D3086-79	GC
TOXAPHENE		
METHOD 14	R29 - P. 1	GC
METHOD 22	R3 - 509A	GC
METHOD 41	R9 - P.24	GC

Table IV-7 Method Performance and Comparison with Drinking Water Standards, Discharge Limitations, and Water Quality Criteria

ARSENIC
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)		50.0	30.0	50.0	0.0022
METHOD 14 R19 - 200.7					
ICP					
Published performance data					
Database range (ug/L)	[69.00 - 1887.00]				
Accuracy (ug/L)	X=1.044T-12.200	40.0	19.1	40.0	OTR
Accuracy (%)	P=104.4-1220.0/T	80.0%	63.7%	80.0%	OTR
Overall precision (ug/L)	S=0.124X+ 2.400	7.36	4.77	7.36	OTR
Intralab MDL*** (ug/L)	53.0				
WS and WP studies (Number of analyses = 185)					
Database range (ug/L)	[13.00 - 468.00]				
Accuracy (ug/L)	X=1.030T+ 2.455	54.0	33.4	54.0	OTR
Accuracy (%)	P=103.0+ 245.5/T	107.9%	111.2%	107.9%	OTR
Overall precision (ug/L)	S=0.083T+ 3.709	7.86	6.20	7.86	OTR
Interlab MDL+ (ug/L)	5.13 (MDL meets all criteria.)				
METHOD 15 R24 - 206.2					
AA; FURNACE					
Published performance data					
Database range (ug/L)	[9.78 - 237.00]				
Accuracy (ug/L)	X=0.965T+ 2.112	50.4	31.1	50.4	OTR
Accuracy (%)	P= 96.5+ 211.2/T	100.7%	103.6%	100.7%	OTR
Overall precision (ug/L)	S=0.141X+ 1.873	8.98	6.26	8.98	OTR
Intralab MDL*** (ug/L)	1.00				
WS and WP studies (Number of analyses = 4458)					
Database range (ug/L)	[13.00 - 468.00]				
Accuracy (ug/L)	X=0.975T+ 0.433	49.2	29.7	49.2	OTR
Accuracy (%)	P= 97.5+ 43.3/T	98.4%	98.9%	98.4%	OTR
Overall precision (ug/L)	S=0.108T+ 0.423	5.82	3.66	5.82	OTR
Interlab MDL+ (ug/L)	4.85 (Does not meet criterion 1.)				
METHOD 16 R24 - 206.3					
AA; GASEOUS HYDRIDE					
Published performance data					
Intralab MDL*** (ug/L)	2.00				
WS and WP studies (Number of analyses = 1120)					
Database range (ug/L)	[13.00 - 468.00]				
Accuracy (ug/L)	X=0.937T+ 0.420	47.3	28.5	47.3	OTR
Accuracy (%)	P= 93.7+ 42.0/T	94.5%	95.1%	94.5%	OTR
Overall precision (ug/L)	S=0.195T+ 1.034	10.8	6.88	10.8	OTR
Interlab MDL+ (ug/L)	6.93 (MDL meets all criteria.)				

Table IV-7 (Continued)

ARSENIC
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)		50.0	30.0	50.0	0.0022
METHOD 17 R24 - 206.4					
SILVER DIETHYLDITHIOCARBAMATE					
Published performance data					
Database range (ug/L)	[20.00 - 292.00]				
Accuracy (ug/L)	X=0.850T- 0.250	42.3	25.3	42.3	OTR
Accuracy (%)	P= 85.0- 25.0/T	84.5%	84.2%	84.5%	OTR
Overall precision (ug/L)	S=0.198X+ 5.930	14.3	10.9	14.3	OTR
Intralab MDL*** (ug/L)	10.0				
WS and WP studies (Number of analyses = 107)					
Database range (ug/L)	[15.00 - 112.00]				
Accuracy (ug/L)	X=1.011T- 2.555	48.0	27.8	48.0	OTR
Accuracy (%)	P=101.1- 255.5/T	96.0%	92.6%	96.0%	OTR
Overall precision (ug/L)	S=0.091T+ 3.993	8.54	6.72	8.54	OTR
Interlab MDL+ (ug/L)	17.4 (Does not meet criteria 2 and 3.)				
METHOD 24 R3 - 404A AFTER B(4)					
SILVER DIETHYLDITHIOCARBAMATE					
Published performance data					
Intralab MDL*** (ug/L)	(Not available.)				
WS and WP studies (Number of analyses = 106)					
Database range (ug/L)	[15.00 - 112.00]				
Accuracy (ug/L)	X=0.955T+ 0.613	48.4	29.3	48.4	OTR
Accuracy (%)	P= 95.5+ 61.3/T	96.7%	97.5%	96.7%	OTR
Overall precision (ug/L)	S=0.169T+ 2.189	10.6	7.26	10.6	OTR
Interlab MDL+ (ug/L)	14.6 (Does not meet criteria 1 and 3.)				
METHOD 25 R3 - 301A-VII					
AA;GASEOUS HYDRIDE					
Published performance data					
Intralab MDL*** (ug/L)	(Not available.)				
WS and WP studies (Number of analyses = 301)					
Database range (ug/L)	[15.00 - 112.00]				
Accuracy (ug/L)	X=0.985T+ 0.150	49.4	29.7	49.4	OTR
Accuracy (%)	P= 98.5+ 15.0/T	98.8%	99.0%	98.8%	OTR
Overall precision (ug/L)	S=0.211T- 0.381	10.2	5.95	10.2	OTR
Interlab MDL+ (ug/L)	8.74 (Does not meet criterion 1.)				

Table IV-7 (Continued)

ARSENIC
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)		50.0	30.0	50.0	0.0022
METHOD 26 R53 - 303E					
AA; GASEOUS HYDRIDE					
Published performance data					
Intralab MDL*** (ug/L)	2.00				
WS and WP studies (Number of analyses = 203)					
Database range (ug/L)	[13.00 - 468.00]				
Accuracy (ug/L)	X=0.929T+ 0.312	46.8	28.2	46.8	OTR
Accuracy (%)	P= 92.9+ 31.2/T	93.5%	93.9%	93.5%	OTR
Overall precision (ug/L)	S=0.307T- 0.259	15.1	8.95	15.1	OTR
Interlab MDL+ (ug/L)	10.1 (Does not meet criterion 3.)				
METHOD 27 R53 - 304					
AA;FURNACE					
Published performance data					
Intralab MDL*** (ug/L)	1.00				
WS and WP studies (Number of analyses = 162)					
Database range (ug/L)	[13.00 - 468.00]				
Accuracy (ug/L)	X=0.965T+ 1.148	49.4	30.1	49.4	OTR
Accuracy (%)	P= 96.5+ 114.8/T	98.8%	100.3%	98.8%	OTR
Overall precision (ug/L)	S=0.101T+ 2.487	7.54	5.52	7.54	OTR
Interlab MDL+ (ug/L)	10.8 (Does not meet criteria 1 and 3.)				
METHOD 32 R25 - D2972-78B					
AA; GASEOUS HYDRIDE					
Published performance data					
Intralab MDL*** (ug/L)	1.00				
WS and WP studies (Number of analyses = 68)					
Database range (ug/L)	[15.00 - 112.00]				
Accuracy (ug/L)	X=0.998T- 1.118	48.8	28.8	48.8	OTR
Accuracy (%)	P= 99.8- 111.8/T	97.6%	96.1%	97.6%	OTR
Overall precision (ug/L)	S=0.188T- 0.512	8.89	5.13	8.89	OTR
Interlab MDL+ (ug/L)	8.07 (Does not meet criterion 1.)				

Table IV-7 (Continued)

ARSENIC
(CONCENTRATIONS are in ug/L)

NSC - No standard or criterion
OTR - Outside the range for extrapolating the regression equations. Range is one-half the lower database range value to 2 times the upper database range value.

(a) Final regulations, 40CFR141.11
(b) Proposed BAT, Option 1, 50FR29082
(c) Proposed PSES, Option I, 50FR29086
(d) Human health, drinking and fish ingestion

* See note 1 (regression equations), at beginning of Appendix.
** See note 2 (limit concentrations), at beginning of Appendix.
***See note 3 (published intralab MDL), at beginning of Appendix.
\+ See note 4 (calculated interlab MDL), at beginning of Appendix.

Criteria for calculated MDL:
(1) The lowest true concentration of the analyte is less than or equal to 10 times the published MDL in reagent water.
(2) The lowest true concentration of the analyte is greater than the calculated MDL.
(3) Eighty percent (80%) of the laboratories (i.e., analytical results) are within plus or minus 40 percent of the lowest true concentration.

Table IV-8 Method Performance and Comparison with Drinking Water Standards, Discharge Limitations, and Water Quality Criteria

BARIUM
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)		1000.			
METHOD 14 R24 - 208.1					
AA					
Published performance data					
Intralab MDL*** (ug/L)	100.0				
WS and WP studies (Number of analyses = 2223)					
Database range (ug/L)	[63.00 - 882.00]				
Accuracy (ug/L)	X=0.968T+ 5.004	973.0	NSC	NSC	NSC
Accuracy (%)	P= 96.8+ 500.4/T	97.3%	NSC	NSC	NSC
Overall precision (ug/L)	S=0.075T+ 7.134	82.1	NSC	NSC	NSC
Interlab MDL+ (ug/L)	33.1 (MDL meets all criteria.)				
METHOD 15 R24 - 208.2					
AA; FURNACE					
Published performance data					
Database range (ug/L)	[56.50 - 437.00]				
Accuracy (ug/L)	X=0.827T+59.460	OTR	NSC	NSC	NSC
Accuracy (%)	P= 82.7+5946.0/T	OTR	NSC	NSC	NSC
Overall precision (ug/L)	S=0.247X+ 6.436	OTR	NSC	NSC	NSC
Intralab MDL*** (ug/L)	2.00				
WS and WP studies (Number of analyses = 1545)					
Database range (ug/L)	[63.00 - 882.00]				
Accuracy (ug/L)	X=0.974T+ 3.701	977.7	NSC	NSC	NSC
Accuracy (%)	P= 97.4+ 370.1/T	97.8%	NSC	NSC	NSC
Overall precision (ug/L)	S=0.105T+ 4.166	109.2	NSC	NSC	NSC
Interlab MDL+ (ug/L)	27.1 (Does not meet criterion 1.)				
METHOD 22 R3 - 301A-IV					
AA					
Published performance data					
Intralab MDL*** (ug/L)	30.0				
WS and WP studies (Number of analyses = 397)					
Database range (ug/L)	[63.00 - 882.00]				
Accuracy (ug/L)	X=0.943T+10.458	953.5	NSC	NSC	NSC
Accuracy (%)	P= 94.3+1045.8/T	95.3%	NSC	NSC	NSC
Overall precision (ug/L)	S=0.112T+13.018	125.0	NSC	NSC	NSC
Interlab MDL+ (ug/L)	60.3 (Does not meet criterion 3.)				

Table IV-8 (Continued)

BARIUM
(CONCENTRATIONS are in ug/L)

NSC - No standard or criterion
OTR - Outside the range for extrapolating the regression equations. Range is one-half the lower database range value to 2 times the upper database range value.

(a) Final regulations, 40CFR141.11
(b) No guideline
(c) No guideline
(d) No criterion

* See note 1 (regression equations), at beginning of Appendix.
** See note 2 (limit concentrations), at beginning of Appendix.
***See note 3 (published intralab MDL), at beginning of Appendix.
\+ See note 4 (calculated interlab MDL), at beginning of Appendix.

Criteria for calculated MDL:
(1) The lowest true concentration of the analyte is less than or equal to 10 times the published MDL in reagent water.
(2) The lowest true concentration of the analyte is greater than the calculated MDL.
(3) Eighty percent (80%) of the laboratories (i.e., analytical results) are within plus or minus 40 percent of the lowest true concentration.

Table IV-9 Method Performance and Comparison with Drinking Water Standards, Discharge Limitations, and Water Quality Criteria

ALDRIN
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)					0.000074
METHOD 16 R54 - 608					
GC					
Published performance data					
Intralab MDL*** (ug/L)	0.0040				
WS and WP studies (Number of analyses = 1446)					
Database range (ug/L)	[0.07 - 0.82]				
Accuracy (ug/L)	X=0.797T+ 0.004	NSC	NSC	NSC	OTR
Accuracy (%)	P= 79.7+ 0.4/T	NSC	NSC	NSC	OTR
Overall precision (ug/L)	S=0.220T+ 0.005	NSC	NSC	NSC	OTR
Interlab MDL+ (ug/L)	0.051 (Does not meet criteria 1 and 3.)				
METHOD 18 R46 - P. 7					
GC					
Published performance data					
Intralab MDL*** (ug/L)	(Not available.)				
WS and WP studies (Number of analyses = 64)					
Database range (ug/L)	[0.07 - 0.82]				
Accuracy (ug/L)	X=0.788T+ 0.000	NSC	NSC	NSC	OTR
Accuracy (%)	P= 78.8+ 0.0/T	NSC	NSC	NSC	OTR
Overall precision (ug/L)	S=0.159T+ 0.004	NSC	NSC	NSC	OTR
Interlab MDL+ (ug/L)	0.087 (Does not meet criteria 1,2, or 3.)				
METHOD 23 R33 - 509A					
GC					
Published performance data					
Intralab MDL*** (ug/L)	(Not available.)				
WS and WP studies (Number of analyses = 89)					
Database range (ug/L)	[0.07 - 0.82]				
Accuracy (ug/L)	X=0.768T+ 0.012	NSC	NSC	NSC	OTR
Accuracy (%)	P= 76.8+ 1.2/T	NSC	NSC	NSC	OTR
Overall precision (ug/L)	S=0.197T+ 0.013	NSC	NSC	NSC	OTR
Interlab MDL+ (ug/L)	0.054 (Does not meet criteria 1 and 3.)				

Table IV-9 (Continued)

ALDRIN
(CONCENTRATIONS are in ug/L)

NSC - No standard or criterion
OTR - Outside the range for extrapolating the regression equations. Range is one-half the lower database range value to 2 times the upper database range value.

(a) No standard
(b) No guideline
(c) No guideline
(d) Human health, drinking and fish ingestion

* See note 1 (regression equations), at beginning of Appendix.
** See note 2 (limit concentrations), at beginning of Appendix.
***See note 3 (published intralab MDL), at beginning of Appendix.
\+ See note 4 (calculated interlab MDL), at beginning of Appendix.

Criteria for calculated MDL:
(1) The lowest true concentration of the analyte is less than or equal to 10 times the published MDL in reagent water.
(2) The lowest true concentration of the analyte is greater than the calculated MDL.
(3) Eighty percent (80%) of the laboratories (i.e., analytical results) are within plus or minus 40 percent of the lowest true concentration.

Table IV-10 Method Performance and Comparison with Drinking Water Standards, Discharge Limitations, and Water Quality Criteria

1,1,1-TRICHLOROETHANE
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs (a)	CWA ELG (b)	CWA PTRT (c)	GOLD BOOK (d)
Standard/Criterion, T** (ug/L)		200.0	10.0	10.0	18400.
METHOD 13 R54 - 624					
GC/MS					
Published performance data					
Database range (ug/L)	[5.00 - 600.00]				
Accuracy (ug/L)	X=1.060T+ 0.730	212.7	11.3	11.3	OTR
Accuracy (%)	P=106.0+ 73.0/T	106.4%	113.3%	113.3%	OTR
Overall precision (ug/L)	S=0.210X- 0.390	44.3	1.99	1.99	OTR
Intralab MDL*** (ug/L)	3.80				
WS and WP studies (Number of analyses = 679)					
Database range (ug/L)	[4.08 - 73.80]				
Accuracy (ug/L)	X=1.024T+ 0.187	OTR	10.4	10.4	OTR
Accuracy (%)	P=102.4+ 18.7/T	OTR	104.3%	104.3%	OTR
Overall precision (ug/L)	S=0.148T+ 0.331	OTR	1.81	1.81	OTR
Interlab MDL+ (ug/L)	2.21 (MDL meets all criteria.)				
METHOD 14 R54 - 601					
GC					
Published performance data					
Database range (ug/L)	[8.00 - 500.00]				
Accuracy (ug/L)	X=0.900T- 0.160	179.8	8.84	8.84	OTR
Accuracy (%)	P= 90.0- 16.0/T	89.9%	88.4%	88.4%	OTR
Overall precision (ug/L)	S=0.200X+ 0.370	36.3	2.14	2.14	OTR
Intralab MDL*** (ug/L)	0.030				
WS and WP studies (Number of analyses = 764)					
Database range (ug/L)	[4.08 - 73.80]				
Accuracy (ug/L)	X=1.021T+ 0.139	OTR	10.3	10.3	OTR
Accuracy (%)	P=102.1+ 13.9/T	OTR	103.5%	103.5%	OTR
Overall precision (ug/L)	S=0.162T+ 0.671	OTR	2.29	2.29	OTR
Interlab MDL+ (ug/L)	3.63 (Does not meet criteria 1 and 3.)				

Table IV-10 (Continued)

1,1,1-TRICHLOROETHANE
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs(a)	CWA ELG(b)	CWA PTRT(c)	GOLD BOOK(d)
Standard/Criterion, T** (ug/L)		200.0	10.0	10.0	18400.
METHOD 11 R55 - 502.1					
PURGE AND TRAP, HALIDE GC					
Published performance data					
Database range (ug/L)	[Not available.]				
Accuracy (ug/L)	X=0.920T+ 0.020 (Not calculated, no database range.)				
Accuracy (%)	P= 92.0+ 2.0/T (Not calculated, no database range.)				
Overall precision (ug/L)	S=0.270X- 0.760 (Not calculated, no database range.)				
Intralab MDL*** (ug/L)	0.0030				
WS and WP studies	(Number of analyses = 237)				
Database range (ug/L)	[10.50 - 182.50]				
Accuracy (ug/L)	X=1.001T+ 0.289	200.5	10.3	10.3	OTR
Accuracy (%)	P=100.1+ 28.9/T	100.2%	103.0%	103.0%	OTR
Overall precision (ug/L)	S=0.223T+ 0.086	44.7	2.32	2.32	OTR
Interlab MDL+ (ug/L)	5.73 (Does not meet criterion 1.)				
METHOD 15 R55 - 524.1					
PURGE AND TRAP, GC/MS					
Published performance data					
Intralab MDL*** (ug/L)	0.26				
WS and WP studies	(Number of analyses = 138)				
Database range (ug/L)	[10.50 - 182.50]				
Accuracy (ug/L)	X=1.015T+ 0.402	203.4	10.6	10.6	OTR
Accuracy (%)	P=101.5+ 40.2/T	101.7%	105.5%	105.5%	OTR
Overall precision (ug/L)	S=0.251T- 0.780	49.4	1.73	1.73	OTR
Interlab MDL+ (ug/L)	4.41 (Does not meet criterion 1.)				
METHOD 16 R55 - 524.2					
PURGE AND TRAP, CAP. COLUMN GC/MS					
Published performance data					
Intralab MDL*** (ug/L)	0.080				
WS and WP studies	(Number of analyses = 74)				
Database range (ug/L)	[10.50 - 182.50]				
Accuracy (ug/L)	X=1.003T+ 0.860	201.5	10.9	10.9	OTR
Accuracy (%)	P=100.3+ 86.0/T	100.7%	108.9%	108.9%	OTR
Overall precision (ug/L)	S=0.273T- 0.257	54.3	2.47	2.47	OTR
Interlab MDL+ (ug/L)	6.35 (Does not meet criteria 1 and 3.)				

Table IV-10 (Continued)

1,1,1-TRICHLOROETHANE
(CONCENTRATIONS are in ug/L)

METHOD	REGRESSION EQUATIONS*	SDWA MCLs(a)	CWA ELG(b)	CWA PTRT(c)	GOLD BOOK(d)
Standard/Criterion, T** (ug/L)		200.0	10.0	10.0	18400.
METHOD 17 R56 - 502.2					
PURGE AND TRAP, CAP. COLUMN GC					
Published performance data					
Intralab MDL*** (ug/L)	0.030				
WS and WP studies (Number of analyses = 31)					
Database range (ug/L)	[10.50 - 182.50]				
Accuracy (ug/L)	X=0.751T+ 1.259	151.5	8.77	8.77	OTR
Accuracy (%)	P= 75.1+ 125.9/T	75.7%	87.7%	87.7%	OTR
Overall precision (ug/L)	S=0.554T- 2.372	108.4	3.17	3.17	OTR
Interlab MDL+ (ug/L)	8.96 (Does not meet criteria 1 and 3.)				

NSC - No standard or criterion
OTR - Outside the range for extrapolating the regression equations. Range is one-half the lower database range value to 2 times the upper database range value.

(a) Final regulations, 40CFR141.61
(b) Final regulations, 40CFR433, Stds are sum of specified TTO's above 10 ug/L
(c) Final regulations, 40CFR433, Stds are sum of specified TTO's above 10 ug/L
(d) Human health, drinking and fish ingestion

* See note 1 (regression equations), at beginning of Appendix.
** See note 2 (limit concentrations), at beginning of Appendix.
***See note 3 (published intralab MDL), at beginning of Appendix.
\+ See note 4 (calculated interlab MDL), at beginning of Appendix.

Criteria for calculated MDL:
(1) The lowest true concentration of the analyte is less than or equal to 10 times the published MDL in reagent water.
(2) The lowest true concentration of the analyte is greater than the calculated MDL.
(3) Eighty percent (80%) of the laboratories (i.e., analytical results) are within plus or minus 40 percent of the lowest true concentration.

Table IV-11 List of Approved Biological Test Procedures in 40 CFR 136.3

Parameter and units	Method[1]	EPA[2] Page #	Standard Methods 15th Ed.	ASTM	USGS
Bacteria:					
1. Coliform (fecal number per 100 mL)	MPN, 5 tube, 3 dilution; or, membrane filter (MF)[4], single step	132 124	908C 909C		B-0050-77
2. Coliform (fecal) in presence of chlorine number per 100 mL	MPN, 5 tube, 3 dilution; or, MF[4], single step	132 124	908C 909C		B-0050-77
3. Coliform (total), number per 100 mL)	MPN, 5 tube, 3 dilution; or, MF[4] single step or two step	114 108	908A 909A		B-0025-77 B-0025-77
4. Coliform (total) in presence of chlorine, number per 100 mL	MPN, 5 tube, 3 dilution; or MF[4] with enrichment	114 111	908A 909(A + A. 5c)		
5. Fecal streptococci, number per 100 mL	MPN, 5 tube, 3 dilution; MF[4] or, plate count	139 136 143	910A 910B 910C		B-0055-77

[1]The method used must be specified when results are reported.

[2]"Microbiological Methods for Monitoring the Environment, Water and Waste, 1978", EPA-600/8-78-017, U.S. Environmental Protection Agency.

[3]Greeson, P.E., et al., "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples", U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A4, Laboratory Analysis, 1977.

[4]0.45 um membrane filter or other pore size certified by the manufacturer to fully retain organisms to be cultivated, and free of extractables which could interfere with their growth and development.

[4A]Since the membrane filter technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.

[5]Approved only if dissolution of the KF Streptococcus Agar (Section 5.1, USGS Method B-0055-77) is made in a boiling water bath to avoid scorching of the medium.

material use. In this form, these are not useful for assessing the adequacy of analytical methods for documenting compliance or noncompliance. EPA's Development Documents for Effluent Limitations Guidelines and Standards, however, present the basis for the guidelines and standards, and identify the concentration basis for the limits which are expressed as mass per unit of production. However, by reviewing all available promulgated and recently proposed guidelines and standards, concentration ELG and PS which are representative of the minimum pollutant concentrations the Agency has used for all of its categorical guidelines and

standards were determined. Therefore, these ELG and PS minimum concentrations represent the most stringent test of the performance of the analytical methods for precision, mean recovery, and detection limits.

For certain of the organic chemical pollutants, the EPA has promulgated ELG and PS based on total toxic organics (TTO). TTO is defined as the sum of the concentrations of all of a specified list of organic priority pollutants which are present in a sample at a minimum concentration of 10 µg/L. Thus, 10 µg/L is used as the required limit on all such pollutants listed, since determination of compliance with the TTO standard requires quantitation of each specified chemical at or above 10 µg/L. Each table for each pollutant references the specific source of the concentrations used as ELG and PS limits.

The last column in the table presents the currently most restrictive water quality criterion. These criteria are taken from the EPA Gold Book (Quality Criteria for Water, 1986, EPA 440/5-86-001, May, 1986). The specific criterion used for the method performance evaluation is either an aquatic life or human health criterion, whichever is most restrictive for the particular chemical.

In addition to information relating to precision and mean recovery, Tables IV-7 through IV-10 present data relating to the published method detection limit (MDL) and an MDL calculated from the WP and WS data. The published MDL's are found in the EPA analytical method manuals and in 40 CFR 136. The published MDL's are usually generated by a single EPA laboratory, and are matrix-specific (usually they represent contaminant-free reagent water). A detection limit based on a non-replicative interlaboratory study would be expected to be significantly higher than an MDL.

The published MDL's are considered by EPA to be the maximum achievable sensitivity of a method for a specific water quality constituent and are not necessarily routinely attainable (see 50 FR 46907, 52 FR 25699). Because of this, EPA has defined a *practical quantitation limit* (PQL) for many analytical methods which must measure analytes at low concentration levels (see 50 FR 46907, 52 FR 25699). The PQL for certain volatile SDWA analytes was defined as the lowest concentration at which 80 percent of the laboratories in the WS studies could obtain results within plus or minus 40 percent of the true concentration standard. It was stated to be about 5 to 10 times the published MDL.

In this analysis the WS and WP data bases were used to calculate what might be called an interlaboratory detection limits (IDL). This is what is identified as the "calculated MDL" in Table IV-7 through IV-10 and was conceived as a possible procedure for establishing PQL directly from a WS or WP data base. The IDL was estimated as follows:

- Use only those method data bases with enough data to calculate regression equations. Although the regression equations are not used in the IDL calculation, this step assures that sufficient data are available to provide some statistical confidence in the calculation.

- Calculate the IDL as the interlaboratory standard deviation times the Student's t value for the 99 percent confidence level and appropriate degrees of freedom (number of analyses used to calculate the standard deviation minus 1).

- Establish criteria for evaluating the detection limit. If these criteria are not met, the calculated detection limit is flagged.

The criteria used to evaluate the interlaboratory detection limit were as follows:

1)As stated in Appendix B to 40 CFR 136, MDL calculations should be based on replicate analyses of spike samples containing the analyte at one to ten times the expected detection limit. Although no replication was involved in WS or WP, if the lowest "true value" from the WS and WP studies exceeded the interlaboratory detection limit by a factor greater than 10, the "calculated MDL" was flagged.

2)The method for determining a method detection limit specifies that the MDL should be below the spike level. If the IDL was not below the lowest "true value" in the WS and WP studies, the "calculated MDL" was flagged.

3)The IDL were evaluated against the PQL criteria developed by EPA, to ensure that 80 percent of the laboratories must obtain results within 40 percent of the true value. If these PQL criteria were not achieved, the "calculated MDL" was flagged.

As shown in Table IV-7 through IV-10, several of the "calculated MDL's" did not meet criteria 1 (indicating WS/WP concentrations were too high) and 3 (indicating that the data quality objective stated for PQL were not always met by IDL).

This approach uses elements from the MDL estimation methodology given by the Agency at 40 CFR 136, Appendix B and the PQL methodology. Comparison of the IDL to the published MDL for a given method and chemical provides a semi-quantitative basis for assessing the interlaboratory effects on MDL's.

Evaluation of Method Performance Data

The data presented in these tables can be used to assess the adequacy of the test methods where specific data quality objectives (DQO's) are identified. For example, Table IV-7 indicates that arsenic could be measured using method 200.7. At a concentration (true value) of 50 µg/L, the method would indicate arsenic at a concentration of 54 ± 15 µg/L at a 95% confidence level.

In a similar manner, at the MCL of 200 µg/L for 1,1,1-trichloroethane, method 502.1 would measure 200.5 ± 87.6 µg/L. Thus, the assessment of adequacy must answer the question of how good a measurement must be. The assessment in this report was limited to a comparison of MDL's with water quality criteria and standards or NPDES effluent limitations. The adequacy of the 304(h) methods cannot be further evaluated for precision and mean recovery in the absence of detailed DQO's.

Availability of Biological Testing Methods

The discussion on availability and adequacy has been separated into two sections due to the proposed significant additions to the available 304(h) methods in early 1988. The EPA proposes to amend 40 CFR 136 by adding new measurements and new test methods to Table IA, "List of Approved Biological Test methods." These methods include (1) methods for measuring the toxicity of pollutants in effluents, drilling muds, and receiving waters, including short-term methods for acute and chronic toxicity to freshwater and marine organisms; (2) methods for measuring mutagenicity; (3) methods for monitoring viruses in wastewaters and sludges; and (4) updated citations to microbiological methods. Under the 1984 national policy for development of water quality-based permit limits, EPA expected toxicity tests to play an important role in the issuance of NPDES permits. EPA recognized the need for uniformity in the test methods, drafted a proposed amendment, and sought public comments. Since the proposed changes to the list of available methods is still in the comment period, the two parts were separated to facilitate possible revisions. Methods are listed as four separate categories for discussion.

Standardized Methods Currently Approved

There are currently five biological parameters that are approved and included in 40 CFR 136. All five parameters are microbiological measurements (Table IV-11) for indicating fecal pollution or for measuring the overall microbiological quality of ambient waters and wastewaters. The methods are described in detail in the EPA manual, "Microbiological Methods for Monitoring the Environment" (4-2). These same analytes have also been described by the United States Geological Survey (USGS) (4-3) as well as the American Public Health Association (4-4). The Fifteenth Edition of the APHA "Standard Methods" cited in Table IA has been updated. Only microbiological methods have been approved. The list does not include any methods for aquatic toxicity test, viruses, or pathogens. As previously discussed, EPA has

proposed to amend the list in order to provide standardized methods for monitoring programs.

Standardized Methods Proposed for Approval

The proposed amendments to the list of approved biological methods in 40 CFR 136 are listed in Table IV-12. In the proposed amendments, the citations to the existing microbiological methods are updated to coincide with the Sixteenth Edition of the APHA Standard Methods (4-4). In addition, methods are proposed for detecting enteroviruses in water and sludge; mutagenicity (Ames Test); acute toxicity methods for freshwater and marine organisms; and chronic toxicity methods for freshwater organisms. A brief description of each method and the rationale supporting the proposed amendments follows.

Enteroviruses in Water and Sludge

Pathogenic viruses are assumed to be included in the definition of "toxic pollutants" to be controlled under the FWPCA. In the past several years, an increased awareness of the risks of waterborne human pathogenic viruses has developed with the agencies responsible for surface waters, effluent, and sludge monitoring. As a result of these concerns and at the recommendation of the World Health Organization (WHO), virus standards have been included in the water quality standards of two states. It is expected that additional states will soon introduce virus standards and requirements for monitoring viruses. Arizona has set a limit of one enteric virus unit per 40 liters of sample for effluent-dominated recreational waters in which there is full body contact. For incidental contact, 125 enteric virus units per 40 liters is allowed. Montgomery County, Maryland has also adopted a virus standard for discharges limiting the number of detectable infectious virus units to 1 per 40 liters.

The methods for detecting enteroviruses in water or sludge are described in the EPA manual of Methods for Virology (4-5). The method consists of instructions for sampling, concentration, detection, and identification. Because of the high infectivity of viruses, it may be necessary to concentrate them from large volumes of sample if they are present only in small numbers. The concentration technique is based on virus adsorption, followed by elution. Viruses are detected and quantified by innoculating an aliquot of the sample concentrate into mammalian cell cultures. Viruses are identified by neutralization tests using specific antisera.

Mutagenic Test Methods

Mutagenic substances are also defined in the FWPCA as toxic substances and are subject to control. Mutagenic activity has been reported in both domestic and industrial waste discharged to surface waters, and has been included in the Agency's toxics control strategy. Mutagenicity tests are performed routinely on effluents in some municipal and EPA field monitoring laboratories, and are included in state toxics control programs. Substances which test positive in the Ames Test for mutagenicity have a high potential for being mammalian mutagens and carcinogens. Chemicals which damage DNA in reproductive cells may cause birth defects and genetic disorders. DNA damage in body or somatic cells may result in the initiation of cancer.

The proposed test method is based on the Ames Test (4-6) and has been described in detail for routine use (4-7). Mutagens in water and wastewater samples are usually concentrated by organic extraction techniques before being used in the test. The test involves the use of mutant bacterial cultures (Salmonella) to detect mutagenic activity. The Salmonella strains developed specifically for this test revert to the "wild" type when acted upon by mutagenic substances. The results of the test are expressed in terms of the number of "revertants" (number of bacteria that mutated) per unit volume of sample or as the number of revertants per gram of organic matter (extract) per liter.

Acute Toxicity Tests for Freshwater and Marine Organisms

The 1984 EPA National Policy for establishing water quality-based permit limitations for toxic pollutants (4-8) proposed the use of toxicity tests to assess and control the discharge of toxic

Table IV-12 List of Proposed Biological Test Procedures for 40 CFR 136.3, Table 1A

	Parameter and Units	Method[1]	EPA	Standard Methods 16th Ed.	Other
1.	Coliform (fecal), number per 100 mL	MPN, 5 tube, 3 dilution, or Membrane filter (MF)[2], single step	p.132[3] p.124[3]	908C 909C	— B-0050-77[4]
2.	Coliform (fecal) in presence of chlorine, number per 100 mL	MPN, 5 tube, 3 dilution, or MF, Single Step[5]	p.132[3] p.124[3]	908C 909C	— —
3.	Coliform (total), number per 100 mL	MPN, 5 tube, 3 dilution, or MF[2] single step or two step	p.114[3] p.108[3]	908A 909A	— B-0025-77[4]
4.	Coliform (total), in presence of chlorine, number per 100 mL	MPN, 5 tube, 3 dilution, or MF[2] with enrichment	p.114[3] p.111[3]	908A 909 (A+A.5c)	— —
5.	Fecal streptococci, number per 100 mL	MPN, 5 tube, 3 dilution MF[2] or plate count	p. 136[3] p. 136[3] p.143[3]	910A 910B 910C	— B-0055-77[4] —
6.	Enteroviruses in water, plaque forming units per Liter	Absorption, elution, organic flocculation followed by: Plaque assay (cell culture infectivity)	Ch. 6[7] Ch. 9[7]	913A (I or II) 913E	— —
7.	Enteroviruses in sludge, plaque forming units per Liter	Beef extract elution, organic flocculation followed by: Plaque assay (cell culture infectivity)	Ch. 7[7] Ch. 9[7] Ch. 10[7]	913D 913E	— — —
8.	Mutagenicity (revertants per Liter)	Ames Test, test strains TA97, TA98, TA100, and TA102	Note 8	—	—
9.	Toxicity, acute, fresh water organisms, percent effluent	*Daphnia* and *Ceriodaphnia*, 48-hour static mortality, Fathead minnow, 48-hour static mortality, or 48- to 96-hour flow-through mortality.	p. 39[9] p. 41[9]	— —	— —
10.	Toxicity, acute, estuarine and marine organisms, percent effluent	Mysids, 48-hour static mortality or 48- to 96-hour flow-through mortality. Silversides, 48-hour static mortality, or 48- to 96-hour flow-through mortality.	p.40[9] p.42[9]	— —	— —
11.	Toxicity, acute, drilling fluids, percent suspended particulate phase	Mysids, 96-hour static mortality	Note 10	—	

(Continued)

Table IV-12 (Continued)

	Parameter and Units	Method	EPA[2-7]	Standard Methods 16th Ed.	Other
12.	Toxicity, chronic, fresh water organisms, percent effluent	Fathead minnow larval survival and growth.	1000.0[11]	—	—
		Fathead minnow embryo-larval survival and teratogenicity.	1001.0[11]	—	—
		Ceriodaphnia survival and reproduction.	1002.0[11]	—	—
		Selenastrum growth.	1003.0[11]	—	—
13.	Toxicity, chronic, estuarine and marine organisms, percent effluent	Sheepshead minnow larval survival and growth.	1004.0[12]	—	—
		Sheepshead minnow embryo-larval survival and teratogenicity.	1005.0[12]	—	—
		Menidia beryllina larval survival and growth.	1006.0[12]	—	—
		Mysidopsis bahia survival, growth, and fecundity.	1007.0[12]	—	—
		Arbacia punctulata fertilization.	1008.0[12]	—	—
		Champia parvula reproduction.	1009.0[12]	—	—

1. The method must be specified when results are reported.
2. 0.45 µm membrane filter or other pore size certified by the manufacturer to fully retain organisms to be cultivated, and to be free of extractables which could interfere with their growth.
3. Bordner, R. H., and J. A. Winter, eds. 1978. Microbiological Methods for Monitoring the Environment, Water, and Wastes. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/8-78/017.
4. Greeson, P. E., T. A. Elke, G. A. Irwin, B. W. Lium, and K. V. Slack. eds. 1977. Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples," U. S. Geological Survey Techniques of Water- Resources Investigations, Book 5, Chapter A4, Laboratory Analysis, U. S. Geological Survey, U. S. Department of Interior, Reston, Virginia.
5. Since the MF technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.
6. Approved only if dissolution of the KF Streptococcus Agar (Section 5.1, USGS Method 8-0055-77) is made in a boiling water bath to avoid scorching the medium.
7. Berg, G., R. S. Safferman, D. R. Dahling, D. Berman, and C. J. Hurst. 1984. USEPA Manual of Methods for Virology. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-84/013. (Chapter 9 revised January 1987; Chapter 10 revised December 1987.)
8. Williams, L. R., and J. E. Preston. eds. 1983. Interim Procedures for Conducting the Salmonella/Microsomal Mutagenicity Assay (Ames Test). Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Las Vegas, Nevada. EPA/600/4-82/068.
9. Peltier, W.H., and C.I. Weber, eds. 1985. Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-85/013.
10. FR 50(165):34592; FR 51(131):24897
11. Horning, W. B., and C. I. Weber, eds. 1985. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Surface Waters to Freshwater Organisms. Environmental Monitoring and Support Laboratory, U.\S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-85/014.
12. Weber, C. I., W. B. Horning, II, D. J. Klemm, T. W. Neiheisel, P. A. Lewis, E. L. Robinson, J. Menkedick, and F. Kessler, eds. 1988. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-87/028.

substances to the nation's waters through the NPDES permits program. The policy states that "biological testing of effluent is an important aspect of the water quality-based approach for controlling toxic pollutants." All states have water quality standards which include narrative statements prohibiting the discharge of "toxic materials in toxic amounts." In the technical support document issued after the national policy was published, (4-9) the application of biological methods for regulating effluents was specifically discussed. It stated that "EPA will use an integrated strategy consisting of both biological and chemical methods to address toxic and non-conventional pollutants from industrial and municipal sources." In addition to enforcing specific numerical criteria, EPA and the States "will use biological techniques and available data on chemical effects to assess toxicity impacts and human health hazards."

Since the early 1970's there has been a steady increase in the use of effluent toxicity tests within the Agency and state NPDES programs to identify and control toxic discharges. To meet the program needs, EPA prepared standardized methods for effluent toxicity tests. The first acute toxicity test methods developed specifically for effluents were published in 1978 (4- 10) and revised and expanded in 1985 (4-11).

The manual includes a preliminary range-finding test, a screening test, and multi-concentration (definitive) static and flow-through toxicity tests. Also included are guidelines on laboratory safety, quality assurance, facilities and equipment, effluent sampling and holding, dilution water, test species selection and handling, data interpretation and utilization, report preparation, organism culturing, and dilutor and mobile bioassay laboratory design. The 1985 (4-11) acute toxicity test methods manual includes a list of 50 recommended freshwater and marine test organisms. The tests are used to determine the effluent concentration, expressed as a percent volume, that causes the death of 50 percent of the organisms (LC50) or a measured effect in 50 percent of the test population (EC_{50}).

The manual also includes a brief discussion of an effluent fractionation technique that is useful in Toxicity Reduction Evaluation (TRE). Should toxicity be demonstrated in the effluent, the NPDES permit writer's guidelines (4-12) state that the Regional office or the State agency with responsibility for that permit should require the permittee to reduce toxicity by determining the causative toxicants or an appropriate treatment method. Using the fractionation technique, the source of toxicity can be possibly discovered. The effluent is subjected to a series of ion exchange resins to separate out particulates from the effluent and split the remaining liquid into an organic and inorganic fractions. If either fraction exhibits toxicity, subfractionation under basic and acidic conditions is completed and each tested for toxicity. The fractionation procedure is now being updated and field tested.

Chronic Toxicity Tests for Freshwater, Marine, and Estuarine Organisms

The use of short-term, partial chronic toxicity tests in the NPDES permits program was recommended in the 1984 National Policy on water quality-based permit limits. The methods were designed to provide a more direct measurement of the "safe" concentration of effluent in receiving waters (NOEC) than was provided in acute toxicity tests at only a slight increase in the time required to produce data. Compared to the traditional full life-cycle chronic tests for fish (months to years) and the cladoceran tests (21-28 days), these short- term chronic tests for freshwater and marine organisms are relatively quick (4- 9 days) and several can be run within nearly the same time period as acute tests. The endpoints used in the proposed chronic tests are survival, growth, and reproduction. The effects include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components which adversely affect the physiological and biochemical functions of the test organisms.

At this time, EPA proposes to approve chronic methods for freshwater, marine and estuarine organisms (4-13, 4-14). The short-term chronic toxicity tests are proposed to estimate one or more of the following: (1) the chronic toxicity of effluents collected at the end of the discharge pipe and tested with a standard

dilution water, (2) the chronic toxicity of effluents collected at the end of the pipe and tested with nontoxic receiving water collected upstream from the outfall or with uncontaminated surface water having the same characteristics (salinity, hardness) as the receiving water, (3) toxicity of the receiving water downstream or within the zone of influence of the outfall, and (4) the effects of multiple discharges on the quality of the receiving water. These tests may also be useful to conduct Toxicity Reduction Evaluations (TRE) and to develop site-specific water quality criteria.

The four methods described for freshwater organisms include a freshwater fish, an invertebrate, and an alga. Each is described briefly:

(1) EPA Test Method 1000.0. Fathead Minnow (*Pimephales promelas*) Larval Survival and Growth Test is a seven-day, static renewal, larval survival and growth test. Less-than-24-hour-old larvae are exposed to control water, receiving water, and at least five concentrations of the effluent. Test results are based on survival and growth (weight increase) of the larvae.

(2) EPA Test Method 1001.0. Fathead Minnow (*Pimephales promelas*) Embryo Survival and Teratogenicity Test is an eight-day, static renewal, embryo-larval survival and teratogenicity test. Embryos and larvae are exposed to a series of effluent concentrations or to receiving water from shortly after fertilization of the eggs through four days posthatching (total of eight days). Test results are based on the combined frequency of mortality and gross morphological deformities (terata).

(3) EPA Test Method 1002.0. Ceriodaphnia Survival and Reproduction Test is a test with the cladoceran, *Ceriodaphnia dubia* during seven days (three broods) in a static renewal test. Test results are based on survival and reproduction. If the test is conducted as described, the control organisms should produce three broods of young (20-30) during the seven days.

(4) EPA Test Method 1003.0. Algal (*Selenastrum capricornutum*) Growth Test is a four-day static growth test. A Selenastrum population is exposed to a series of concentrations of effluent or to receiving water. The response of the population is measured in terms of changes in cell density (cell counts per milliliter), biomass, chlorophyll content, or absorbance, compared to the control.

Six short-term chronic methods for estimating toxicity to marine and estuarine organisms were published in May, 1988 (4-14). The chronic marine methods are briefly reviewed as follows:

(1) EPA Test Method 1004.0. Sheepshead Minnow (*Cyprinodon variegatus*) Larval Survival and Growth Test is a seven-day, subchronic, static renewal, larval survival and growth test.

(2) EPA Test Method 1005.0. Sheepshead Minnow (*Cyprinodon variegatus*) Embryo-Larval Survival and Teratogenicity Test is a nine day, subchronic, static renewal embryo-larval survival and teratogenicity test.

(3) EPA Test Method 1006.0. Inland Silversides (*Menidia beryllina*) Larval Survival and Growth Test is a seven day, subchronic, static renewal test.

(4) EPA Test Method 1007.0. Mysid (*Mysidopsis bahia*) Survival, Growth, and Reproduction Test is a seven day, subchronic, static renewal test.

(5) EPA Test Method 1008.0. Sea urchin (*Arbacia punctulata*) Fertilization Test is a one and one-half hour sperm cell toxicity test to determine the concentration of a test substance that reduces fertilization of exposed eggs.

(6) EPA Test Method 1009.0. Red algae (*Champia parvula*) Sexual Reproduction Test is a two day exposure and 5-7 day recovery period test in which the formation of reproductive structures called cystocarps (indicating fertilization) resulting from sexual reproduction is monitored. The

number of cystocarps per female are counted and compared to the controls.

The results of these tests with effluents are expressed as the "safe" concentration (percent effluent volume), which is the highest concentration in the dilution water at which no adverse effect is observed (No-Observed-Effect-Concentration or NOEC). To ensure quality data, three reference toxicants are available from the EPA Environmental Monitoring and Support Laboratory in Cincinnati (sodium dodecylsulfate, copper sulfate, and cadmium chloride). Instructions for the use and the expected toxicity values for the reference toxicants are provided with the samples.

Additional Available EPA Methods

Methods for performing field surveys and damage assessments due to toxic substances discharged or inadvertently released are available but are not being considered for approval by EPA at this time. These methods were developed by EPA to provide guidance for Agency and state biological monitoring programs (4-15). Biological monitoring methods for field assessments of phytoplankton, zooplankton, periphyton, macroplyton, macroinvertebrates, and fish were described in 1973 (4-16). Although this manual requires some updating, it is still widely used by EPA and other monitoring programs.

Methods for quantitative ecological assessments have also been developed by other EPA research labs for specific needs. Under the direction of the EPA Environmental Research Lab at Corvallis, Oregon, a series of methods specifically designed for the marine environment were developed and published for intertidal macrofauna, macrophyta, benthos, zooplankton, and phytoplankton (4-17,18). Methods were also developed for ecological surveys of water bodies in semi-arid regions by the Environmental Monitoring and Systems Lab at Las Vegas (4-19). Included in these methods were methods for sampling macroinvertebrates in streams in arid and semi-arid regions with intermittent flow patterns.

A significant amount of additional methods have been developed by EPA for specific needs that have been published but not included in any of the primary methods manuals. For instance, the EPA Environmental Research Laboratory at Gulf Breeze, FL has developed extensive methods for culturing specific test organisms (4-20), including brine shrimp (*Artemia* sp), a mixohaline rotifer (*Brachionus plicatilis*), green alga (*Chlorella* sp), and four atherinid fish (*Menidia beryllina, M. menidia, M. peninsulae,* and *Lauresthes tenuis*). Included with the culturing methods were also methods for toxicity testing.

Lastly, FWPCA program-specific methods have been developed by EPA that were tailored to a specific monitoring need and sample matrix. For instance, in order to satisfy the requirements of the Ocean Dumping Program, EPA developed bioassay methods for a wide variety of marine species (4-21). In conjunction with the U.S. Army Corps of Engineers, EPA also developed bioassay methods for dredged and fill material being discharged into marine and estuarine environments (4-22). Bioassay methods were also developed for evaluating the toxicity to marine organisms of oil and oil dispersants (4-23). These methods are outdated and are not being proposed for approval as a §304(h) method. Dredged material bioassays are conducted extensively using these methods within each Corps of Engineers District in support of maintenance dredging.

Various other methods and guidelines are available for biomonitoring under other federal statutes. For instance, extensive guidelines were developed by EPA to support pesticide registrations under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (4-24). These guidelines for developing an acceptable protocol border on being a complete method since a great deal of procedural information is incorporated by reference. Many additional methods have been developed by associations outside of the federal government. Voluminous methods, including methods for microbiology, bioassay testing and field assessments, have been published by the American Society for Testing and Materials (ASTM). In many cases,

these methods were developed in parallel with equivalent EPA methods.

Adequacy of Biological Testing Methods

In this section, adequacy will be evaluated by comparing the inventory of environmental analytes required under the FWPCA against the available test methods identified in the preceding section. Those methods that monitor a required analyte will then be reviewed as to development status (approved, standardized, available, or in development). Approved or standardized methods will then be compared to the criteria for determining adequacy already discussed. The minimum requirements for a demonstration of adequacy is that the methods have been subjected to ruggedness testing, and that single and multilaboratory precision of the methods have been established. Lastly, the section will discuss the need for determining whether laboratory methods are predictive of impacts of effluents on the biological integrity of receiving waters.

Prior to a detailed discussion of the adequacy of each test method it should be recognized that overall, the number and types of approved biological test methods are inadequate to support the FWPCA monitoring program. Only five microbiological parameters are on the approved list. Clearly, these five parameters cannot be used to totally satisfy the Congressional mandated goals of "fishable and swimmable waters." Methods are needed for determining the health of ecosystems and their components, for detecting human pathogens in water, for preventing possible impacts on fish and other aquatic biota and man from toxic chemicals and effluents, for developing water quality criteria that the states will use in developing numerous water quality standards, and for satisfying numerous other requirements of the FWPCA, the Safe Drinking Water Act and related statutes. In anticipation of these programmatic needs, EPA has developed numerous methods over the last few years.

These methods represent state-of-the-art knowledge at the time of their development in each area. Often, EPA has been the motivating force behind significant scientific advances in microbiology, virology, aquatic toxicology and ecology. Since the development of these methods, there has continued to be additional scientific advances, additional new environmental problems have been discovered, and Congress has established more stringent clean-up goals. For these reasons, EPA needs to improve outdated methods, continue to develop new methods, and continue to assess the adequacy of its methods for monitoring the environment.

Adequacy of Approved Methods

The microbiological test procedures that are approved in 40 CFR 136 have been extensively used across the nation and internationally for decades. Fecal coliforms are routinely used to monitor municipal effluents, certain industrial effluents, and receiving waters. The ratio of fecal coliform to fecal streptococci methods is used to differentiate between non-human and human sources of fecal pollution. Nonfecal members of the coliform group occur naturally in water, soil, and vegetation, and usually survive longer in water than fecal coliforms; therefore, the recency of pollution or proximity to the pollution source can be determined by the fecal coliform test. As discussed in the inventory section, a survey of NPDES permits in four regions found that fecal coliforms were a frequently required analyte.

Adequacy of Proposed Methods

As previously discussed in the availability section of this chapter, the Agency recognized that the list of approved methods in 40 CFR 136 are inadequate to support the biological monitoring programs under the FWPCA. There are no EPA-approved methods for viruses, mutagens, acute or chronic toxicity test methods. In early 1988, EPA proposed that the list of approved biological methods will be amended to rectify this inadequacy. Each

proposed addition is discussed below as to adequacy.

Enteroviruses in Water

The enterovirus in water method being proposed by the EPA has been evaluated for ruggedness (4-25), single laboratory precision (4-25), and multilaboratory precision (4-26). A coefficient of variation (CV) for single lab precision of 10-18% was calculated. The multilaboratory precision of the method was in the 60-70% range. Based on the available data, these methods would appear to be adequate. The EPA methods manual for virology (4-4) is quite complete and well documented but should be revised to incorporate recently available data on test precision and replication of results.

Enteroviruses in Sludge

Ruggedness and multilaboratory precision studies are available for the method. Ruggedness (4-25) was determined to be adequate and multilaboratory precision was estimated to be within the range of 60-70% (4-27). These data are considered by EPA to be adequate to support the proposed rulemaking.

Ames Test for Mutagenicity

Ruggedness data, and single and multilaboratory precision studies are all available on the Ames Test. Overall single laboratory precision was reported to average ± 12% (4-28) and was < 10% CV for 72% of the groups of three replicate plates. Several studies of the interlaboratory precision of the test have been conducted (4-29).

Acute Toxicity Methods for Freshwater and Marine Organisms

While some 50 species are recommended for acute toxicity testing, depending on the nature of the discharge or study site, all of the results with these various species have been pooled for comparison. Designed experiments to evaluate ruggedness are limited to temperature, pH, and age of test organisms for fathead minnows. Particularly, few studies appear to be available that examine the sources of problems in culturing the organisms, the necessary first step in toxicity testing.

Precision of acute toxicity tests depends upon a number of factors, such as the species used, the age, condition, or health of the organisms, and test conditions such as temperature, dissolved oxygen, food, water quality, and the number of test organisms used at each toxicant concentration. Single laboratory test precision has been estimated by using the same species of organisms under the same test conditions, and employing a reference toxicant. Most of the precision data available were obtained with four standard test organisms (i.e., Daphnia spp., fathead minnows, sheepshead minnows and mysids). Limited data exist for the remaining species. Data on single laboratory precision (CV) from 92 reference toxicant tests with three species ranged from 10% to 86% with a weighted mean of 38% (4-30). The values for multilaboratory precision from 153 reference toxicant tests with six species ranged from 22-167% and had a weighted mean of 50%. For the 48 effluents for which single laboratory data were available, 89.6% of the effluents had coefficients of variation of less than 40% and 89.6% of the effluents had coefficients of variation of less than 30%. For the 141 effluents used in multilaboratory studies, 81.6% of the effluents yielded coefficients of variation of less than 40% and 74.5% yielded coefficients of variation of less than 30% (4-11). EPA considers the single and multilaboratory precision to be acceptable and the methods to be suitable for the proposed rulemaking action.

Drilling Fluids Toxicity Test

Although it is also an acute toxicity test, the test method for drilling fluids (4-30) being proposed for 40 CFR 136 is a stand-alone method without reference to the above protocols. A specifically designed ruggedness test has not yet been performed on this test method. A criticism of the method by the regulated industrial community using the method for compliance, is that the method is vague or ambiguous at several critical steps (4-31). A single lab estimate of precision of

73% was calculated and a 90% variability was calculated for multilaboratory variability (mean estimates). Estimates of precision (CV) made by EPA at two of its environmental research labs and with 10 outside contract labs are 35.7% for single lab precision and 45% for interlaboratory comparisons (4-32,33).

Chronic Methods for Freshwater Organisms

Some ruggedness studies of these four test methods (1000.0; 1001.0; 1002.0; 1003.0) have been performed. Single lab precision data are available on all four tests with reference toxicants and with an effluent for the fathead minnow embryo-larval survival test. Variability (CV) ranged from 6-29% for Method 1000.0 on survival and 6-17% for growth data (4-13). For Method 1001.0, survival data for fatheads varied within a single lab by 41-62% for reference toxicants and maximum precision was obtained with a trickling filter effluent. For Method 1002.0, maximum precision was also obtained (values reported in NOEC-LOEC; calculation of coefficient of variation not possible) in 9 of 10 LOEC calculations and in 6 of 10 NOEC calculations. For Method 1003.0, three reference toxicants were tested and variability ranged from 47-83% for 6-11 replicate tests. Multilaboratory precision data are available for 3 of the 4 test methods with an effluent (4-13).

Developmental Methods for Future Consideration

The chronic methods for marine organisms has been identified by EPA for future consideration as approved methods. Single lab precision data are available for both sheepshead minnow tests as well as the sea urchin method. A multilaboratory evaluation with the mysid survival, growth and reproduction test is planned for reference toxicants and an effluent. Ruggedness data has yet to be developed, but additional multilaboratory studies are planned.

Comments received by the EPA during circulation of the initial draft included the following:

- A ten laboratory participant multilaboratory evaluation of the fathead minnow larval growth test (which was the basis for the Menidia and Cyprinodon methods) has been completed by industry and EPA labs. Those results should be considered by EPA for inclusion into the manual.
- Test standardization between the freshwater and marine chronic methods is advisable as well as between the marine methods. For instance, it was believed that the number of fish per replicate, the number of replicates, and the size of the test containers should be consistent to allow for minimal equipment and set-up costs.
- Photoperiods between the freshwater methods and marine methods are different (14:10 and 16:8, respectively) and should be standardized so that a lab can use one environmental chamber for both types of testing.
- Number of test concentrations between marine chronic methods is inconsistent or not specified. The design of the mysid rapid chronic toxicity test should be modified to conform to other EPA tests.
- Additional standard toxicants are needed and EPA should publish a list of target toxicity ranges based on multilaboratory methods.
- Salinity of effluents should be determined by ionic ratios rather than refractometry or conductance to avoid false results.
- Reporting of LC_1 alone is inappropriate. EMSL-Cincinnati is modifying the computer programs to calculate LC_1, LC_{10}, and LC_{50} to adjust the results for control mortality.
- Teratogenicity measurements are subjective and open to interpretation.
- Drying times and temperatures for larvae should be standardized to achieve consistency.

- The design of the drilling mud acute toxicity test should be modified to correspond to other acute toxicity tests.

EPA has considered these comments and made changes as required before proposing the methods for comment as part of 40 CFR 136 rulemaking.

Summary of Adequacy

The currently approved biological methods in 40 CFR 136 are insufficient for performing the types of analyses required by the various FWPCA programs. Test methods for enteroviruses in water and sludge, Ames Test, acute toxicity test methods for freshwater and marine organisms, and chronic methods for freshwater and marine organisms and field survey methods should be formulated in 40 CFR 136. EPA has recognized this need and proposed to adopt available, standardized methods to address these specific needs.

Further standardization for the chronic toxicity test methods for freshwater and marine organisms is necessary in order to reduce the costs of performing the experiments and to ensure consistent data. Ruggedness, single laboratory, and multilaboratory precision studies are still needed for several test methods.

The coefficient of variation (CV) for biological methods typically ranged from less than 10% up to 90%. Based on these results, biological laboratory results are comparable to the variability observed within and between laboratories for chemical analyses.

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CHAPTER FIVE
COMPARABILITY OF TESTING METHODS

Introduction and Summary

The explosive demand for environmental monitoring data over the past ten years has resulted in a proliferation of analytical methods. Many of these methods are similar to but inconsistent with methods already developed. The consequences resulting from the use of these methods are that data of varying, and to a large degree unknown, quality are being generated at an increasing rate.

This chapter compares methods established by the EPA and other organizations to methods established under §304(h). Due to the sheer number of methods available for any given analyte, it was impossible to provide detailed comparisons of all methods.

Detailed comparisons were performed for the following generic techniques:

- Selenium by graphite furnace atomic absorption spectrometry (GFAAS)
- Metals by inductively coupled plasma spectroscopy (ICP)
- Volatile organics by purge and trap gas chromatography/mass spectrometry (GC/MS)
- Semivolatile organics by solvent extraction Gas Chromatograph/Mass Spectrometry (GC/MS)
- Halogenated volatile organics by purge and trap gas chromatography with electrolytic conductivity detection (GC/HECD)
- Organochlorine pesticides and PCB's by gas chromatography with electron capture detection (GC/ECD)

These six techniques cover a range of widely used techniques which form the basis for the measurement of the toxic priority pollutants in the FWPCA, the Appendix IX compounds under RCRA and the target analytes of the Superfund Contract Laboratory Program.

Based on the detailed comparisons of these six techniques and a general review of other methods, the following findings were obtained:

- Although many methods are available for a given analyte, the procedures are essentially the same. Specific operational details differ among the methods, typically for no apparent reason. Although the various versions of a procedure may indicate different method performance characteristics (e.g., lower detection limits, better precision) the procedural details do not clearly support these stated differences in performance.
- The EPA methods for toxic chemicals in 40 CFR 136 are highly developed, documented and standardized relative to other methods for environmental measurements.
- The QA/QC requirement in the methods vary significantly, are generally deficient in non-EPA methods, inconsistent among

EPA programs, and confusing in many situations (e.g., SW-846).

- Virtually all of the methods reviewed were based on methods originally developed under §304(h).

These findings suggest that the EPA methods that have been enhanced by QA/QC practices should supersede the non-EPA methods that have not been so enhanced, and that the various EPA methods and QC requirements should be consolidated.

Definition of and Approach to Reviewing Test Methods

The test methods used by EPA and other organizations are usually highly technically detailed and involve dozens of discrete steps. For example, the Statement of Work (5-1) for determination of organic analytes under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA; "Superfund") Contract Laboratory Program contains 426 pages of mostly single spaced text defining innumerable steps. As a result, it was not possible within the time available to compare in detail all test methods for a given analyte. Therefore, the comparisons of test methods in this study are generally based upon review of condensations of these methods. As with the selection of the test methods to be compared and with all condensations, certain features of the methods are emphasized over others. These are the features most important to control the quality of results produced.

The EPA test methods for toxic pollutants have come under microscopic scrutiny by Agency scientists, by various offices within EPA, by EPA contractors, by non-EPA organizations using these methods, by manufacturers of analytical equipment, and by the industries that EPA regulates. In response to notices in the Federal Register, the Agency has received many comments on its test methods, and has strived to modify and expand its test methods to address the concerns set forth in the comments. Over the last decade, the comments and criticisms have been leveled at EPA methods for determination of toxic organic and trace metal analytes as well as bioassay methods, and most recently at the quality assurance/quality control (QA/QC) requirements and specifications in these methods. In this study, EPA has therefore given principal attention to the comparison of test methods for determination of the organic and trace metal analytes and aquatic toxicity.

Background for Comparison of Testing Methods

EPA methods for determination of pollutants in environmental samples are necessitated by the Agency's requirement to monitor environmental pollution. This monitoring can be pro-active, as in the case of the National Pollutant Discharge Elimination System (NPDES) program or reactive, as in the case of clean-up at abandoned hazardous waste disposal sites. These varying monitoring requirements result in different characteristics for the analytical methods developed under these programs. A brief background of the evolution of certain of the Agency's methods resulting from differing monitoring requirements is described in this sub-section.

Federal Water Pollution Control Act

Section 304(h) of the FWPCA requires the EPA Administrator to promulgate guidelines establishing test methods for analysis of pollutants that must be provided in any certification pursuant to §401 of the Act or permit application pursuant to §402 of the Act. The Administrator has also made these test methods applicable to monitoring and reporting of NPDES permits (40 CFR 122, 122.21, 122.41, 122.44, and 123.25), and implementation of the pretreatment standards issued under §307 of the Act (40 CFR 403, 403.10 and 403.12). The test methods for these purposes have been promulgated at 40 CFR 136. A structure and history of 40 CFR 136 has been given in the preamble to the promulgation of the methods (49 FR 43234, October 26, 1984).

The methods for organic toxic pollutants in 40 CFR 136 were developed in response to a Consent Decree (Natural Resources Defense Council, Inc., et al. vs. Train, 8 ERC 2120, D.D.C. 1976). These methods comprise a

methods set, and are designed to determine the 114 organic "priority pollutants" listed in the Consent Decree. The methods were first proposed in the Federal Register in 1979 (44 FR 69469, December 3, 1979), and were promulgated as Appendix A of 40 CFR 136 in the October 26, 1984 notice.

The methods were validated through interlaboratory studies between proposal in 1979 and promulgation in 1984. These methods form the basis for almost all subsequent EPA methods for organic pollutants in water (including drinking water, groundwater, surface water, seawater, and waters from all other sources), and for subsequent American Society for Testing Materials (ASTM) methods, U.S. Geological Survey (USGS) methods, and "Standard Methods for Examination of Water and Wastewater" (Standard Methods). The methods developed by the RCRA and Superfund programs for the analysis of soils, wastes and biological tissue are all based on the FWPCA methods.

The inorganic methods to support the FWPCA and Safe Drinking Water Act (SDWA) were published in Environmental Monitoring and Support Laboratory (EMSL- Cincinnati), Methods for Chemical Analyses of Water and Wastes (5-2), ASTM's Annual Book of Standards (5-3), USGS's methods manual (5-4), and Standard Methods (5-5). The methods are written for analytical chemists and contain most of the steps necessary to assure a given level of data quality. However, the EPA method for metals by Inductively Coupled Plasma Spectroscopy (ICP), Method 200.7 (5-6) does the best job of defining the quality control requirements. While the method for the analysis of metals by ICP are well defined, the other inorganic methods lack performance characteristics and specific criteria for method performance. EPA has remedied these deficiencies to some degree as a result of a settlement agreement (5-7) by publishing interlaboratory method validation study data for a number of EPA inorganic methods directly in 40 CFR 136. To date, the Agency has yet to publish performance criteria for any of the methods for inorganics in 40 CFR 136.

Superfund Contract Laboratory Program (CLP) Protocols

The test methods used by the CLP are more properly called protocols than methods because they have very explicit contractual and reporting requirements included within the methods. These protocols were designed to supply legally defensible environmental data. In addition to methods for determination of organic and inorganic pollutants in waters, the protocols contain provisions for determination of the pollutants in other sample matrices. The Agency conducts approximately 7,000,000 determinations per year on over 90,000 samples with a wide variety of matrices using these protocols through contracts with commercial analytical laboratories.

The significant feature of these protocols is that substantial evidentiary materials are embedded in the methods. Therefore, if the protocol is used for general analytical uses not involving court proceedings, a large amount of unnecessary paperwork is delivered at significant additional cost per analysis. To date, laboratories performing work for potentially responsible parties (PRP's), have not been required to follow the CLP protocols.

Office of Solid Waste Methods

These methods are contained in a comprehensive document titled "Test Methods for Evaluating Solid Waste" (SW-846) (5-8). These methods are primarily designed for determining if a given waste is hazardous or if groundwater contamination is occurring and are prepared to address a wide variety of sample matrices. The manual separates the analytical methods into components such as sample preparation and analysis. For example, the FWPCA and SDWA methods and the Superfund CLP protocols give separate, fully contained methods for the analysis of a sample type, and include continuous steps for extraction, concentration, extract cleanup, instrument calibration, analysis, quality control, and, in the case of the CLP protocols, data reporting. The RCRA manual separates these steps into separate methods and gives separate method numbers to each step. The major advantage is

that it tends to force standardization of common procedures such as determinative steps for multiple sample types. The major disadvantage is that the compilation becomes quite large (the Third Edition of SW-846 is distributed in four volumes) and accumulates, of necessity, much extraneous discussion for the user who desires to analyze for a relatively simple matrix such as groundwater. In addition, editing the huge document for consistency is a formidable task; careful reviews of the Third Edition reveal that the general quality control requirements sometimes directly contradict the specific requirements within a method.

Drinking Water Methods

Under the SDWA, approved analytical methods are promulgated in 40 CFR 141. The sources for the approved methods for inorganic analyses are the same as those under the FWPCA, which includes EMSL-Cincinnati, ASTM, Standard Methods, and the U.S.G.S. For organics, however, EMSL-Cincinnati provided a new series of organic methods for compliance monitoring of organic compounds in finished drinking water and raw source water. EPA's organic methods for SDWA are known as the "500 Series" (i.e., 502.1, 502.2, 503.1, 504, 524.1 and 524.2). EMSL-Cincinnati's "600 Series" methods promulgated for priority toxic organics under FWPCA, although technically nearly identical, were considered for the regulation of volatiles, but were abandoned after public comment because the analytical objectives were different and therefore the quality control requirements were much different. The "500 Series" methods are designed to provide data at concentration levels at and below the promulgated maximum contaminant levels (MCL).

Comparison of Testing Methods

The remainder of this section presents the detailed method comparisons for the six techniques discussed previously (4 chemical, 2 biological). For each technique, a comprehensive table was prepared that documents key method characteristics (e.g., detection limits, instrument condition, QA/QC requirements) for the methods reviewed. Not all of the method characteristics lend themselves to easy tabulation. For example, the holding times in the Superfund program are a contractual requirement for the analytical laboratory. Thus, the holding times begin upon receipt at the laboratory rather than at time of collection.

Comparison of Methods for Determination of Organochlorine Pesticides

Organochlorine pesticides have been one of the most important groups of compounds to EPA since the Agency's founding. Many of the analytes in this group have caused significant environmental damage. Among the organochlorine pesticides are lindane, heptachlor, chlordane, toxaphene, and DDT. Most Agency methods for organochlorine pesticides also measure polychlorinated biphenyls (PCB's). For these reasons, methods for determination of these compounds are available for all of the major water-related programs within EPA (FWPCA, SDWA, Superfund, and RCRA), and from other organizations (ASTM, USGS, and Standard Methods). Therefore, this technique was selected to represent a wide variety of the organic methods available that involve solvent extraction followed by gas chromatography analysis.

Table V-1 compares the salient characteristics of eight methods studied for the determination of chlorinated pesticides and PCB's in water by extraction and gas chromatography with electron capture detection. The major characteristics of these methods are given in the method title; i.e., they all use an extraction technique to remove the pesticide from the wastewater; they all use gas chromatography for separation and identification of the analytes; and they all use electron capture for detection of the analytes. Gas chromatography is a technique used for separation of the components of mixtures of organic compounds; electron capture is an instrumental measurement technique whereby the molecule detected captures a free electron, resulting in a net decrease in current through the detector. Gas chromatographs with electron capture detectors are available from more than

Table V-1 Methods for Determination of Chlorinated Pesticides and Polychlorinated Biphenyls (PCB's) in Water by Extraction and Gas Chromatography with Electron Capture Detection

Method Characteristic	Water Regulations	Drinking Water	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Method Number (if any)	608	505	508	8080	CLP-MM	D 3086-85	D 3104-83	509
Revision Date	1984	1986	1986	1986	1987	1985	1983	1985
Number of analytes covered	25	18	32	26	26	20	24	19
Format	EMSL-Ci	EMSL-Ci	EMSL-Ci	No formal document	No formal document	ASTM D	TWRI	
Sample								
Holding time	<72 hr or pH 5 - 9	<14 days	No spec	No spec	<5 days	No spec	No spec	No spec
Preservation	4 C + sodium thio	4 C + sodium thio	4 C + merc chlor	No spec	4 C, in dark	No spec	No spec	No spec
Volume required	1 Liter	35 mL	1 Liter	1 Liter	1 Liter	1 Liter for ECD	1 Liter implied	1 Liter
Extraction								
Solvent	Methylene chloride	Hexane	Methylene chloride	Methylene chloride	Methylene chloride	MeCl2 + Hexane	Hexane	MeCl2 + qB B qHexane
Technique	Sep funnel/cont	Micro-extraction	Sep funnel/ tumble	Sep funnel/cont	Sep funnel/cont	Sep funnel	Sep funnel	Sep funnel
Concentration								
Technique	Kuderna-Danish	None	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish
Final solvent	Hexane	Hexane	MTBE	Hexane	Hexane	Hexane	Hexane	Hexane
Final extract volume	5 mL	2 mL	5 mL	5 mL	1 mL	1 mL	1 mL	10 mL
Cleanup techniques	Florisil/sulfur	None	None	Florisil/sulfur	GPC/Alumina/sulfur	Flor/Alum/SG/TLC	Alumina/Silica Gel	Florisil
Gas chromatograph								
Column temperature	Iso @ 200 C	180-260 @ 4 C/min	60-300 @ 4 C/min	See Method 608	Isothermal @ 192 C	Isothermal @ 200 C	Not given	Isothermal @ 200 C
Column								
Type	Packed	Capillary	Capillary	Packed	Packed/Capillary	Packed	Packed	Packed
Primary	SP-2250/SP-2401	DB-1	SPB-5	SP-2250/SP-2401	OV-17/OV-210	OV-17/OV-210	SP-2100	OV-1
Confirmatory #1	OV-1	Durawax DX-3	DB-1701	OV-1	OV-1	OV-210	SP-2250/SP-2401	OV-210
Confirmatory #2	Not given	OV-17	Not given	Not given	OV-210	OV-1	Not given	OV-17/SP-2401

(Continued)

Table V-1 (Continued)

Method Characteristic	Water Regulations	Drinking Water	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Confirmatory #3	Not given	Not given	Not given	Not given	DB-5 or DB-1701	OV-210/SB-30	Not given	OF-1/SE-30
Calibration								
Technique	Int or ext std	External standard	Int or ext std	Int or ext std	External standard	Not given	External standard	Not given
Number of points	3 minimum	3 minimum	3 minimum	5 minimum	3	Not given	2	Not given
Linearity	<10% RSD RF or CF	<10% RSD of CF	Cal curve only	<20% RSD RF or	<10% RSD of CF	Not given	Calibrate daily	Not given
Frequency of verification	Daily	Daily	Each shift	Daily	Each 72 hr	Not given	Calibrate daily	Not given
Verification specification	+/- 15% RF or CF	+/- 15% CF	+/- 10% RF or CF	+/- 15%	+/- 20%	Not given	Calibrate daily	Not given
Qualitative identification								
Retention time agreement	+/- 3 std dev RT	No spec	+/- 3 std dev RT	+/- 3 std dev RT	+/- 3 std dev RT	No spec	Not given	Not given
DDT/Endrin breakdown	No spec	Endrin <50%	No spec	<20%	<20%	No spec	No spec	No spec
Determination of Lindane								
Concentration range	0.016 - 4.0 µg/L	Not given	0.075 - 1.0 µg/L	Method 608 data	0.01 - 0.1 µg/L	0.01 - 0.1 µg/L	Not given	See ASTM data
Detection limit	MDL=0.004 µg/L	MDL=0.003 µg/L	MDL=0.006 µg/L	MDL=0.004 µg/L	MDL=0.004 µg/L est	DL-0.001 µg/L	DL-0.01 µg/L	DL-0.01 µg/L
Quantitation limit	0.012 ug/L est	PQL=0.015 µg/L	PQL=0.030 µg/L	MQL=0.040 µg/L	CROL=0.05 µg/L	Not given	Not given	Not given
Percent recovery	80 (Inter-lab)	91 (Single lab)	93 (Single lab)	Method 608 data	Not given	97 (Inter-lab)	86 (Single lab)	ASTM data
Precision (% RSD)	22 (Inter-lab)	7 (Single lab)	4 (Single lab)	Not given	Not given	55 (Inter-lab)	12 (Single lab)	ASTM data
Quality Control/Assurance (QA/QC)								
Initial accuracy	Spec in table	No test	Spec in table	Method 608 data	No test	No test	No test	No test
Initial precision	Spec in table	No spec	No test	Method 608 data	No test	No test	No test	No test
Blanks								
Frequency	Each sample set	Daily	Daily	Each set or 5%	Each sample set	Not required	Each sample set	Not required
Specification	No spec	<MDL	< 1/2 MDL	No spec	No spec	No spec	No spec	No spec
Surrogate recovery								
Frequency	Every sample	No test	Every sample	Every sample	Every sample	No test	No test	No test
Specification	No spec	No spec	TBD	+/- 3 SD	In table	No spec	No spec	No spec

(Continued)

Table V-1 (Continued)

Method Characteristic	Water Regulations	Drinking Water	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Matrix spike recovery								
Analytes covered	All	All	All	All	Subset	No test	No test	No test
Frequency	10% minimum	10%	10%	10% minimum	5% minimum	No test	No test	No test
Specification	In table	No spec	No spec	In table	In table	No spec	No spec	No spec
Duplicate analyses								
Analytes covered	No test	No test	Those in samples	All	Subset	No test	No test	No test
Frequency	No test	No test	10% minimum	5% minimum	5% minimum	No test	No test	No test
Specification	No test	No spec	No spec	No spec	In table	No spec	No spec	No spec
Statement of data quality	Recovery +/- 2 SD	Not required	Not required	Recovery +/- 2 SD	Not required	Not required	Not required	Not required
Safety	Explicit warnings	Explicit warnings	Explicit warnings	Not given	Not given	Explicit warnings	Not given	Not given

References:

Method 608--Organochlorine Pesticides and PCBs, 40 CFR Part 136 [49 FR 43234, October 1984].

Method 505: "Analysis of Organohalide Pesticides and Aroclors in Drinking Water by Microextraction and Gas Chromatography", Supplement to "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati Ohio 45268, September 1986.

Method 508: "Determination of Chlorinated Pesticides in Ground Water by Gas Chromatography with an Electron Capture Detector", Supplement to "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati Ohio 45268, September 1986.

Method 8080: "Organochlorine Pesticides and PCBs", "Test Methods for Evaluating Solid Waste", SW-846, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Office of Wolid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460, Third Edition, November 1986.

Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program, Analytical Support Branch, Office of Emergency Response, U.S. Environmental Protection Agency, Washington DC 20460, October 1986.

ASTM Standard D3086-85: "1986 Annual Book of Standards", Section 11: Water and Environmental Technology, Volume 11.02: Water, American Society for Testing Materials, 1916 Race St, PhiladelphiaPA 19103, 1986.

"Organochlorine and organophosphorus compounds, total recoverable (O-3104-83) and dissolved (O-1104-83), gas chromatographic", "Methods for the Determination of Organic Substances in Water and Fluvial Sediments", U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A3, Open-File Report 82-1004, U.S. Geological Survey, Room 5A420, National Center, 12201 Sunrise Valley Drive, Reston, VA 22092, 1983.

Section 509A, "Organochlorine Pesticides", "Standard Methods for the Examination of Water and Wastewater", Prepared and published jointly by American Public Health Association, American Water Works Association, Water Pollution Control Federation, Publication Office: American Public Health Association, 1015 Fifteenth St NW, Washington DC 20005, Sixteenth Edition, 1985.

five major instrument manufacturers and as many as 30 minor manufacturers.

The data in Table V-1 reveal that all of the methods use nearly identical materials, equipment, and operating conditions. The most significant difference is in the use of capillary GC columns in the method chosen to represent the most current drinking water methods. The Agency is actively pursuing the incorporation of capillary column technology into all appropriate methods.

However, the methods are shown to provide different performance. For example, the method detection limit for a typical analyte, lindane, varies from 0.001 to 0.01 µg/L. Furthermore the methods use different detection limit terms (MDL, DL, PQL, CRDL, MQL).

The QA/QC requirements vary from no requirements to requirements that specify the type, frequency and acceptance criteria for all QC samples. For example, calibration requirements are specified as "daily", "each shift" and "each 72 hours" or in some cases not specified.

The data in Table V-1 also reveal that although there are numerous inconsistencies among the EPA methods, they are more highly developed than non-Agency methods. Major deficiencies exist in the calibration and quality assurance/quality control (QA/QC) section of the non-EPA methods. Unless these details are carefully specified in the methods, laboratories performing analyses will produce results of unknown and, probably, less than optimal quality.

Comparison of Methods for the Determination of Halogenated Volatile Organics

Halogenated volatile organic compounds are a group of low molecular weight compounds that are of concern because of their widespread use and toxic and carcinogenic effects. Many of the compounds in this group have been detected in drinking water supplies. The compounds in this group typically contain one to six carbon atoms with one or more halogenated (chlorine, bromine, fluorine or iodine) atoms. Examples of these compounds include vinyl chloride, chloroform, trichloroethylene and ethylene dibromide.

Compounds in this class typically have boiling points of less than 200°C and water solubilities of less than 1%. These two physical properties enable the compounds to be measured by a technique involving: 1) gas stripping the compound from water (purging); 2) trapping the compounds on a solid sorbent (trapping); 3) transferring the compounds from the solid sorbent to a gas chromatograph with high temperature and gas flow (desorbing); and 4) separating and identifying the compounds by means of a gas chromatograph (GC). This technique, termed "purge and trap GC" has been adapted into many Agency methods.

Compounds which can be purged, trapped, desorbed and chromatographed also include non-halogenated compounds such as benzene and carbon disulfide. Described elsewhere in this chapter is a technique using purge and trap GC with a mass spectrometer (MS) as a detector. Purge and trap GC/MS techniques can measure a broad range of volatile compounds, including halogenated volatiles.

However, GC/MS techniques have several limitations, including the cost and complexity of the instrumentation and the limited sensitivity of the MS detector. An alternative detector, the Hall electrolytic conductivity detector (HECD), can be coupled with the purge and trap GC technique to selectively measure halogenated species. This detector system, developed commercially by Coulson and Hall, is based on the pyrolysis of halogenated organics in a hydrogen atmosphere to inorganic acids (e.g., HX) extraction of the monitored species from the gaseous reaction products stream into the conductivity solvent and the detection of the monitored species by the change in resistance of the conductivity solvent.

As shown in Table V-2, six methods for halogenated volatile organics were reviewed. A review of the operational details of the methods reveals that all of the methods use virtually identical reagents, equipment and operating conditions. The only significant difference in these methods is in the use of a capillary GC

Table V-2 Comparison of Methods for the Determination of Halogenated Volatile Organics in Water by Purge and Trap Gas Chromatography with Electrolytic Conductivity Detection

Method Characteristics	Water Regulations	Drinking Water	Drinking Water	Solid Waste	ASTM	Standard Methods
Method Number	601	502.1	502.2	8010	D3871-84	514
Revision Date	1984	1896	1986	1986	1984	1985
Number of Analytes	29	38	58	39	NS	NS
Sample Collection	25 mL minimum volume	Duplicate samples, 40-120 mL	Duplicate samples, 40-120 mL	Duplicate 40 mL	NS	Duplicate
Sample Preservation	4°C	4°C,1:1 HCl to pH<2	4°C,1:1 HCl to pH<2	4 drops conc. HCl,4°C	4°C	4°C
Holding Time	14 days	14 days	14 days	14 days	a few hours if possible, or 15 days	as soon as possible
Purge Gas	N_2 or He	N_2 or He	N_2 or He	N_2 or He	N_2 or He	N_2 or He
Purge Rate, mL/min.	40	40	40	40	40	40
Purge time, minutes	11.0	11.0 + 0.1	11.0 + 0.1	11.0 + 0.1	12 or longer	11.0
Trap Size	25 cm	25 cm	25 cm		150 mm	25 cm
Trap Packing	1.0cm 3%OV-1 7.7 cm Tenax 7.7 cm Silica Gel 7.7 cm charcoal	1/3 Tenax 1/3 Silica Gel 1/3 Charcoal	1/3 Tenax 1/3 Silica Gel 1/3 Charcoal	1/3 Tenax 1/3 Silica Gel 1/3 Charcoal	100 mm Tenax 50 mm Silica Gel	1cm 3% OV-1 15 cm Tenax 8 cm Silica Gel
Desorb temp.,°C	180	180	180	180	180 ± 5	180
Desorb time, min.	4	4.0 ± 0.1	4.0 ± 0.1	4	4	4.0
GC Column Type	Packed	Packed	Capillary	Packed or	Packed Capillary	Packed
Primary Column	1% SP-1000	1% SP-1000	VOCOL	1% SP-1000	Suitable Packing	0.2% Carbowax 1500
GC Conditions	3 min. at 45°C 8°C/min. to220°C	3 min. at 45°C 8°C/min. to 220°C	8 min. at 100°C 4°C/min. to 180°C	3 min. at 45°C 8°C/min. at 220°C	4 min. at 60°C 8°C/min. to 170°C	3 min. at 60°C 8°C/min. to 160°C
Confirmatory Column	n-Octane on Porasil C	n-Octane on Porasil C	NS	n-Octane on Porasil C	NS	n-Octane on Porasil C
Calibration Technique	Internal or External	Internal or External	Internal or External	Internal or External	External	External
Number of Calibration points	3	5	5	5	NS	NS

(Continued)

Table V-2 (Continued)

Method Characteristics	Water Regulations	Drinking Water	Drinking Water	Solid Waste	ASTM	Standard Methods
Linearity check	±10% RSD	±15% RSD	±15% RSD	±20% RSD	NS	NS
Calibration Frequency	Daily	Daily	Daily	Daily	NS	NS
Calibration Specification	Acceptance Criteria for each parameter	RF ± 20%	RF ± 20%	RF ± 15%	NS	NS
Retention time Specification	NS	<10% over 8 hours	<10% over 8 hours	NS	NS	NS
Identification Specification	Retention time agreement within 3 T	NS	NS	± 3 T of three absolute retention times	NS	NS
second Column Confirmation	Can be used	Can be used	NS	Normally is required	NS	Required for unknown samples
Method Performance Data, Detection Limits µg/l	Trichloro-ethylene MDL, 0.12	MDL, 0.001	MDL, 0.0	PQL, 1.2	NS	LOD for each sample
Accuracy %	87 est	92 est	96	601 Data	NS	NS
Precision, SD	20 est	29 est	3.5	601 Data	NS	NS
QA/QC Requirements						
Initial Demon-stration	NS	7 replicates at 2 µg/l	7 replicates at 2 µg/l	NS	NS	NS
Accuracy Check	4 QC check samples	MDL Study	MDl Study	4 QC check samples	NS	NS
Accuracy Specifi-cation	Compare to table	90-100%	80-120%	601 Data	NS	NS
Recovery Check	4 QC check samples	MDL Study	MDL Study	4 QC check samples	NS	NS
Recovery Specifi-cation	Compare to table	<35% RSD	<30% RSD	601 Data	NS	ND
Requirements - Ongoing						
Blanks	Daily	Daily	Daily	Daily	NS	Daily
Spikes	10% or 1/month	NS	NS	One per batch	NS	NS
Duplicate	Recommended	NS	NS	Recommended	NS	NS
QC Checks	Varies	10%	10%	Varies	NS	Daily
QC Accept-ance Criteria	Provided	60-140%	60-140%	Provided	NS	NS
Certification	NS	Required in program	Required in program	NS	NS	NS
PE Samples	Recommended	Recommended	Recommended	Recommended	NS	NS

(Continued)

Table V-2 (Continued)

References

Method 601: "Purgeable Halocarbons", 40 CFR Part 136

Method 502.1: "Volatile Halogenated Organic Compounds in Water by Purge and Trap Gas Chromatography," Physical and Chemical methods Branch, Environmental Monitoring and Support Laboratory, USEPA,Cincinnati, OH, September 1986.

Method 502.2: "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series", Physical and Chemical Methods, Branch, Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, OH, September 1986.

Method 8010: "Halogenated Volatile Organics", "Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Volume 1B "Office of Solid Waste and Emergency Response, USEPA, November 1986.

ASTM Standard

D3871-84: "Organic Compounds, Purgeable, Headspace Sampling", "1987 Book of Standards", Section 11:Water and Environmental Technology, Volume 11.02: Water, American Society for Testing Materials, Philadelphia, PA.

Section 514: "Halogenated Methane and Ethane, by Purge and Trap", "Standard Methods for the Examination of Water and Wastewater", APHA/AWWA, Sixteenth Edition, 1985.

column in Method 502.2. This method is the most recently developed of the six methods. Because of the improved characteristics of this method, it is expected that the other methods will evolve toward this technique.

A review of these methods reveals trivial differences that may or may not affect the performance. For example, all methods but one specify an eleven minute purge time. One method, ASTM Method D-3871-84, specifies a twelve minute purge time. The methods all use a 25-cm trap. However, the packings and relative amount of each packing varies. As in the other methods, the QA/QC requirements vary tremendously.

Although most of the methods specify a holding time of 14 days, the preservation varies from 4°C to 1:1 HCl to pH <2 to "4 drops of concentrated HCl". The methods are stated to provide different levels of performance. For example, the "detection limits" (MDL, PQL, etc.) for trichloroethylene ranged from 0.001 to 1.2 µg/L. As in the other examples, the EPA methods were more developed and the method details, especially QA/QC requirements, were more fully documented than the non-EPA methods.

Comparison of Methods for the Determination of Organic Compounds by Gas Chromatography/Mass Spectrometry

The use of gas chromatography/mass spectrometry (GC/MS) techniques for the analysis of organic constituents in water has gained widespread use because of the ability of the mass spectrometer to detect and measure a large variety of compounds. Furthermore, the technique can be used to deduce the structure of a compound based on mass fragmentation patterns. This latter aspect of the technique is particularly important in the analysis of samples containing hundreds of contaminants.

Although many specialized GC/MS techniques have been developed (e.g., the methods for dioxins) the predominant use of GC/MS techniques is for the general analysis of a sample for a specific list of compounds. GC/MS techniques usually involve the following steps:

- isolation of the target analytes from the sample matrix,
- concentration of the target analytes,
- separation of the components on a gas chromatograph, and
- detection and quantitation of the analytes with the mass spectrometer.

These general operations are used for both the "analyzed for" approach and the approach used to deduce the structure of unknown compounds.

However, the "analyzed for" approach adds two additional steps: 1) calibration with known reference materials; and 2) additional criteria for compound identifications. These two steps can result in reliable identification and quantitation of specific compounds when

Table V-3 Comparison of Methods for the Determination of Halogenated Volatile Organics in Water by Purge and Trap Gas Chromatography with Electron Capture Detection

Method Characteristic	Water Regulations	ITD	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Method Number	624	1624 Rev. C	524	8240	CLP-MM	D 3871/D 4128	D-3115-83	514/516
Revision Date	1984	1986	1985	1986	1987	1984/1982	1983	1985
Number of analytes covered	31	55	51		34	5	27	25
Format	EMSL-Ci	EMSL-Ci	EMSL-Ci	No formal document	No formal document	ASTM	TWRI	APHS
Sample								
Holding time	<14 days	<14 days	<14 days	<14 days	<10 days	<15 days	No spec	<2 weeks
Preservation	4 C + sodium thio	4 C + sodium thio	4 C + pH <2	4 C + sodium	2 - 6 C, in dark	4 C + dechlor	No spec	4 C + sodium thio
Volume required	>25 mL	>20 mL	60 - 120 mL	2 x 40 mL	40 mL	45 mL	>10 mL implied	2 x 40 mL
Sample preparation								
Technique	Purge & trap	Purge & trap	Purge & trap	Purge and trap	Purge and trap	Purge and trap	Purge and trap	Purge and trap
Gas chromatograph								
Column temperature								
Initial	45 C for 3 minutes	45 C for 3 minutes	45 C for 3 minutes	45 C for 3 minutes	45 C for 3 minutes	Room temp desorb	45 C for 4 minutes	60 C for 3 minutes
Program	45 - 220 @ 8 C/min	45 - 240 @ 8 C/min	45 - 200 @ 8 C/min	45 - 200 @ 8 C/min	45 - 200 @ 8 C/min	60 - 170 @ 8 C/min	45 - 210 @ 8 C/min	60 - 160 @ 8 C/min
Final	15 minutes	Until BFB elutes	15 minutes	220 for 15 minutes	220 for 15 minutes	170 for 12 minutes	To end of acquire	Until compounds elute
Column								
Type	Packed	Packed	Packed	Packed	Packed	Packed	Packed	Packed
Primary	SP-1000/ Carbopak	SP-1000/ Carbopak	SP-1000/ Carbopak	SP-1000/ Carbopak	SP-1000/ Carbopak	Carbowax /Carbopak	SP-1000/ Carbopak	Carbowax/ Carbopak
Calibration								
Technique	Internal standard	Isotope dilution	Internal standard	Internal standard	Internal standard	Internal standard	Int or ext standard	Not given
Number of points	3 minimum	5	5	5 minimum	5	Not given	Not given	Not given
Linearity	<35% RSD of RF	<20% RSD of RR	<10% RSD of RF	<30% RSD of RF	<30% RSD of RF	Not given	Not given	Not given

(Continued)

Table V-3 (Continued)

Method Characteristic	Water Regulations	ITD	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Frequency of verification	Daily	Each 8 hr shift	Daily	12 hours	12	Not given	Not given	Not given
Verification specification	Spec in table	Spec in table	+/- 20%	+/- 25%	+/- 25%	Not given	Not given	Not given
Qualitative identification								
Retention time agreement								
Absolute	+/- 30 s of std	No spec	+/- 30 s of std	No spec	No spec	Not given	<5% of std	Not given
Relative	No spec	+/- 6 sec	No spec	+/- 0.06 RRT	+/- 0.06 RRT	Not given	Not given	1 - 2 percent
m/z's must maximimize	Within one scan	<2 consec scans	No spec	No spec	No spec	Not given	Within +/- 1 scan	Not given
Mass spectral agreement	+/- 20 percent	+/- 50 percent	+/- 10 Abs abund	+/- 20 Abs abund	+/- 20 Abs abund	Not given	Not given	Fit > 950
Average Characteristics for Determination of Compounds Listed								
Concentration range (min-max)	5 - 600 µg/L	10 - 200 µg/L	Not given	Not given	20 -200 µg/L	"low ug/L-low mg/L"	Not given	0.5 - 1500 µg/L
Detection limit (min-max)	MDL: 1.6-7.2 µg/L	ML: 10 - 50 µg/L	MDL: .07-2.0	PGL: 5 - 100 µg/L	CROL: 5 - 10 µg/L	DL: 5 µg/L est	DL: 3 µg/L	0.5 µg/L
Quantitation limit (min-max)	5 - 600 µg/L	10 - 200 µg/L	Not given	Not given	20 -200 µg/L	Not given	Not given	Not given
Percent recovery (average)	99 (est; Inter-lab)	100 (est; Inter-lab)	97 (est; One lab)	Method 608 data	Not given	102 (est; Inter-lab)	Not given	102 (est; One lab)
Precision (average % RSD)	26 (est; Inter-lab)	12 (est; Inter-lab)	9 (est; One lab)	Method 608 data	Not given	25 (est; Inter-lab)	Not given	10 (est; One lab)
Determination of Benzene as a Specific Example of Method Characteristics								
Concentration range	5 - 600 µg/L	10 - 200 µg/L	Not given	Not given	20 -200 µg/L	"low µg/L-low mg/L"	Not given	Not given
Detection limit	MDL=4.4 µg/L	ML=10 µg/L	MDL: 0.1 µg/L	PQL: 5 µg/L	CRQL: 5 µg/L	DL: 1 µg/L est	Not given	Not given

(Continued)

Table V-3 (Continued)

Method Characteristic	Water Regulations	ITD	Drinking Water	Solid Waste	Superfund CLP	ASTM	USGS	Standard Methods
Quantitation limit	5 ug/L est	10 ug/L	Not given	Not given	20 -200 ug/L	Not given	Not given	Not given
Percent recovery	93 (Inter-lab)	99 (est; Inter-lab)	97 (Single lab)	Method 608 data	Not given	96 (Inter-lab)	Not given	Not given
Precision (% RSD)	25 (Inter-lab)	11 (est; Inter-lab)	3.6 (Single lab)	Method 608 data	Not given	40 (Inter-lab)	Not given	Not given
Quality Control/ Assurance (QA/QC)								
Tuning	BFB	BFB	BFB	BFB	BFB	BFB	BFB	BFB
Initial accuracy (% recovery)	Spec in table	Spec in table	95 - 110	Method 608 data	No test	No test	No test	No test
Initial precision (% RSD)	Spec in table	Spec in table	<35	Method 608 data	No test	No test	No test	No test
Measurement of detection limit	Not required	Required	Not required	Not required	CROL required	Not required	Not required	Not required
Blanks								
Frequency	Each sample set	Each sample set	Daily	Each sample set	Each sample set	Not required	Each sample set	Daily
Specification	No spec	<5 ug/L	No spec	No spec	<5x CRQL	No spec	Not required	Not required
Surrogate recovery								
Frequency	Every sample	Every sample	No test	Every sample	Every sample	No test	Not specified	Not given
Specification	No spec	Spec in table	No spec	+/- 3 SD	Spec in table	No spec	70-130 percent	No spec
Matrix spike recovery								
Analytes covered	All	All	No test	All	Subset	No test	No test	No test
Frequency	10% minimum	100% (labeled)	No test	10% minimum	5% minimum	No test	No test	No test
Specification	In table	In table	No spec	In table	In table	No spec	No spec	No spec
Duplicate analyses								
Analytes covered	No test	No test	No test	All	Subset	No test	No test	No test
Frequency	No test	No test	No test	5% minimum	5% minimum	No test	No test	No test
Specification	No test	No spec	No spec	No spec	Spec in table	No spec	No spec	No spec
Statement of data quality	Recovery +/- 2 SD	Recovery +/- 2 SD	Not required	Recovery +/- 2 SD	Not required	Not required	Not required	Not required
Safety	Explicit warnings	Explicit warnings	Explicit warnings	Not given	Not given	Explicit warnings	Not given	Explicit warnings

(Continued)

Table V-3 (Continued)

References:

"Method 624--Purgeables," 40 CFR Part 136 [49 FR 43234, October 1984].

Method 1624, Revision C, "Volatile Organic Compounds by Isotope Dilution GC/MS," Industrial Technology Division (WH-552), USEPA, 401 M St SW, Washington, DC 20460, November 1986.

Method 524.1: "Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry," Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati Ohio 45268, September 1986.

Method 8240: "Gas Chromatography/Mass Spectrometry of Volatile Compounds," "Test Methods for Evaluating Solid Waste," SW-846, Volume 1 B: Laboratory Manual, Physical/Chemical Methods, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460. Third Edition, November 1986.

Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program, Analytical Support Branch, Office of Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460, Occtober 1986.

ASTM Standard D3871-84: "Purgeable Organic Compounds in Water Using Headspace Sampling" and D 4128-82: "Identification of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry," "1986 Annual Book of Standards," Section 11: Water and Environmental Technology, Volume 11.02: Water, American Society for Testing Materials, 1916 Race St., Philadelphia PA 19103, 1986.

"Purgeable organic compounds, total recoverable, gas chromatographic/mass spectrometric, purge and trap (O-3115-83)," "Methods for the Determination of Organic Substances in Water and Fluvial Sediments," U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A3, Open-File Report 82-1004, U.S. Geological Survey, Room 5A420, National Center, 12201 Sunrise Valley Drive, Reston, VA 22092, 1983.

Section 514: "Halogenated Methanes and Ethanes by Purge and Trap," and Section 516: Organic Contaminants, Gas Chromatographic/Mass Spectrometric Method," "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, American Water Works Association, Water Pollution Control Federation, Publication Office: American Public Health Association, 1015 Fifteenth St NW, Washington DC 20005, Sixteenth Edition, 1985.

standardized methods are properly used. GC/MS is a powerful tool in its ability to provide structural information. However, there are varying degrees of confidence in the ability of this technique to unequivocally "identify" an unknown compound. For this reason, the "analyzed for" approach is generally preferred to techniques oriented at identifying unknown compounds.

Two general techniques are used for GC/MS analyses. These techniques, were developed based on the volatility of the compounds. Compounds of high volatility and low water solubility are termed "volatile" organics and typically measured by "purge and trap" GC/MS. The concepts of purge and trap GC were discussed previously. The second technique involves the solvent extraction of compounds from the sample matrix with subsequent analysis. Compounds measured by this technique have been defined as "semivolatile" or "extractable" compounds. Due to pH adjustments that are sometimes incorporated in the solvent extraction step, subcategories of analytes have evolved that reflect the fractionation of the bases and neutral organics (B/N) together, separate from the acid analytes.

Tables V-3 and V-4 compare the methods that have been developed for the determination of volatile and semivolatile organics by GC/MS. Table V-3 compares the characteristics of eight methods which use the purge and trap GC/MS technique developed in Method 624 for volatile organics. As shown in this table, the methods have virtually identical operational conditions. However, the methods have different specifications for "identifying" a compound. For example, Method 624 specifies that the retention time must agree within 30 seconds from the standard retention time, the key fragment ions must maximize within one scan and the relative ion intensities must be within ±20% of the reference spectra. Method 8240 specifies a relative retention time (±0.06) has no specification for maximization of key ions and specifies that absolute ion intensities must be ±20%.

Other similar "differences" are documented in Table V-3. It is unclear as to whether any of these differences contributed to the differences in method performance (detection limits, precision, etc.) that are stated in the methods.

Table V-4 compares six GC/MS methods for semivolatile organics. As in the other tables, the methods shown in this table have similar operational analytes, and, as in the other tables, some differences are contained in the methods. For example, the mass spectral agreement criteria are specified as ±20% of the standard, ±50% relative abundance, ±20% absolute abundance and >950 FIT.

Comparison of Methods for Determining Metals by Graphite Furnace and ICP Emission Spectroscopy

Many metals such as lead, cadmium, selenium, arsenic, etc., are of environmental concern and have been tested for years. Methods for the determination of metals are included among EPA's 304(h), SDWA, Superfund and RCRA method compilations as well as from other organizations such as ASTM, USGS and Standard Methods. Table V-5 compares the salient characteristics of methods for the determination of metals in water by acid digestion and analysis with graphite furnace atomic absorption spectrophotometry (GFAAS). Table V-6 compares the sample preparation and analysis for metals by spectroscopy.

The three major EPA programs are listed in the tables along with the comparable methods from ASTM and Standard Methods. The FWPCA and SDWA both use MCAWW methods and, therefore, are combined in Tables V-5 and V-6. Table V-5 lists the general atomic absorption (AA) methods with the number of analytes covered in the general method. The method for determining selenium (Se) in water was selected as a representative of the individual "200" series AA methods. Table V-6 compares the ICP methods for all the analytes. Cadmium was selected as a representative metal.

The major characteristics of the AA methods are the same. They use acid digestion with nitric acid and hydrogen peroxide, the same matrix modifiers and instrument conditions, and have nearly identical ranges and detection limits. There are small differences in the digestions

Table V-4 Methods for Determination of Semivolatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry

Method Characteristic	Water Regulations	ITD	Solid Waste	Superfund	USGS	Standard Methods
Method Number (if any)	608	1625, Revision C	8270	CLP-MM	O-3117 &	516
Revision Date	1984	1986	1986	1987	1983	1985
Number of analytes covered	81	176	118	64	59	13
Format	EMSL-Ci	EMSL-Ci	No formal document	No formal document	TWRI	APHS
Sample						
Holding time	<7 days	<7 days	<7 days	<5 days	<48 hr	<1 week
Preservation	4 C + sodium thio	4 C + sodium thio	4 C + sodium thio	4 C, in dark	4 C	4 C, in dark
Volume required	1 Liter	35 mL	1 gallon	1 Liter	1 Liter implied	1 Liter
Extraction						
Fractions	B/N; Acid	B/N; Acid; Semi-	B/N; Acid; Semi-	B/N; Acid; Semi-	B/N; Acid; Semi-	B/N; Acid
Solvent	Methylene chloride	Methylene chloride	Methylene chloride	Methylene chloride	Methylene chloride	Not specified
Technique	Sep funnel/cont	Continuous	Sep funnel/cont	Sep funnel/cont	Sep funnel	Not specified
Concentration						
Technique	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Kuderna-Danish	Not specified
Final solvent	Methylene chloride	Methylene chloride	Methylene chloride	Methylene chloride	Methylene chloride	Not specified
Final extract volume	1 mL	1 mL	1 mL	1 mL	1 mL	Not specified
Cleanup techniques	None	GPC	GPC; many other	GPC	Not given	Not given
Gas chromatograph						
Column temperature						
Initial	4 min @ 50 C	5 min @ 30 C	4 min @ 40 C	4 min @ 40 C	2.5 min @ 45	Not given
Program	50 - 270 @ 8 C/min	30 - 280 @ 8 C/min	40 - 270 @ 10 C/min	40 - 270 @ 10 C/min	45 - 300 @ 6 C/min	Not given
Final	270 until elution	280 until elution	270 until elution	10 min @ 270	15 min @ 300 C	Not given
Column						
Type	Packed	Capillary	Capillary	Capillary	Capillary	Not given
Base/neutral	3% SP-2250	0.25 mm DB-5	.25 or .32 mm DB-5	.25 or .32 mm DB-5	0.20 mm SE-54	Not given
Acid	1% SP-1240DA	0.25 mm DB-5	.25 or .32 mm DB-5	.25 or .32 mm DB-5	0.20 mm SE-54	Not given
Semivolatile (B/N + acid)	Not applicable	0.25 mm DB-5	.25 or .32 mm	.25 or .32 mm DB-5	0.20 mm SE-54	Not given
Calibration						
Technique	Internal standard	Isotope dilution	Internal standard	Internal standard	Internal standard	Not given

(Continued)

Table V-4 (Continued)

Method Characteristic	Water Regulations	ITD	Solid Waste	Superfund	USGS	Standard Methods
Number of points	3 minimum	5	5 minimum	5	3	Not given
Linearity	<35% RSD of RF	<20% RSD of RF	<30% RSD RF	<30% RSD of RF	Not given	Not given
Frequency of verification	Daily	Each 8 hr shift	12 hour	12 hour	Not given	Not given
Verification specification	+/- 20% RF	Specs in table	+/- 30%	+/- 25% RF	Not given	Not given
Qualitative identification						
Retention time agreement						
Absolute	< +/- 30 s of std	No spec	No spec	No spec	25 scan window	No spec
Relative	Not given	Specs in table	+/- 0.06 RRT	+/- 0.06 RRT	No spec	1 - 2 percent
m/z's must maximize	< +/- 1 scan	<2 consec scans	No spec	No spec	No spec	No spec
Mass spectral agreement	+/- 20% of std	+/- 50% rel abund	+/- 20 Abs abund	+/- 20 Abs abund	No spec	>950 FIT
Average Characteristics for Determination of Compounds Listed						
Concentration range (min-max)	5 - 1300 ug/L	10 - 200 ug/L	Method 625 data	5 - 160 ug/L	Not given	Not given
Detection limit (min-max)	MDL: 0.9-36 ug/L	MDL: .002-15 ug/L	Not given	Not given	Not given	Not given
Quantitation limit (min-max)	4 - 100 times MDL	10 - 200 ug/L	PQL: 10 - 50	CROL: 10 - 50 ug/L	Not given	Not given
Percent recovery (average)	80 (est; Inter-lab)	98 (est; Inter-lab)	Method 625 data	Not given	81 (est; One lab)	95 (est; One lab)
Precision (average % RSD)	30 (est; Inter-lab)	15 (est; Inter-lab)	Method 625 data	Not given	30 (est; One lab)	12 (est; One lab)
Determination of Naphthalene as a Specific Example of Method Characteristics						
Concentration range	Not given	20 - 200 ug/L	Method 625 data	5 - 160 ug/L	Not given	Not given
Detection limit	MDL: 1.6 ug/L	ML: 10 ug/L	Not given	Not given	DL: 1 ug/L	Not given
Quantitation limit	4.8 ug/L	10 ug/L	PQL: 10 ug/L	CRQL: 10 ug/L	Not given	Not given
Percent recovery	78 (Inter-lab)	99 (est; Inter-lab)	Method 625 data	Not given	81 (Single lab)	95 (Single lab)
Precision (% RSD)	29 (Inter-lab)	14 (est; Inter-lab)	Method 625 data	Not given	17 (Single lab)	4 (Single lab)
Quality Control/Assurance (QA/QC)						
Tuning	DFTPP	DFTPP	DFTPP	DFTPP	Not given	Not given
Initial accuracy	Spec in table	Spec in table	Method 625 data	No test	No test	No test
Initial precision	Spec in table	Spec in table	Method 625 data	No test	No test	No test

(Continued)

Table V-4 (Continued)

Method Characteristic	Water Regulations	ITD	Solid Waste	Superfund	USGS	Standard Methods
Measurement of detection limit Not required	Required	Not required	Not required	CRDL required	Not required	Not required
Blanks						
Frequency	Each sample set	Each sample set	Each set or 5%	Each sample set	Each sample set	Not required
Specification	No spec	<10 ug/L	No spec	>(1 - 5) x CRQL	No spec	No spec
Surrogate recovery						
Frequency	Every sample	Every sample	Every sample	Every sample	No test	No test
Specification	No spec	In table	In table	In table	No spec	No spec
Matrix spike recovery						
Analytes covered	All	All	All	Subset	No test	No test
Frequency	10% minimum	100% (labeled)	5% minimum	5% minimum	No test	No test
Specification	In table	In table	In table	In table	No spec	No spec
Duplicate analyses						
Analytes covered	Not required	Not required	All	Subset	No test	No test
Frequency	No spec	No spec	5% minimum	5% minimum	No test	No test
Specification	No spec	No spec	No spec	In table	No spec	No spec
Statement of data quality						
Samples	Recovery +/- 2 SD	Recovery +/- 2 SD	Recovery +/- 2 SD	Not required	Not required	Not required
Laboratory	Not required	Recovery +/- 2 SD	Not required	Not required	Not required	Not required
Safety	Explicit warnings	Explicit warnings	Not given	Not given	Not given	Not given

References:
"Method 625--Base/Neutrals and Acids", 40 CFR Part 136 [49 FR 43234, October 1984].
Method 1625, Revision C: "Semivolatile Organic Compounds by Isotope Dilution GCMS", Industrial Technology Division (WH-552), USEPA, 401 M St SW,
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American Public Health Association, 1015 Fifteenth St NW, Washington DC 20005, Sixteenth Edition, 1985.

Table V-5 Comparison of Methods for the Determination of Seleniumin in Water by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)

Method Characteristic	EPA			Othera	
	Drinking Water & MCAWW	Solid Waste SW-846	Superfund-CLP CLP-SOW 787	ASTM	Standard Methods
Method Number	270.2	7740	270.2 CLP-M	D3859	323A
Revision Date	1978	1986	1987	1985	1985
General Method					
(GFAAS)	200.0	7000	IFB - Ex. D & E	D3919	304
No. Analytes Covered	29	11	9	13	17
Sample					
Holding Time	6 mos.	6 mos.	6 mos.	6 mos.	6 mos.
Preservation	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3
Digestion					
Acids, Reagents	HNO_3, H_2O_2	HNO_3, H_2O_2	HNO_3, H_2O_2		
Concentration	Conc., 30%	Conc., 30%	(1+1), 30%	Conc., 30%	Conc., 30%
Instrument Conditions					
Specified	Yes	No	Yes	No	No
Backgound Correction	Recom-mended	Required	Required	Recom-mended	Recom-mended
Matrix Modifier	$Ni(NO_3)_2$	$Ni(NO_3)_2$	$Ni(NO_3)_2$	$Ni(NO_3)_2$	
Calibration					
Number of Points	4, 5	4, 5[c]	4	4	4
Frequency	-	Hourly	Daily	Every New Run	Daily
Verification Specs.	±10%	±20%	±10%	-	-
Determination of Se					
Conc. Range (mg/l)	5-100	-	5-100	2-100	5-100
Detection Limit (mg/l)	2	2	2	2	2
% Recovery	94-112%	94-112%	97%[b]	92%	-
Precision	4-14%	4-14%	7%[b]	3-30%	6-18%
QA/QC Blanks					
Frequency	Each calib.	Each batch	10%	-	Each batch

(Continued)

Note
a USGS does not list the method in its manual.
b ASTM STP 925, (1986), Quality Control in Remedial Site Investigations.
c SW-846 (1986) Manual often contains several conflicting requirements between the chapters on Quality Control, General Method and Specific Methods

Table V-5 (Continued)

Method Characteristic	EPA Drinking Water MCAWW	EPA Solid Waste SW-846	EPA Superfund-CLP CLP-SOW 787	Othera ASTM	Othera Standard Methods
Specification	±10%	-	±5 ppb	-	-
Calibration Checks					
Frequency	5%	10%, 6.6%[c]	10%	10%	-
Specification	±10%	±20%	±10%	-	-
Analytical Spike (post-digest)					
Frequency	Each Matrix	All Complex Matrices	100%	Each Matrix	-
Specification	-	-	±15%	±10%	-
Replicate Injections	Recom-mended	Recommended	Two-Required	Recom-mended	Two-Required
Matrix Spike Sample (Pre-digest)					
Analytes Covered	-	All	All	-	-
Frequency	-	5%, 10%[c]	5%	-	-
Specifications	-	-	±25%	-	
Duplicate Sample					
Analytes Covered	All	All	All	-	-
Frequency	10%	5%, 20%	5%[c]	-	-
Specification	-	-	±20%	-	-
Duplicate Matrix Spike					
Frequency	-	10%, 5%[c]	-	-	-
Specification	-	-	-	-	-

Note
a USGS does not list the method in its manual.
b ASTM STP 925, (1986), Quality Control in Remedial Site Investigations.
c SW-846 (1986) Manual often contains several conflicting requirements between the chapters on Quality Control, General Method and Specific Methods.

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Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U.S. Geological Survey, Books, Chapter A1 (1979)

regarding the amount and concentrations of acids used. The major differences occur in the QC and calibration requirements. The number of standards required for calibration vary from four to five at frequencies ranging from hourly and daily to "unspecified". The calibration verification criteria ranged from ±10% and ±20% to unspecified.

Table V-6 Comparison of Methods for the Determination of Metals in Water by Inductively Coupled Plasma (ICP) Spectroscopy

Method Characteristic	EPA Drinking Water MCAWW	EPA Solid Waste SW-846	EPA Superfund-CLP CLP-SOW 787	Other[a] ASTM	Other[a] Standard Methods
Method Number	200.7	6010	200.7 CLP-M	D4190 (DCP)[d]	305
Revision Date	1979	1986	1987	1982	1985
No. Analytes Covered	25	25	25	16	25
Sample					
Holding Times	6 mos.	6 mos.	6 mos.	6 mos.	6 mos.
Preservation	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3
Digestion					
Acids, Reagents	HNO_3, HCl	HNO_3, HCl	HNO_3, HCl	HNO_3, HCl	HNO_3, HCl
Concentration	(1+1), (1+1)	Con., (1+1)	(1+1), (1+1)	Con., Con.	Con., (1+1)
Background Corrections	Required	Required	Required	-	Required
Interelement Corrections	If needed	Required	Required	-	Recommended
Linearity Check	-	-	± 5%	-	-
Calibration					
Number of Points	2 min.	3, 5[c]	3 min.	5	-
Frequency	-	-	daily	each run	-
Verification Spec	± 5%	± 10%	± 10%	-	-
Determination of Cd					
Concentration Range	-	-	-	50-1000 ppb	-
Detection Limit (µg/l)	4	4	4		4
% Recovery	93-116%	93-116%	97%b	97%b	
Precision	12-16%	12-16%	14-16%[b]	11% (100 ppb)	
QA/QC					
Accuracy Check	weekly	weekly	daily		
Accuracy Specification	± 5%	± 10%			
Initial Precision	± 5%	± 5%	± 10%		
Blanks					
Frequency	10%	10%	10%	-	-
Specification	± 2 std. dev.	± 3 std. dev.	± CRDL(5 ppb)[e]	-	-
Calibration Checks					
Frequency	10%	10%	10%	-	-
Specification	± 5%	± 10%	± 10%	-	-
Low Level Check	-	-	2x CRDL(10 ppb)	-	-
Interference Checks					
Type	Spiked Sample	Spiked Ck. Soln	Program Ck. Std.	-	-
Frequency	Every calibration	Every 8 hours	Every 8 hours	-	-
Specification	± 1.5 Std. dev.	± 20%	± 20%	-	-
Replicate Exposures	Recommended	Min. two	Min. two	-	-
Serial Dilution					
Frequency	Each matrix	Each matrix	5%	-	-
Specification	± 5%	± 10%	± 10%	-	-
Matrix Spike (Pre-Digest)					
Analytes Covered	-	All	All	-	-
Frequency	-	20%, 5%[c]	5%	-	-
Specification	-	± 20%	± 25%	-	-

(Continued)

Table V-6 (Continued))

Method Characteristic	EPA			Other[a]	
	Drinking Water MCAWW	Solid Waste SW-846	Superfund-CLP CLP-SOW 787	ASTM	Standard Methods
Duplicate Sample Analyses					
Analytes Covered	-	All	All	-	-
Frequency	-	20%, 5%[c]	5%	-	-
Specification	-		± 20%	-	-
Duplicate Matrix Spike					
Frequency	-	10%, 20%[c]	-	-	-
Specification	-	± 20%	-	-	-
Matrix Spike (post-digest)					
Frequency	Each matrix	Each matrix	Pre-Dig. Spike Fails		
Specification	± 10%	± 25%	-	-	-

Note
a USGS does not list the method in its manual.
b ASTM STP 925, (1986), Quality Control in Remedial Site Investigations.
c SW-846 (1986) Manual often contains several conflicting requirements between the chapters on Quality Control, General Method and Specific Methods.
d Direct Current Plasma only.
e CRDL in the CLP Contract Required Detection Limit (5 ug/l for Cd)

The number, frequency, and specifications for blanks are different among methods, the frequency and specifications of calibration checks are different, and the analytical spike and the number of injections are different as are the requirements for matrix spikes, duplicate samples, and duplicate matrix spikes. In the SW-846 manual for solid waste, the QC requirements are sometimes inconsistent between AA methods for the individual metals.

The comparison of ICP methods shows the same results found for AA. The methods are nearly identical, including the same acids for digestion. Again, however, there are small, apparently unnecessary, differences in the amounts and concentration of the acids. The concentration range, detection limits, and general percent recovery and precision statements are also the same among methods.

The major differences in the ICP methods, as with the AA methods, occur in the quality control requirements. The number of standards, the frequency, and verification specification in the calibration methods are different. Although the frequency of the blanks for ICP are similar among methods, the criteria range from ±2 standard deviations (std. dev.) for MCAWW and ±3 standard deviations for RCRA to ±detection limit for Superfund. Calibration checks, interference checks, serial dilutions, and replicate exposure requirements are all different as are the specifications for duplicates, matrix spikes and duplicate matrix spikes. The QC requirements for the ICP methods in ASTM and Standard Methods are non-existent. The data in Tables V-5 and V-6 reveal that all the methods use nearly identical materials, equipment and operating conditions but have differences in digestion methods.

Major deficiencies exist in the QA/QC requirements of the non-EPA methods and there is inconsistency among EPA programs, particularly within the solid waste program. The data also indicate that the EPA inorganic methods are more highly developed than non-EPA methods, with Superfund's Contract Laboratory Program being the most complete for frequency and specification requirements. EPA has found that unless detailed QA/QC requirements are contained in the methods and followed correctly, laboratories performing analyses will produce results of unknown and

often less than optimal quality. Consistent detailed methodology and QC requirements should be developed by EPA for the analysis of inorganics to ensure that data from the various programs are comparable and with a known and stated quality.

Biological Methods

Numerous organizations establish test protocols for biological methods, including the American Public Health Association (APHA); the American Society for Testing and Materials (ASTM); States, and individual testing laboratories. Although there are often many similarities between these methods, the precise requirements may be significantly different and could result in variability in the test results. In reviewing single and multilaboratory precision studies in the previous chapter, several investigators performing "round robin" evaluations attributed variable test results to either use of different protocols or variable interpretation of language in the same protocol. To examine the extent of these potential differences, the acute toxicity test method for Daphnia spp. in effluents, developed by APHA, ASTM, and EPA, is compared in Table V-7. This is one of the few biological tests that exist in a similar fashion from several organizations.

There was considerable difference in the format used for writing the method. The APHA method required constant reference back to previous sections that appeared to be general guidelines for any toxicity tests and not specific to this test. The APHA method left several analytes (e.g., length of test) in question, even after careful review of the applicable section. All three methods used a different definition of death and suggested different methods for determining death. This could considerably alter the LC_{50} since only those data collected at the end of the test period are used to calculate the LC_{50}. Control mortality restrictions were roughly equivalent. Only the EPA method required a standard reference toxicant. The number, size, and amount of test solution in each test container was significantly different. APHA had few clear specifications for water quality in the test solutions or required conditions during the test. Of the three methods, EPA's method was the most thorough method with the clearest specifications and instructions for performing the test. Any comparisons among methods developed for the various program offices of EPA or between EPA and other federal agencies is largely nonproductive. The targeted sample matrix for each method (e.g., dredged material, oil dispersants, municipal sludge) is typically so dissimilar as to mandate a matrix specific method. These methods have different goals due to the wording of the authorizing legislation or the site or disposal specific analytes (e.g., dilution rates).

While no significant benefits are gained by additional comparisons of specific techniques, comparisons of terminology and standardization of terminology used in biomonitoring would be useful. For instance, in aquatic toxicity testing, the definition of critical terms such as "death", "chronic", or "strain" are quite confused due to slightly different wording in the definition or different techniques associated with the concept (e.g., how to demonstrate or determine death).

Table V-7 Comparison of Daphnia spp. Acute toxicity test procedure from three sources

Parameter	EPA (1985)	ASTM (1987)	APHA (1985)
1. Test organism			
a. species	a. Daphnia pulex (preferred)	a. D. pulex or magna	a. Daphnia
b. age	b. 1-24 h neonates	b. <24 h neonotes	b. <24 h neonates
2. Test conditions			
a. temperature	a. 20+oC	a. 20+	a. 20oC, 25oC (?) +1oC
b. dissolved oxygen	b. >40% of saturation	b. not specified; within 10% of natural	b. within 10% if naturals: >60% saturation; no problem if 15%
c. dilution water	c. receiving water, surface water, ground water, synthetic water (mod. hard for D. magna; mod. or soft for D. pulex)	c. receiving, surface, ground, reconstituted	c. receiving water; reconstituted
d. pH	d. 6.0-9.0	d. no specification	d. pH = receiving water p,H adjust if necessary to +0, 4
e. light intensity	e. 50-100 ft. candles	e. <800 lux = 74 ft.	e. no specification
f. photo period	f. 8-16 h light/24 h	f. 16L:8D	f. no specification
g. cover	g. none	g. none	g. no specification
h. aeration	h. none unless DO below 40% saturation	h. not discussed	h. no specification
i. size of container	i. 100 ml beaker	i. 250 ml beaker	i 125 mL
j. no. per container	j. 10	j. 5	j. 10
k. no. of replicates	k. 2 l. 50 ml	k. 4 l. = 200 ml	k. 2
l. amount of test solution	l. 100 ml		l. 100 mL
m. no. of concentrations	m. screening - 1 to 4; definitive = 1 to 4	m. 5 + control	m. 5 + control
n. feeding scheduling	n. no feeding during 48 hr., every other day if longer	n. no feeding	n. no feeding
o. test duration	o. screening = 24 h	o. 48 h	o. 5 days or as long as live = short term tes;t long term test = 21-30 days
p. endpoint	p. LC50	p. LC50	p. LC50
3. Data			
a. standard toxicant	a. yes	a. no	a. no
b. frequency of observations	b. 0,1,2,4,8 hrs; daily	b. 24, 48 hr	1, 2, 4, 8, 16 hr; 24 hr - afterwards
c. method for calculating	c. choice of manuals or several computer programs	c. manual or computer - various procedures	c. various manual procedures
d. control mortality	d. <10%	d. <10%+d. <10%; prefer <5%	

Chapter Five References

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2. *Methods for Chemical Analysis of Water and Wastes,* Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA 600/4-70-020.

3. *Annual Book of ASTM Standards,* Volume 11: Water, American Society for Testing and Materials, Philadelphia, PA 19103.

4. *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments,* U.S. Department of the Interior, U.S. Geological Survey, Techniques of Water-Resources Investigation, Book 5, Chapter A1, 1979.

5. *Standard Methods for the Examination of Water and Wastewater,* American Public Health Association, 1015 Fifteenth Street, N.W. Washington, D.C. 20036.

6. Appendix C to 40 CFR 136.

7. National Resources Defense Council v. Train (8 ERC 2120, D.D.C. 1976).

8. *Test Methods for Evaluating Solid Waste,* SW-846. Office of Solid Waste and Emergency Response.

CHAPTER SIX

ADEQUACY AND COMPARABILITY OF QUALITY ASSURANCE AND QUALITY CONTROL PROGRAMS AND PROCEDURES

Introduction and Summary

While a fully validated and standardized method is desirable, it alone is not sufficient for the generation of valid data. A quality assurance and quality control (QA/QC) program including QA/QC procedures incorporated into methods are essential to detect and correct problems in the measurement process and to assure that the results generated are of a known and acceptable quality. The basic concepts of quality control, the techniques used to control errors, and quality assurance, the mechanism used to verify that the QC activities are acceptable, are described in detail in the literature (6-1 to 6-5). The QA/QC procedures contained in 40 CFR 136 methods were reviewed to determine their adequacy to control and document the quality of data produced for Federal Water Pollution Control Act (FWPCA) programs. These procedures were also compared to the procedures developed for other programs. Many QA/QC requirements developed by the Agency are not contained within the methods, but, are mandated by the program. These requirements were also reviewed.

Collaborative method validation studies have been conducted, reports completed, and precision and accuracy generated on 63 of the 175 EPA methods in 40 CFR 136. For 14 of these methods which cover the 114 priority pollutants the data from the studies have been used to establish minimal QC performance criteria for users of the methods. The need exists to generate this type of information for other analytes in 40 CFR 136 and for those matrices that have not been so validated.

The quality assurance activities established under EPA's legislatively mandated programs differ, and are lacking in some aspects. In addition, the quality control procedures contained in analytical methods addressing the same analytes are unnecessarily different, often conflicting and in many cases, insufficient. The Agency should attempt to establish uniform quality assurance criteria for all of its regulatory program efforts. Both chemical and biological methods established under each program office for a group of analytes should have consistent quality control requirements to enhance data quality and reduce costs for the regulated community. The laboratory approval and certification activities in the Agency are diverse, duplicative, and inconsistent among its operating programs. These differences result in much greater costs to the regulated communities and much greater complexity in regulations, for no useful purpose. The Agency should determine the feasibility of establishing a single uniform certification function within its QA program for all monitoring and regulating activities.

Quality Assurance Programs

Analytical methods developed by EPA contain specific QA/QC procedures related to activities such as calibration, laboratory control samples, spike samples, etc. However, incorporation of QC requirements into the methods is not sufficient to ensure the generation of valid data. In recognition of the need to provide additional guidance, each program has incorporated additional QA/QC activities to enhance the quality of the analytical data.

Before one can understand the past activities and future needs in QA/QC, one must understand the history of QA/QC in the Agency and the several levels now operating.

National Quality Assurance Program

EPA established a formal Quality Assurance (QA) Program in 1972 with the responsibility for QA assigned to the Office of Acid Deposition, Environmental Monitoring, and Quality Assurance (OADEMQA) within the Office of Research and Development (ORD). Technical responsibility for QA was assigned to three OADEMQA laboratories by matrix area:

Water and Wastes	Environmental Monitoring and Support Laboratory - Cincinnati, OH (EMSL-Cincinnati)
Air	Environmental Monitoring Systems Laboratory - Research Triangle Park, NC (EMSL-RTP)
Radiochemistry Toxic and Hazardous Materials	Environmental Monitoring Systems Laboratory - Las Vegas, NV (EMSL-Las Vegas)

EMSL-Cincinnati provides the following QA support to the Agency's water and waste programs including the programs under the FWPCA:

1. Collaborative Method Validation Studies
2. Method Equivalency Program
3. Intra-laboratory Quality Control Support:
   - Manuals/Guidelines for Quality Control
   - Quality Control Sample Program
   - The Repository for Toxic and Hazardous Materials (calibration standards for trace organics)
4. Interlaboratory QC Support:
   - Performance Evaluation (PE) Studies

Mandatory QA Requirement

In 1979, the Administrator established requirements for QA in the Agency:

May 30, 1979:

> . . .I am making participation in the quality assurance effort mandatory for all EPA supported or required monitoring activities... Monitoring is defined as all environmentally related measurements which are funded by the EPA or which generate data mandated by EPA.

June 14, 1979:

> In order to assure. . .usable data of known quality, I am making. . Quality Assurance Requirements mandatory for all EPA contracts, grants, cooperative agreements, and interagency agreements that involve environmental measurements.

The Agency requires the development of Quality Assurance Project Plans covering each activity of a project. The Quality Assurance Management Staff (QAMS) has been established in the Office of Acid Deposition, Environmental Monitoring, and Quality Assurance (OADEMQA) to develop, coordinate, and direct the implementation of these efforts.

QA Within Programs of the Agency

Although the concepts of standardized methodology and standardized QA across Agency programs are accepted and can be shown to be more efficient than separate efforts, each water and waste program differs somewhat in: analytes, concentrations of analytes, sample matrices, and interferences; and in legislative timetables for regulation and compliance. As a

result, the Agency's operating programs have established conceptually similar but not identical methods of analyses and QA/QC requirements.

Quality Control Within Methods

As regulations progressed, the three EMSL laboratories realized that the key to ensuring proper application of QC was to make QC an integral part of the analytical method which is required for use under regulations. Consequently, the methods for toxic organic analytes in 40 CFR 136 became the first water methods to contain a quality control section requiring start-up and ongoing performance demonstrations and to provide performance criteria. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA, Superfund) Contract Laboratory Program (CLP) program followed with a similar response.

Laboratory Certification/Laboratory Accreditation

Any discussions of laboratory approval, accreditation or certification first require a definition of terms. EMSL-Cincinnati, responding to the QA/QC needs of the Office of Water, uses the following definitions:

Laboratory Accreditation	a generic term used in a variety of ways by different organizations to describe some form of approval.
Laboratory Certification	the official EPA approval by a regulating authority based on exact Agency criteria, for a laboratory to perform some required function.

There is only one Certification Program in EPA, that for certification of laboratories regulated under the Safe Drinking Water Act (SDWA) and its amendments. The certification requirements include critical elements on sampling, sample preservation, and analytical methods, laboratory facilities, personnel, instrumentation, quality control, data reporting, successful participation required in evaluation studies for each analyte to be certified, and lastly, an on-site inspection of the laboratory operations based on the above criteria.

Laboratory Performance Evaluation

In order to assure that laboratories are performing in accordance with requirements in the program or the methods, the Agency established external laboratory evaluation procedures. The external laboratory evaluations include formal laboratory certification, laboratory approval blind performance evaluation samples, and/or on-site laboratory audits. While there is no doubt that these programs have improved the quality of data generated and that some overlap is desirable, there are inconsistencies and deficiencies in the various QA programs. The external laboratory evaluation programs established in the regulatory program of the Agency are summarized below.

FWPCA - There is no formal EPA certification program established under FWPCA. Wastewater treatment facilities are regulated under the National Pollution Discharge Elimination System (NPDES), one of the most extensive monitoring networks operated by the Agency. Within this system, dischargers monitor themselves and are required to immediately report any NPDES permit violations. Enforcement actions initiated by reported self-monitoring data are legally and technically equitable only if the data generated within the NPDES system are of known quality and are intercomparable. The Discharge Monitoring Report Quality Assurance (DMR-QA) program was instituted in 1980 to evaluate data quality from NPDES permittees. The primary mechanism in the DMR-QA program is the performance evaluation study. A performance evaluation study is conducted annually to measure the ability of discharger laboratories to generate good quality DMR data submitted by the 7500 major industrial wastewater dischargers to show compliance with their NPDES permits. The DMR-QA program provides a cost-effective mechanism by which this data quality is monitored.

Performance evaluation samples contain 29 of the most frequently occurring analytes listed on NPDES permits. Acceptance criteria are derived from analyses of these samples by EPA and state enforcement laboratories. Samples are distributed as unknowns to approximately 6500 laboratories representing 7500 major dischargers. Results are used to evaluate quality of self-monitored data. Quality control samples and other corrective actions are taken to bring poor performers back to acceptable levels and to help to maintain enforcement and compliance laboratories in control and intercomparable.

In the first two studies for the DMR-QA program, (1980 and 1982) 73-76 percent of the data were acceptable. The performance level has improved year by year to the present 86.5 percent acceptability.

Within available resources, the regions and states use DMR-QA results to flag laboratories with the most serious problems for follow-up such as on-site visits. However, although there may be some follow-up action from the states or EPA regional offices on poor performance by laboratories, direct action is not required. Only a few states (e.g., Wisconsin) perform formal compliance inspections of laboratories with recurring problems.

Although the most commonly regulated contaminants are addressed in the DMR- QA studies, these are only 29 out of the 252 analytes in 40 CFR 136. It is recognized that if resources were available, the studies should challenge analysts for at least representative compounds in each major pollutant category under regulation, the studies should be performed at least twice per year and that the group tested should be expanded to include the 5000-6000 "major-minor" dischargers, for a total of 13,000-14,000 permittees.

Laboratory Performance Evaluation Under Other Environmental Programs

SDWA - Under the SDWA, a formal certification program has been instituted to certify laboratories analyzing drinking water for compliance with the SDWA and the Drinking Water Regulation promulgated in 40 CFR 141 & 142. A certification manual, currently in revision, includes critical elements for certification, requirements to maintain certification, and methods to downgrade the laboratory certification status. Laboratories are certified for microbiology, chemistry or radiochemistry on an analyte-by-analyte basis.

In order to be certified, a laboratory must fulfill the following initial requirements: 1) satisfactory analysis of performance evaluation (PE) samples for those analytes for which it seeks certification; 2) acceptable on-site inspection; and 3) meet the minimal requirements stated in the certification manual (i.e., acceptable QA plan, use of approved methods, qualified personnel, and adequate equipment). This certification is valid for up to three years and in order to maintain it, the laboratory must satisfactorily analyze one PE sample per year, use approved analytical methodology, notify the certifying authority of any major changes in the laboratory, and pass an on-site evaluation every three years. Provisional certificates are also issued to laboratories which met most of the criteria and can demonstrate that they can produce valid data. These laboratories have up to one year to correct deficiencies. A one time extension of six months can be granted if progress is made in correcting the deficiencies. The mechanisms for provisional certification and de-certification are specified in the certification manual.

While these requirements provide some measure that the data generated are of a known and acceptable quality, the individual criteria vary among state to state certification programs. The periodic checks (PE samples and on-site inspections) for maintaining the certification are not designed to monitor laboratory ongoing performance.

Resource Conservation Recovery Act (RCRA) - Although the EPA program (Office of Solid Waste) establishes performance criteria and evaluates laboratory performance, it has no formal evaluation program for laboratories performing analyses under RCRA regulations. The Office of Solid Waste (OSW) sends out quarterly PE samples (through EMSL-Cincinnati) to EPA contractors and state laboratories performing RCRA analyses. The state RCRA requirements for laboratories vary

from state to state. Several states, such as New Jersey, allow laboratories to perform RCRA analyses if they are certified by the state to perform water and wastewater analyses or if the laboratories either participate in the EPA Superfund CLP or are contracted specifically by the state. Other states, such as California, have certification programs for solid waste analyses that involve performance evaluation samples, acceptable analytical methods and QA programs, as well as on-site inspections. There is no uniformity in the QA programs developed in the fifty states.

CERCLA - Superfund's CLP has developed an extensive QA program for contract analytical laboratories performing analytical services for EPA. Although the CLP does not have a formal certification program, it has stringent requirements which a laboratory must meet before a contract is awarded:

- The laboratory must satisfactorily analyze a set of at least two PE samples (water and solids) designed as typical waste samples.
- The laboratory must submit with its bid for a contract all the laboratory's standard operating methods (SOP's), a list of equipment to be used on the contract, and resumes to show staff qualifications.
- The laboratory must pass a pre-award on-site laboratory inspection designed to assess the laboratory's sample capacity and ability to meet the terms and conditions of the contract.

Once a laboratory has received a CLP contract to perform organic or inorganic analyses, an ongoing QA program is required which assesses the performance of the laboratory with quarterly (at a minimum) PE samples, routine on-site audits, and detailed audits of all data reported. Historically, 50-70% of the laboratories have failed to pass the pre-award PE samples. The laboratories with CLP contracts are generally regarded as among the better laboratories in the country. With the constant monitoring for lab performance and the high level of QA/QC, the CLP reputation gives Agency programs a strong "comfort factor" choosing CLP laboratories for other analytical services. The CLP has become a de-facto certification program for the laboratories performing analysis of waste samples.

However, since the controls in the CLP are only monitored for those laboratories under contract and providing analytical services to the Agency, there is no assurance that data generated by industry, or by CLP laboratories on non-CLP samples are of the same quality. Fully-qualified laboratories which may choose not to compete for purely business reasons, or were not selected for CLP contracts may be implied to be second class.

The Superfund program sends out blind PE samples to about 70 CLP laboratories through EMSL-Cincinnati and EMSL-Las Vegas. These samples simulate typical natural matrices such as mining waste. The PE samples are sent to laboratories who take part in the pre-award process, to determine which contractors are capable of performing chemical analyses on toxic wastes within established limits. Even when laboratories know they are being tested and presumably use their best people and equipment, some cannot successfully analyze PE samples. The percentages of laboratories passing organic and inorganic samples are nearly the same. Although validated methods and rigorous QA/QC requirements are critical for valid results, they cannot ensure reliable results. In addition QC requirements should be built into Agency programs and methods, and the QC records should be available with the data results.

Other Quality Assurance Support

The Agency provides other QA support for data generated by the user community:

- Method validation studies,
- Manuals and guidelines on sampling, analyses, and quality control,
- Analytical reference materials.

This section describes the QA support developed for FWPCA methods and for methods developed in RCRA, SDWA, and CERCLA programs.

Method Validation Studies

The formal collaborative study design has evolved over the past 10-12 years. At present, EMSL-Cincinnati conducts method validation studies (MVSs) inhouse and extramurally for water analytes. A prime contractor is assigned the task order for preparation of spiking solutions, water samples, instructional materials, verification analyses, formal conduct of the study, and screening of the study data from participating laboratories. EMSL-Cincinnati obtains the participating laboratories through the competitive procurement process based on technical qualifications, performance evaluation, and costs. The prime contractor conducts the study, EMSL-Cincinnati evaluates the results of using computerized data treatment, and prepares the final reports.

EMSL-Cincinnati processes data from the participating laboratories using a computer program entitled, "Interlaboratory Method Validation Study (IMVS)," which follows the American Society of Testing and Materials (ASTM) - D2777 guidelines. The IMVS program uses two outlier removal tests, the Youden laboratory-ranking test and a repetitive Thompson t-test, both at the 5 percent significance level. The retained data are processed to provide statistics such as the bias, overall precision and single analyst precision. The IMVS program computes a weighted linear regression equation for accuracy as a function of the true value, and for single analyst and overall precision as functions of the mean recovery of the analyte. Finally, the IMVS program compares each of the industrial and municipal water types against reagent water and indicates which of the water types exhibit a matrix effect.

Method validation studies have been conducted, reports completed, and precision and accuracy generated on the methods listed in Table VI-1. The data from these studies have been used to establish performance criteria limits for all of the 600 series methods. The need exists to generate this type of information for those analytes and listed in 40 CFR 136 that have not been so validated.

Table VI-1. Approved EPA Methods in 40 CFR 136 Supported by Formal EMSL-Cincinnati Method Validation Studies

Analytes	EPA Method #
pH	150.1
Specific Conductance	120.1
Non-Filterable Residue	160.2
Total Hardness	130.1
Sodium	273.1
Potassium	258.1
Alkalinity/Acidity	310.1/305.1
Chloride	325.3
Sulfate	375.4
Ammonia-Nitrogen	350.2
Nitrate-Nitrogen	352.1
Kjeldahl-Nitrogen	351.3
Orthophosphate	365.2
Total Phosphorus	365.41
BOD	405.1
COD	410.2/410.1
TOC	415.1
Aluminum	202.1, 202.2
Arsenic	206.3
Cadmium	213.1, 213.2
Chromium	218.1, 218.2
Copper	220.1, 220.2
Iron	236.1, 236.2
Lead	239.1, 239.2
Manganese	243.1, 243.2
Mercury	245.1, 245.2
Selenium	270.3
Zinc	289.1, 289.2
Trace Metals - ICP (27)	200.7
Purgeable Halocarbons (28)	601
Purgeable Aromatics (7)	602
Phenols (11)	604
Benzidines (2)	605
Phthalate Esters (6)	606
Nitrosamines (3)	607
Pesticides and PCBs (24)	608
Nitroaromatics and Isophorone (4)	609
Polynuclear Aromatic Hydrocarbons (16)	610
Haloethers (5)	611
Chlorinated Hydrocarbons (9)	612
2,3,7,8-Tetrachlorodibenzo-p-Dioxin (1)	613
Purgeables (31)	624
Base/Neutrals, Acids, and Pesticides (64)	625
Cyanide, Total	335.2
Cyanide, Amenable to Chlorination	335.1

Method validation studies have been completed or are in progress on the following analytes and methods in other EPA legislation:

Table VI-2. Method Validation Studies Completed for Other EPA Legislation

Analytes	EPA Method #
PCBs in Oils	--
Maximum Trihalomethane Potential	510.1
Total Organic Halides (TOX)	OSW-9020
Ignitable Organics	OSW-1010
Chlorophyll (Spectrophotometric and Fluorometric)	--
Macroinvertebrate Organisms	--
Petroleum Hydrocarbons in Brine	418.1

Table VI-3. Method Validation Studies - In Progress for Other EPA Legislation

Trace Metals in Water and Sludges	OSW 3005, 3010 and 3050
Volatile Organics (GC/MS)	OSW 8240/5030 (in conjunction with 524.2)
Semi-Volatile Organics (GC/MS)	OSW 8270/3510
Volatile Organics (GC/MS)	DW-524.2
EDB/DBCP	DW-504
Pesticides/PCBs	DW-525
Aldicarbs/Carbofurans	DW-531
Volatile Organics (GC/PID/ECD)	DW-502.2
Chlorinated Herbicides	DW-515

Manuals and Guidelines

Manuals and guidelines are an integral part of EMSL-Cincinnati's §304(h) quality assurance (QA) program. As the state-of-the-art changes, manuals/ guidelines are revised for sampling, sample preservation and analyses of waters/wastewaters for physical and chemical pollutants and biological forms commonly found in the environment. By setting and enforcing standards and limits, the Agency can ultimately enhance the quality of the environment. The guidance provided in the manuals such as the examples below supports these requirements.

1. Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, EMSL-Cincinnati, 1982.

   The quality of the data generated by monitoring activities is only as good as the sample collected, its preservation and analysis. Therefore, guidance is provided on collecting representative samples in ambient waters, and wastewaters, measuring flow rates to meet National Pollutant Discharge Elimination System (NPDES) mass loading requirements, statistical methods for sampling, automatic and manual sampling techniques, and preservation techniques.

2. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79/020, EMSL-Cincinnati, Revised March, 1983.

   Guidance is provided for analytical methods to monitor water supplies, waste discharges, and ambient waters. The objective of the manual is to provide the best analytical methods currently available for use in environmental monitoring, compliance monitoring, enforcement, and research activities of the Agency for water and wastewater.

3. Handbook for Analytical Quality Control (QC) in Water and Wastewater Laboratories – EPA-600/4-79-019, EMSL-Cincinnati, 1979.

   Continuing QA/QC programs must be established in the monitoring laboratories to assure the reliability and veracity of field and analytical data generated in water and wastewater pollution control activities. This handbook addresses those QC activities and provides general guidelines to establish the integrity of the data. It includes laboratory services, instrumentation selection, glassware, reagents, solvents, gases, QC charts, data handling and reporting, laboratory safety, and other guidance.

Reference Materials

Reliable reference materials are essential to assure the generation of quality data. The quality control samples, analytical method standards and performance evaluation samples prepared by EMSL-Cincinnati provide QA support for a variety of EPA programs.

Quality Control Samples

Water and wastewater laboratories generating data for enforcement, compliance, or to study long-term pollution trends must provide reliable data of the known quality to assure that a proper decision is made. One support activity is the provision of QC samples to the analysts as independent checks on analytical technique, calibration standards, and understanding of the analytical protocol.

Analytes contained in the QC sample program address the priority pollutants under the Consent Decree and other inorganic and physical analytes regulated under NPDES. Chemicals are purchased from commercial sources, checked for their identity and purity, purified if necessary, and combined with other compatible analytes. The analytes are normally dissolved in water or a water-miscible solvent such as acetone, methylene chloride or methanol, and flame sealed in all glass ampuls, then monitored for stability over a 90-day period. Upon successful conclusion of the stability studies, the QC samples (1-15 analytes) are produced in 3,000 to 10,000 ampul batches. Random samples from the production lot are analyzed by the producing contractor then sent to independent analytical laboratories to verify the true concentration for each analyte. Upon verification, new sample series are added to the QC sample list published in the semi-annual EPA QA Newsletter prepared by EMSL-Cincinnati. User instructions direct the analyst to dilute a specified volume in a water or wastewater. The true value for each analyte therein is provided with the 95 percent confidence limits (C.L.) within which the analyst's results should fall. The 95 percent C.L. for each analyte are developed from EPA method validation studies or EPA performance evaluation studies.

The ampul concentrates are designed for storage and shipment at ambient temperatures. Annual checks are conducted on each analyte by independent referee laboratories to assure that no degradation or change has taken place. There are 25 QC sample series containing about 235 analytes to support FWPCA programs, which are available to EPA, state, local, EPA contract laboratories and the commercial sector. The annual distribution rate for FWPCA programs use is about 75,000 ampuls. There are specific requirements in the 600 series methods in Table VI-1 that use these samples to demonstrate acceptable performance. Other federal and state programs which specify the use of these QC samples have varying frequency and use requirements.

In addition to the QC samples supplied for FWPCA methods, QC samples are designed to support the other Agency water programs as well as RCRA, Superfund, and Toxic Substances Control Act (TSCA). Some QC samples are produced as natural matrix samples. These samples contain the pollutants as they occur naturally or as they are added through actual pollution in the environment. Solid samples are collected from a waste site, a river, estuary, or lake. They are dried, homogenized, and reference values established by independent referee laboratories. Such samples include PCBs in sediments and fish, metals in fish, inorganics and general organics in municipal digested sludge and organic pollutants in Chesapeake Bay sediment. A complete list of the QC Sample Series and analytes is provided in the Table in the Appendix. Such reference samples are important to non-point source monitoring, ocean-dumping and marine/estuarine programs as well as RCRA.

The Repository for Toxic and Hazardous Materials

The EPA Repository for Toxic and Hazardous Materials was established to provide calibration standards to EPA, state, local, and EPA contract laboratories utilizing §304(h) methods. The Repository is a "permanent" source of organic calibration standards. The highest purity chemicals are procured or synthesized if unavailable or too costly, and provided to the requestor with a certified purity for each of the calibration materials.

The Repository purchases chemicals in neat form from the commercial sector and analyzes each to verify identity and purity. The purity is established primarily using gas chromatography (GC) with a capillary column followed by a flame

ionization detector. If the purity is greater than or equal to 99 percent, it is classified as a quality assurance standard (QAS) material. Purity in the range of 95 to 99 percent is classified as a quality assurance reagent (QAR) material and those multi-peak compounds such as PCBs and toxaphene are classified as quality assurance technical (QAT) grade materials. A major activity of the Repository is to upgrade as many analytes as possible into the QAS category through such purification techniques as high performance liquid chromatography (HPLC), spinning band distillation or recrystallization techniques. Upon establishment of the purity, samples are sent to independent referee laboratories to confirm the purity of the neat chemical. After purification, an average of 5,000 ampuls are produced for a single analyte in a suitable solvent at a concentration ranging from 1500 to 10,000 µg/mL. The single-analyte solutions are sent to independent referee laboratories to confirm the final concentrations.

Upon verification, the new calibration standards are added to the list of available standards in the EPA QA Newsletter. Some 108 organic compounds of the 114 priority pollutants specified in the Consent Decree are available as "certified" calibration standards. Approximately 51,000 standards were distributed in FY87 to 871 requesters to support analyses performed under the FWPCA. See the list of calibration standards in the Appendix.

Performance Evaluation Samples

To assure the legal defensibility and reliability of data generated, environmental monitoring activities must have viable intralaboratory and interlaboratory QA programs. An interlaboratory QA program includes use of unknown samples to challenge the ability of laboratories to perform acceptable analyses of regulated chemicals in a formal study.

In the performance evaluation studies conducted by EPA for water programs, stable concentrates of regulated analytes are produced at two levels, verified for true values, homogeneity, and stability over time, and distributed to participants for dilution with reagent water and analyses. Analytical results returned through state and regional program offices to EMSL-Cincinnati, where the data are computer-processed to determine performance acceptability. Statistics are accumulated over a number of studies and pooled to establish relationships (regressions) between test concentration and method performance. PE study limits on a given study are developed from EPA/state laboratory data in the current study or from previous studies. If limits from the current study are not completely enclosed within the limits based upon the previous six studies, the current study limits are used to evaluate the study data. A performance evaluation study report for each laboratory is sent to the ten EPA regional offices and through them to the regulating state authorities who use the results to confirm good laboratory performance, to identify problems and provide technical assistance on analytical techniques, calibration, and QC methods to the participating laboratories. Ultimately, these studies upgrade data quality.

There are three major types of PE studies for water and wastewater conducted by EMSL-Cincinnati: (1) Water Pollution (WP) PE studies with 900-1100 laboratories/study which are conducted to support the FWPCA, (2) the major discharger PE studies conducted with about 6500 laboratories/study conducted specifically for the Discharge Monitoring Report - QA (DMR-QA) supporting the NPDES program, and (3) Water Supply (WS) Studies with 1200-1500 laboratories/study conducted to support the Drinking Water Certification Program.

The 95 percent confidence limits were selected as acceptance limits for the Drinking Water Program's WS studies, while 99 percent limits were selected for WP and DMR-QA Studies. As a result, the overall performance levels of participant laboratories over time in the three study types have generally reflected the 4 percent difference (99-95) between the two sets of limits.

From an initial 83 percent overall acceptable data in the first WP study, the next two studies showed a slight decline as other laboratories participated for the first time. However, performance then showed only a slow

improvement to an 85 percent acceptance level which has remained relatively constant to this time. The DMR-QA studies showed a significant improvement initially and have remained relatively constant at about 84 percent acceptable data for the past four years. The WS studies began with 63 percent acceptable data in 1978 and have improved to an 80-81 percent over the last three years. The EPA will need to make additional effort and resource commitments for follow-up activities if the acceptance levels are to be further improved.

Quality Control Requirements

Quality control procedures are the practices used on an ongoing basis to make certain that the analytical method performed properly and to define the quality of the data that was generated. The quality control (QC) requirements in the methods promulgated by EPA or required by the various EPA programs can be divided into the following groups:

- Method performance testing,
- Instrument calibration and verification,
- Blank analysis,
- Ongoing method performance checks,
- Sample-specific QC, and
- Data reporting requirements.

Method performance testing involves the demonstration, prior to the analysis of any samples, that the laboratory is capable of performing the method.

Instrument calibration involves the initial calibration of the instrument using multiple standards at a specified frequency to define the relationship of concentration to instrument response and to ensure the instrument is capable of producing acceptable quantitative data. Instrument calibration should include verification of accuracy and precision using quality control samples. Ongoing instrument performance involves continuing use of calibration standards to monitor instrument performance and calibration stability during the analytical runs. Blanks include field blanks, calibration blanks, reagent or preparation blanks and spiked blanks to check for contamination and/or carryover in the analytical process and instrument baseline drift.

Ongoing method performance checks involve the use of quality control samples and standards to verify that the method and instrument were used properly. Laboratory control samples (LCS), method blanks and surrogates are carried through the entire analytical method to monitor method performance.

Sample-specific quality control includes matrix spikes, duplicate matrix spikes and duplicate sample analyses to determine the method performance on the samples. The matrix spikes give an indication of the accuracy of the method for each compound in the matrix of interest. Duplicate samples and matrix spike duplicates indicate the precision of the analysis in the matrix which includes errors due to analytical imprecision and sample non-homogeneity.

The frequency of these QC requirements, the acceptance criteria or specifications, and the corrective action required vary significantly between the methods established by different EPA programs. A summary comparison of the QA/QC requirements for the organic and inorganic methods for the various EPA programs is summarized in Tables V-1 through V-5 and VI-4, Frequency of QC Sample Checks.

Method Performance Testing

Prior to the analysis of any samples, many methods require testing to demonstrate the proficiency of the laboratory to properly perform the method. These initial start-up tests may also include an instrument or method detection limit determination study. With the exception of the Superfund CLP program, laboratories are not required to submit the data to a regulatory agency to prove the test was done. The external lab evaluation generally consists of formal certification programs, blind performance evaluation samples, and/or on- site laboratory audits.

FWPCA. Initial start-up tests are contained in seventeen methods in 40 CFR 136. In the 600 Series for organics, each analyst must analyze

four aliquots of a QC check sample (available from EMSL-Cincinnati or prepared by the laboratory) and generate statistics to show that the test results are within the acceptance criteria for precision and recovery listed in the methods. Problems that cause an analytical result to be out of acceptance limits must be corrected. The analytical methods for inorganics do not as yet require initial QA tests.

SDWA. The 500 series methods that have been approved in 40 CFR 121.24 for the determination of volatile organic chemicals have incorporated a formal QC program that specifies rigid start-up acceptance criteria that have not been directly derived from interlaboratory method validation data. The laboratory is required to analyze seven replicate samples containing the target analytes at defined spike concentrations (typically one-fifth the MCL). The results from these analyses are used to calculate an MDL as specified in Appendix B to 40 CFR 136. The results are also compared to acceptance criteria specified both for the average recovery and the standard deviation. For example, Method 502.1 requires that the average recovery be between 90% and 110% of the true value and the standard deviation must be less than 35%.

RCRA. The initial internal laboratory validations required for the RCRA program are contained in the methods specified in the SW-846 manual. For organics, where corresponding 600 series methods exist, the initial laboratory requirements are the same as those in the 600 Series promulgated under the CWA. For example, the requirements and acceptance criteria for Methods 8250 (GC/MS for semi-volatile organics - packed column techniques) and 8270 (GC/MS for semi-volatile organics - capillary column techniques) are not only identical to each other but are taken directly from Method 625 (40 CFR 136). Where no corresponding 600 series method exists (e.g., 8015, 8280), there are no initial performance requirements. For inorganic compounds there are no initial laboratory tests required under the RCRA program.

CERCLA. Under Superfund's Contract Laboratory Program, the laboratories contracting for organic and inorganic analyses must show that they can initially meet all the QC requirements (i.e., tuning, calibrations) specified in the contracts when analyzing the pre-award performance evaluation samples. In addition, the laboratories must determine and submit instrument detection limits for all the analytes on all the instruments to be used on the contract. For inorganics, the inter-element corrections and linear ranges used for the ICP are also submitted. The raw data for the initial tests must be submitted with the pre-award PE samples before a contract can be awarded.

Instrument Calibration and Verification

A review of the calibration requirements revealed differences in the methods developed within each Agency program. These differences included different numbers of calibration points, different frequencies of use and different acceptance criteria. As an example of the differences, the calibration requirements for the GC/MS methods for volatiles (624, 1624, 8240, etc.) are summarized below.

FWPCA. Under the FWPCA, the "600 Series" has two GC/MS methods for volatile organics (624 and 1624). Instrument tuning is required with bromofluorobenzene (BFB) prior to calibration and analysis of samples. Method 1624 requires a five-point calibration curve for each analyte while 624 requires only a three-point calibration. Both methods require the response factors (RF) used for quantitation to be constant at all concentrations with percent relative standard deviations (RSD's) ranging from less than 10% to less than 35% in order to use the mean RF for calculation. In 624, ongoing calibration and BFB tuning verification is required at least daily, while in 1624 it is required every eight hours when the systems are in use. Tables with specific acceptance criteria for each compound are provided in the 600 methods.

SDWA. Under the SDWA, the "500 Series" includes two similar GC/MS methods for volatile organics, Methods 524.1 (packed column) and 524.2 (capillary column). The instruments must be tuned with BFB prior to calibration and analysis, same as with the 600 Series for VOA's. The criteria for key ion abundances are also

Table VI-4 Approved EPA Methods in 40 CFR 136 Supported by Formal EMSL-Cincinnati Method Validation Studies

Analytes	Methods	Method Blank	Field Blank	Field Dup.	Dup. Sample	Spike Dup.	Matrix Spike Sample	Lab Control Sample	Sur-rogates	PE Samples
Clean Water Act Water & Wastewater Samples										
GC Purgeables	601-602	Daily	-	NS	-	-	10%	Daily	-	-
GC "600" Series	603-619	ESS	-	NS	-	-	10%		-	-
GC/MS Purgeables (VOA)	624	Daily	-	NS	-	-	5%	Daily	Req	-
GC/MS Semivolatiles	625	ESS	-	NS	-	-	5%		Req	-
AAS Metals	200.0	ESS	-	NS	Opt., 10%	-	-	-	-	Yearly
ICP Metals	200.7	ESS	-	NS	-	-	-	-	-	-
Safe Drinking Water Act Finished Drinking Water and Raw Source Water										
Organic "500" Series	502.1-531	Daily	ESS	10%	-	-	-	10%		Qtrly.
Metals - Same as CWA										
CERCLA - Superfund (CLP) Water, soil, waste samples										
GC - Pest. & PCB's	608-CLP	5%, ESS	Rec	-	-	5%, ESS	5%,	-	Req.	Qtrly.
Dioxin (2378)	613-CLP	ESS	Rec	-	-	5%, ESS	5%, ESS	-	ACC	ESS
GC/MS Purgeables (VOA)	624-CLP	Daily,ESS	Rec	-	-	5%, ESS	5%,	-	ACC	Qtrly.
GC/MS Semivolatiles	625-CLP	5%, ESS	Rec	-	-	5%, ESS	5%,	-	ACC	Qtrly.
Metals - AA	200.0-CLP	5%, ESS	Rec	-	5%	-	5%, ESS	ESS	-	Qtrly.
ICP	200.7-CLP	5%, ESS	Recom.	-	5%	-	5%, ESS	ESS	-	Qtrly.
RCRA Soil, waste samples										
GC "8000" Series	8010-8150	ESS	NS	-	ESS	ESS	ESS		100%	-
GC/MS VOA	8240	Daily	NS	-	ESS	ESS	ESS		CLP	-
GC/MS Semi-Vol.	8250,8270	ESS	NS	-	ESS	ESS	ESS		CLP	-
Dioxin & Furans	8280	ESS	NS	NS	ESS	-	ESS		CLP	NS
HPLC (PAH)	8310	ESS	NS	-	ESS	-	ESS		-	-
Metals - Acid Dig.	3000	ESS	NS	NS	20%	-	ESS		ESS	-
AA	7000	ESS	NS	NS	5%	5%, 10%	20%	-	-	-
ICP	8010	ESS	NS	NS	5%	20%	5%	-	-	-

ESS - Each samples set NS - Not Specified Opt - Optional Qtrly - Quarterly Recom - Recommended
Req - Surrogates required, no acceptance criteria CLP - CLP criteria are used
ACC - Surrogate required; acceptance criteria established

similar to the 600 Series except for differences in the requirements for mass 173 in Method 524.1. Both methods require five-point calibrations with constant RF's at all concentrations (percent RSD ranging from less than 10 to less than 35) for mean RF calculations. Similar to the 600 Series methods, ongoing calibration checks and BFB tuning are required at least daily. Unlike the 600 Series methods, however, the 500 Series require the daily calibration check for every compound to respond within 20% of the initial calibration.

CERCLA. The method adopted by the CLP for VOA's is Method 624-CLP-M which is basically the same as 624 except that a five-point calibration is required. In addition, key compounds, termed system performance check compounds (SPCC), must meet minimum RF's. Calibration check compounds (CCC) must have RF's within 30% RSD. Ongoing calibration checks and BFB tuning verification are required for every 12 hours of analyses. The minimum RF criteria for the SPCC's (0.3) and the CCC's (RF's - 25% of the initial calibration) must be achieved every 12 hours.

RCRA. Under RCRA, the SW-846 Manual has one method (8240) for GC/MS analysis of volatile organics which operationally contains requirements virtually identical to the CLP requirements.

Laboratory Control Samples

Laboratory control (LCS) samples are samples that are analyzed to verify that the method performance was within specified control limits. Laboratory control samples include method or reagent blanks and check samples containing known amounts of analyte. The quality control samples supplied by EMSL-Cincinnati are frequently used as LCS's. The use of LCS's does not measure the performance of the method on the samples analyzed, but does demonstrate that the method was properly performed.

FWPCA. For organics, most of the QC samples required by the 600 Series organic methods are generated in the laboratory and include method blanks, sample spikes and laboratory control samples. For inorganics, the only QC sample specification contained in the 200.0 AA method is an "optional requirement" to analyze a reference sample once per quarter. The results for the reference sample should be within the control limits established by EPA. The ICP method (200.7) requires the analysis of a "quality control sample" obtained from an outside source to be used for the verification of the calibration. The quality control sample "should be prepared" in the same acid matrix as the calibration standards. This does not necessarily require that the QC sample is carried through the entire sample preparation and analysis methods. The "200" Series metal methods do not, therefore, require a laboratory control sample.

SDWA. For organics, the SDWA 500 Series methods for volatile organic compounds (VOCs) emphasize detectability at low concentrations near the MCLs. Laboratory control samples at a 10% frequency or at least 2 samples per month are required. The SDWA methods have also specified the analysis of a low level QC check sample on a weekly basis. The inorganic QC requirements for SDWA are the same as those under FWPCA.

CERCLA. The CLP methods under Superfund require method blanks or preparation blanks for every sample matrix or every 20 samples, whichever is more frequent, and lab control samples for inorganics. There are no LCS requirements for organics.

RCRA. Under the RCRA program, the SW-846 Manual, 3rd Edition, has quality control requirements in several sections, which sometimes have confusing specifications. The RCRA methods specify the collection of field duplicate samples, field blanks, and equipment blanks (rinsates) in the general QA section but do not specify a frequency. For inorganics the only QC sample required for AA or ICP is the preparation blanks. Method 6010 also requires the preparation of a "quality control sample" in the same acid matrix as the calibration standards, similar to Method 200.7. Unlike Method 200.7, however, the RCRA method does not indicate when or if that sample should be

analyzed. Requirements for the analyses of LCS's for organics are not specified.

Sample Specific Quality Control

Sample specific QC requirements are contained in the analytical methods to document the performance of the method for the samples analyzed. The QC requirements include matrix spikes, duplicate matrix spikes, duplicates, and surrogate spikes. A lab sample duplicate is a sample that is a split at the laboratory and both the splits are carried through the entire sample preparation and analysis procedures as separate samples. A sample spike is the addition of standard(s) to a sample before sample preparation. A sample spike duplicate is a sample split at the lab with both splits spiked with the same standard and then carried through the entire sample preparation and analysis procedure as separate samples. Most programs require either duplicate samples and a spike sample or sample spike and duplicate sample spikes. Only the RCRA program requires all three in some cases, a duplicate sample, a spiked sample and a duplicate spiked sample.

FWPCA. The 600 Series methods for organics require a laboratory spiked sample at a frequency of 10%, except for methods 624 and 625 which require a frequency of 5% (one per 20 samples). The GC/MS methods require the addition of surrogate spikes to each sample. Neither duplicate samples nor duplicate spike samples are required in the organic methods.

For inorganics, neither the 200.0 AA method nor the 200.7 ICP method requires duplicate samples or spiked samples, although a duplicate sample is recommended in the AA method (200.0). An analytical (post-digest) spike is recommended in method 200.7 (ICP) for new or unusual sample matrices and is required in the individual AA methods for every sample matrix to verify that standard additions are not required. There are no criteria specified for the AA spiked sample, while a criteria of 100 ± 10% recovery is specified for the spike in the ICP method to indicate possible interferences.

SDWA. The 500 Series methods for organic compounds do not require laboratory duplicates, spike samples, or surrogates. The inorganic methods have the same requirements as those under FWPCA.

CERCLA. The organic CLP methods require a spike sample and a spike sample duplicate at a frequency of 5% or per sample batch, whichever is more frequent, and surrogates in each sample. The criteria for the matrix spike and matrix spike duplicate recoveries for each compound are contained in tables in the SOW. The inorganic CLP methods require a matrix spike sample and a duplicate sample at a frequency of 5% or per sample set, whichever is more frequent. The duplicate samples must be within ± 20% and the matrix spike recovery must be 100 ± 25%. If the matrix spike is out of control, an analytical spike (post-digest) is required to separate the analytical method performance from the digestion performance.

RCRA. The sample specific QC procedures contained in the 3rd Edition of SW-846 is somewhat confusing since the QC section, the general sections, and each individual method, often have different requirements. The QC chapter, 1.3, requires a detection limit and quantification limit of all analytes to be evaluated by determining the noise level of response for each sample. Method 6010 for ICP specifies only a duplicate sample at 5% frequency and a spiked sample duplicate (i.e., two separate spiked samples) at a 20% frequency (every 5 samples). The general AA method (7000) specifies a duplicate and a spike sample every twenty samples (5% frequency), while the individual AA methods often specify a third requirement. Method 7060 for arsenic, for example, requires "duplicates, spiked samples, and check standards should be routinely analyzed" in 7.8, but the QC Section 8 requires only a spike duplicate sample every 20 samples (5% frequency), not a duplicate sample and not the 20% frequency specified in the ICP method. Method 7470 for mercury requires a spike duplicate every 10 samples (a 10% frequency). Thus, for AA methods, the QC requirements include 5% and 10% frequencies, sometime a spike and duplicate and sometimes a spiked duplicate without a duplicate sample. The ICP method requires a duplicate spike sample at a 20% frequency. The QC requirements in the

digestion methods specify a duplicate sample at a 20% frequency (every 5th sample) which contradicts both the AA and the ICP methods. There is no obvious reason why the QC requirements should be so dramatically different between methods and analytes and it adds significant confusion to the laboratory attempting to analyze the sample according to the recommended methods.

For organic analyses, a spiked sample and a spiked sample duplicate are required at a frequency of 5% (one every 20 samples) with surrogates required on all samples. The surrogate spikes are not identified in the GC methods. Duplicate samples are not required. There is some confusing language in the method however. For example, method 8250, 5.6, states that the matrix spike standard is injected "into the GC/MS to determine recovery of surrogate standards in all blanks, spikes and extracts". Although most of these problems are probably due to typographical errors, these inconsistencies become requirements for the laboratory community when the methods are quoted in the regulations.

A summary comparison of the QC requirements for the various programs is shown in Table VI-2. Another summary comparison of the QA/QC requirements including criteria are given for some methods in the methods comparisons in Tables V-1, V-2 and V-3.

Computerized Quality Assurance

Because EPA realized that the exponential increase in the volumes of data generated places a burden on its ability to monitor the integrity of analytical results, the Agency is moving toward computerized evaluation of environmental data quality.

As an example of this, the Industrial Technology Division (ITD) in EPA's Office of Water Regulation and Standards has been evaluating results of gas chromatography/mass spectrometry (GC/MS) analyses on EPA's mainframe computer. The advantages of computerized evaluations are the removal of subjectivity of human judgment and drudgery and the rapid availability of quality-assured results.

ITD's need for computerized quality assurance was brought about by the large volume of data generated in analyses of wastewaters. In ITD's programs, data generated by the contract laboratories are placed on magnetic tape in a raw data format used to archive data for subsequent testing as a part of the 1976 Consent Decree paragraph 4(c) and in a reduced data format for reporting final results. Magnetic tapes of the raw data are shipped to EPA's Environmental Research Laboratory in Athens, Georgia for identification and quantification of unknown pollutants. The reduced data are shipped to EPA's National Computer Center in Research Triangle Park, North Carolina for computerized data quality evaluation. After evaluation, reports of final pollutant concentrations and statements of data quality are printed out at EPA Headquarters for ITD use in developing effluent limitations and guidelines.

Based on the concepts provided by ITD, and on the commonality of quality assurance in EPA's GC/MS methods, instrument manufacturers have begun producing software packages capable of computerized evaluation of data quality. In turn, EPA has had to refine the quality control requirements in its contracts to make them more definitive. The obvious advantage of monitoring data quality at the point of generation is that data will be of acceptable quality when received by the user and rejections and reruns will be reduced.

Data Reporting Requirements

In nearly all of the Agency's environmental monitoring programs, the reporting requirements are external to the analytical methods. This separation permits the method to be used by organizations external to EPA (e.g., industry). One exception to this separation is the Superfund Contract Laboratory Program (CLP), in which the reporting requirements are included in the analytical methods. This inclusion is desirable for the CLP because the methods and data are intended almost exclusively for Agency use, whereas nearly all

other Agency methods are intended for use by EPA and the analytical community at large.

For other methods, each regulatory program has defined its reporting requirements, leading to a variety of reporting formats through EPA and adding to the difficulties in comparing environmental data between programs. Data reporting requirements, whether internal or external to methods, are not always consistent. Inconsistencies result from varying program requirements, or changes in method technology.

One example is the problem of reporting pollutant contaminants at concentrations which cannot be measured accurately or which cannot be quantitated. Many of the different and accepted "codes" for reporting these levels are contained in RCRA's SW-846 Manual Table 11-2. Unfortunately, RCRA allows 14 variations to be used. Other programs have similar reporting codes as follows: LOD (Limit of Detection), LOQ (Limit of Quantification), PQL (Practical Quantitation Limit), MQL (Method Quantitation Limit), MDL (Method Detection Limit), IDL (Instrument Detection Limit), CRDL (Contract Required Detection Limit), LT (Less Than), BDL (Below Detection Limit), < (Less Than #), - (i.e., <0.01), "trace" or "t", ND (Not Detected), "K" (i.e., K0.01), "u" (i.e., STORET),– (dash), large numbers (i.e., 99999), zeros, {} (i.e., [0.01]), and of course blanks. In many cases, the symbols are ambiguous because the meanings could be that the value was at the limit of detection or the constituent was not present. This problem is exacerbated when samples must be diluted.

Once the data are reported, the problem arises as to how calculations are performed for the various requirements such as spike recoveries, duplicate precisions, etc. In some cases, zero is used and in other cases one of the many types of detection or quantitation limits are used. Many methods include general method detection limits, but provide little guidance for determining a practical quantitation limit for real samples. The following section summarizes the few data reporting requirements specified in the various EPA programs.

FWPCA. The organic "600" series methods specify that "all QC data obtained should be reported with the sample results". Exactly how or what QC is to be reported is not specified, and often this requirement is not followed by laboratories. The methods also specify that the concentrations should be reported as µg/L without correction for recovery. The inorganic "200" series AA methods specify only that results entered into EPA's STORET database must be in µg/L. The ICP method (200.7), however, requires data be reported in mg/L up to three significant figures as well as corrected for the reagent blank.

SDWA. The inorganic requirements for SDWA are the same as in FWPCA methods. The organic "500" series methods all require reporting in units of µg/L. The methods also require that "all QC data obtained should be reported with the sample results". Additional requirements are specified under the National Primary Drinking Water Regulations (NPDWR): results of all analytical methods including negatives (i.e., not detected); the name and address of the system that supplied the sample; contaminants; analytical methods used and the dates of sampling and analysis. The SDWA set the PQL's for 7 regulated VOCs at 5 µg/L, and at 2 µg/L for vinyl chloride, which was described as approximately 5 to 10 times the MDL.

CERCLA. The reporting requirements under Superfund's Contract Laboratory Program are very detailed and quite extensive to permit independent review by other chemists. Nearly every aspect of the analysis is documented with rigid format and specified as a deliverable. All the QC to be reported and its format is specified in detail. Specifications are also given for calculations, units, detection limits, etc. The most recent CLP requirement for reporting all the data results on computer diskette has resulted in exact directions and formatting for the reports to allow direct reading into the EPA computers. The organic deliverables include, but are not limited to: summary of GC and GC/MS calibrations, GC/MS tuning results, calibration verifications, sample and QC samples tabulated results (blanks, surrogates, spikes, spiked duplicates, etc.), raw data (i.e., mass spectra and chromatograms) and results for the tentatively identified compounds.

The inorganic deliverables include the summary of the AA ICP calibrations, the calibration verifications (initial and continuing), the sample results and sample description, the QC samples results (blanks, spikes, spiked duplicates, etc.), and the raw data (i.e., direct readout from the instrumentation). Despite the perception that the CLP requires tremendous amounts of extra results, the CLP protocols do not require exceptional amounts of QC, but only that all the QC have criteria, that these criteria be met, and that all QC be reported and delivered with the results.

RCRA. The third edition of SW-846 stipulates that the QC data must be available from the laboratory upon request and adopted most of the reporting requirements of Superfund's CLP, including all the forms. Unfortunately, some of the QC requirements do not always fit with the CLP forms and confusion can arise. Many contract analytical laboratories assess an additional fee to cover the cost of providing the cost of the data packages for RCRA. Both RCRA and CLP require the reporting of percent moisture or percent solid content of the samples without blank correction.

The determination of PQL's for organic compounds in various matrices are specified in SW-846 and are calculated by multiplying the MDL by a matrix "factor". The MDL's and the matrix factors are provided with each method. For example, in method 8250 (GC/MS for semi-volatiles), the factors are 10 for groundwater; 70 for low level soil; 10,000 for high level soil; and 100,000 for non-water miscible waste. The PQL's do not take into account any dilution or pre-concentration and the matrix "factors" may be a somewhat simplistic approach to the problem of reporting limits in different matrices.

In general, most methods do not provide sufficient information for reporting requirements. Documentation should be available to provide information sufficient to support all claims made from the results including the QA and QC data. Measurements should be reported in consistent units only to the number of significant figures consistent with their limits of uncertainty. Reports should make clear which results, if any, were corrected for blank and recovery measurements. Reports should be written to include sufficient information so that the users of the data can understand the results without having to return to the raw data to make their own interpretation. Finally, and most importantly, data should be reported with enough information to establish the quality of the results.

Quality Assurance and Quality Control for Biological Methods

Quality assurance guidance for the various biological methods is very diverse in its goals, requirements, and adherence. A solid QA/QC program for microbiological methods has been established by the Agency for the SDWA Drinking Water Certification Program and can serve as a standard against which other EPA programs can be compared. The SDWA QA program includes analyses of performance evaluation (PE) samples on an annual basis, on-site visits, initial certification and recertification procedures, investigation methods for problems and rigid inhouse requirements for precision studies. In response to the 1986 Amendments to the Safe Drinking Water Act, this program will need to be expanded to include samples for viruses, heterotrophic plate counts and presence/absence tests for total and fecal coliform bacteria.

A similar program does not yet exist for FWPCA biological tests. It should be developed for all biological or bioassay methods promulgated in 40 CFR 136.

A national program for the certification of toxicity testing laboratories would be useful in insuring the quality of test data. At present, two states (California and New Jersey) have laboratory certification programs for toxicity testing laboratories. QC support for a toxicity laboratory certification program has been started within the Quality Assurance Branch at the EPA EMSL-Cincinnati. Standard reference toxicants (copper sulfate, cadmium chloride, and sodium dodecylsulfate) are available upon request. Ampuls are supplied with instructions and an expected range of LC50 results. While this reference toxicant program is conceptually sound, it has been very limited in scope in the absence of a national certification program for

the FWPCA. Sample distribution is limited due to current funding problems. While temporary, this may inhibit the development of the QA/QC practices necessary for the technique-oriented biological and biomonitoring methods in testing laboratories. EPA should accelerate the development of a full QA/QC program for biology and seek to make the use of QC and PE samples mandatory for aquatic toxicity.

The QA section of the acute toxicity methods manual includes a cumulative summary (cusum) graph or control chart developed from data for a specific reference toxicant and species of test organism. This running plot is maintained by adding new data each time a standard reference toxicant test is performed. The LC50 should fall between the upper control limit (mean plus two standard deviations) and the lower control limit (mean minus two standard deviations), the sensitivity of the test organisms or the credibility of the test system are suspect. The reference toxicant test should be repeated with the same organisms or a different source of test organisms.

The maintenance of a control chart is a useful concept to ensure quality data and should be required. In the "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms Manual", a frequency for reference toxicant tests is specified. This requirement should be incorporated into all toxicity test methods.

Chapter Six References

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CHAPTER SEVEN
IMMEDIATE AND LONG-TERM TECHNOLOGY AND TESTING METHODS NEEDS

The regulatory programs directed and managed by EPA have significantly motivated the development and commercialization of the analytical technology required to support environmental monitoring. In addition, the Agency has been the principal developer of testing procedures and methods and provider of testing methods to perform chemical and biological monitoring required to support all environmental programs in the United States. Although the EPA has made significant strides in developing the technology and methods in use today, the recent pace of environmental regulation has created a demand for testing technology and methods greater than ever before. The demands for new technology and improved methods are based on program needs attributable to increased emphasis on the measurement of more analytes in more complex matrices at lower levels and with better performance. In order to ensure continued success to meet these increased demands, EPA should continue its role as the leader in the development of methods in a number of areas.

Some of these areas require immediate attention to meet a specific program need (e.g., methods to measure organic chemicals and metals in POTW sludges). Other areas are broader based and will require the implementation of new technology (e.g., methods for the measurement of polar water-soluble organics). In addition, there are needs to improve the reliability of existing methods and to develop generic methods that are suitable for many needs (e.g., multiresidue pesticide methods). This chapter discusses these immediate and long-term needs and the process used, or that should be used, to meet these needs.

Overview and Summary

The ability of laboratories to detect and measure pollutants in environmental samples has improved exponentially over the past 25 years. For example, in 1951, the U.S. Public Health Service first reported the presence of organic chemicals in drinking water (7-1). The method required the collection of up to 80,000 gallons of water for each analysis. Extensive, laborious operations were performed to demonstrate that the water contained organic chemicals in the parts per billion (ppb) range at an analytical cost of several thousand dollars (today's dollars). The specific chemicals present could not be identified. By comparison, a routine analysis for halogenated volatile organic compounds can now be performed on as little as 5 milliliters (mL) of sample (0.0002% of the sample required in 1951). Today, reliable identification and accurate measurements of these compounds can be performed at the sub part per billion level for about $100 per analysis.

This improvement in technology has also been reflected in other ways. At the time of the Natural Resources Defense Council (NRDC) Consent Decree in 1976 (7-2), environmental analyses for toxic chemicals were typically performed at universities or research centers. There were few commercial laboratories operating gas chromatography/mass spectrometry (GC/MS) instrumentation and

there were virtually no standardized methods for the measurement of specific pollutants in water. In the decade since the Consent Decree, the improvements in instrumentation, the quality of the analytical methods and the growth of laboratories capable of performing these analyses has been astronomical. It has been estimated that in 1986 over 500,000 environmental samples were analyzed in the United States (7-3). Similarly, there have been dramatic improvements in the sensitivity of short-term toxicity tests and in the development of new genotoxicity tests.

Despite these improvements, much remains to be done. Based on the increasing demands from existing regulations, existing testing methods will require significant improvement and new technology must be developed and standardized to satisfy these demands. Specifically, new technology, or modifications to existing methods are required to improve sensitivity, precision, accuracy, specificity, applicability and reliability. Many of these methods require highly skilled analysts and complex, expensive instrumentation. The explosive demand for analytical data has resulted in a proliferation of commercial analytical laboratories, and a shortage of trained and experienced personnel. These factors contribute to the need for significant improvements in the methods and technology available today. These factors also contribute to the need for training of analytical chemists, continued support in supplying methods, reference materials, and guidance to the regulated community. Significant limitations are inherent in existing technology and will require development of completely new technologies to solve some analytical problems. The combination of needs to improve the performance of existing methods and to develop new technology will require a concerted intensive effort by the Program Offices and ORD.

As explained in more detail in subsequent sections, there are a multitude of immediate needs which need to be addressed. These needs range from improving an existing method to developing a new method in response to legislative mandates. Beyond these immediate needs, the Agency plans to continue its investigations into new technologies which will provide solutions to tomorrow's environmental problems. The Agency must maintain a leadership role in analytical methods development if it is to maintain technical credibility in this area.

Until the early 1980's, the scientific and regulated community, as well as technical staff within the Agency, believed that there was a good balance between the available technology and methods and the regulatory requirements. However, in the last five years, the consensus is that the monitoring demands have significantly outstripped the Agency's ability to provide technology and methods capable of fully supporting these programs. The Agency with its current organization and resources cannot provide the technology and methods required to fully support the immediate and long-term monitoring requirements established under current environmental laws. While the Agency's resources must be greatly increased to solve priority problems, federal efforts need to be more sharply focused on developing technology and improving existing methods. Novel and innovative programs need to be implemented to encourage the commercial sector (e.g., instrument manufacturers) to develop the technology evolving from federal laboratories or academia. The use of mechanisms contained in the Technology Transfer Act of 1986 (Public Law 99-502) needs to be implemented to enhance the commercial-ization of new technology. A more organized effort within the Agency is essential to eliminating the tremendous duplication of efforts being expended in solving the same basic problems.

Immediate Methods Needs

Near term methods needs arise principally from environmental legislation. The Program Offices typically are faced with demands to develop regulations that require either new methods or improvements in the existing methods. The development of methods in this situation requires close coordination between the Program Offices and ORD. The method needs are very specific, for example, the measurement of specific organic compounds in

POTW sludges, and the time available to develop the method is typically very short. Due to the tremendous and varied needs from the Program Offices, the researchers are overloaded and many development programs are not being done or are being done at contract laboratories. Furthermore, due to the lack of a focused effort, each Program Office is developing methods for its program resulting in inconsistent approaches to the development process.

The formation of an Environmental Methods Management Group (EMMG) will resolve many of these problems. The fact is that many methods needs cross program lines. For example, an improved extraction technique for pesticides will result in better data for all of the Agency programs which require measurement of pesticides. For this reason it is important that all Agency methods development work be coordinated.

One of the objectives of the EMMG is to coordinate Agency-wide short term methods development activities. One of the first activities of this group should be to review and prioritize the immediate methods development needs of the Agency. Based on a review of Program Office needs, over 200 different short-term needs were identified which directly impact monitoring required under the Federal Water Pollution Control Act (FWPCA).

These needs encompass the technical disciplines of inorganic chemistry, organic chemistry, microbiology and aquatic biology. Some of these needs are well defined and should be readily achieved, e.g., a capillary method for volatile organics. Others will require more intensive efforts, e.g., establishment of definitive holding times. In some cases, a generic need (e.g., better cleanup techniques, better pollutant identification techniques) may solve both short-term and long-term problems. For example, it may be possible to develop a cleanup technique based on existing technology which improves an existing method. New technology may in the future provide even better performance.

Most of the short term methods development needs are oriented towards improving the performance (cost, sensitivity, reliability, accuracy, etc.) of an existing method or increasing its applicability (new matrices, additional analytes). Some of these needs are listed in Table VII-1. It should be noted that this table is not a complete inventory of immediate needs, but examples of the types of needs that require solutions. Virtually all of these needs are also needs in other programs.

Long-Term Technology Needs

The methods developed by the Agency that are used today are based on the best demonstrated technology that is available to the regulated community. Research efforts are ongoing to improve these methods. However, every method has limitations. These limitations are generally caused by:

- the chemical and/or physical property of the analyte being measured;
- interferences present in the sample matrix;
- the adequacy of the method to unambiguously determine the analyte at the specificity and sensitivity required; or
- insufficient knowledge of the biology of commonly used test organisms.

The Agency is conducting research into new technologies that address these concerns. For example, liquid chromatography coupled with mass spectrometry is being investigated as a technique for the measurement of polar water-soluble organic compounds.

It should be noted that while some of these research areas may soon result in improvement to current methods, it is more likely that it will be years before these research efforts will have any real impact. In fact, it is likely that some of these techniques will never prove useful. This factor should not deter the ongoing efforts.

As an example of this process, Table VII-2 traces the development of three technical areas which are related to environmental analyses:

- Gas Chromatography - Fourier Transformer Infrared Spectrometry (GC/FT-IR)
- Open Tubular (capillary) Column GC

Table VII-1 Examples of Immediate FWPCA Methods Development Requirement Needs

- Effective extraction and digestion methods for metals and organic analysis of complex matrices, e.g., sludges, sediments, fish tissue.
- Standardized clean-up methods for metals and organics in sample extracts from complex and variable matrices, e.g., sludges, tissues.
- Determination of scientifically valid and legally defensible sample holding times in all sample matrices.
- Reliable sampling protocols for all environmental media.
- Artificial intelligence systems for inferring substance identity from instrumental analytical data when the compound does not match any spectra available in the libraries.
- Computer data processing systems capable of performing routine QA/QC evaluation of monitoring data.
- Direct methods (no-preconcentration) for quantitation of toxic and related organic compounds.
- Methods to measure organics and metals at lower levels.
- Methods to analyze for longer target lists of chemicals which also can identify the presence of other toxic metals and organics.
- Automation of organics sample preparation techniques.
- Ion chromatographic procedures for anions.
- Development of solid sorbents for water sampling.
- Incorporation of capillary column GC methods.
- Methods for measuring effects of wastewaters on fish and aquatic life.
- Rapid methods to detect and quantify sublethal aquatic toxicity in industrial and municipal discharges.
- Rapid methods to detect pathogens in sludges.

- Ion Chromatography

These three examples illustrate the time required for a technique available at the research level to become commercially available and fully standardized. These three areas are discussed below.

The GC/FT-IR technique is under investigation as a technique for environmental analysis. The technique holds promise as a technique for rapid screening of samples to determine compound class assignments. In the 20 years since the technique first appeared in the literature, instrument costs have decreased and the sensitivity of the techniques has increased. However, the technique is still considered to be under development. GC/FT-IR is not being used on a routine basis for environmental analyses.

By comparison, the development of capillary column GC technology has had a very rapid (10 year) growth with continued improvements. The glass capillary columns available in the 1970's were very cumbersome to use and were less efficient than the fused silica columns available today. Capillary column technology has essentially replaced the packed column method originally developed for Method 625. In addition to the improvements in column efficiency, the newer columns have improved the precision and accuracy of the measurements and now require less skill in their installation and maintenance.

Ion chromatography was patented in 1975 for measuring anions in water. In essentially a 10-year period, the technique has been refined to measure both cations and organic ions. Over

Table VII-2 Examples of the Development of Environmental Analytical Instrumentation

(1) GC-FT/IR

Date	Detection Limit, µg	Price	Event
1965		N/A	First publication
1969	10^{-5}	$200K	First commercial instrument • Very slow scan rate • No library search
1975	10^{-7}	$_____	Gold light pipe & MCT detector technology became commercially available
1980	_____	$180K	Research began on new sources and FT technology
1986	10^{-8}	$40K	1980 technology became commercially available as a GC-only detector; result was major price breakthrough
1987	10^{-8} 10^{-10}	$70K	High sensitivity; capillary GC
		$150K	Matrix isolation
1989?	10^{-8}	<$100K	First EPA method verified and published

(2) Open Tubular (Capillary) Column GC

Date	Column Efficiency	Event
1977	2000 plates/meter	Glass capillary columns and capillary injectors became widely available commercially
1980	4000 plates/meter	Fused silica (physically rugged) capillary columns developed.
1980	4000 plates/meter	Bonded phase (chemically rugged) capillary columns developed.
1984	-	First EPA capillary GC methods finalized.
	N/A	Megabore™ columns developed.
1987	10,000 plates/meter	100μm I.D. capillary columns commercially available <5% of EPA methods using capillary GC technology

(3) Ion Chromatography (IC)

Date	Incremental Capability	Price	Event
1975	Anions(-)	$10K	Patent issued to Dow Chemical Dionex Incorporated
1980	Cations(+)	-	-
1985	Organic Ions	-	Development of gradient elution; election; able to elute organic and inorganic ions
	Anions	-	First EPA method published (Method 300 - drinking water)
1986	Reverse phase	$10-40K	Technique merges w/HPLC

6000 instruments are used in environmental laboratories. The time from the development of the instrumentation until the approval of the first EPA method was less than ten years, one of the fastest developments of technology and methods.

The EMMG should focus its energies on prioritizing the long-term research goals of the Agency, in cooperation with instrument manufacturers, universities and commercial laboratories. These long-term research needs should address the major limitations, such as those listed below, associated with today's technology.

Table VII-3 lists some examples of new technologies which are currently being investigated. These technologies hold promise not only for superseding the performance of existing methods (i.e., better sensitivity, lower cost, more reliable identification) but also in solving additional needs such as:

- measurement of polar water-soluble organics,
- speciation of organometallic or inorganic species,
- providing on-line continuous monitoring, and
- use of immunoassay and gene probes to detect pathogens.

These techniques are discussed in more detail subsequently.

Discussion of Emerging Technologies and Methods

The previous section discussed generically both short-term and long-term methods development needs. This section provides more detailed discussion of some areas that are undergoing development, organized into inorganic chemistry, organic chemistry and biology.

Inorganic Chemistry

With the increased emphasis on the measurement of toxic metals to determine compliance with health based regulations, more metals will need to be measured simultaneously in a broader suite of sample matrices. Several new emerging technical and commercial developments over the next five years will have a significant impact on environmental analyses for inorganic analytes. These new technologies should decrease the cost of analyses, increase laboratory productivity and the quality of the analytical data and lower the effective detection limits in a wide variety of sample matrices. Some of these technologies are described below.

Table VII-3 Examples of New Technology for Potential Routine Use

Gradient Ion Chromatography
Continuous Monitoring Electrodes
Enzyme Electrodes
Inductively Coupled Plasma/Mass Spectrometry
Inductively Coupled Plasma - Hydride - Optical Emission Spectroscopy
Inductively Coupled Plasma - Fourier Transform - Optical Emission Spectroscopy
X-Ray Fluorescence
Anodic Stripping Voltametry
High Performance Liquid Chromatography/Electrochemical Detection
Immuno Assay
High Performance Liquid Chromatography/Mass Spectrometry
Super Critical Fluid - Mass Spectrometry
High Performance Liquid Chromatography/Fourier Transform Infrared Spectroscopy
Gas Chromatography/Fourier Transform Infrared Spectroscopy
Super Critical Fluid/Fourier Transform Infrared Spectroscopy
High Resolution Mass Spectrometry
Triple Quadrupole Mass Spectrometry
Robotics
Super Critical Fluid Extraction
Gas Chromatography Atomic Emission Spectroscopy
Super Critical Fluid Atomic Emission Spectroscopy.

The area of sample preparation is the most labor intensive segment of environmental analyses. Unfortunately, EPA and other government agencies have established digestion methods for many different metals which are basically the same except for small differences (e.g, acid strength, amounts added, etc.). In the coming years, there should be a consolidation of digestion methods which would improve the comparability of data. Microwave digestion techniques could significantly impact the sample preparation for inorganics. In this method, the sample is placed in a pressurized digestion vessel, acidified, and then heated in a special microwave oven. Preliminary studies indicate that this technique may result in a more complete digestion in less time than conventional heating on hot plates. More studies must be done on this and other digestion methods for various matrices to ensure precision and accuracy in the digestions and the comparability of results with existing techniques. Microwave digestion methods can be developed for oily wastes to finally resolve the problems of analyzing metals in very difficult matrices.

While not a significant problem for water samples, getting a representative sample of all other matrices is the most significant factor controlling the precision of a test. Another improvement in sample preparation will be in the development of standardized sample homogenization methods to permit more reproducible analyses of soil, sediment and waste samples. Standard sample preparations must also be developed for biological tissues as more and more environmental studies are addressing bioaccumulation.

For mercury, multiple sample preparations are presently used within EPA and in other agencies. Studies should be conducted to determine the significance of the differences in the various digestions and develop a consolidated method to permit better comparison of the data. Improved sample preparation techniques must also be developed for silver and antimony, particularly in soils and sludges.

In the next decade, the application of inductively coupled plasma/mass spectrometry (ICP/MS) to environmental analyses could result in the single greatest impact on the analysis of metals. The ICP/MS technique has all the advantages of optical ICP/atomic emission spectroscopy (AES) in that it can perform rapid, multielement determination of almost all elements in the periodic table in a sample, but ICP/MS also has very low detection limits, nearly equal to graphite furnace atomic absorption spectroscopy (GFAA). Similar to GC/MS, ICP/MS is very specific for the identification and quantification of a specific target list of elements and can identify and semi-quantitate other metals that may be present in the sample by operating in the scanning mode. ICP/MS also has a much wider linear working range than GFAA (i.e., 0.001 to 100 ppm). ICP/MS can also provide isotope measurement capability, improve the accuracy of measurements by using isotope dilution methods, and provide analyses for radionuclides.

The ICP/MS could perform many of the traditional radiochemical methods and perform the analyses in minutes instead of days.

The ICP/MS can be used in the scan mode, as mentioned earlier, to provide a quick screen for metals in environmental samples by the rapid identification, and semi-quantitative measurements of most elements. ICP/MS will also be used in conjunction with liquid chromatography (LC) to measure organometals and other metal species.

Improvements in ICP optical systems should occur with the computerization and automation of the instrumentation, improved selectivity and sensitivity, and in the use of the hydride technique to measure low levels of critical elements (i.e., arsenic and selenium) in a simultaneous, multielement mode. Although presently a difficult method to perform correctly, recent studies have indicated that improved hydride methods will be developed for application to routine production analyses.

Ion chromatography (IC), particularly gradient ion chromatography, will become more routine in the future. Currently approved only for analysis of drinking waters for nitrate, the technique has not been widely applied for routine analyses in other matrices. The advantages of the method are that it is relatively fast, has good sensitivity and determines several analytes at once. Further improvements in column technology and experience with this technique will aid in the expansion of IC into routine chemical analysis for many matrices.

Inorganic analytical instrumentation as a whole is evolving towards an emphasis in automated sampling and analysis including computerization of the quality control decisions with corresponding action to be taken (i.e., reanalysis, respiking, etc.), networks and electronic communication (instruments to and from main computers), Laboratory Information Management Systems (LIMS), and environmental-specific software. These developments are being driven by the need to interface with LIMS systems to allow automated data acquisition, automated quality assurance/ quality control (QA/QC) review, data archival and result reporting packages, all of which lag significantly behind the more computerized organic analytical instrumentation. The prices of instrumentation will continue to decrease as ICP's become as common as atomic absorption spectrophotometers. ICP/MS will be refined and used routinely as instrument conditions and interference corrections are better defined. For EPA work, on-line communications will be used to transport and review data results, at least for the CLP laboratories. AA instrumentation, particularly, will be computerized and programmed to make the QC checks and decisions now performed by the analyst with the data transmitted to a central computer which will correlate the incoming data and write the reports for the laboratories.

Holding times for samples is fast becoming a critical issue as sample loads increase for laboratories. Studies will need to be completed to determine scientifically supportable holding time requirements for organic and inorganic compounds in a variety of matrices including waters, soils, wastes, sludges and biological tissue. Important inorganic analytes that should be studied are the unstable elements such as mercury, cyanide and chromium (particularly hexavalent Cr). Efforts to develop and improve analytical methods will continue for a variety of inorganic analytes such as Total Organic Halides (TOX) in sediments and soils, cyanide in the presence of sulfide, fluoride, ammonia, Total Kjehldahl Nitrogen (TKN), sulfate and phenols.

In addition, requirements for the analysis of asbestos in air and water will increase the development of improved, standardized asbestos analysis, probably by Transmission Electron Microscopy (TEM) or other optical techniques. Hopefully, a method will be standardized for the analysis of hexavalent chromium, Cr (VI), to meet environmental program requirements to assess the fate and effects of this important but very difficult analyte to measure.

Organic Chemistry

A large number of new technical and commercial developments will evolve during the next five years. These will be available to environmental laboratories and should significantly impact the quality of analytical

data, laboratory sample throughput, and/or cost of analysis.

Some of these techniques are currently available and used in applications other than of environmental analysis. It is clear that major emphasis must be placed on the enhancement of existing GC/MS techniques and the development of other multi-analyte technologies such as LC/MS.

Laboratory Robotics

Benchtop laboratory robotics will begin to replace labor intensive tasks such as weighing, diluting, pipetting standards and loading autosampler vials. The benefit is increased sample throughput, with decreased labor content in each sample, and precision equal to or better than manual operations. For these reasons, sample analysis done with robotics are perceived to be more defensible in litigation.

Laboratory robotics systems are not faster but can work longer hours. They are designed only for laboratory scale tasks which require lifting less than 1500 grams. They will therefore not be capable of manipulating sample containers or large pieces of laboratory apparatus (e.g., liquid-liquid extractors). Overall, use of robotics should result in a significant savings in the total cost of analysis.

Sample Preparation Techniques

Numerous new methods of sample preparation are needed to separate and measure the broad range of organic compounds currently of concern. These techniques represent a trend towards increasing the amount of in-situ analyte extraction and, consequently, require little or no prior sample preparation. Many of these techniques will be capable of sample preconcentration, thereby effectively lowering the detection limits of the technique. Bar code readers/writers enhance the chain of custody in sample tracking from field sampling through generation of the final report, including error checking each time the sample is manipulated, transferred or analyzed. Note that all of the techniques listed are amenable to automation, and may be directly coupled on- line to GC's and/or SFC's.

These techniques are expected to have the largest single impact on quality, credibility, sample throughput, and cost of analysis in the near term. For these reasons, a subcommittee on Sample Preparation Methods is proposed for the Environmental Methods Management Group.

Capillary Column Technology

A very wide range of open tubular (capillary) columns should be incorporated into GC methods and replace all packed column GC methods in use today. The benefits of each are outlined below.

Open Tubular GC Column Analytical Characteristics

I.D.	Compatibility with Spectroscopic Detectors	Resolution	Analysis Time	Ease of Use
0.76 mm	Yes	Slow	Slow	Fair
0.53 mm	Yes	Intermediate	Intermediate	Excellent
0.32 mm	Yes	High	Intermediate	Good
0.25 mm	No	High	Fast	Fair
0.18 mm	No	High	Fast	Difficult
0.10 mm	No	High	Fast	Difficult

It is expected that the 0.5 mm ID columns will become the de-facto standard for environmental applications. Research problems and dioxin analyses will require columns of <0.25 mm because of the very high separation efficiency capability.

HPLC Technology

HPLC separation methods will be the major new development in environmental methodologies. This development will be driven by potential future monitoring requirements pertaining to the analysis of polar, ionizable, and thermally labile compounds. Based on 15 years of GC/MS experience, it is clear that the method of choice will be HPLC/MS because of the need for separation, sensitivity, and direct identification. High resolution columns are now available for compounds with molecular weights consistent with environmental regulatory requirements. They will emerge for both

analytical (with MS) and sample preparation/cleanup applications.

Super-Critical Fluid Chromatography

Super-critical fluid chromatography (SFC) became commercially available in 1986 and will extend the molecular weight limit from nominally 1000 amu for GC to 30,000 amu. SFC allows the use of gas phase detectors, including MS, and therefore is capable of both high sensitivity detection and high efficiency separations with open tubular columns. It will, therefore, compete with HPLC for some applications and the Agency needs to begin environmental methods development in this technique immediately.

Spectroscopic Identifications

Spectroscopic identification of GC and HPLC effluents will expand because of the requirements of both positive qualitative identification and low detection limits. Secondly, the cost of spectroscopic identification has decreased by as much as a factor of four during the last six years; (e.g., FT/IR).

Environmental analyses in the 1990's will involve an increasing number of analytes and complex matrices. Coupled with the fact that chromatographic separations are now at their theoretical limit of efficiency, the advent of more "hyphenated techniques" has the potential to improve the information content and the confidence and quality of the final result.

Thus, Fourier Transform infrared detection (FT/IR) and identification will be used as a complimentary on-line technique to GC-MS. New interface technologies will allow HPLC/MS to give electron impact (EI), chemical ionization (CI), and/or fast atom bombardment (FAB) spectra which can be matched to standard library spectra for the first time. It has been projected that there will be as many HPLC/MS systems in world-wide use by the turn of the century as there are GC/MS systems in use today. Therefore, the Agency has an immediate need to develop LC/MS methods as discussed in the Separations Section above.

Atomic emission spectroscopic detectors represent a new capability for increasing the specificity of detection for both GC and SFC effluents. These will be heteroatom specific detectors (ex., Cl and/or N-, S-, O- containing compounds) and may lead to measurements and calculation of the empirical formula of GC effluents. This hyphenated technique will therefore be complimentary to MS (structural analysis) and FT/IR (function group and structural analysis) techniques. Data reduction of one or more of these detectors will require either high level, experienced organic analytical chemists or expert (computer-software) systems for unambiguous qualitative identification. Thus the information content of each sample analysis will increase substantially and require more, faster and advanced computation power in order to maintain the current level of sample throughput in the laboratory.

Computer Systems

Computer systems for environmental laboratories will continue to evolve with emphasis on networks, communications (terminal-to-terminal, instrument- to- computer, and computer-to-computer), LIMS, and environmental specific software. These developments are driven by the needs for (a) greater sample and result integrity, (b) QA/QC and management review of data, (c) need to archive and retrieve data into and out of data bases, (d) edit and consolidate result and report files, and (e) accommodate updates in computer system hardware and software.

Market specific software packages will begin to be effective in the 1990's. This development will increase the quality of data, make it easier for noncomputer people to manipulate data, results, and reports by having software which is designed for specific environmental tasks, methods, data bases, spectral libraries, etc. This will make it easier and faster for nonexpert analysts to produce results without the overhead of large, general purpose software. The laboratory-computer developments can be expected to follow the trends in office automation, thus standard networks and communication protocols will converge towards industry standards.

Biology

During the description of the FWPCA programs, the inventory of required analytes, and determination of availability and adequacy of test methods, the following future development needs were identified. The needs are grouped for convenience even though several are interrelated and no specific order of priority is implied.

Microbiological Needs

- As a result of the amendments to the Safe Drinking Water Act (SDWA), methods should be developed for detecting pathogenic bacteria, protozoa, and parasites for wastewaters, sludges, and sediments. Pathogenic candidates include *Salmonella, Shigella, Clostridium botulinum, Pseudomonas aeruginosa, Vibrio cholerae, Aeromonas hydrophila, Leptospira, Crypstosporidium, Giardia lamblia, Entamoeba histolytica, nematodes, Ascaris* (ova), and *Taenia* (ova).
- Improved and new methods for microbial toxicity and mutagenicity are needed. Candidate tests include Microtox (Photo*bacterium phosphoreum*) (7-4), Microscreen (*Escherichia coli*), Bacillus, and *Saccharomyces cerevisiae*. The degree of correlation between these tests and aquatic toxicity tests should be determined, particularly for toxic organics, and single lab precision studies should be performed. Stormwater discharges should be included in the media tested.
- Methods are needed for the rapid identification and verification of pathogens and indicator species when detected in traditional methods. Candidate methods include gene probes and immunological tests (monoclonal and polyclonal antibodies).
- Integrated microbiological monitoring systems using analytical instrumentation to characterize microbial communities and measure toxicity (sensitivity to pollutants and toxicants) are needed.
- The EPA Manual of Methods for Microbiology needs to be updated to address the program needs for monitoring pathogens and indicator organisms.

Virology Needs

- The EPA Manual of Methods of Virology (1984) needs to be updated periodically, consistent with scientific advances. Additional research is necessary to further improve virus sampling, extraction, and concentration techniques in the manual. A section should be added on precision and replication.
- Standardized methods are needed for virus detection in shellfish- growing waters. Edible shellfish are known to concentrate viruses from fecal-contaminated waters during feeding. Since they are often eaten raw or insufficiently cooked, subjecting shellfish-growing waters to human waste constitutes a public health risk. Microbiological acceptance of the sanitary quality of these estuarine and coastal growing areas is based on coliform standards. However, growing areas that have been bacteriologically approved for shellfish have been a source of viral disease outbreaks. To effectively establish an acceptable and practical program for virological monitoring of shellfish and shellfish growing waters, new techniques that rely on a virological index need to be made available.
- Aerosolized sewage due to the production of aerosols from domestic sewage treatment plants and wastewater spray from irrigation and land disposal systems are known to contain enteric viruses, but only the most rudimentary technology exists for their detection in air. The potential for virus disease dispersed through aerosolized sewage spotlights the need for development of methods for their detection.
- Better detection and identification techniques are needed for waterborne viruses. The existing gene probe technology entails development of nucleic

acid hybridization probes. If applicable, it would be a much more rapid and cost-effective technique than current enteric virus methods.

- More suitable indicators of the presence of viruses in water, wastewater, sludges and soils are needed.

Aquatic Toxicity Methods

- EPA should develop methods to assess toxicity persistence in receiving waters, sediment toxicity, and bioaccumulation, teratogenic, mutagenic, or carcinogenic potential or waste.
- EPA should also standardize procedures for conducting toxicity tests in combination with low dissolved oxygen or high temperature since these are common additional stresses. EPA should seek to standardize the format and requirements of all toxicity test procedures.
- EPA should develop methods for monitoring the toxicity of municipal and industrial sludges. Emphasis should be placed on microbial toxicity and on methods for toxicity tests with suspended solids.
- EPA should finalize criteria and required testing requirements for sediment disposal to support the §404 program.
- At the request of several EPA Regional offices and State agencies, EPA should consider the development of methods for determining toxicity to tropical organisms. These methods would support NPDES permits programs in Hawaii, California, and Puerto Rico.
- EPA should continue its developmental work on the duckweed toxicity test including the production of a manual and demonstration of single lab precision.
- EPA should initiate research into the basic biology of the principal aquatic toxicity tests organisms that are the basis for effluent monitoring. Inadequate information is available on many of the test species. This research should be directed at a better understanding of the basis for the responses of the organisms during testing and for developing better culture techniques for producing consistently healthy test organisms in the quantities needed.
- Methods are needed to relate toxic substances detected in fish tissues with the health of fish. Standardized methods for detection and quantification of toxic material in target tissue of fish and shellfish should be a future requirement. This will include developing a relationship between (acute and chronic) toxicity and the distribution of toxics in cellular proteins (cytosol).
- EPA should also develop a method for determining the amount of biomass inhibition at treatment plants due to toxic effluents.
- Cost effective methods are also needed for multispecies test procedures using standardized microcosms.

Field Surveys and Damage Assessment

- The EPA SAB recommends that EPA update existing guidelines and develop methods for field studies for monitoring the biological integrity of aquatic communities in receiving waters. This will include methods needed to evaluate and define ecosystem stability and resilience which is necessary to better define the acceptable degree of biological effects and the frequency of exposures under the water quality based approach for controlling toxic discharges.
- The ecoregion methods of defining regional patterns in water chemistry and aquatic biota can be a valuable tool to help states define attainable goals in water quality and aquatic community improvements. The EPA SAB recommends that EPA continue to refine these methods so that they can be used in state regulatory programs.

Quality Assurance/Quality Control

- Due to continued requests from States and EPA Regional offices administering the NPDES permits program and to requests

from the regulated industries, the EPA should develop a certification program for labs that perform aquatic toxicity testing and related biological tests. These data are subject to legal review and challenge in enforcement efforts and must be legally defensible. This program would parallel or be a part of the existing SDWA lab certification program for drinking water analyses.

- The EPA should increase its technology transfer program for training commercial testing laboratories, state laboratories, and EPA regional laboratories in the major testing methods to ensure consistency between laboratories in data quality. Emphasis should be placed on implementing the QA/QC recommendations associated with the various test methods. This effort would include further reliance on the EPA Quality Assurance Branch of EMSL-Cincinnati and the availability of reference standards.

Chapter Seven References

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APPENDIX

Approximate Ranges of Concentration for Quality Control (QC) Samples-Water Quality Analyses

QC Samples Series	Analytes
DEMAND ANALYSES (1-200 mg/L)	BOD, COD, and TOC in water
EPA/API STANDARD REFERENCE OILS (Neat Oils)	Arabian Light Crude Oil, Prudhoe Bay Crude Oil, South Louisiana Crude Oil, No. 2 Fuel Oil (high aromatics), and No. 6 Fuel Oil (high viscosity) Bunker C (laboratory must request specific oil)
LINEAR ALKYLATE SULFONATE (5-6%)	LAS, the anionic surfactant standard for the MBAS in water
MINERAL/PHYSICAL ANALYSES (1-100 mg/L)	sodium, potassium, calcium, magnesium, pH, chloride, fluoride, alkalinity/acidity, total hardness, total dissolved solids, and specific conductance in water
NONIONIC SURFACTANT (CTAS TEST) STANDARD (Neat Compound)	Reference Nonionic Surfactant, C12-18 E11. Standard Methods Method 512 C
NUTRIENTS (0.5-5 mg/L)	nitrate-N, ammonia-N, Kjeldahl-N, orthophosphate, and total P in water
OIL AND GREASE (20 mg/L)	analyzable by IR and gravimetrically in propanol
PESTICIDES IN FISH (0.01-3 mg/Kg)	alpha-BHC, endrin, DDD, DDE, and DDT
PHENOLS, TOTAL (4AAP Method) (45 ug/L)	total phenols in water
POLYCHLORINATED BIPHENYLS (PCBs) IN OILS (10-500 ug/L)	Aroclor 1016, 1242, 1254, and 1260 in transformer, hydraulic, and capacitor oils, (specify Aroclor and oil)
PCBS IN SEDIMENTS (5-10 mg/Kg)	Aroclor 1242 and 1254
SUSPENDED SOLIDS (0-500 mg/L)	non-filterable, volatile and total filterable residue
TRACE METALS - WP I (1-500 ug/L)	aluminum, arsenic, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, vanadium, and zinc in 0.5% nitric acid solution
TRACE METALS - WP II (10-20 ug/L)	antimony, silver, and thallium in 0.5% nitric acid solution
TRACE METALS - WP III (0.1-10 ug/L)	barium, calcium, potassium, sodium, magnesium, and molybdenum in 0.5% nitric acid solution
TRACE METALS IN FISH (0.1-50 mg/Kg)	arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc

Approximate Ranges of Concentration for QC Samples-Priority Pollutants/Hazardous Wastes/Toxic Chemicals

QC Samples Series	Analytes
n-ALKANES (0.05-2 ug/L)	dodecane, eicosane, heptadecane, hexacosane, tetradecane, tricosane in acetone
CHLORINATED HYDROCARBONS (Method 612) (10-100 ug/L)	hexachloroethane, hexachlorobenzene, 1,2,4-trichloro-benzene, o-dichlorobenzene, p-dichlorobenzene, m-dichlorobenzene, hexachlorobutadiene, 2-chloro-naphthalene in acetone
CHLORINATED HYDROCARBON PESTICIDES - WP I (Method 608) (2-10 ug/L)	aldrin, dieldrin, DDT, DDE, DDD, and heptachlor in acetone
CHLORINATED HYDROCARBON PESTICIDES - WP II (Method 608) (50 ug/L)	chlordane in acetone
CHLORINATED HYDROCARBON PESTICIDES - WP III (Method 608) (2-10 ug/L)	alpha-BHC, beta-BHC, heptachlor epoxide, endrin, aldehyde, and alpha and beta endosulfan in acetone
CYANIDE, TOTAL (500 ug/L)	in water, pH greater than 9.0
EP METALS (1-100 mg/L)	arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver in acetic acid
EP PESTICIDES & HERBICIDES (10-5,000 ug/L)	lindane, endrin, methoxychlor, 2,4-D, and Silvex in acetone
GC/MS ACIDS (Method 625) (100 ug/L)	2-chlorophenol, 2-nitrophenol, phenol, 2,4-dimethyl-phenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-chloro-3-methylphenol, pentachlorophenol, and 4-nitrophenol in methanol
GC/MS BASE NEUTRALS - I (Method 625) (100 ug/L)	bis-2-chloroethyl ether, 1,3-dichlorobenzene, 1,2-dichlorobenzene, nitrosodipropylamine, bis-2-chloroethoxy methane, 1,2,4-trichlorobenzene, hexachlorobutadiene, 2-chloronaphthalene, 2,6-dinitro-toluene, 2,4-dinitrotoluene, diethyl phthalate, hexachlorobenzene, phenanthrene, dibutyl phthalate, pyrene, benzo(a)anthracene, dioctyl phthalate, benzo(k)fluoranthene in methanol
GC/MS BASE NEUTRALS - II (Method 625) (100 ug/L)	1,4-dichlorobenzene, bis-2-chloroisopropyl ether, hexachloroethane, nitrobenzene, naphthalene, dimethyl phthalate, acenaphthene, fluorene, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, anthracene, fluoranthene, butyl benzyl phthalate, benzo(a)pyrene, benzo(b)fluoranthene, benzo(a,h)anthracene, benzo(g,h,i) perylene, chrysene, and bis (2-ethyl-hexyl phthalate) in methanol
GC/MS BASE NEUTRALS - III (Method 625) (100 ug/L)	4-chlorobenzotrifluoride, m-chlorotoluene, 2,4-dichloro-toluene, 1,3,5-trichlorobenzene, 1,2,4,5-tetrachloro-benzene, 1,2,3,4-tetrachlorobenzene, 2,4,6-trichloro-aniline, 1,2,3-trichlorobenzene, and pentachlorobenzene in acetone
GC/MS PESTICIDES - I (Method 625) (100 ug/L)	heptachlor, heptachlor epoxide, dieldrin, endrin, DDD, alpha BHC and gamma BHC in acetone
GC/MS PESTICIDES - II (Method 625) (100 ug/L)	beta-BHC, aldrin, alpha and beta Endosulfan, 4,4'-DDE, and 4,4'-DDT in acetone
HALOETHERS (Method 611) (10-150 ug/L)	bis (2-chloroisopropyl) ether, bis (2-chloroethoxy) methane, bis (2-chloroethyl) ether, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether in acetone
ICAP - 19 (1 mg/L)	As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V and Zn in dilute nitric acid
ICAP - 7 (0.5-10 mg/L)	Ag, Al, B, Ba, K, Na, and Si in dilute nitric acid
NITROAROMATICS AND ISOPHORONE (Method 609) (1-150 ug/L)	isophorone, nitrobenzene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene in acetone

Approximate Ranges of Concentration for QC Samples-Priority Pollutants/Hazardous Wastes/Toxic Chemicals

QC Samples Series	Analytes
n-ALKANES (0.05-2 ug/L)	dodecane, eicosane, heptadecane, hexacosane, tetradecane, tricosane in acetone
PHENOLS (GC) (Method 604) (2-275 ug/L)	phenol, 2,4-dimethylphenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichloro-phenol, pentachlorophenol, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol in acetone
PHTHALATE ESTERS (Method 606) (10-50 ug/L)	dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, butyl benzl phthalate, diethyl hexyl and dioctyl phthalate in acetone
POLYCHLORINATED BIPHENYLS (Method 608) (50 ug/L)	separate samples available for Aroclor 1016, 1221, 1232, 1242, 1248, 1254, and 1260 in acetone (laboratory must request specific Aroclor needed)
POLYNUCLEAR AROMATICS - I (Method 610) (5-100 ug/L)	acenaphthene, anthracene, benzo(k)fluoranthene, naphthalene, and pyrene in acetone
POLYNUCLEAR AROMATICS - II (Method 610) (10-100 ug/L)	acenaphthylene, benzo(a)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, dibenzo(a,h) anthracene, fluoranthene, and phenanthrene in acetone

Approximate Ranges of Concentration for QC Samples-Biology/Microbiology

QC Samples Series	Analytes
ALGAE FOR IDENTIFICATION	Samples contain algae preserved in 5% formalin for microscopic identification: Sample No. 1 contains: 1 green, 1 bluegreen Sample No. 2 contains 3 bluegreens Sample No. 3 contains: 1 green, 1 bluegreen Sample No. 4 contains: 1 diatom (Hydrax mounted slide) (Laboratory must specify sample needed.)
BACTERIA INDICATOR STRAINS (108-109 organisms/vial)	Enterobacter aerogenes, Escherichia coli, pneumoniae, Pseudomonas aeruginosa and Streptococcus faecalis, lyophilized (laboratory must request specific organisms needed). Also available are sterile lyophilized blanks for evaluation of aseptic technique.
CHLOROPHYLL (3-80 ug/L) CHLOROPHYLL (0.20-80 mg/L)	fluorometric analyses, 1 calibration sample approximately 80 ug/L pure chlorophyll; 1 check sample approximately 3 ug/L pure chlorophyll; 1 check sample approximately 20 ug/L mix of pigments. A 3 ampul set.
CHLOROPHYLL (0.20-80 mg/L)	spectrophotometric analyses, (#1 is pigment #2 is pure chlorophyll __), two levels in acetone. A 2 ampul set.
REFERENCE TOXICANTS	sodium lauryl sulfate (30-60 mg/mL) in aqueous solution cadmium chloride (10 mg/mL) in aqueous solution. copper (4 mg/mL) in aqueous solution (available 9/1/87) (laboratory must specify toxicant(s) needed)
SIMULATED PLANKTON	20 mL aqueous suspension of latex spheres for particle counting, and a permanent, glass slide mount of latex spheres for particle size distribution determinations.

Approximate Ranges of Concentration for QC Samples-Drinking Water Analyses

QC Samples Series	Analytes
CORROSIVITY/SODIUM (0.1-15 mg/L)	Langlier's Index Value and Sodium in water
HERBICIDES (10-100 ug/L)	2,4-D, 2,4,5-TP (Silvex) in methanol
NITRATE/FLUORIDE (0.1-10 mg/L)	nitrate-N and flouride in water
CHLORINATED HYDROCARBON PESTICIDES - WS I (0.20-20 ug/L)	lindane, endrin, and methoxychlor in acetone
CHLORINATED HYDROCARBON PESTICIDES - WS II (50 ug/L)	toxaphene in acetone
RESIDUAL FREE CHLORINE (1 mg/L)	solvent is water
TRACE METALS - WS (1.0-500 ug/L)	arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver in 0.3% nitric acid solution
TRIHALOMETHANES (20 ug/L)	chloroform, bromoform, dichlorobromomethane, and chlorodibromomethane in methanol
TURBIDITY (0.5-5 NTU)	in water
VOLATILE ORGANIC CONTAMINANTS - I (Methods 503, 524, 602 and 624) (20 ug/L)	benzene, ethylbenzene, m-xylene, n-propylbenzene, p-chlorotoluene, 1,3,5-trimethylbenzene and p-dichlorobenzene in methanol
VOLATILE ORGANIC CONTAMINANTS - II (Methods 503, 524, 602 and 624) (20 ug/L)	trichloroethene, p-xylene, o-xylene, t-butylbenzene, p-cymene and m-dichlorobenzene in methanol
VOLATILE ORGANIC CONTAMINANTS - III (Methods 503, 524, 602 and 624) (20 ug/L)	toluene, chlorobenzene, isopropylbenzene, sec-butylbenzene, 1,2,4-trimethylbenzene, n-butylbenzene, and o-dichlorobenzene in methanol
VOLATILE ORGANIC CONTAMINANTS - IV (Methods 502, 524, 601 and 624) (20 ug/L)	1,1-dichloroethylene, cis-1,2-dichloroethylene, 1,1,1-trichloroethane, 1,1-dichloropropene, 1,1,2-tri-chloroethane, 1,1,2,2-tetrachloroethylene, bromoform, and bis(2-chloroethyl) ether in methanol
VOLATILE ORGANIC CONTAMINANTS - V (Methods 502, 524, 601 and 624) (20 ug/L)	bromochloromethane, chloroform, carbon tetrachloride, 1,1,2-trichloroethylene, 1,2-dibromoethane, 1,1,1,2-tetrachloroethane, pentachloroethane, 1,2-dibromo-3-chloropropane and m-dichlorobenzene in methanol
VOLATILE ORGANIC CONTAMINANTS - VI (Methods 502, 524, 601 and 624) (20 ug/L)	dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, bromodichloromethane, 1,3-dichloropropane, 2-chloroethyl ethyl ether, 1,2,3-trichloropropane, chlorobenzene, bromobenzene and o-dichlorobenzene in methanol
VOLATILE ORGANIC CONTAMINANTS - VII (Methods 502, 524, 601 and 624) (20 ug/L)	trichlorofluoromethane, trans 1,2-dichloroethene, dibromomethane, 1,2-dichloropropane, chlorodibromo-methane, 1,1,2,2-tetrachloroethane, chlorohexane, o-chlorotoluene, and p-dichlorobenzene in methanol

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E001	Acenaphthene
E002	Acrolein**
E003	Acrylonitrile (10,000 ug/mL)
E004	Benzene
E005	Benzidine
E006	Chlorobenzene
E007	1,2,4-Trichlorobenzene
E008	Hexachlorobenzene (1000 ug/mL)*
E009	1,2-Dichloroethane
E010	1,1,1-Trichloroethane (10,000 ug/mL)(QAR)
E011	Hexachloroethane
E012	1,1-Dichloroethane (5,500 ug/mL)
E013	1,1,2-Trichloroethane (QAR)
E014	1,1,2,2-Tetrachloroethane (10,000 ug/mL)(QAR)
E015	Chloroethane (11,000 ug/mL)***
E016	bis(2-Chloroethyl) ether
E017	2-Chloroethyl vinyl ether (QAR)
E018	2-Chloronaphthalene
E019	2,4,6-Trichlorophenol
E020	p-Chloro-m-cresol
E021	Chloroform
E022	2-Chlorophenol
E023	1,2-Dichlorobenzene
E025	1,4-Dichlorobenzene
E026	3,3'-Dichlorobenzidine
E027	1,1-Dichloroethylene (1,000 ug/mL)
E028	trans-1,2-Dichloroethylene (11,500 ug/mL)
E029	2,4-Dichlorophenol
E030	1,2-Dichloropropane (10,000 ug/mL)
E033	2,4-Dinitrotoluene
E034	2,6-Dinitrotoluene
E036	Ethylbenzene (10,000 ug/mL)
E037	Fluoranthene
E038	4-Chlorophenyl phenyl ether
E039	4-Bromophenyl phenyl ether
E040	bis(2-Chloroisopropyl) ether (QAR)
E041	bis(2-Chloroethoxy) methane (QAR)
E042	Methylene chloride (10,000 ug/mL)
E043	Methyl chloride***
E044	Methyl bromide (9940 ug/mL)***
E046	Dichlorobromomethane
E047	Fluorotrichloromethane
E050	Hexachlorobutadiene (QAR)
E051	Hexachlorocyclopentadiene
E052	Isophorone
E053	Naphthalene
E054	Nitrobenzene
E055	2-Nitrophenol

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E056	4-Nitrophenol
E057	2,4-Dinitrophenol (QAR)
E058	4,6-Dinitro-o-cresol
E059	N-Nitrosodimethylamine
E060	N-Nitrosodiphenylamine
E061	N-Nitrosodi-n-propylamine
E062	Pentacchlorophenol
E063	Phenol
E064	bis(2-Ethyl hexyl) phthalate
E065	Butyl benzyl phthalate
E066	Di-n-butyl phthalate
E067	Di-n-octyl phthalate
E068	Diethyl phthalate
E069	Dimethyl phthalate
E070	Benzo(a)anthracene (1,000 ug/mL)
E071	Benzo(a)pyrene (1,000 ug/mL)(QAR)*
E072	Benzo(b)fluoranthene (2,500 ug/mL)*
E073	Benzo(k)fluoranthene (1,000 ug/mL)*
E074	Chrysene (1,000 ug/mL)*
E075	Acenaphthylene (QAR)
E076	Anthracene (1,000 ug/mL)*
E077	Benzo(g,h,i)perylene (1,000 ug/mL)**
E078	Fluorene (QAR)
E079	Phenanthrene
E081	Indeno(1,2,3-c,d)pyrene (500 ug/mL)*
E082	Pyrene (1,000 ug/mL)
E083	Tetrachloroethylene
E084	Toluene (10,000
E085	Trichloroethylene (10,000 ug/mL)
E088	Dieldrin (1,000 ug/mL)
E089	Chlordane (QAT)
E091	4,4'-DDE
E092	4,4'-DDD
E093	alpha-Endosulfan (1,000 ug/mL)**
E094	beta-Endosulfan (1,000 ug/mL)**
E095	Endosulfan sulfate (1,000 ug/mL)(QAR)**
E096	Endrin (QAR)
E097	Endrin aldehyde (2,500 ug/mL)
E098	Heptachlor
E099	Heptachlor epoxide (2,500 ug/mL)
E100	alpha-BHC (2,500 ug/mL)
E101	beta-BHC (2,500 ug/mL)*
E102	gamma-BHC (Lindane)
E103	delta-BHC (1000 ug/mL)
E104	PCB-Aroclor 1242 (QAT)
E105	PCB-Aroclor 1254 (QAT)
E107	PCB-Aroclor 1232 (QAT)
E108	PCB-Aroclor 1248 (QAT)

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E110	PCB-Aroclor 1016 (QAT)
E111	Toxaphene (QAT)
E124	4,4'-DDT (QAR)
E125	PCB-Aroclor 1016 (1,000 µg/mL)(QAT)++
E126	PCB-Aroclor 1221 (QAT)++
E129	PCB-Aroclor 1260 (500 µg/mL)(QAT)++
E129	PCB-Aroclor 1260 (1,000 µg/mL)(QAT)++
E129	PCB-Aroclor 1260 (3,000 µg/mL)(QAT)++
E130	PCB-Aroclor 1262 (QAT)++
E131	PCB-Aroclor 1268 (2,500 µg/mL)* (QAT)
E132	PCB-Aroclor 1242 (500 µg/mL)(QAT)++
E132	PCB-Aroclor 1242 (1,000 µg/mL)(QAT)++
E132	PCB-Aroclor 1424 (3,000 µg/mL)(QAT)++
E135	PCB-Aroclor 1254 (500 µg/mL)(QAT)++
E135	PCB-Aroclor 1254 (1,000 µg/mL)(QAT)++
E135	PCB-Aroclor 1254 (3,000 µg/mL)(QAT)++
E136	Bromochloromethane (10,000 µg/mL)
E149	2,4-Dichlorotoluene
E150	2-Chlorotoluene
E151	3-Chlorotoluene
E152	4-Chlorotoluene (QAR)
E153	4-Chlorobenzotrifluoride
E156	Pentachloronitrobenzene
E168	alpha,alpha,2,6-Tetrachlorotoluene
E169	Benzyl chloride (QAR)****
E170	2,3-Dichloro-1-propylene (10,000 µg/mL)
E171	1,2-Dibromoethane (EDB) (10,000 µg/mL)
E173	cis-1,2-Dichloroethylene (10,000 µg/mL)(QAR)
E175	1,2,3-Trichlorobenzene
E176	1,3,5-Trichlorobenzene
E177	1,2,4,5-Tetrachlorobenzene (2,500 µg/mL)(QAR)****
E179	2,4,5-Trichlorophenol (QAR)
E180	2,4,6-Trichloroaniline
E182	3-Chlorophenol
E183	4-Chlorophenol
E200	Chlorodibromomethane (10,000 µg/mL)(QAR)
E201	ortho-Xylene
E202	meta-Xylene
E203	para-Xylene
E212	Bromoform
E214	1,3-Dichlorobenzene
E218	cis & trans 1,3-Dichloropropylene (QAR)
E219	Mirex (1,000 µg/mL)*
E220	Aldrin
E222	2,3,5-Trichlorophenol (QAR)
E224	2,4-Dimethylphenol
E225	1,2,3,4-Tetrachlorobenzene (2,500 µg/mL)
E231	Dibenzo(a,h)anthracene (1,000 µg/mL)

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E236	n-Decane
E237	n-Undecane
E238	n-Dodecane
E239	n-Tridecane
E240	n-Tetradecane
E241	n-Pentadecane
E242	n-Heptadecane (2,500 µg/mL)
E244	n-Nonadecane (1,000 µg/mL)
E250	ortho-Cresol (QAR)
E251	meta-Cresol (QAR)
E252	para-Cresol
E255	Dibutyl ether
E257	Styrene
E258	Epichlorohydrin****
E260	Pentachlorobenzene (2,500 µg/mL)
E261	Dibenzofurane
E262	Diphenyl ether
E263	Diphenylamine
E270	Acrylamide (10,000 µg/mL)
E271	Pyridine (10,000 µg/mL)
E282	Diisodecyl phthalate
E284	Acetone
E285	Diethyl ether (4,500 µg/mL)
E286	1,2-Epoxybutane****
E295	Phenacetin
E298	N-Nitrosopyrrolidine
E299	2-Fluoroacetamide
E300	Pentachloroethane
E305	4-Chloroaniline
E306	Urethane (Ethyl carbamate)
E311	Methyl ethyl ketone
E322	Methylene bis (o-chloroaniline)
E324	o-Nitroaniline
E325	m-Nitroaniline
E327	Vinyl acetate****
E329	Ethylenethiourea
E330	2,4-Dichlorophenoxyacetic acid (2,4-D)****
E334	N-Nitrosodiethylamine
E335	1,1,1,2-Tetrachloroethane (QAR)
E337	Malononitrile
E338	Propionitrile
E342	p-Nitroaniline
E349	4-Methyl-2-pentanone
E360	Carbon tetrachloride (10,000 µg/mL)
E363	Carbon disulfide
E364	Hexachloropropylene (1,000 µg/mL)
E366	Safrole
E368	1,2,3-Trichloropropane

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E369	Saccharin (2,000 µg/mL)
E375	3-Chloropropionitrile (1,000 µg/mL)
E406	Bromobenzene
E411	Acetophenone
E439	Methyl methacrylate (1,000 µg/mL)
E455	Dinoseb****
E458	1-Nitrosopiperidine
E470	PCN Halowax 1099 (QAT)
E471	PCN Halowax 1001 (QAT)
E472	PCN Halowax 1000 (QAT)
E473	Acetonitrile***
E475	Allyl alcohol (1,000 µg/mL)
E480	para-Dioxane (10,000 µg/mL)
E536	Vinyl chloride***
E541	Benzoic acid****
E542	Aniline
E543	Propargyl alcohol (1,000 µg/mL)+ + +
E548	N,N-Dimethylformamide
E552	2,4,5-TP (Silvex) (QAR)****
E560	Ethyl parathion (1,000 µg/mL)****
E565	2-Naphthylamine (1,000 ug/mL)
E567	7,12-Dimethylbenz(a)anthracene (1,000 µg/mL) (QAR)
E572	Methyl parathion (1,000 µg/mL)****
E573	Kepone (1,000 µg/mL) (QAR)+ + +
E662	3-Nitrophenol
E669	1-Methyl ethyl benzene (Cumene)
E686	Methacrylonitrile (1,000 µg/mL)
E687	Ethyl methacrylate (1,000 µg/mL)
E688	2-Picoline
E700	Resorcinol
E713	Picloram (1000 µg/mL)****
E715	Carbofuran
E856	Isodrin
E952	p,p'-Methoxychlor
E954	Aldicarb (1,000 µg/mL)****
E993	1,2-Dibromo-3-chloropropane
E995	Aldicarb sulfone (1,000 µg/mL)****
E996	Aldicarb sulfoxide (1,000 µg/mL)****
E1089	Alachlor (1,000 µg/mL)
E1090	Atrazine (1,000 µg/mL)
E1097	Dibromomethane
E1103	1,3,5-Trimethylbenzene (Mesitylene)
E1104	sec-Butylbenzene
E1105	n-Butylbenzene
E1106	tert-Butylbenzene
E1107	1,2,4-Trimethylbenzene (QAR)
E1108	4-Isopropyltoluene (p-Cymene) (QAR)
E1109	1,3-Dichloropropane

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

Concentrations are 5,000 µg of QAS-Pure Compound per mL of Methanol Solvent Unless Otherwise Noted

E1112	n-Propylbenzene
E1166	1,1-Dichloro-1-propylene (QAR)
E1167	2,2-Dichloropropane
	Surrogates and Internal Standard for USEPA GC/MS Methods 624 and 625
E188	Phenanthrene - d10 (150 µg/mL)(QAR)(100 µg/mL)*
E189	Phenol - d5 (100 µg/mL)*
E190	2,4-Dimethylphenol-3,5,6-d3 (QAR)(100 µg/mL)*
E191	Pentachlorophenol-13C6 (100 µg/mL)*
E192	Dimethyl phthalate - d6 (150 µg/mL)*
E193	2-Fluorophenol (QAR) (100 µg/mL)*
E194	2-Fluorobiphenyl (100 µg/mL)*
E195	1-Fluoronaphthalene (100 µg/mL)*?
E196	1,4-Dichlorobutane-d8 (150 µg/mL)
E197	2-Bromo-1-chloropropane-d6 (150µg/mL)(QAT)
E198	Bromochloromethane-d2 (150 µg/mL)
E199	Benzo (g,h,i) perylene-13C12 (100 µg/L)
E232	Fluorobenzene (150 µg/L)
E233	4-Bromofluorobenzene (150 µg/L)
E234	4,4-Dibromooctafluorobiphenyl (100 µg/L)*
E776	1,2-Dichlorobenzene-d4 (150 µg/L)

*In Acetone **In para-Dioxane ***In 2-Propanol ****Acetonitrile
+In Methylene Chloride ++In Isooctane +++In Cyclohexanone

* U.S. GOVERNMENT PRINTING OFFICE: 1989 - 648-163/87049

Environmental Protection
Agency

Information
Cincinnati OH 45268

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