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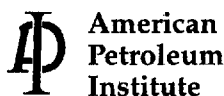
LABORATORY ANALYSIS OF PETROLEUM INDUSTRY WASTEWATERS

ARRANGING FOR ANALYSIS AND UNDERSTANDING LABORATORY REPORTS

REGULATORY AND SCIENTIFIC AFFAIRS
PUBLICATION NUMBER 4694
DECEMBER 1999



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Laboratory Analysis of Petroleum Industry Wastewaters

Arranging for Analysis and Understanding Laboratory Reports

Regulatory and Scientific Affairs

API PUBLICATION NUMBER 4694

PREPARED UNDER CONTRACT BY:

TISCHLER/KOCUREK
ROUND ROCK, TEXAS

DECEMBER 1999



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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Roger Claff, Regulatory and Scientific Affairs

MEMBERS OF THE WATER TECHNOLOGY TASK FORCE

Robert Goodrich, Exxon Research and Engineering Company, Chairperson

David Pierce, Chevron Research and Technology Company, Vice Chairperson

Terrie Blackburn, Williams Pipeline Company

Deborah Bolton, Chevron Products Marketing Company

Vic Carlstrom, Mobil Exploration and Production US Incorporated

Leanne Kuncce, BP Oil Company

Jim Mahon, FINA Company

William Martin, ARCO Products Company

Gary Morris, Mobil Technology Company

Arnold Marsden, Jr., Equiva Services LLC

Barbara Padlo, Amoco Research Center

Gerry Sheely, Marathon Ashland Petroleum LLC

Paul Sun, Equilon Enterprises LLC



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Preface

The American Petroleum Institute's (API's) Health and Environmental Sciences Department, through the API Water Technology Task Force, has conducted a multi-year research program to identify and evaluate practical and environmentally sound technologies for water/wastewater treatment for petroleum facilities. The Task Force has also sponsored work that will help petroleum facilities and government agencies to improve treatment efficiencies to change and comply with regulations. The results of this program are intended to inform decision-makers on appropriate treatment alternatives for individual petroleum manufacturing or distribution facilities.

The Task Force has sponsored and published a significant amount of work in prior years on handling and treating petroleum waters. A listing of some key published reports and guidance documents is summarized below. The goal of this report is to assist individual petroleum facilities to understand, interpret, and arrange for the proper laboratory analyses of petroleum industry wastewaters, whether done by in-house staff or through another resource. The report should be applicable to several types of petroleum facilities, including refineries, marketing and pipeline terminals, production facilities, and underground storage tank sites.

This report is very comprehensive; it covers development of cost-effective analytical plans, selecting a laboratory, key considerations in evaluating laboratory reports, detection limits, QA/QC, available resources, and statistical calculations. The report is structured in a tiered fashion, with the most critical information, in a simple format, presented first. More detailed material covering specialized topics follows. Case studies, sample laboratory reports and reviews, and data calculations are provided to illustrate the material on this complex but necessary topic of laboratory report review and assessment. In some situations, given stringent NPDES monitoring requirements, the cost implications of erroneous laboratory data or poorly prepared laboratory reports can be tens to hundreds of thousands of dollars from fines, investigation costs, follow-up sampling and analysis, etc., not to mention publicity implications. Through this report, the reader will gain useful information and insight that may help prevent realizing these implications.

The Task Force gratefully acknowledges and appreciates the fine work performed by Tishler/Kocurek, Round Rock, Texas, in preparing this comprehensive study.

Other Studies Sponsored by the Water Technology Task Force

- Publ. 4664 Mixing Zone Modeling and Dilution Analysis for Water-Quality-Based NPDES Permit Limits, April 1998.

- Publ. 4665 Analysis and Reduction of Toxicity in Biologically Treated Petroleum Product Terminal Tank Bottoms Water, April 1998.

- Publ. 1612 Guidance Document for Discharging of Petroleum Distribution Terminal Effluents to Publicly Owned Treatment Works, November 1996.

- Publ. 4581 Evaluation of Technologies for the Treatment of Petroleum Product Marketing Terminal Wastewater, June 1993.

- Publ. 4582 Comparative Evaluation of Biological Treatment of Petroleum Product Terminal Wastewater by the Sequencing Batch Reactor Process and the Rotating Biological Contactor Process, June 1993.

- Publ. 4602 Minimization, Handling, Treatment, and Disposal of Petroleum Product Terminal Wastewaters, September 1994.

- Publ. 4606 Source Control and Treatment of Contaminants Found in Petroleum Product Terminal Tank Bottoms, August 1994.

Abstract

A guidance manual is presented by the American Petroleum Institute (API) to assist in arranging for and understanding laboratory analysis of petroleum industry wastewaters. The manual is designed for environmental coordinators, managers, corporate staff, field personnel, and others who must address environmental compliance reporting and regulatory issues. This manual is applicable to wastewaters from petroleum refining, marketing and pipeline terminals, underground storage tank cleanups, and petroleum production facilities. Guidance and information are provided for setting data quality objectives; planning analyses; selecting a laboratory; and reviewing laboratory reports, detection and quantification limits, quality assurance/quality control practices, method references, method-defined analytes, and statistical calculations. The manual contains information on two levels: The first presents the most critical information in a simple format that can be read quickly, and the second discusses additional detail and related topics. Examples of case studies, laboratory reports, and data calculations are given throughout the manual. Checklists are provided to help users understand, plan, and review laboratory data.

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Introduction

This manual is designed for environmental coordinators, managers, corporate staff, and others who must address environmental compliance reporting and regulatory issues. It is also useful for field personnel responsible for obtaining wastewater sample analyses to fulfill environmental regulatory requirements.

This manual assumes that users have some familiarity with wastewaters in the petroleum industry and with the basic requirements of wastewater permits. It is helpful if users also have some basic knowledge of wastewater constituents, analytical methods, analytical laboratories, and environmental regulatory agencies.

Types of Wastewaters Covered

This manual addresses wastewaters associated with the petroleum industry, including:

- 1) Petroleum refining
 - Treated process effluent for direct discharge,
 - Pretreated process effluent for indirect discharge (for example, to a publicly-owned treatment works or deep well), and
 - Storm water.
- 2) Marketing and pipeline terminals
 - Treated process effluent for direct discharge,
 - Pretreated process effluent for indirect discharge,
 - Storm waters, and
 - Untreated process wastewater such as tank water draws.
- 3) Underground storage tank cleanups
 - Leaks and spills to ground water.
- 4) Petroleum production facilities
 - Produced water from crude oil extraction.

Most of these wastewaters are direct or indirect point source discharges to surface waters, which are regulated under the U.S. Environmental Protection Agency's (EPA's) National Pollutant Discharge Elimination System (NPDES) under authority of EPA or an NPDES-authorized state. Thus, most of the discussion and examples in this manual relate to the NPDES program.

Purpose of This Manual

The purpose of this manual is to help the user:

- Understand the technical and regulatory issues associated with obtaining analytical data on wastewater samples as well as the interpretation of the data.
- Understand data quality objectives (DQOs) and articulate DQOs at the beginning of a project.
- Select analytical methods and evaluate their pros and cons.
- Understand and specify method detection limits, quantification limits, reporting levels, minimum levels, and other related terms.
- Understand the concepts of laboratory QA/QC and be able to specify, request, and interpret QA/QC data such as spikes, duplicates, and blanks.
- Understand how matrix interference affects analyses and how to work with the laboratory to resolve such problems.
- Evaluate and select a laboratory.
- Review laboratory reports.
- Understand what to do if a QA/QC requirement is failed.

What's in This Manual

This manual contains information on two levels. Part I is designed to provide the most critical information in a simple format that can be read quickly. Checklists for various topics based on the information in Part I have been developed for practical use and are found in Part IV. Part II of the manual contains additional detail on the topics discussed in Part I, as well as other related topics. Part III of the manual includes references and acronyms. Examples of case studies, laboratory reports, and data calculations are given throughout the manual.

Users of this manual who need information very quickly about a particular topic should go to **Quick Start** at the end of this **Introduction**. For other users who have less pressing needs, the following outline gives a brief overview of each chapter in the manual.

Overview of Manual

Part I— Essential Information

Chapter 1, **Setting Objectives**—introduces the concept of Data Quality Objectives for setting goals prior to conducting laboratory analyses, to ensure data quality. The Checklist for this chapter is **Data Quality Objectives**.

Chapter 2, **Planning Analyses**—discusses how the selection of analytical methods is determined by regulatory specified methods, detection and quantification limits, matrix interferences, and quality assurance/quality control requirements. Checklists for this chapter are **Selecting the Right Analytical Method**, **Resolving Detection/Quantification Limit Problems**, **QA/QC Items for Initial Discussion with Laboratory**, **QA/QC Data in Laboratory Report**, and **Developing an Analytical Schedule**.

Chapter 3, **Selecting a Laboratory**—discusses what should be considered when selecting a laboratory for analyzing environmental samples, including required analyses, staffing, support services, recordkeeping, reporting, reputation, size, and costs. Checklists for this chapter are **Selecting a Laboratory**, **Developing an Analytical Schedule**, **Elements of a Good Laboratory Recordkeeping System**, and **Items for Onsite Laboratory Evaluation**.

Chapter 4, **Reviewing Laboratory Reports**—outlines the basic contents of an analytical laboratory report, and discusses checking the basic elements of a report as soon as it is received, including identifying typical problems that would require immediate response, and reviewing sample results in detail. Checklists for this chapter are **Identifying Parts of a Laboratory Report**, **Initial Review of Laboratory Report**, **Problems Requiring Immediate Response**, and **Checking If Results are Reasonable**.

Part II— Additional Detail and Special Topics

Chapter 5, **Detection and Quantification Limits**—discusses different terms often used in relation to detection and quantification limits, why these limits are important in laboratory analyses and regulatory compliance, and how to apply and interpret these limits.

Chapter 6, **Quality Assurance/Quality Control**—discusses common quality assurance/quality control terms (spikes, duplicates, blanks, etc.) and requirements specified in analytical methods and laboratory programs. The Checklist for this chapter is **QA/QC Data in Laboratory Report**.

Chapter 7, **Method References**—describes the references for analytical methods for the NPDES program and EPA's analytical manual, SW-846, used primarily for nonNPDES analyses.

Chapter 8, **Method-Defined Analytes**—describes the most common of the method-defined analytes for wastewater (for example, BOD, TSS, COD, TOC, oil and grease, and TPH), and how they are related to each other.

Chapter 9, **Statistical Calculations**—discusses statistical terms and calculations likely to be encountered in environmental analyses and laboratory reports such as precision, bias, accuracy, outliers, nondetects, and method detection limits. Checklists for this chapter are **Indications of Analytical Bias** and **Errors That Can Result in Outliers**.

Part III—References and Acronyms

This part lists the references and acronyms cited in the manual.

Part IV—Checklists

This part contains Checklists to help the user understand, plan, and review laboratory data. These Checklists are:

- **Data Quality Objectives**
- **Selecting the Right Analytical Method**
- **Resolving Detection/Quantification Limit Problems**
- **QA/QC Items for Initial Discussion with Laboratory**
- **QA/QC Data in Laboratory Report**
- **Developing an Analytical Schedule**
- **Selecting a Laboratory**
- **Elements of a Good Laboratory Recordkeeping System**
- **Items for Onsite Laboratory Evaluation**
- **Identifying Parts of a Laboratory Report**
- **Initial Review of Laboratory Report**
- **Problems Requiring Immediate Response**
- **Checking If Results Are Reasonable**
- **Indications of Analytical Bias (Too High or Too Low)**
- **Errors That Can Result in Outliers**

Quick Start

For readers who must find information in this manual quickly, some of the most common questions/problems with laboratory analyses are listed below with directions where to find relevant information in the manual.

Deciding What to Analyze

Where to look in this manual:

- Chapter 2, **Planning Analyses**
- Chapter 5, **Detection and Quantification Limits**
- Chapter 6, **Quality Assurance/Quality Control**
- Chapter 8, **Method-Defined Analytes**
- Part IV, Checklists:
 - **Selecting the Right Analytical Method**
 - **Developing an Analytical Schedule**
 - **Resolving Detection/Quantification Limit Problems**
 - **QA/QC Items for Initial Discussion with Laboratory**
 - **QA/QC Data in Laboratory Report**

Getting the Right Detection Limit

Where to look in this manual:

- Chapter 2, **Detection and Quantification Limits** (introduction)
- Chapter 5, **Detection and Quantification Limits** (additional detail)
- Chapter 9, **EPA Method Detection Limit**
- Part IV, Checklist:
 - **Resolving Detection/Quantification Limit Problems**

Resolving Matrix Interferences

Where to look in this manual:

- Chapter 2, **Matrix Interferences**
- Chapter 5, **Detection and Quantification Limits**
- Chapter 6, **Matrix Spike**
- Chapter 9, **EPA Method Detection Limit**
- Part IV, Checklist:
 - **Resolving Detection/Quantification Limit Problems**

Evaluating a Laboratory for Potential Work

Where to look in this manual:

- Chapter 3, **Selecting a Laboratory**
- Chapter 4, **Reviewing Laboratory Reports**
- Part IV, Checklists:
 - **Selecting a Laboratory**
 - **QA/QC Items for Initial Discussion with Laboratory**
 - **Elements of a Good Laboratory Recordkeeping System**
 - **Items for Onsite Laboratory Evaluation**
 - **Identifying Parts of a Laboratory Report**

Checking a Laboratory Report

Where to look in this manual:

- Chapter 4, **Reviewing Laboratory Reports**
- Chapter 6, **Quality Assurance/Quality Control**
- Chapter 7, **Method References**
- Chapter 9, **Statistical Calculations**
- Part IV, Checklists:
 - **Identifying Parts of a Laboratory Report**
 - **Initial Review of Laboratory Report**
 - **Problems Requiring Immediate Response**
 - **Checking If Results Are Reasonable**
 - **QA/QC Data in Laboratory Report**
 - **Indications of Analytical Bias (Too High or Too Low)**
 - **Errors That Can Result in Outliers**

Identifying Problems and Solutions

Where to look in this manual:

- Chapter 4, **Problems Requiring Immediate Response**
- Chapter 5, **Detection and Quantification Limits**
- Part IV, Checklists:
 - **Problems Requiring Immediate Response**
 - **Resolving Detection/Quantification Limit Problems**
 - **Indications of Analytical Bias (Too High or Too Low)**
 - **Errors That Can Result in Outliers**

Part I

Essential Information

Chapter 1

Setting Objectives

Whether samples are to be analyzed or a laboratory report is to be reviewed, one should decide what the objectives are so that the analytical results will be the best they can be.

Data Quality Objectives (DQOs) is a term used to describe the goals or objectives for a particular data collection activity. By setting goals prior to collecting the data, one helps ensure that the quality of the data is good and that the data satisfy the project needs. DQOs include both qualitative and quantitative objectives. An example of a qualitative DQO is “to obtain measures of metals in a wastewater effluent.” An example of a quantitative DQO is “to meet a minimum analytical level for lead of 5 micrograms per liter ($\mu\text{g/L}$).”

Some projects are simple enough that DQOs do not require a lot of planning, where the data needs are simple and clear and a call to the laboratory suffices. Larger and more complicated projects require more planning. At a minimum, DQOs should be written in outline form, for example, as an analytical schedule table showing analytes, minimum analytical limits, and reasons for analysis (permit application/monitoring, cleanup confirmation, and so on). Depending on the type of project and regulatory requirements, the DQOs may be formally stated in a written plan, which can be quite detailed.

DQOs can be established for various tasks within a project, such as sample collection, in addition to sample analysis. However, because this manual focuses on analyses of wastewater, the discussion of DQOs here is limited to analytical issues.

Before samples are collected and analyzed, DQOs are established to ensure that the analytical results meet a project's requirements. DQOs for analytical data should address the elements of data quality: accuracy, precision, detection/quantification limits, completeness, representativeness, and comparability. Table 1-1 includes examples of general DQOs for each of these elements. Part IV of this manual contains a Checklist based on this table, **Data Quality Objectives**, that can be copied and used to prepare DQOs for a particular project.

Typically, when developing DQOs for analytical data and where there are multiple DQOs to address a given data quality element, one of the DQOs will

control. For example, a ground water cleanup standard may require a detection limit that is lower than the reporting limit for the laboratory, but higher than the published method detection limit. The cleanup standard sets the final DQO and obviously will require some discussion with the laboratory on how to achieve a lower reporting limit.

The level of detail in DQOs will depend on the particular activity or project. DQOs can be included in a written sampling and analysis plan, or outlined in summary fashion in a table. A copy of the DQOs should be provided to the laboratory. If the DQOs are very extensive or complicated, extra care will be needed to ensure that the laboratory understands what is required. If the DQOs are included in a detailed plan, the laboratory should be provided with an outline summary of the requirements as well. The DQOs also should be discussed verbally with the laboratory, even if the DQOs are given to the laboratory in written form and made part of the service contract. The more effort and planning done before the actual analyses, and the more communication with, and involvement of, the laboratory, the more likely the DQOs will be satisfied and the analytical results will be valid and useful.



*See the
checklist in
Part IV, Data
Quality
Objectives.*

Table 1-1. Example of General DQO Statements for Analytical Data

Representativeness

- Include all analytes to meet regulatory requirements.
- Include any additional analytes needed for material characterization, for example, those affecting material handling or treatment.
- Collect type of sample representative of material and/or needed to meet analytical/regulatory requirements (grab, composite).
- Collect sufficient samples representative of material and/or needed to meet regulatory requirements.
- Collect samples to meet minimum frequency of regulatory requirements.

Detection/Quantification Limits

- Meet detection/quantification limits of analytical method.
- Meet any specific detection/quantification limits for project, including regulatory requirements.

Accuracy

- Meet recovery criteria of analytical method.
- Meet recovery criteria set by laboratory.
- Meet any specific recovery criteria for project, including regulatory requirements.

Precision

- Meet precision criteria of analytical method.
- Meet precision criteria set by laboratory.
- Meet any specific precision criteria for project, including regulatory requirements.

Completeness

- Laboratory analyzes all samples as requested.
- Laboratory reports results for all requested analyses.
- Laboratory reports all QA/QC data as requested.

Comparability

- Sample results comparable to similar materials.
 - Relationships between certain analytes logical and reasonable (for example, COD to BOD ratio).
-

Chapter 2

Planning Analyses

There are four major factors affecting the selection of laboratory analyses:

- 1) Regulatory specifications for certain methods,
- 2) Detection and quantification limits,
- 3) Matrix interferences, and
- 4) Quality assurance/quality control (QA/QC) requirements.



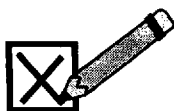
NOTE

The ultimate responsibility for the quality of the analytical data lies with the person being regulated.

The choice of analytical method often is left up to the laboratory. While most laboratories routinely performing analyses for regulatory programs will know which methods to use, some laboratories will not. Consequently, the analyses, although they may be precise and accurate, may not meet legal requirements of the regulatory program. Detection and quantification limits refer to the sensitivity of an analytical method. These limits are important because they may be specified by regulatory agencies or they may be needed to demonstrate compliance with a regulatory standard, permit limit, or cleanup standard. Matrix interferences refer to materials in the sample that interfere with analysis, which may affect detection and quantification limits or method performance in recovery and precision. QA/QC is important because it ensures the quality of the analyses.

In regulatory programs, the ultimate responsibility for the quality of the analytical data lies with the person being regulated. This is made clear by the number of certification statements that must accompany data submittals and permit applications. Thus, it is important to know these requirements and ensure that the laboratory uses the correct methods.

This chapter discusses how the above four factors affect the selection of analytical methods. Part IV includes a Checklist, **Selecting the Right Analytical Method**, which is based on these factors and which can be used to set up an analytical schedule.



See the checklist in Part IV, **Selecting the Right Analytical**

Methods Specified by Regulation

Regulatory programs may specify certain analytical methods. For example, under the National Pollutant Discharge Elimination System (NPDES) program, only methods listed at 40 Code of Federal Regulations (CFR) 136 may be used unless the NPDES permit explicitly specifies an alternate method. Other regulatory programs related to the types of wastewaters covered by this manual generally do not require specific analytical methods; however, it is always wise to check before selecting a method.



NOTE

The NPDES program allows only methods listed at 40 CFR 136, unless the NPDES permit specifies an alternate method.

The most common method references for wastewater are found at 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act;" and in SW-846, the U.S. Environmental Protection Agency's (EPA's) "Test Methods for Analysis of Solid Waste." SW-846 methods are most commonly used in the Resource Conservation and Recovery Act (RCRA) program. A laboratory will sometimes inappropriately use an SW-846 method for wastewater, because SW-846 methods are often very similar to those at 40 CFR 136. Notwithstanding their similarities, however, SW-846 methods are not allowed and may not be used for NPDES reporting.

NPDES-approved methods and SW-846 methods are described in the next two sections.

NPDES-Approved Methods

Analytical methods for NPDES monitoring must be:

- 1) A method approved at 40 CFR 136, or
- 2) An alternate method specified in the NPDES permit.

For most NPDES analyses, a method at 40 CFR 136 will be suitable. Occasionally, an alternate method is negotiated with the permit agency, usually when wastewater characteristics cause matrix interferences (see **Matrix Interferences** later in this chapter). For a discussion of alternate methods, see **Alternate Methods** following this section.

Requirements at 40 CFR 136

All of the approved analytical methods for NPDES analyses are listed in Tables IA-IE of 40 CFR 136. For each analyte, there are one or more

approved methods. Table II of 40 CFR 136 contains requirements for sample containers and preservation. The contents of the 40 CFR 136 tables are summarized in Table 2-1 of this chapter.

The references for the methods approved at 40 CFR 136 are listed in Table 2-2 of this chapter; they are described more fully in Chapter 7, **Method References**. Of the references for analytical methods listed in Table 2-2, the most common are:

- *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, D.C., 1992 (*Standard Methods*), and,
- *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, U.S. Environmental Protection Agency, Cincinnati, 1979.

Table 2-1. Description of Analytical Specifications at 40 CFR 136

Table IA

Approved biological test procedures, including tests for pathogenic bacteria and bacterial indicators (total coliform, fecal coliform, *Escherichia coli*, *Enterococci sp.*) and the acute and chronic whole effluent toxicity procedures (fresh and saline waters).

Table IB

Entitled "List of Approved Inorganic Test Procedures," which is somewhat misleading. Includes the inorganic analytical procedures for metals, salts, dissolved and suspended solids, and inorganic forms of nitrogen; also lists the approved methods for *organic* materials such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), oil and grease, and organic nitrogen. Contains all NPDES analytes with the exception of specific organic chemicals and pesticides that are measured using gas chromatography (GC) or high performance liquid chromatography (HPLC) methods.

Table IC

Approved methods for non-pesticide organic compounds. Compounds listed are individual organic chemicals (with the exception of the polychlorinated biphenyls, which are mixtures identified by chlorine content) and analytical

procedures are all GC or HPLC methods, with various types of detectors that are specific to the chemicals being analyzed.

Table ID

Approved methods for pesticides. Methods are GC methods and thin layer chromatography (TLC) methods.

Table IE

Approved methods for radiological analytes, including alpha and beta particles, and radium.

Table II

Required sample container materials, preservation methods, and holding times for each analyte and method specified in Tables IA-IE.

Table 2-2. Analytical Method References at 40 CFR 136

Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency

Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Water Environment Federation (WEF), American Society of Civil Engineers (ASCE)

Annual Book of ASTM Standards, Water and Environmental Technology, American Society for Testing and Materials (ASTM)

“Official Methods of Analysis of the Association of Official Analytical Chemists,” Association of Official Analytical Chemists (AOAC)

U.S. Geological Survey (USGS) method references

Proprietary method references

Alternate Methods

An alternate method that is not listed at 40 CFR 136 may be used for NPDES analyses if it is specified in the NPDES permit. If an alternate method is specified in the permit, it takes precedence over the 40 CFR 136 methods. The method specified in the permit must be used for compliance demonstration. Use of an alternate method is described in the next example.

EXAMPLE - Example of Alternate Method in NPDES Permit

A chemical plant in Texas had demonstrated a significant matrix interference problem with all approved modifications of the analytical methods for total cyanide and cyanide amenable to chlorination. The plant had conducted extensive method development work and found that replacing the colorimetric determination in the approved cyanide methods by ion chromatography (IC) as a determinative method eliminated most of the interference. The method development work and the demonstration of matrix interferences with the approved cyanide methods were presented to the permit authority. The permit writer included the modified cyanide method (IC determination) in the NPDES permit, to be used to demonstrate compliance with the permit limits. The permit writer did this because of the extensive time that would be required to obtain EPA approval for the modified method.

Alternate methods may be specified in an NPDES permit for a number of reasons:

- monitoring for an analyte for which there is no 40 CFR 136 method
- avoiding an analytical interference unique to the permittee's effluent
- attaining a lower detection limit or improved method sensitivity
- attaining improved resolution or selectivity for the analyte of interest
- improving method precision and accuracy
- reducing analytical costs
- simplifying analytical procedures

An important principle of analyses for NPDES permit compliance is that only approved 40 CFR 136 methods may be used unless the permit explicitly requires or allows an alternate method. It is important for the permittee to inquire about and fully understand why an alternate method has been specified in his/her permit, and to include discussion of analytical methods as part of the permit negotiation process. In this discussion, the permittee should consider the following concerns:

- 40 CFR 136 is intended to provide the permit writer with a complete compendium of EPA-approved and fully validated methods for analysis of pollutants under the Clean Water Act. The permit writer must provide a

technically sound justification, beyond application of “professional judgment,” for selecting a method outside of this compendium; and this justification should clearly indicate why the permit writer believes that 40 CFR 136 methods are not appropriate for the particular permit.

- In many cases in effluent guidelines development, the use of specific analytical methods was assumed. Use of a different analytical method for compliance monitoring could invalidate the effluent guideline. For example, EPA has specified in the refinery effluent guidelines the analytical procedure for phenolic compounds given in the 14th edition of *Standard Methods*. To ensure consistency and accuracy in compliance determinations, refineries should be required to use this same analytical method for compliance monitoring. In particular, refineries should not be required to use phenolics methods specified in later editions of *Standard Methods*.
- The appropriate 40 CFR method may have a method detection limit above the concentration in the effluent. It is quite acceptable and consistent with EPA policy to use the 40 CFR 136 method and report zero concentration in this case. If a permit writer insisted upon an alternate method, perhaps unvalidated but with a lower method detection limit, and then specified a stringent water-quality-based permit limit near or at this detection limit, the permittee might be unable to comply with the permit limit. The permittee should insist that inasmuch as 40 CFR 136 methods are fully validated (see below), no unvalidated or improperly validated methods can or should be substituted for them.
- Section 304(h) of the Clean Water Act and 40 CFR 136.3 require all analytical methods used for compliance monitoring be subjected to a rigorous method validation process, including round robin testing to establish interlaboratory performance and variability. The permit writer is obligated to specify in permits only analytical methods which have undergone this rigorous method validation process. The permittee should insist that all methods specified in the permit be properly validated as per 40 CFR 136.3 and section 304(h) of the Clean Water Act.

Typically, the best resource for analytical methods for analytes not listed at 40 CFR 136 is SW-846 (see the next section, **SW-846 Methods**). Methods for metals and organics such as volatiles and semivolatiles in SW-846 are similar to those at 40 CFR 136; however, SW-846 methods cover a wider range of analytes than the NPDES methods. Thus, for analytes identified in NPDES permits and permit applications for which no 40 CFR 136 method exists, there often will be an acceptable analytical method in SW-846. *Standard Methods* and the ASTM methods (see Chapter 7, **Method References**) are also sources of

analytical procedures that may be suitable for analytes not covered by approved NPDES methods.

If there is not any published method available for the analyte, then the laboratory and its client should work together to develop a method. In this case, the laboratory must be sure to perform the same type of QA/QC specified for similar types of analytes with approved analytical methods. Examples of such procedures include the measurements of blanks, initial and ongoing precision and recovery, and matrix spikes and matrix spike duplicates. The analytical method used should also be documented carefully in writing. These steps will assure that the resulting data are valid.

Many NPDES permittees would like the option to use one of the new, proprietary analytical methods and equipment which are constantly being introduced by the chemical analysis industry, but cannot do so until the methods are formally approved at 40 CFR 136. Even relatively minor modifications to an approved method, if such modifications are not explicitly allowed by the method, must be approved by EPA, even though the current EPA procedures at 40 CFR 136 for approval of alternate methods are very cumbersome and time-consuming.

This situation will change once EPA promulgates its proposed streamlining procedures for alternative analytical methods (62 Federal Register [FR] 14976, March 28, 1997). The streamlining procedures provide for simplified approvals of alternate or modified analytical methods for most analytes listed at 40 CFR 136, if the alternate method can meet specified performance criteria based on approved methods. Under streamlining, a single laboratory, single matrix, modified analytical method can become an approved method without even contacting EPA, provided the reference method performance criteria can be achieved and the modifications do not include changes in instruments used for detection. The new method approval procedures will allow companies and laboratories to obtain EPA approval much more quickly than has been possible in the past. EPA's objective is to encourage the development and implementation of improved analytical methods.

Once the streamlined approval procedures for modified and alternate analytical methods become available, facilities will have greater opportunities to adopt more efficient and sensitive analytical methods, and it should also be easier to deal with matrix interference problems (see **Matrix Interferences** later in this chapter).

SW-846 Methods

Outside of the NPDES program, EPA's SW-846 is the most common analytical method reference. This reference is used primarily for the analysis of samples under the RCRA hazardous waste regulations. When NPDES analytical methods are not required for a wastewater sample or when the sample is not taken for NPDES monitoring, SW-846 methods may be suitable. SW-846 contains methods for metals, organic analytes such as volatile and semivolatile organics, and other analytes such as cyanide, sulfides, sulfates, and oil and grease. SW-846 also includes tests for hazardous waste characteristics of ignitability, corrosivity, reactivity, and toxicity (Toxic Characteristic Leaching Procedure, TCLP).

Detection and Quantification Limits

The discussion of detection and quantification limits in this chapter provides an overview of this topic; for more detail, the reader should see Chapter 5, **Detection and Quantification Limits**.

There are so many terms that are used to define or relate to detection and quantification limits that the whole subject can be very confusing. In simple terms:

- A detection limit is the concentration at which the analyte can just be identified, but at which there is so little of it that its concentration cannot be measured.
- A quantification limit is the concentration at which there is barely enough of the analyte to both identify it and to measure its concentration. The quantification limit is greater than the detection limit.

Detection and quantification limits are important because:

- They may be required by regulatory agencies in permits, permit applications, or other regulatory documents, or
- They may be needed to demonstrate compliance with a regulatory standard, permit limit, or cleanup standard.

The difference between detection and quantification limits is important in regulatory compliance monitoring such as for NPDES permit limits. Using quantification limits lessens the chance of a false positive, that is, a laboratory result that says the analyte is there, when it actually is not. Thus, when

compliance limits are very low, it is important to base them on quantification limits rather than detection limits.

Detection limits and quantification limits have become progressively more important as regulatory limits on some pollutants have decreased to levels close to the maximum performance capabilities of the available methods. This is particularly true for substances that are potentially toxic and are regulated by water quality standards. Examples include mercury and 2,3,7,8-tetrachlorodibenzo-p-dioxin, both of which have water quality standards that are set well below the detection capabilities of the most sensitive available methods. Table 2-3 shows some examples. It is important to note that the method detection limit (MDL) and minimum level (ML, a type of quantification limit) values shown in Table 2-3 are based on analyses of samples in reagent (clean) water, not complex wastewater effluents. Therefore, they may not be achievable for some wastewaters. In many cases, low concentration water quality standards result in water-quality-based *permit limits* that are below analytical method detection capabilities.

Table 2-3. Examples of Water Quality Criteria That Are Below Analytical Method Detection and Quantification Capabilities

Chemical	Criterion Type*	Criterion* µg/L	Method Detection Limit (µg/L)**	Minimum Level (µg/L)**
Cyanide	Salt water, aquatic	1	20	NA
Benzo(a) pyrene	Human health	0.0028	0.023	NA
Acrylonitrile	Human health	0.059	0.5	NA
Mercury	Human health	0.012	0.2	NA
PCB-1242	Human health	0.000044	0.065	NA
2,3,7,8-TCDD	Human health	0.000000013	NA	0.00001

*From EPA's National Toxic Rule, 40 CFR 131.36
 **For most sensitive 40 CFR 136 method

The need to consider detection limits and quantification limits is not limited to pollutants for which water quality standards have been established. Even though the permit limits for a specific pollutant may be above the analytical detection and quantification limits, these limits will become important if the pollutant is sometimes at very low concentrations. A common example is oil and grease, which in a biologically-treated effluent or in runoff from a clean area, will be below the quantification limit. In such cases the regulatory agency will usually have a reporting policy that specifies how to report

individual values that are below quantification and/or detection limits and how to compute averages when the data include values below detection or quantification limits. Therefore, it is important that the users of analytical data understand the differences between detection limits and quantification limits, and the origin and definitions of the most commonly used forms of these limits. An example of permit language that describes how to handle values less than quantification limits is given below.

**EXAMPLE - Example NPDES Permit Language for Compliance Reporting
of Values Below the Quantification Limit**

The text shown below is taken from standard NPDES permit language of EPA Region 6.

PART II — OTHER CONDITIONS

A. MINIMUM QUANTIFICATION LEVEL (MQL)

If any individual analytical test result is less than the minimum quantification level listed below, a value of zero (0) may be used for that individual result for the Discharge Monitoring Report (DMR) calculations and reporting requirements.

METALS AND CYANIDE MQL (µg/L)

Cadmium (total)	1
Copper (total)	10
Cyanide (total)	20

VOLATILE COMPOUNDS MQL (µg/L)

Benzene	10
Toluene	10

Typically, there will be many regulated pollutants in a permit or permit application for which detection limits and quantification limits will not be an issue. Such measurement limitations are not a concern for any pollutant that is always present in an effluent at concentrations well above the quantification limit. For example, for many industrial effluents, quantification limits for BOD, TOC, COD, total suspended solids (TSS), and ammonia-nitrogen are not a problem.

It cannot be assumed that even the most experienced laboratories will automatically report data at the required detection or quantification limits. There are many examples of NPDES permit applications that have been returned to applicants as incomplete because the detection or quantification limits did not meet the criteria. In fact, because of these problems some

regulatory agencies now include on their permit application forms minimum detection or quantification limits for certain chemicals. Typically, these are chemicals for which the state has water quality standards. In these instances, an easy way to ensure that the laboratory achieves the required limits is to provide it with a copy of the permit application and state that the specified limits must be achieved. Below is an example of a typical detection limit problem with metals.

EXAMPLE - Typical Metal Detection Limit Problem

In situations where water quality standards for heavy metals are very restrictive with low concentrations, it is important that the laboratory use a method with low detection limits. Most laboratories prefer to analyze water samples for metals using the inductively coupled plasma/atomic emission spectrometry (ICP/AES) method because it is fast and inexpensive. However, for certain metals such as copper and cadmium, the ICP/AES method does not have a sufficiently low detection limit to allow a regulatory agency to evaluate compliance with water quality standards. In these cases, the water samples must be analyzed using the more sensitive graphite furnace atomic absorption (GFAA) method or ICP-mass spectrometry (ICP/MS) method.

In some cases, a laboratory will not be able to achieve the detection or quantification limits specified in NPDES permits, permit applications, or the published analytical methods. Simply telling the regulatory agency that a detection or quantification limit cannot be met is insufficient. The following steps should be taken when there is a problem in achieving a detection or quantification limit.



See the checklist
in Part IV,
**Resolving
Detection/
Quantification
Limit Problems.**

- 1) Make sure the laboratory has tried all of the sample clean-up steps (sample preparation steps to separate the analyte from its matrix) allowed by the analytical method. For example, many of the gas chromatography/conventional detector (GC/CD) and gas chromatography/mass spectrometer (GC/MS) methods promulgated at 40 CFR 136 allow sample clean up techniques to eliminate or reduce matrix interferences. They also allow alternate GC column packing and detectors and changing the temperature program to provide better resolution. The proposed EPA streamlining procedures for changes to existing analytical methods or alternate analytical methods (see **Alternate Methods** earlier in this chapter) will make it much easier than it has been in the past to use matrix clean up procedures that are not included in the approved analytical methods, provided acceptable method performance can be demonstrated.

- 2) If approved clean up steps do not provide the required sensitivity, use a more sensitive approved analytical method, if available. For example, EPA states that its isotope dilution methods for analysis of volatile (EPA 1624) or semivolatile (EPA 1625) organic analytes will often resolve matrix interferences for the non-isotope dilution methods EPA 624 and 625.
- 3) If neither of these approaches achieves the required detection or quantification limit, then it will be necessary to meet with the regulatory agency to discuss how to solve the problem. One alternative is the development of a matrix-specific detection or quantification limit. In many cases, the agency will allow a deviation from the reporting limits required in a wastewater permit application if the discharger can provide convincing evidence, such as that based on process knowledge, that the specific analyte of concern is not likely to be present in the wastewater.

Part IV includes a Checklist, **Resolving Detection/Quantification Limit Problems**, which is based on the above steps. The Checklist can be used when discussing analyses with a laboratory or regulatory agency, or as a simple reminder of what steps should be taken to resolve this type of problem.

Matrix Interferences

The term matrix refers to the characteristics of a sample, not only the physical form (water, liquid, solid), but also the components of the sample (specific constituents, oils, etc.). The matrix of a sample affects the efficiency of analysis, including recovery. In general, the more complex a matrix, the greater the effect on the analysis.

Because the target analyte typically constitutes a very small portion of the sample matrix (for example, measurements of “micro” [10^{-6}] and “pico” [10^{-12}] gram per liter are not uncommon), other chemical constituents in the matrix or its physical characteristics can interfere with the ability of an analytical method to measure the target analyte. Typically, this interference is experienced as the inability to achieve the required detection/quantification limits, poor recovery of spikes of the target analyte, or poor precision results from replicate analysis. An example of matrix interference from total dissolved solids is given below.

EXAMPLE - Example of Matrix Interference from Total Dissolved Solids (TDS)

High concentrations of total dissolved inorganic salts, such as sodium and chloride, interfere with the sensitivity of the ICP/AES and GFAA methods, which are used for analyzing most trace metals in effluents. Trace concentrations are typical of water quality-based effluent limits. An effluent that contains high concentrations of such salts requires sample clean up methods before it can be analyzed for trace levels of certain metals such as copper and lead. For example, the GFAA procedures for certain heavy metals include a chelation-solvent extraction step to eliminate this interference.

Typically, matrix interferences are consistent for a specific wastewater matrix. This is especially true for treated effluents, which have relatively constant characteristics. Therefore, matrix interferences are usually discovered when a particular analysis is performed for the first time. Interferences can be identified when samples are analyzed for a permit application, and when the application requires testing for analytes that were not required to be tested for previous applications. Screening studies that some facilities conduct on their treated effluents may also identify matrix interferences.

If testing is being performed on relatively high strength, untreated wastewater streams, then matrix interferences will be more common and potentially more difficult to eliminate. This is not uncommon in the case of facilities that must comply with pretreatment standards for specific organic chemicals. For example, if a discharger has limits on benzene and toluene, and the untreated wastewater contains xylenes at a concentration 50 to 100 times greater, it may be very difficult to quantify the target analytes (benzene and toluene).

Most of the approved analytical methods include a description of common matrix interferences and recommend approaches for eliminating them. As discussed in the previous section, **Detection and Quantification Limits**, these procedures can include sample clean up steps to remove the interferences, and changing the column packing or temperature program in a GC method to provide better resolution. As discussed in an earlier section, **Alternate Methods**, if and when EPA's analytical methods streamlining procedures are finalized, they would allow a laboratory to make changes to the approved analytical methods that are not described in the procedure, provided that the laboratory can meet specified method performance levels.

Normally, when matrix interferences are encountered, the laboratory will attempt to eliminate them by following procedures for such in the method. Often, there is sufficient sample to allow limited, additional analyses for this purpose. However, it will sometimes be necessary to collect additional samples.

If it is impossible to resolve the matrix interferences with any of the EPA-approved analytical methods and allowable sample clean up procedures, several options remain. The regulatory authority may be asked to approve an alternate method that is not subject to the interference, to change the detection or quantification limit, or to allow analysis for a surrogate chemical that is not subject to matrix interference. Before such alternatives are approved by the regulatory authority, the discharger will have to thoroughly document that all approved analytical methods, including all the allowable clean-up steps related to the observed interference, have been considered and exhaustively evaluated.

In general, regulatory authorities are reluctant to allow major method changes to or to relax performance requirements for approved methods, including the published detection and quantification levels. In the case of detection and quantification limits in permits, it is helpful if the permit already includes a provision allowing development of effluent specific detection/quantification limits (see Chapter 5, **Detection and Quantification Limits**). This provision makes it much easier to obtain agency approval of alternative detection/quantification limits when matrix interference problems occur.

Quality Assurance/Quality Control

In general usage, the terms “quality assurance” and “quality control” are usually lumped together and referred to in shorthand fashion as QA/QC. In laboratory usage, however, each term has a distinct definition. Although not critical, in certain situations it is helpful to know the distinction between quality control and quality assurance.

Quality control consists of practices and procedures in the laboratory with the objective of achieving high quality in the services the laboratory provides. Quality assurance consists of practices and procedures in the laboratory designed to assure that quality control is implemented properly. Examples of elements in a quality control program are listed in Table 2-4. Examples of program elements for quality assurance are listed in Table 2-5.

An introduction to the most common quality control elements is given next, followed by a discussion of what is acceptable QA/QC and what to do in practical situations. More detailed QA/QC topics are discussed in Chapter 6, **Quality Assurance/Quality Control**.

Table 2-4. Example Elements of Quality Control Program

Suitable facilities and equipment, properly maintained
 Technical competence
 Training
 Standard operating procedures
 Good laboratory and measurement practices
 Inspection
 Validation
 Documentation
 Protocols for specific purposes

Table 2-5. Example Elements of Quality Assurance Program

Sample control and management
 Record control and management
 Internal and external audits
 Corrective action procedures
 Interlaboratory collaborative tests
 Intralaboratory internal tests
 Statistical control techniques
 Independent reference samples
 Methods evaluation
 Laboratory design
 Reporting to management
 Training
 Quality objectives and planning
 Program review and revision

Common Terms

A brief description of the common QA/QC terms—spikes, duplicates, and blanks—is given here. These and other QA/QC terms are discussed in more detail in Chapter 6, **Quality Assurance/Quality Control**.

Spikes

A spike is a quantity of material added to a sample, the spiked material being whichever analyte(s) is(are) of interest. There are different types of sample spikes used in the laboratory for different purposes and at different steps in

analytical procedures. Typical types of sample spikes are listed in Table 2-6. Figure 2-1 illustrates the points in the analytical process where the various spikes are introduced or analyzed, and how these spikes relate to each other.

A spiked sample is used to calculate the recovery of an analyte (see **Accuracy and Recovery** in Chapter 9, **Statistics** for calculation examples). The recovery information is either used directly in the calculation of the analyte concentration or is used merely to judge whether the analytical process is in control and producing accurate results.

Table 2-6. Common Types of Sample Spikes

Standard solutions
Matrix spike and matrix spike duplicate
Surrogate spike in volatile and semivolatile organic analyses
Isotope spike
Internal standard spikes for volatile and semivolatile organic analyses
Method of standard addition spike for metal analyses

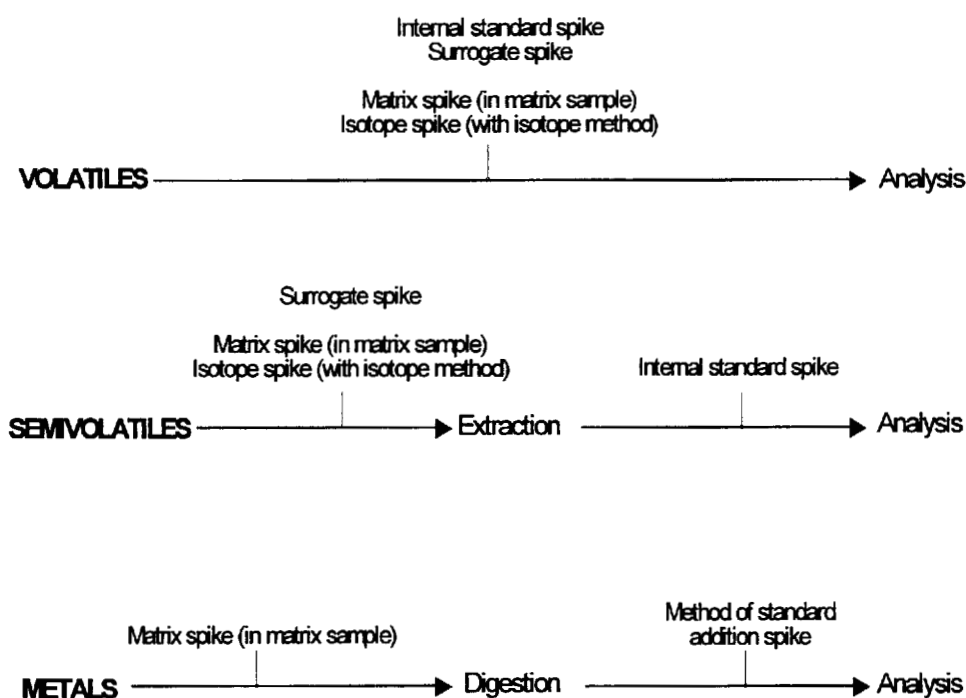


Figure 2-1. Different Types of Sample Spikes

Duplicates and Replicates

Duplicate analyses (and replicates of two or more) are used to evaluate sample variance or precision. When evaluating duplicates, it is important to know what “activities” have been duplicated. For example, a duplicate pair could be two split samples prepared at the time of collection (field duplicate) or it could be only the analytical step that is duplicated on the same sample (duplicate measurement). Therefore, when variability in sample measurement is an important issue, care must be taken to define where and how duplicates will be made. For example, if sample uniformity or heterogeneity is a question, field duplicates will be important. If analytical precision is a question, laboratory duplicate measurements will be important.

Blanks

A blank is a sample that is not supposed to contain the target analyte(s), and is prepared with reagent or distilled water. The purpose of the blank sample is to detect contamination or interference problems, or document their absence. Such problems can be caused by field conditions where the sample is collected, the person collecting the sample, laboratory conditions, reagents used in the analysis, laboratory equipment, and the person(s) performing the analysis.

Like duplicates, blanks can be prepared at different points in the sample collection and measurement process. The most common types of blanks are laboratory blanks, field blanks, and trip blanks.

Outlining QA/QC Requirements with the Laboratory

To minimize QA/QC problems, QA/QC requirements should be agreed upon with the laboratory before samples are sent for analysis. Table 2-7 presents sample questions to ask the laboratory when initially inquiring about analyses. Part IV includes a Checklist, **QA/QC Items for Initial Discussion with Laboratory**, which is based on the questions in Table 2-7. Another Checklist in Part IV, **QA/QC Data in Laboratory Report**, can be used to identify exactly which QA/QC data are to be included in the laboratory report. The latter Checklist contains a recommended “minimum” QA/QC list, as well as additional QA/QC that may be needed for a particular project.

What should a client request of a laboratory in the way of QA/QC data? Initially, the QA/QC request depends on the laboratory’s routine QA/QC program and what it can and is willing to do for the client. If the laboratory cannot or does not want to provide a certain type of QA/QC, it is up to the

client to decide if the information can be omitted or if it is critical and another laboratory must be used. It also depends on the particular needs of the project, including both the client's needs and any regulatory specifications.

At a minimum, the client should discuss with the laboratory what normal QA/QC procedures will be conducted for the type of samples and analyses that will be performed. The discussion should at least cover matrix spikes, duplicates, quality control standards, and blanks analyses, including the frequency of each type. Required detection or reporting limits should be clearly spelled out and reviewed. If the client requires QA/QC procedures in addition to the laboratory's normal routine, these requirements need to be specified and preferably in writing. There may be a cost for additional QA/QC, which needs to be discussed and agreed upon. Other questions that should be asked of the laboratory include whether payment is required for any analysis that does not meet agreed upon QA/QC requirements or for any reanalysis that must be done because the laboratory made a mistake. QA/QC requirements, costs, and response actions can be written into a service contract with the laboratory.



See the
checklists in Part
IV, QA/QC Items
for Initial
Discussion with
Laboratory and
QA/QC Data in
Laboratory
Report.

Costs for additional QA/QC are negotiable with the laboratory. Additional QA/QC may be in the form of matrix spikes, trip blanks, field blanks, blind duplicates, and so on. There may or may not be any extra cost for additional QA/QC. The cost will depend on the laboratory, how much the requested QA/QC differs from normal laboratory procedures, the number and frequency of samples, and other considerations.

Table 2-7. Sample Questions on QA/QC for Initial Discussion with Laboratory

-
- Are matrix spikes, duplicates, QC standards, and blank samples analyzed?
 - What is the frequency of analysis for matrix spikes, duplicates, QC standards, and blanks?
 - What detection or reporting limits are required?
 - If additional QA/QC procedures/samples are required, what is the additional cost?
 - When laboratory errors occur, will the sample be reanalyzed at no additional cost?
 - Is payment for analysis required if agreed upon QA/QC requirements are not met?
 - What is done when matrix interferences are indicated? Is the sample reanalyzed?
-

Developing an Analytical Schedule

The following steps can be used to help develop an analytical schedule for routine monitoring or a particular project. Part IV includes a Checklist, **Developing an Analytical Schedule**, based on the these steps.

- 1) Identify every analyte specified in the applicable permit, permit application, or other regulatory requirement. Also identify any other analyte that might affect wastewater handling or treatment, and so should be included in the analytical report.
- 2) Identify the total number of samples and sampling frequency required for each analyte.
- 3) Identify the type of sample (grab, composite) for each analyte. Analytes normally requiring grab samples include pH, temperature, dissolved oxygen, chlorine, volatile organics, oil and grease, coliforms, total phenols, sulfites, sulfides, and hexavalent chromium.
- 4) Identify sample holding times for each analyte. Analytes with relatively short holding times include pH, coliforms, aquatic toxicity, chlorine, hexavalent chromium, nitrate (not nitrate and nitrite combined), dissolved oxygen, sulfite, surfactants, and turbidity.
- 5) Identify the most restrictive detection/quantification limit among all the requirements for each analyte.
- 6) Identify any particular analytical methods that are specified by the regulations, permit, or project. In NPDES permits, special analytical requirements are sometimes included as footnotes to the limits or monitoring requirements, or may be included in the "Other Conditions."
- 7) For each analyte for which there is no analytical method specified in the permit, identify the approved methods at 40 CFR 136. Identify appropriate methods for non-NPDES analyses.
- 8) Based on knowledge of the waste matrix and the required detection/quantification limits, select one or more analytical methods for each analyte. Preliminary screening of the wastewater may be needed to define the matrix characteristics.



See the checklist in Part IV, **Developing an Analytical Schedule**.

Typically, Steps 7 and 8 will be performed by the laboratory, if it is provided with the analyte list and required detection/quantification limits. However, it is good practice to verify the laboratory's selections to identify potential problems before any analyses are performed.

Analytical schedules can be as simple or detailed as needed. Two examples are given here. It is important to keep in mind that these are only examples, and analytical schedules for any particular facility and sampling activity will depend on the needs of that facility.

EXAMPLE - Example of Analytical Schedule for Pretreated Wastewater

Analyte	Reason for Analysis			Sample Frequency	Minimum Number of Samples
	EGL	NPDES	Treatment Characterization		
BOD ₅	x	x	x	1/wk	4
CBOD ₅	-	-	x	2/wk	8
TSS	x	x	x	2/wk	8
COD	x	x	x	2/wk	8
TOC	x	x	x	2/wk	8
Chloride (a)	-	-	-	2/wk	8
TDS	-	-	x	1/wk	4
Conductivity	-	-	x	2/wk	8
Oil and grease	x	-	x	2/wk	8
Total phenols	x	x	x	1/wk	4
Ammonia-N	x	x	x	1/wk	4
TKN	-	-	x	1/wk	4
Ortho-P	-	-	x	1/wk	4
pH	x	x	x	2/wk	8
Cyanide	-	x	-	1/wk	4
Sulfide	x	-	x	1/wk	4
Chromium	x	x	-	1/wk	4

EGL - parameter limited by EPA Effluent Guidelines and Limitations for petroleum refining, 40 CFR 419

NPDES - required for NPDES permit application

(a) - To determine if COD or TOC should be used as effluent parameter; petroleum refining guidelines allow TOC in lieu of COD when chlorides are greater than 1,000 mg/L.

EXAMPLE - Example of Analytical Schedule for Ground Water Remediation

Analyte	Remediation Cleanup Standard (mg/L)	Minimum Analytical Level (mg/L)
Chromium	0.1	0.1
Lead	0.015	0.015
Mercury	0.002	0.002
Nitrate	10	10
Nitrite*	1	1
Benzene	0.005	0.005
1,2-Dichloroethane	0.005	0.005
1,1-Dichloroethene	0.007	0.005
Ethylbenzene	0.7	0.25
1,1,2,2-Tetrachloroethane	0.0143	0.01
Tetrachloroethene	0.005	0.005
Toluene	1	0.025
Trichloroethylene	0.005	0.005
Vinyl chloride	0.002	0.002
Xylenes	10	0.025

*For nitrite analyses alone (not combined as nitrate plus nitrite), no preservation chemicals (acid) can be used and maximum holding time is 48 hours.

Chapter 3

Selecting a Laboratory

Selection of a qualified laboratory for environmental analyses is very important for obtaining good, reliable data for waste stream characterization and regulatory compliance. The basic principles of selecting a laboratory for wastewater analyses are the same whether the laboratory is an in-house facility (either at the plant site or a corporate laboratory) or a commercial laboratory.

The person or persons responsible for selecting the laboratory to perform analyses for compliance monitoring or permit applications must bear in mind that the permittee ultimately has responsibility for the quality of the data. Therefore, the permittee must have confidence in the laboratory's knowledge and its ability to produce reliable, valid data. The following sections discuss several factors that may be considered when selecting a laboratory for analyzing environmental samples.



See the checklist
in Part IV,
**Selecting a
Laboratory.**

Part IV contains a Checklist, **Selecting a Laboratory**, which covers topics such as required analyses, staffing, support services, recordkeeping, reporting, reputation, size, and costs.

Required Analyses

The first step in selecting a laboratory is to identify what data are needed. Data may be needed for NPDES compliance, NPDES permitting, ground water clean up, wastewater characterization, or some other activity. If the number of samples or analytes is large, it is helpful to prepare an analytical schedule or list showing each analyte and its sampling and analytical requirements (see Chapter 2, **Developing an Analytical Schedule**). The schedule should include whatever information is critical to ensuring that the analytical data will meet regulatory and project requirements. Such information may include sampling frequency, sample holding times (particularly for analytes with very short holding times), detection/quantification limits, minimum number of samples, and reason for sampling (which regulatory or project requirement). An analytical schedule can be sent to the laboratory to ensure that the laboratory understands the analytical requirements. When the laboratory report is received, the schedule also is useful for checking that the required analyses were done.



See the checklist in
Part IV, **Developing
an Analytical
Schedule.**

In-House or Commercial Laboratory

The next step is to determine if some or all of the analyses will be performed by an in-house laboratory. Many facilities will perform relatively simple wet chemistry tests (for example, TSS and COD) for routine monitoring with an in-house laboratory and send more time-consuming tests (for example, BOD, ammonia) to a commercial laboratory. Other facilities send all analytical work to a commercial laboratory that routinely performs these types of tests for many clients. Obviously, there are many ways of delegating laboratory analyses. One should select laboratories based on such factors as laboratory capabilities, availability of personnel, project timing, and cost structure.

Capabilities

The laboratory must have the capabilities to conduct the required analyses and related services. The client can evaluate these capabilities initially by reviewing the laboratory's promotional materials and qualifications (for commercial laboratories) and asking for opinions and recommendations from colleagues and other business contacts. It is a good idea to visit the laboratory. The visit can be announced or unannounced, brief or very detailed as in a formal performance audit (see later discussion in **Site Visit**). All laboratory analyses are important and should be performed well and correctly; however, the more critical the analyses, the more one should take care in selecting a laboratory and evaluating its capabilities and ongoing performance.

Whether or not one makes an onsite visit or audit, there are many aspects of a laboratory operation that can be evaluated, either when initially selecting a laboratory or when performing an evaluation as part of routine performance checks. These are discussed in the following sections.

Staffing

The laboratory should have trained personnel who are competent to perform the analyses. The education and experience of the staff should be reviewed to assure that they are qualified to conduct the analyses. There should be sufficient analysts and support personnel to handle the workload and to assure that illness or vacations do not interfere with performing analyses in a timely manner and most importantly, within maximum holding times. If the laboratory conducts analyses requiring sophisticated analytical equipment with high sensitivity (for example, GC and HPLC methods, graphite furnace atomic absorption spectrometry, inductively coupled plasma atomic emission

spectrometry), the laboratory should have trained chemists that specialize in the use of these instruments.

Equipment

The laboratory should have all of the necessary equipment to conduct the analyses. Equipment should be clean, well maintained, and situated in a working area that is organized and uncluttered. The laboratory should perform regular, scheduled maintenance and calibration of the equipment and keep records of these activities. It is essential that for instrumental analyses, the laboratory have either spare instruments, replacement parts for all high-maintenance items, or an arrangement with a supplier for rapid replacement of a malfunctioning item.

Subcontracting of Analyses

The commercial laboratory should be asked if it will subcontract any of the analyses—routine or special analyses—to other laboratories. Subcontracting can be a fairly routine practice of some laboratories. If the commercial laboratory has to subcontract for certain routine analyses, this extra step in the chain-of-custody for the samples and results should be considered carefully by the client. If a laboratory is proposing to subcontract specific analyses on a routine basis, the client should provide the same review of the subcontractor laboratory as it does of the prime contract laboratory. Having routine analytical work performed at a laboratory over which the client has no direct contractual control is a potentially risky practice. Subcontracting is not a concern, however, if the subcontract arrangement is directly with the client's laboratory.

It is not uncommon for infrequent and unusually complicated analytical tests (for example, analyses for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans) to be subcontracted. There are relatively few laboratories that perform such analytical work on a routine basis and it is best to use an experienced laboratory for this type of work. Therefore, this type of subcontracting should be acceptable. In fact, it is often convenient to have the prime contract laboratory make the arrangements for the specialized analyses with the subcontractor.

It is most important that the client make clear to the laboratory that the client should be notified before any analyses are performed under subcontract. The client should have the opportunity to approve in advance any subcontract

laboratory, as well as any work that laboratory performs for the client. This should be specified in the contract with the prime contract laboratory.

Support Services

Besides the actual analyses performed by a laboratory, there are other services performed by the laboratory, either directly for the client or as part of the general operation of the laboratory. Such support services include providing sample containers and preservative chemicals, sampling personnel, recordkeeping and reporting, and sample management. These activities are discussed in the following sections.

Sample Containers and Preservatives

Included in the cost of analysis, laboratories should provide the following items and services:

- Precleaned sample bottles appropriate for each type of analysis, either already filled with the necessary preservative or with the preservative provided with instructions for its addition.
- Chain of custody forms.
- Ice chests that can be used to store the samples for shipment from the sampling site to the laboratory. The laboratory may also include a thermometer to document the temperature during shipping.
- Delivery and pickup services, unless travel distance requires the samples to be sent by a commercial carrier.

Sampling Personnel

Many laboratories can provide personnel to collect the samples at the field site. The client may request this service because of the laboratory's expertise, timing, or cost. This is a relatively common practice for commercial laboratories performing whole effluent toxicity (WET) testing on wastewater effluents. Because of the amounts of sample required for the WET tests (in addition to the routine chemical tests), the laboratory will set up its own composite samplers. Usually, this is more convenient for the client than having to purchase and operate the sampling equipment, especially because WET testing usually is relatively infrequent (monthly or quarterly). Other