American Petroleum Institute

STEP
Strategies for Today's Environmental Partnership

LABORATORY ANALYSIS OF PETROLEUM INDUSTRY WASTEWATERS

ARRANGING FOR ANALYSIS AND UNDERSTANDING LABORATORY REPORTS

REGULATORY AND SCIENTIFIC AFFAIRS
PUBLICATION NUMBER 4694
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American Petroleum Institute

STEP Strategies for Today's Environmental Partnership

American Petroleum Institute Environmental, Health, and Safety Mission and Guiding Principles

MISSION

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

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- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emission and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

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
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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.

Contents

Introduction

Part I Essential Information

Table

Table

Figure

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 specificied 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 (µg/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.

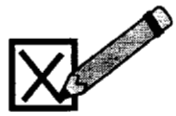
DQOs can be established for various tasks within a project, such as sample collection, in addition to sample analysis. However, because this manual focuses on analyses of wastewater, the discussion of DQOs here is limited to analytical issues.

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:

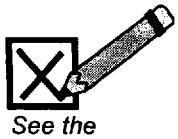
1) Regulatory specifications for certain methods,
2) Detection and quantification limits,
3) Matrix interferences, and
4) Quality assurance/quality control (QA/QC) requirements.

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 Method.**

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

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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.

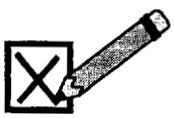
It cannot be assumed that even the most experienced laboratories will automatically report data at the required detection or quantification limits. There are many examples of NPDES permit applications that have been returned to applicants as incomplete because the detection or quantification limits did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

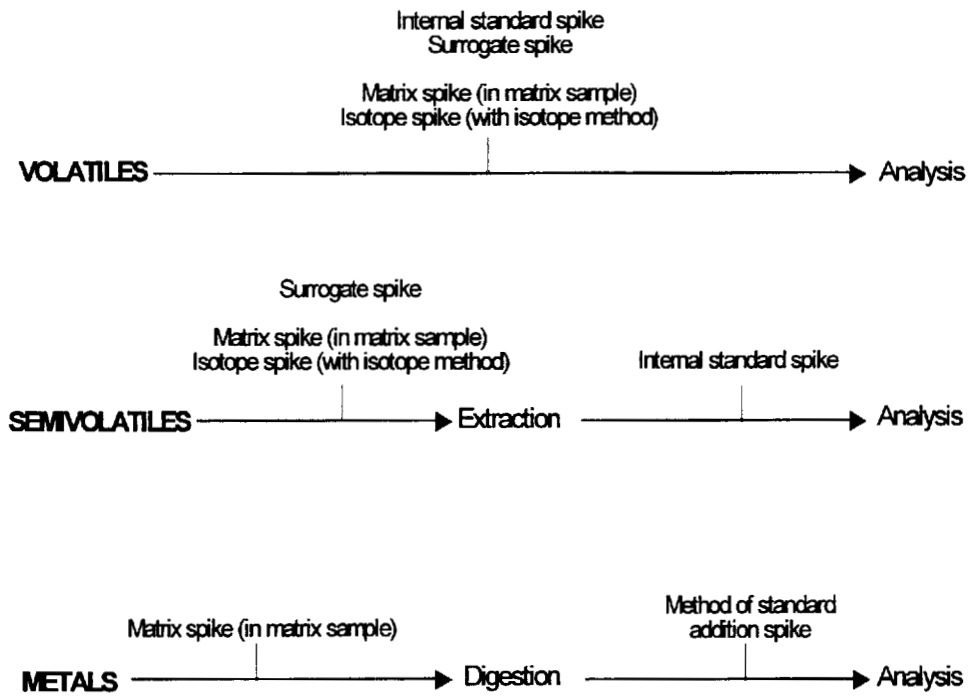


Figure 2-1. Different Types of Sample Spikes

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.

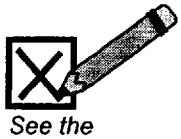
Outlining QA/QC Requirements with the Laboratory

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.

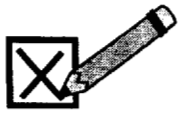
2) Identify the total number of samples and sampling frequency required for each analyte.

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."



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

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.

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

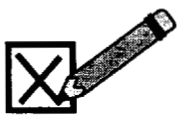
*For nitrite analyses alone (not combined as nitrate plus nitrite), no preservation chemicals (acid) can be used and maximum holding time is 48 hours.

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.

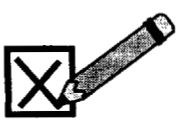


See the checklist in Part IV, **Selecting a Laboratory.**

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.

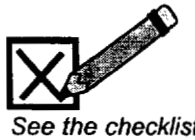
Sampling Personnel

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

types of specialized sampling services may also be provided by a laboratory, such as clean sampling for trace metals.

Recordkeeping and Reporting

Recordkeeping and reporting are essential elements of a laboratory's operation. Laboratory reports should be examined for clarity and to assure that all of the requested analyses and supporting data are included (see Chapter 4, **Reviewing Laboratory Reports**).



See the checklist in Part IV, **Elements of a Good Laboratory Recordkeeping System.**

Many laboratories provide two levels of reporting. The first level is the summary of the analytical results. The second reporting level includes the detail such as the GC/MS chromatograms and spectrograms, calibration curves, and the actual laboratory records for the QA/QC analyses. Typically, the standard laboratory report includes only the basic or level-one data because most clients do not wish or need to see the detailed data for every sample. If requested, most laboratories are able and willing to provide more detailed reports.

The quality of the laboratory's reports can be used as one measure to judge the laboratory's attention to detail and quality. While it is possible to be misled by a well organized and neat report, poorly organized or incomplete reports suggest problems with the laboratory's operation.

The quality of a laboratory's recordkeeping is a very strong indication of its attention to quality in analysis. The best way to determine the adequacy of the laboratory's recordkeeping is by a site visit (see **Site Visit** in this chapter). Table 3-1 lists examples of what would be considered part of a good recordkeeping system. The items in Table 3-1 have also been put together in as a Checklist, **Elements of a Good Laboratory Recordkeeping System**, located in Part IV.

The form of the analytical data—paper report, computer file, or online—may be important to a particular project. For example, if a large amount of data has to be summarized from the laboratory reports, it may be more convenient to receive the data in computer files; it also would avoid transcription errors that can occur when data are re-entered from paper forms.

Table 3-1. Example Elements of a Good Laboratory Recordkeeping System

Sample Management

- Chain of custody documentation of sample collection, transport, and delivery to laboratory.
- Tracking system for initial sample receipt, sample delivery to analysts, sample holding times, and sample storage after analysis.

Analytical Worksheets and Data Records

- Handwritten records by individual analysts kept in bound notebook.
- Handwritten records made in ink, data corrected by crossing out and initialing instead of erasure.
- All necessary analytical information is completed.
- Samples clearly identified and traceable to chain of custody records.
- Times are recorded as necessary at each analytical step.
- Each analyst signs or initials his or her analyses.
- Results recorded in central reporting system in a timely manner.

Files

- Well organized system for maintaining and archiving worksheets, notebooks, chain of custody forms, equipment maintenance records, and other items of laboratory operation.
- Well organized computer data system, including routine data backups.
- System for archiving files and identifying files no longer needed so that they can be destroyed.

Archiving Samples

Most laboratories will archive (store in a traceable system) samples for a period of time after analysis is completed. The client should determine how the laboratory archives samples in case an archived sample is needed for reanalysis or additional testing. In general, it helps to hold samples until the end of the holding time; however, this is not always practical or cost effective.

Reputation and Size

The commercial environmental laboratory business is highly competitive. There are a few large, national companies that offer analytical services

through a number of regional laboratories. There are smaller, regional commercial laboratories, and there are a multitude of small commercial laboratories in some markets. Size and range of services offered are not necessarily indicators of good services and high quality, although in general one can expect that the large national laboratory firms will provide high quality, dependable services. Many small laboratories also are very good, and some that specialize in certain analytical techniques (clean metals analyses, method development) can be excellent. Small commercial laboratories that are local often can be a good choice if they provide services such as delivery of sample bottles and sample pick up, services that a national or regional laboratory may not be able to provide because of its distance from a site.

The client should examine carefully the qualifications and reputations of all candidate laboratories. The laboratories should provide a list of current references. The client should contact at least two or three of a laboratory's references to verify the type and quality of work and to find out if there were any particular problems. An important question to ask a reference is the promptness with which the laboratory issues its reports. Reports that are issued long after completion of the tests may indicate inadequate staffing/resources.

The length of time a laboratory has been operating also indicates stability and quality of work. A laboratory that has been operating for a number of years usually is one that has a stable business with a satisfied clientele. As with any new business that has not been operating long enough to acquire a large client base to give as references, extra care should be taken when evaluating a new laboratory operation.

If there is any question about the fiscal health of a laboratory, the client should review, if possible, general financial statements for the laboratory and whether it has any financial ties to other companies that are having financial problems.

Costs

For many facilities, annual analytical costs for NPDES and other environmental monitoring can be significant. Therefore, cost may be a consideration when selecting a laboratory; however, cost should be considered only after it has been determined that all candidate laboratories are qualified to perform the required testing. No laboratory that has potential deficiencies in its operations that could result in invalid results, regardless of how good its cost structure is, should be used.

If a facility has a large number of samples that have to be analyzed on a routine basis, it should try to negotiate special rate structures with competing laboratories to obtain the best price. Most laboratories are willing to negotiate their rates when there will be a guaranteed backlog, which a large volume of work provides. One way to determine a baseline for costs is to obtain the standard cost schedules from a number of laboratories, including large national and regional laboratories. Although one may negotiate lower rates for a large number of samples or routine samples such as ground water monitoring, the standard rate schedules are a good starting point for evaluating costs.

Finally, a word of caution. There is such a thing as costs being "too good to be true." If one laboratory's costs are much, much lower than other laboratories, it may indicate that the laboratory is taking short cuts, which may produce poor or invalid data, or that it is trying to get work by "low balling" its bid. Laboratory work is no different than any other kind of service — "you get what you pay for." Therefore, a client should balance the costs against other project needs, in particular, obtaining good quality data.

Site Visit

A site visit to a laboratory is very valuable for judging a laboratory's capabilities and work product. Whenever practical, a site visit should be conducted before a laboratory is selected, and then routinely when the contract is renewed. Laboratories do not mind these site visits by their clients, and most welcome them. Many large corporations now have a policy that either corporate or facility representatives visit all commercial laboratories with which they will contract. In many cases the representatives will include both a chemist familiar with environmental analyses and a regulatory compliance person. This is an excellent practice because it shows due diligence in the event a question is raised about the validity of the data.

Table 3-2 lists some items that may be included in an onsite laboratory evaluation. This list has also been made into a Checklist, **Items for Onsite Laboratory Evaluation**, located in Part IV.

Table 3-2. Example Items that may be Included in an Onsite Laboratory Evaluation

General Conditions
Cleanliness
Organization
Storage of chemicals
Condition of work surfaces and areas
Safety equipment
Staffing
Number of degreed chemists (PhD, MS, BS)
Number of non-chemistry degreed analysts
Number of supervisors and qualifications
QA/QC manager onsite
Equipment
Equipment appropriate to each type of analysis
Utility equipment such as refrigerators, ovens, balances, incubators
Cleanliness and routine maintenance
Manuals
Analytical reference manuals
Standard operating procedures
QA/QC procedures
Equipment manuals
Records
Sample chain of custody
Analytical worksheets, logbooks, or computer printouts
Equipment calibration and maintenance
Reports
Organization and clarity of standard analytical report
Contents of standard analytical report
Detail of standard analytical report
Other data that can be reported if requested
Regulatory Requirements
General knowledge of regulatory programs requirements (NPDES, etc.)
Knowledge of analytical requirements for regulatory programs

The site visit should consist of a walk-through of the laboratory facilities, interviews with selected laboratory personnel, and review of recordkeeping and reporting procedures. All aspects of the laboratory's sample management should be included as part of the review. Reviewers should ascertain both the laboratory's analytical capabilities and the laboratory staff's working knowledge of the analytical and general requirements of pertinent regulatory programs. Although not critical, knowledge of and familiarity with environmental regulations makes it easier to work with the laboratory on projects and helps ensure that the data meet regulatory requirements.

The following example highlights why site visits are important when judging a laboratory's capabilities.

See the checklist in Part IV, **Items for Onsite Laboratory Evaluation.**

EXAMPLE - Unusual Practices Discovered on Laboratory Visits

One chemical company visiting a small commercial laboratory found that the laboratory was incubating BOD samples in a closet. The manager stated that because the laboratory was temperature controlled (heated and cooled), it was unnecessary to have an incubator to maintain the required temperature for the BOD test, and that since the closet was dark, all of the requisite conditions of the test were satisfied.

During another site visit, a company discovered that the laboratory's practice for calibrating the weight balance was to use a nickel in lieu of a certified set of standard weights. The laboratory manager believed his calibration was acceptable because the same nickel was used every time.

Evaluating Laboratory Performance with Test Samples

Laboratory performance can be evaluated in a number of ways. In the most basic way, the client can review a laboratory's reports, checking for completeness and acceptable QA/QC. If a client is interested in a more objective evaluation or wants to compare several laboratories, special test samples can be sent to these laboratories. These samples can be incorporated into an audit review or a detailed performance study.

In general, it is best *not* to identify performance test samples as such or tell the laboratory about the performance test. If the client is interested in knowing how the laboratory would perform on a routine basis, the test samples should be "blind," that is, identified only as ordinary samples. Examples of the types of samples that can be used in performance evaluations are given in Table 3-3.

Table 3-3. Examples of Sample Types Used to Evaluate Laboratory Performance

Blind field duplicates
Split field samples to multiple laboratories
Certified check or reference samples
Sample sets with two or more concentration levels
Youden pairs (sample pairs with different, but similar concentrations)

Blind field duplicates are duplicate samples collected at the sample site and sent to the same laboratory, but with different sample labels. Laboratory precision, that is, the agreement between measurements, can be evaluated with blind duplicates.

Split samples collected in the field are sent to multiple laboratories to see how closely the results match and if any of the laboratories have difficulties in detecting a particular analyte or measuring at trace (low) levels. Duplicates of the split samples also can be sent to evaluate laboratory precision.

Certified reference or check samples (obtained from companies who specialize in these types of samples) can be sent to any number of laboratories to see how their results match with the certified concentration. EPA routinely uses certified samples as quality control samples in performance evaluation studies of laboratory water and wastewater analyses.

Certified or prepared samples that cover a range of concentrations can be sent to laboratories to evaluate performance at different concentration levels. Typically, the concentration range reflects expected values for one or more projects the client has in mind. For example, high-concentration samples may be used to assess performance with samples from a recent spill area, and trace-concentration samples may be used for treatment system effluent samples; or post-remediation samples with concentrations approaching cleanup standards.

Youden pairs refers to a particular statistical test developed by W.J. Youden, used for comparing performance among multiple laboratories. Youden's technique was used by EPA in developing method performance equations for the 600-series techniques for volatile and semivolatile organic analyses in Appendix A, 40 CFR 136. A Youden pair is two samples that have been designed to have different, but similar concentrations. The difference is intentional so that even if the laboratory knows it's a performance test, it cannot unconsciously bias the results by expecting the two concentrations to be the same. Analysis of the data from a Youden paired sample interlaboratory

test is relatively simple, but requires more detail than is suitable for this type of manual. Interested readers can refer to several references for these details (Youden and Steiner, 1975; Kocurek and Woodside, 1997; Taylor, 1987; Wernimont, 1985).

The following examples describe laboratory performance studies that have been conducted by some companies.

EXAMPLE - Laboratory Performance Evaluation for BTEX

As part of its ongoing laboratory audit program, a company designed a performance evaluation study for 20 laboratories, focusing on BTEX (benzene, toluene, ethylbenzene, xylenes) analysis for ground water samples. To ensure that the laboratories' routine performance was tested, the samples were not identified as performance samples, rather as ordinary ground water monitoring samples. Each laboratory received 10 samples, which were prepared as sample pairs with similar concentrations for Youden 2-sample plots and analysis. The data results from the laboratories were used to assess precision, accuracy, and detection and quantification limits.

EXAMPLE - Laboratory Performance Evaluation for Volatile Organics, Metals, and Method-Defined Analytes

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This is an example of a truly "blinded" study with respect to both samples and laboratories. A company conducted a unique laboratory performance evaluation of a group of more than 20 commercial environmental laboratories. Those contacting the laboratories posed as engineers working at a gasoline station cleanup. They were to contact the laboratory to discuss analysis of the station's contaminated ground water. Ground water samples were spiked with analytes that were either typical components of gasoline or had been found in the company's monitoring wells. Samples also were spiked with metals, some that were actually present in the ground water and several others that were not. Samples also were spiked for method-defined analytes BOD, COD, TOC, and oil and grease. Data results from the laboratories were analyzed to assess: 1) performance for volatile, metal, and general parameter analyses; 2) effects of recovery correction on volatile organics; and 3) performance for tentatively identified compounds (TICs).

Getting Help from Consultants

There are times when consultants can be helpful in selecting a laboratory, for example, when a project is large, the analyses are complicated, or when a company wishes to develop an "approved list" of laboratories for its facilities. A consultant may be needed to provide expertise in particular types of analysis, to perform an in-depth audit, or to be an objective third party (in laboratory selection). The consultant can either evaluate a particular laboratory or recommend a list of acceptable laboratories.

Depending on the client's need for laboratory services, there are a number of different types of consultants that can help in selecting a laboratory(s). Often, these consultants are with auditing or data validation firms. In order to judge whether a laboratory can provide particular services and produce acceptable work, the consultant should be familiar with environmental analyses and any special regulatory requirements that are critical to the project.

Chapter 4

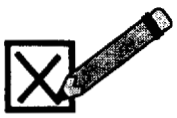
Reviewing Laboratory Reports

This chapter begins with an outline of the basic contents of an analytical laboratory report. Following this outline is a discussion on checking the basic elements of a report as soon as it is received, identifying typical problems that would require immediate response, and reviewing sample results in detail. The sample results discussion includes checking whether data look correct, understanding different method-defined parameters, and understanding and using detection/quantification limits. QA/QC is discussed next, focusing on what to do when performance criteria are not met.

Report Contents

There is no standard reporting format for environmental analyses; therefore, there is a wide variety of styles in laboratory reports. Some reports are quite thick and include detailed quality control data; other reports are slim and provide only summaries of quality control data.

Despite the differences in formats and level of quality control detail, there are elements common to essentially all laboratory reports. A list of these items is shown in Table 4-1. As the table shows, report information can be divided into four categories: client, sample, analytical, and QA/QC information. A Checklist based on Table 4-1, **Identifying Parts of a Laboratory Report**, is located in Part IV. The Checklist can be used to review the general contents of a laboratory report or to list what information is desired in a laboratory report. If a group of laboratories is being evaluated for potential work, the Checklist can also be used to compare each laboratory's level of report detail.



See the checklist in Part IV, **Identifying Parts of a Laboratory Report.**

Client information is very basic. At a minimum, it will include the name of the client. It also may include the client address, phone number, facility contact, and project title or description.

Typical sample information begins with a short description of the sample, usually taken from the sample label. The report will state the type of sample matrix, something general such as "water" or "aqueous" or something a little more specific like "ground water" or "wastewater effluent." In addition to the sample code given by the client on the sample label, the report will show the tracking code, which the laboratory assigned to the sample. The date of sampling, and sometimes the time as well, will be shown along with the date of receipt in the laboratory.

Information in the laboratory report regarding the analyses themselves will include the analyte name and its analytical result with the units of measure. Analytical method numbers or codes will be given, sometimes including a short identifying name such as "ICP" for metals. Dates of special sample preparation will be given such as extraction dates for semivolatile analyses. Normally on the same line as the analytical result will be the analytical limit, which is described and defined differently among laboratories. The limit may be called a detection limit, a reporting limit, or something similar. There may be notations on individual analytical results, describing some particular detail, problem, or special condition. Such notations usually appear more often with analyses of volatile and semivolatile compounds. Also included with the analytical information is the identity of the analyst, by initials or name. An example of analytical information from a laboratory report is shown in Figure 4-1.

Report information on QA/QC will include the chain of custody form, which traces sample handling from collection to receipt at the laboratory. Standard QA/QC information will include data on recovery/accuracy, precision, and method blanks. Recovery data will be presented for spiked standards or control samples, matrix spikes, and "surrogates" in volatile and semivolatile analyses. Precision data will be presented for duplicates/replicates on laboratory control and/or client samples. The laboratory report may include allowable ranges for recovery and precision for each analyte and notations on results that fall outside allowable ranges. QA/QC data will also include results for method blanks. Examples of recovery, precision, and method blank data from a laboratory report are shown in Figure 4-2 (detailed data) and Figure 4-3 (less detail). The laboratory report will be reviewed and approved by laboratory personnel responsible for data quality and will show their identity by initials, name, and/or signature.

Of course, the laboratory report may include information in addition to those items listed in Table 4-1, depending on the samples received, analyses requested, and the laboratory's QA/QC and reporting procedures. Such additional information may include results for trip and field blanks, sample dilution factors, quality control (QC) sample control lot numbers, and so on.

Table 4-1. Items Typically Included in Analytical Laboratory Report

Client Identification

Sample Information
- Sample description
- Sample matrix type
- Sample identification code given by client
- Sample identification code given by laboratory
- Sample collection date and time
- Date of receipt in laboratory

Analyses
- Method reference codes and descriptions
- Dates of sample preparation steps
- Date of analysis
- Analyte or parameter name
- Analytical result
- Analytical units
- Detection, quantification, or reporting limit
- Analytical notes and explanations with key codes
- Identity of analyst

Quality Control and Quality Assurance
- Chain of custody form
- Recovery/accuracy results and allowable ranges
  - Spiked standards or control samples
  - Matrix spikes
  - Surrogates in volatile and semivolatile analyses
- Precision results and allowable ranges
  - Laboratory control sample duplicates/replicates
  - Client sample duplicates/replicates
- Indication of results outside allowable limits
- Method blanks
- Identification and signature of reviewers

Date: 06/06/98	Client Name	Report: AN0777
Time: 13:09:22	Analytical Results/Chronology	Page: 1
	Client Sample ID:	GW-9
	Job Number & Lab Sample ID:	A98-040 A804001
	Sample Date:	06/04/98
	TCLP Date/Holding Time Met:	N/A
	Extraction Date/Holding Time Met:	N/A
	Analysis Date/Holding Time Met:	06/05/98 14:45 YES
	Dilution Factor:	1.0

Analyte	Reporting Limit	Result	
Method 8260 - Volatile Organics (mg/L)			
Benzene	0.005	0.03	
Ethylbenzene	0.2	0.06	J
Toluene	0.02	0.10	
Total xylenes	0.02	0.002	J
Tetrachloroethene	0.005	0.005	U
Internal Standards			
Chlorobenzene-d5	50-200%	91%	
1,4-Difluorobenzene	50-200%	92%	
1,4-Dichlorobenzene-d4	50-200%	87%	
Surrogates			
Toluene-d8	88-110%	104%	
p-Bromofluorobenzene	87-115%	96%	
1,2-Dichloroethane-d4	75-113%	91%	

J Concentration is estimated because result is less than reporting limit.
U Compound was analyzed for but not detected.

Figure 4-1. Example of Analytical Information in Laboratory Report

Laboratory X

Semivolatile Organics by GC/MS

Quality Control Report

Laboratory Sample No.	QC Matrix	QC Category	QC Lot Number (DCS)	QC Run Number (SCS/Blank)
0894-01-SA	Aqueous	EPA 625	06 JUN 98-04A	06 JUN 98-04A

Duplicate Control Sample Report

Analyte	Concentration (µg/L) Spiked	Measured DCS1	DCS2	AVG	Accuracy Average (%) DCS	Limits	Precision (RPD) DCS	Limit
Phenol	200	55.8	65.4	60.6	30	17-55	16	29.0
Pyrene	100	82.2	79.5	80.8	81	57-150	3.3	22.0

Method Blank Report

Analyte	Result	Units	Reporting Limit
Benzo(a)pyrene	ND	µg/L	10
Chrysene	ND	µg/L	10

ND - Not detected
RPD - Relative percent difference
SCS - Single control sample
DCS - Duplicate control sample

Figure 4-2. Example Laboratory Report for QA/QC Data (Detailed Data)

Laboratory Y

Report of Analysis Parameter	Result	Units	RQL	Quality Assurance Data Blank	RPD	Recovery	LCS
CBOD5	360	mg/L	1	<1			
COD	617	mg/L	10	<10	3%	98%	86%
Conductance	8200	µS/cm	1	<1	0%	NA	NA
Oil and grease	31	mg/L	1	<1	2%	NA	NA
pH	8.4	SU	NA	NA	0%	NA	NA
TOC	110	mg/L	1	<1	15%	149%	107%
TSS	43	mg/L	1	<1	3%	NA	NA
NH3-N	56	mg/L	1	<0.01	6%	103%	102%
Chloride	2030	mg/L	50	<0.5	1%	97%	94%

LCS - Laboratory control sample
NA - Not applicable
RPD - Relative percent difference
RQL - Reporting Quantitation Limit
SU - Standard units

Figure 4-3. Example Laboratory Report for QA/QC Data (Less Detail)

Reviewing Reports

This section gives guidance on how to review a laboratory report. The guidance covers checking the basic elements of a laboratory analytical report, something that should be done as soon as the report is received. Guidance is given for problems indicated by the report that would require an immediate response, such as when a permit limit is exceeded or when a sample appears to be missing. Guidance is given on how to check whether data look correct, and understanding detection/quantification limits, QA/QC, and method-defined parameters.

Checking the Basics

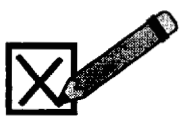
When a laboratory report is initially received, it is a good idea to quickly review its contents in case there are any problems requiring immediate action or that would interfere with project needs or deadlines. Table 4-2 contains sample questions that can be used to perform an initial review of the report. These questions have also been made into a Checklist, **Initial Review of Laboratory Report**, located in Part IV.

The initial report review may indicate some issues or problems that would require immediate action. Some of the more common problems requiring a quick response are discussed in the next section. Following that section is guidance on how to review sample results and QA/QC data.

Table 4-2. Sample Questions to Perform Initial Review of Laboratory Report

Sample Information

- Do all sample descriptions and identification codes match information on the chain of custody form?
- Do all sample dates and times match information on the chain of custody form?
- Were all samples received within required/recommended holding times?
- Were all samples analyzed as requested?



See the checklist in Part IV, **Initial Review of Laboratory Report.**

Analyses

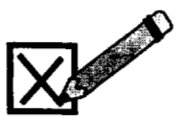
- Are all sample preparation dates within required/recommended holding times?
- Are all sample analysis dates within required/recommended holding times?

- Were all samples analyzed with appropriate/approved methods?
- Do all analytical methods match those that were specified?
- Are all requested analytes reported?
- Are all analyte forms clear (total/dissolved, wet/dry weight, as "N," as "P," etc)?
- Are all measurement units clear and appropriate for the sample type (mg/L, mg/kg, etc)?
- Do all detection/analytical limits meet specifications?

Quality Control and Quality Assurance

- Are all chain of custody forms included, completed properly, and signed by laboratory personnel?
- Are QA/QC data included?
- Do QA/QC data meet performance criteria?
- If there were QA/QC problems, were they resolved?

Problems Requiring Immediate Response



See the checklist in Part IV, **Problems Requiring Immediate Response.**

There may be problems with analytical results that require immediate response by the laboratory client. Quick responses are necessary when the data are to be used in a regulatory report with a reporting deadline, such as the NPDES DMR or a permit application. Responding quickly to an analytical problem is particularly important in cases where the laboratory still has enough sample for reanalysis within sample holding limits.

In some cases, the immediate response may be as simple as asking the laboratory to review its records and correct errors in the report. In some cases, the laboratory may be asked to reanalyze samples if sufficient sample volume is available and sample holding periods have not been exceeded. In other cases, the immediate response will be to resample and repeat the analysis.

This section discusses some typical problems with analytical reports that usually require quick action on the part of the client. Suggestions on ways to deal with these problems also are included. As an introduction to this problem-solving section, the example below provides some actual statements from laboratory reports summarizing problems encountered with sample analyses. Unfortunately, not all problems can be resolved immediately; sometimes additional sampling is required or more extensive laboratory work is needed.

A Checklist, **Problems Requiring Immediate Response**, is located in Part IV. The Checklist lists typical problems and includes suggestions on how to handle them.

EXAMPLE - Examples of Problem Descriptions in Laboratory Reports

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Problem 1

The holding time was exceeded for volatile organics for Sample X due to laboratory error. The sample was originally analyzed using the low level test, but due to elevated levels of certain target compounds the sample was reanalyzed using the medium level test 2 days after the 14-day holding time expired.

Problem 2

Sample X was diluted due to concentrations of target compounds present above the linear calibration range of the instrument. The reporting limits were adjusted relative to the analytical dilution performed.

Problem 3

The 7-day holding time for Method 625 extraction for Sample X was exceeded due to analyst error. The holding time expired on 2/28/97 and the sample was extracted on 3/18/97. In the laboratory tracking system, the code for the extraction was taken to a completed status before the extraction was actually done.

Problem 4

The RPDs for several compounds were outside control limits for the duplicate control sample (DCS) associated with QC Lot 18 FEB 97-1C for semivolatile organics. All spike compounds were within control limits for the matrix spike and spike duplicate associated with this DCS indicating the problem was probably isolated to the DCS.

Problem 5

2-Fluorobiphenyl and p-terphenyl-d14 surrogate recoveries for Sample X were found to be below control limits due to sample matrix interference. The sample was re-extracted and the recoveries were confirmed.

Problem 6

The method blanks associated with Sample X were found to have 25 µg/L and 16 µg/L of acetone present.

Problem 7

Sample X was diluted for selenium, thallium, and lead due to matrix interferences. Sample Y was diluted for arsenic to bring the arsenic concentration within the linear calibration range of the instrument. The reporting limits for these metals were adjusted accordingly.

Permit Limit Exceeded

Typically, the first step in reviewing analytical reports for permit compliance purposes is to determine if any results exceed a permit limit. When a limit is exceeded, the immediate response should be to review all of the analytical information supplied in the report to assure that the sample was correctly collected, preserved, and analyzed. If any potential problems are identified with the sampling or analysis procedures, the laboratory should be contacted to determine if the sample is valid.

Another immediate decision that should be made is whether or not to take another sample and redo the analysis. Resampling may be a wise choice even when the original analysis is valid. Even if the result is valid, resampling may be needed to demonstrate that the permit exceedance was incidental and does not indicate a persistent noncompliant situation. Penalties for exceeding permit limits are directly related to the number of days of noncompliance. Thus, additional samples will be useful in an enforcement context because they will limit the size of potential penalties if a single, random exceedance of a permit limit occurs. Resampling is particularly important when monitoring is infrequent, for example, only once a month or once a week.

Wrong Analytical Method

All analyses for NPDES permits must be performed using a method that is approved in the NPDES regulations (Tables IA, IB, IC, ID, and IE, 40 CFR 136), unless the permit specifies that an alternate analytical method must be used. A very common problem is that in lieu of a 40 CFR 136 method, a laboratory will use and report results from one of the RCRA analytical methods published in SW-846. Although many of the SW-846 methods are virtually identical to their NPDES counterparts, they may not be interchanged for NPDES reporting.

The problem can often be corrected by calling the laboratory and having it verify that the method used for the analysis was the appropriate 40 CFR 136 method. The report can be reissued with the correct method identification. If the correct method was not used, then reanalysis of an archived sample (if the 40 CFR 136 holding time was not exceeded) is the best approach. If an archived sample cannot be used, another sample should be collected and analyzed with the appropriate method.

Holding Time Exceeded

The allowable holding times for NPDES analyses are specified in Table II of 40 CFR 136. Holding times are given for each analyte for which there is an

approved 40 CFR 136 method. Analyses of samples that exceed these holding times are in most cases considered invalid and must be repeated.

Examples of holding times from 40 CFR 136 are given in Table 4-3, which also includes sample container and preservation requirements. Problems with containers and preservation methods are discussed in the next section.

A very common problem with holding times is meeting the "analyze immediately" requirement for pH samples. The requirement is defined in 40 CFR 136 as being within 15 minutes or less of sample collection. To meet this requirement, the pH usually must be measured in the field or immediately after bringing the sample to an onsite laboratory. It is important to know that pH measurements performed by a distant, offsite laboratory do not meet 40 CFR 136 requirements and should not be used for NPDES compliance purposes.

Improper Preservative or Container

Table II of 40 CFR 136 lists required sample containers and preservation methods for analytes with approved 40 CFR 136 methods (see Table 4-3 for examples). If the sample container is improper, or the sample was improperly preserved, then the analysis of the sample is generally considered invalid for regulatory purposes. If the result is valid, another sample must be collected using the correct container and preservation methods.

An example of improper preservation would be when a sample is kept at too high a temperature. As Table 4-3 shows, many analytical tests require that the sample be kept at a 4°C at all times until the sample is used up or discarded. Some deviation from 4°C normally is considered acceptable, but usually is limited to an increase of one to two degrees. During warm or hot weather, temperature is a particular concern right after sample collection and during transport to the laboratory, when conditions cannot be controlled as well as in a laboratory.

Another example of improper preservation would be the use of hydrochloric acid (HCl) instead of sulfuric acid (H_2SO_4) for samples to be analyzed for COD. Because HCl causes positive interferences in the COD test, it cannot be used as a preservative for this analyte. Using HCl incorrectly with a COD sample may happen because preservation requirements can be confused with those for a related analyte, TOC. Allowable preservatives for TOC include not only H_2SO_4, but also HCl and phosphoric acid (H_3PO_4). Only H_2SO_4 is allowed with COD samples.

An example of an improper sample container would be use of plastic for oil and grease samples. Only glass containers are allowed because part of the oil

and grease can stick to the plastic surface when the sample is poured out and thus, will not show up in the analysis. The sample results would be biased low.

Table 4-3. Required Containers, Preservation Techniques, and Holding Times from 40 CFR 136 for Selected Analytes

BOD	P, G	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6 gm ascorbic acid[b]	14 days[e]
COD	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Oil and grease	G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days
Organic carbon	P, G	Cool, 4°C, HCl or H_2SO_4 or H_3PO_4 to pH<2	28 days
pH	P, G	None required	Analyze immediately[a]
Sulfide	P, G	Cool, 4°C, add zinc acetate plus NaOH to pH>9	7 days
TSS	P, G	Cool, 4°C	7 days
Purgeable halocarbons	G, Teflon™-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[b]	14 days
Purgeable aromatic hydrocarbons	G, Teflon™-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$,[b] HCl to pH 2[c]	14 days
Polynuclear aromatic hydrocarbons[d]	G, Teflon™-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$,[b] store in dark	7 days until extraction; 40 days after extraction

P-plastic
G-glass

[a] Usually means within 15 minutes or less of sample collection.
[b] Should be used only in the presence of residual chlorine.
[c] Sample receiving no pH adjustment must be analyzed within seven days of sampling.
[d] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding time should be observed for optimum safeguard of sample integrity. See 40 CFR 136 for additional detail.
[e] Maximum holding time is 24 hours when sulfide is present. See 40 CFR 136 for additional detail.

Wrong Reporting Limits

Many of the 40 CFR 136 analytical methods have specified reporting levels, typically method detection limits or minimum levels, that analysts are expected to achieve on most wastewater matrices. The reporting levels specified in the 40 CFR 136 analytical methods are usually not regulatory reporting levels. However, it is becoming more common for the NPDES permit, or the NPDES permit application form, to specify analytical reporting limits. Reporting limits are most common for pollutants that are regulated by a state's water quality standards, but sometimes permits will specify reporting limits for pollutants regulated by technology-based standards.

If the reporting limit in the analytical report is greater than the reporting limit required in the permit, the laboratory should be contacted immediately. For consistency, laboratories typically use their own standardized reporting limits, which may be higher than what they are actually able to achieve. The laboratory should be asked if the analytical data can support reporting a lower limit. If so, the laboratory simply can reissue the report with the new limit. If the laboratory cannot state that the analysis met a lower limit, the only other options would be to reanalyze an archived sample or collect another sample, and ensuring that the required reporting limit is achieved.

Missing Sample

Occasionally, a sample is altered during transport to the laboratory and cannot be analyzed, such as when the sample container is broken or the preservation temperature has not been maintained. Most laboratories will immediately contact the client so that a new sample can be collected. Unfortunately, sometimes a laboratory will not call and the client does not learn of the damaged sample until the report is sent.

If a sample analysis is missing from a laboratory report, the client should immediately call the laboratory. If the sample container was broken, the preservation requirements were not met, or the sample was otherwise rendered unanalyzable or invalid, then another sample should be collected. If the sample was analyzed, but the laboratory simply forgot to include the results in the report, the report can be corrected and reissued. If the laboratory neglected to analyze the sample, but it still has it in storage and the holding time has not been exceeded, the laboratory needs to complete the analysis and send a report.

Missing Analyte

Laboratory reports should be checked as soon as they are received to make sure that all analytes that were requested are included. Missing analytes can occur for several reasons. The chain of custody form, which lists the requested analyses, may be unclear or incomplete. The laboratory may have forgotten to perform the analysis. Even if the laboratory performed the analysis, the laboratory may have forgotten to mark the analyte or the analytical result because the analyte is unusual and not on standardized analyte lists. Some state wastewater permit applications, for example, require analyses of certain organic chemicals that are regulated by water quality standards but not included in the standard analyte lists for the methods.

NOTE
If the missing analyte is an organic chemical, it may be in the report under an alternate name.

If an analyte is missing from the report, the laboratory should be called to see if the analysis was done. If so, the laboratory may need to simply re-examine the original gas chromatographs, mass spectrographs, and other instrument data to calculate the result. If the analysis was not done, the only options are to reanalyze the original sample if the holding time has not been exceeded, or to collect a new sample.

If the missing analyte is an organic chemical, it may be in the report under an alternate name. Many organic chemicals may be reported under either their common name or International Union of Pure and Applied Chemistry (IUPAC) name. Typical examples are shown in Table 4-4. It is helpful to keep a list of alternate chemical names to check before calling the laboratory with questions about missing analytes.

Table 4-4. Examples of Alternate Names for Some Common Wastewater Analytes

IUPAC Name	Alternate Name
Bromodichloromethane, Dibromochloromethane, Tribromomethane, and Trichloromethane	Trihalomethanes
2-Butanone	Methyl ethyl ketone, MEK
Chloroethene	Vinyl chloride
Dichloromethane	Methylene chloride
1,2-Dimethylbenzene	o-Xylene
1,3-Dimethylbenzene	m-Xylene
1,4-Dimethylbenzene	p-Xylene
2-Methylphenol	o-Cresol

3-Methylphenol	m-Cresol
4-Methylphenol	p-Cresol
4-Methyl-2-pentanone	Methyl isobutyl ketone (MIBK)
2-Propanone	Acetone
Tetrachlorethene	Perchloroethylene, PERC, PCE
Tribromomethane	Bromoform
Trichloroethene	Trichloroethylene, TCE
Trichloromethane	Chloroform

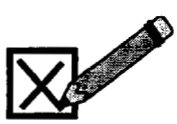
Sample Results

Reliable analytical results are the ultimate objective of sampling and analysis. Because the majority of wastewater data are used for regulatory compliance or permit applications, it is essential that the results be of high quality. Thus, it is important that the person(s) responsible for reviewing the data and preparing regulatory reports or documents understand thoroughly how to review and evaluate the quality of the sample results. This section describes important characteristics of sample results and provides guidance on how to evaluate these results.

Are the Results Reasonable?

The first step in reviewing sample results should address whether they are reasonable in light of: (1) knowledge of the characteristics of the sampled stream; (2) the past performance of any wastewater treatment units; and (3) other characteristics or analytes measured in the sample. Sample results that should alert the reviewer to questionable and potentially invalid results include:

- The presence of an analyte that is not used at the facility and has never been found in previous samples. For example, results showing methylene chloride in an effluent at a plant that does not manufacture, process, or use chlorinated chemicals and has never shown methylene chloride in previously collected samples would be suspect.
- An implausible or unlikely relationship between two analytes that measure the same or related chemical properties, when such a relationship has not been seen previously (see **Method-Defined Analytes** in this chapter). An example would be a sample with a TOC concentration that is equal to or greater than its COD. TOC and COD both measure organic content; however, for most wastewaters the COD always will be greater than the TOC. COD expresses organic



See the checklist in Part IV, **Checking if Results are Reasonable.**

content as oxygen demand whereas TOC expresses organic content as carbon. Because two oxygen atoms are added to one carbon atom (plus one oxygen atom for every two hydrogen atoms attached to that carbon atom) when an organic chemical is completely oxidized, and also because oxygen has a greater atomic weight than carbon, the COD should be greater than the TOC. Also, some inorganic chemicals will introduce a COD, but not a TOC, response. A change in relationship between two analytes in a specific sample could suggest sample contamination or laboratory error. This type of problem can occur for analytes such as BOD, COD, and TOC.

- Notes, flags, or similar type notations on reported results. Laboratories will mark with a flag, or footnote, sample results that involved analytical problems, difficulties, or special handling. Typical examples of such notations include: (1) high detection limits because dilution was required to resolve matrix interferences; (2) peaks on gas chromatographs that could not be resolved for reliable identification of organic analytes; (3) contamination in a blank sample; and (4) QA/QC criteria that were not achieved. Examples of these notations from laboratory reports are shown in Table 4-5. With the exception of blank contamination, these types of problems generally render the analytical result invalid for NPDES permit applications or permit reporting. If a blank is contaminated with an analyte, and the effluent sample is not, then the effluent sample can be reported as a valid analysis (see Part III, **References and Acronyms**, for EPA's "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring"). In its guidance manual, EPA also states that if an analyte is measured in a water sample at least 10 times the blank concentration, then the sample result may be considered valid. If less than 10 times the blank, the sample results should be considered invalid.
- A result that is far outside (either above or below) its typical range. Most facilities will have (or should develop) control charts or similar statistical tools for those pollutants that are monitored for permit compliance. These statistical methods will provide upper and lower bounds based on historical measurements. A measurement that is very far outside these upper and lower bounds may reflect a real change in the water composition (such as due to a spill or a treatment unit upset), or it may be a faulty measurement due to sampling or analytical problems. As discussed in the **Permit Limit Exceeded** section in this chapter, analytical results that are outside the normal range and exceed a regulatory limit should be investigated immediately.
- Obvious and frequent typographical errors in the laboratory report should raise questions about the quality of the results.

Table 4-5. Example of Notations Qualifying Analytical Results

Compound was analyzed for, but not detected
Value is estimated or below reporting limit • Notation used when estimating a concentration for TICs for which the analysis has not been calibrated. • Notation used when the result is less than the reporting limit, but greater than zero.
Analyte found in associated method blank sample
Concentration exceeds calibration range of instrument
Sample was diluted for analysis
Spiked sample recovery not within control limits
Duplicate analysis not within control limits

Method-Defined Analytes

There are certain commonly used analytical methods in which the analyte is defined by the actual procedures of the method. These methods do not analyze for individual chemicals such as chromium or benzene, rather they analyze chemical groups or chemical properties as a whole. Examples of method defined analytes are BOD, TSS, COD, TOC, oil and grease, and total petroleum hydrocarbons (TPH). Some of these method-defined analytes are often reasonably well correlated, especially in a specific wastewater matrix. It is important for a reviewer and user of laboratory data to understand what the method-defined analytes actually represent, and how the results of one method relate to another. The most common of the method-defined analytes for wastewater are listed in Table 4-6 with a brief description. A more detailed description of these method-defined analytes, and their relationships, are discussed in Chapter 8, **Method-Defined Analytes.**

Table 4-6. Examples of Method-Defined Analytes for Wastewater

Biochemical oxygen demand (BOD)—measure of biologically oxidizable substances.

Chemical oxygen demand (COD)—measure of the amount of all substances that can be oxidized by a strong solution of chromic acid at high temperature in the presence of a silver catalyst.

Total organic carbon (TOC)—measure of the amount of organic carbon by combustion of the organic compounds to carbon dioxide in a furnace.

Oil and grease (O&G)—measure of biodegradable animal greases and vegetable oils along with relatively non-biodegradable mineral oils.

Total petroleum hydrocarbons (TPH)-measure of relatively non-biodegradable mineral oils.

Phenols—measure of a wide range of hydroxy (OH) derivatives of benzene and its condensed nuclei, including phenol, ortho- and meta-substituted phenols, and para-substituted phenols when the substitution is a carboxyl, halogen, methoxyl, or sulfonic acid group.

Total solids (TS)—measure of total residue remaining in a sample after drying at 103° to 105° C.

Total suspended solids (TSS)—measure of nonfilterable residue, that is, the solids that do not pass through the test filter. TSS is a portion of the total solids in a sample.

Total dissolved solids (TDS)—measure of filterable residue, that is, the dissolved solids that pass through the test filter. TDS is a portion of the total residue in a sample.

Surfactants—measure of methylene blue active substances (MBAS), based on the production of color by the reaction of certain anionic surface active agents with methylene blue.

Whole effluent toxicity (WET)—a measure of adverse toxicity effects on the test species (vertebrates, invertebrates, or plants), including interactive effects of different chemicals and physical properties of the samples.

Detection and Quantification Limits

Detection and quantification limits in laboratory analyses 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.

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 there is so little of it that it cannot be measured.
- A quantification limit is greater than a detection limit and is the concentration at which enough analyte is present to both identify analyte and measure its concentration.

In Chapter 2, **Planning Analyses**, the importance of selecting the right detection or quantification limit for laboratory analyses was discussed. After receiving the laboratory report, it is very important to check that the required detection or quantification limits were achieved. If not, action must be taken to correct this problem (see **Wrong Reporting Limits** earlier in this chapter).

For a more detailed discussion of detection and quantification limits and their importance in laboratory analyses and regulatory compliance, the reader should see Chapter 5, **Detection and Quantification Limits**.

Quality Assurance/Quality Control

This section discusses how to check whether laboratory analyses meet QA/QC performance criteria and what to do when they do not. Part IV contains a Checklist, **QA/QC Data in Laboratory Report**, that can be used to verify that all of the requested QA/QC data are included in a laboratory report. This checklist contains a recommended "minimum" QA/QC list, as well as additional QA/QC that may be needed for a particular project.

For an overview of QA/QC for laboratory analyses, the reader should see Chapter 2, **Planning Analyses**. For a more detailed discussion of QA/QC procedures, the reader should see Chapter 6, **Quality Assurance/Quality Control**.

Sometimes an analysis will not meet QA/QC performance criteria set by the laboratory or analytical method. This may happen because the sample has a complex matrix or a constituent that interferes with the analysis or the laboratory could be performing poorly. When a laboratory encounters performance problems, the analyst may reanalyze the sample if enough sample remains to determine whether the problem is with the sample or the analysis itself. The problem should be noted in the laboratory report. What the laboratory does to resolve the problem also may be described in the report or just the final results may be given. At times, the problem cannot be resolved and the available data are reported as is.

When a laboratory encounters a quality control problem, it should attempt to resolve the problem following its quality control program. When a problem is initially observed, the laboratory should analyze a QC standard to determine if the method was being performed correctly. If the results of the QC check standard are not within control limits, laboratory performance is considered out of control and the source of the problem must be identified and corrected. If the problem cannot be resolved, the analytical result for the sample is considered suspect and may not be reported for regulatory compliance purposes.

Certain situations such as compliance monitoring require that quality control problems caused by the sample matrix or analytical interferences be resolved. General guidance for this type of problem is discussed in Chapter 2, **Matrix Interferences.** If, however, a laboratory appears to have frequent performance failures within its regular quality control program, the laboratory may not have the technical expertise for the analysis and another laboratory should be used.

Two of the most common terms related to QA/QC performance criteria are accuracy (or recovery) and precision. Recovery is calculated for spiked samples, measuring what percentage of a spike is recovered from a sample. Precision is the difference in repeated measurements and represents random error. The first item to check for recovery and precision data is whether the laboratory report contains any remarks or notes that it did not meet all the performance criteria. The report also may include the performance criteria (usually an allowable range, for example, 80%-120% for recovery). These criteria can be compared to the recovery and precision data for spike and duplicate samples. These terms and others related to laboratory analyses are discussed in more detail in Chapter 9, **Statistical Calculations**.

Part II
Additional Detail and Special Topics

Chapter 5

Detection and Quantification Limits

This chapter discusses the 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.

Definitions

Table 5-1 defines some of the most commonly used terms related to detection and quantification limits. Many of the terms and their definitions sound very similar and refer to statistical terms, which can be confusing and sometimes difficult to understand. Perhaps the most important point to keep in mind, however, is the basic difference between a detection limit and a quantification limit. If an analyte is present below the detection limit, it is at such a low level that it is difficult to say that it is really there. If an analyte is present above the quantification limit, it is easier to detect the analyte and to measure how much is there. A simple analogy would be measuring lengths with a ruler. For example, even though the "." at the end of this sentence can be seen, it would be difficult to measure its width with a ruler; however, it would be easier to measure the length of "....." because it has more periods and is longer.

Of the terms shown in Table 5-1, the most common ones encountered in regulatory compliance are MDL, ML, MQL, MAL, and PQL. A brief introduction to some of these terms is given here. The next section discusses in detail how detection and quantification terms are applied in regulatory situations.

The term, detection limit, refers to the concentration of an analyte, for a specific measurement method and sample matrix, at which the analyte can be reported to be present in a sample of the same matrix, at a stated statistical confidence level which is typically 99%. A reported value at or near the detection limit does not provide a usable measurement of the true quantity of the analyte in the sample. It is important to understand that detection limits are not fixed values. They are subject to the analytical method used, laboratory technique and analytical instruments, and the properties of the analyte and sample matrix.

The quantification limit is defined as the level at which the analytical method can produce a quantitative result within a defined interval for a given

confidence level. For example, a quantification limit might be defined as the minimum concentration at which the quantity of chemical A can be measured within ± 25% at a 95% confidence level. A third term which is sometimes used by laboratories is the reporting limit. Laboratories may establish their own protocols for reporting results that differ from the commonly used definitions of detection limits and quantification limits. Examples of laboratory reporting limits include the lowest concentration that is included in an instrumental calibration curve, a fixed multiplier of an instrument signal-to-noise ratio, or statistical analyses of multiple detection and/or quantification limits from reagent water studies.

Table 5-1. Definitions of Terms Commonly Used in Reference to Detection and Quantification Limits

Method Detection Limit (MDL)	The minimum concentration of a substance that can be measured with a 99% confidence that the analyte concentration is greater than zero based on analysis of a specified sample matrix (40 CFR 136, Appendix B). Reagent water MDLs have been published by EPA for a number of 40 CFR 136 methods.
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 of a blank. (American Chemical Society, ACS)
Contract Required Detection Limit (CRDL)	Reporting limits specified for laboratories under contract to EPA for Superfund investigations.
Instrument Detection Limit (IDL)	The smallest signal above background noise that an instrument can detect at a 99% confidence level. (ACS)
Practical Quantitation Limit (PQL)	The lowest level that can be reliably determined within specified limits of precision and accuracy during routine laboratory operating conditions. Operationally defined in the drinking water rules as 5 to 10 times the MDL (50 FR 46907, November 13, 1985)
Minimum Level (ML)	The lowest concentration that gives recognizable signals and an acceptable calibration point. It is the equivalent concentration of the lowest calibration standard analyzed by a specific analytical procedure. MLs are matrix-specific. ML values have been published by EPA for a number of 40 CFR 136 methods. EPA has provisionally defined the ML as 3.18 times the MDL for a specific analyte, method, and matrix.

Limit of Quantitation (LOQ)	The level above which quantitative results may be obtained with a specified degree of confidence. The operational LOQ is 10 times the standard deviation measured in a blank and is assumed to provide a quantitative uncertainty of ± 30% at a 99% confidence level. (ACS)
Minimum Quantification Level (MQL) Minimum Analytical Level (MAL)	Examples of quantification levels set by regulatory agencies for NPDES compliance reporting. The MQL is used for NPDES permits issued in EPA Region VI and is the same as the MAL used by the Texas Natural Resource Conservation Commission. Both are based on the PQL/ML definitions.

There is only one regulatory definition of detection limit that is specific to analyses for NPDES permit compliance. This is the MDL, which is promulgated at 40 CFR 136, Appendix B. It is estimated by analyzing seven or more replicate samples of the target matrix or reagent water, spiked with the analyte of interest at a concentration within a factor of five of the expected detection limit.

The ML is a type of quantification limit. EPA's definition of the ML is 3.18 times the MDL for a specific analyte, method, and matrix. In recent years, EPA has published MLs in a number of 40 CFR 136 methods.

It is important to note that a reporting limit specified by a laboratory is not necessarily a predefined detection or quantification limit, such as described in Table 5-1, nor is it necessarily a permit limit, condition, or constraint. It is the responsibility of the permittee to ensure that laboratory results used to demonstrate NPDES permit compliance meet all of the limits, conditions and constraints of the permit, including permit-specified quantification and detection limits. The permittee should ask and understand what the laboratory means by "reporting limit;" and in designing the sampling and analytical program, the permittee should work with the laboratory to ensure that DQOs properly reflect all permit limits and constraints, including quantification and detection limits.

Application and Interpretation

There are important characteristics of detection limits and quantification limits that must be understood when interpreting laboratory results. First, both the detection limit and the quantification limit are matrix-specific. Second, published MDLs typically are based on tests performed on a reagent water

matrix by a single laboratory. Third, published MLs, which may be based on data from more than one laboratory, are not statistically-based and may also be derived from reagent water matrices.

In addition to the target analyte, a water sample matrix will contain a complex mixture of inorganic and organic chemicals. The complexity of the mixture may make it difficult to identify or quantify the target analyte, much like the conversation in a crowded room makes it difficult to hear and understand a single person. Complex matrices may increase detection and quantification limits for any specific target analyte. The published MDLs and MLs for the EPA methods are based on analyses of reagent water, which is essentially free of impurities. Thus, these MDLs and MLs represent the lowest and best results achievable, and a particular laboratory may not be able to achieve them for a specific analyte.

Interlaboratory uncertainty, which is the difference in results between laboratories that are using identical analytical procedures, influences whether a laboratory can achieve the MDLs or MLs published by EPA. Published MDLs are often based on the results from a single laboratory, which do not account for the differences or variability that would be seen among laboratories as a whole. In the case of EPA's published MLs, they are often developed from evaluation of data from multiple laboratories and matrices for a specific method and analyte, but are not statistically-based and therefore cannot be directly used to estimate precision.

Fortunately, there are approaches that can be used to address both the matrix interference and interlaboratory problems with published MDLs and MLs, if one is willing to expend the time, effort, and costs to resolve them. The MDL procedure at 40 CFR 136, Appendix B, specifically states that a matrix-specific MDL can be determined. Most regulatory agencies recognize the significance of matrix interferences and will allow matrix-specific MDLs and quantification limits to be substituted for the published values of the MDL and ML, if the necessary technical documentation is provided. As shown in the next example, an NPDES permit may have specific language allowing a matrix-specific MDL. The information required to support a matrix-specific MDL is a study as prescribed at 40 CFR 136, Appendix B, using the applicable analytical method and the specific matrix.

EXAMPLE - Example NPDES Permit Language for Matrix-Specific Detection and Quantification Limits

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

The permittee may develop an effluent specific detection limit (MDL) in accordance with Appendix B to 40 CFR 136. For any pollutant for which the permittee determines an effluent specific MDL, the permittee shall send to the EPA Region 6 Permits Branch (6WQ-P) a report containing QA/QC documentation, analytical results, and calculations necessary to demonstrate that the effluent specific MDL was correctly calculated. An effluent specific minimum quantification level (MQL) shall be determined in accordance with the following calculation:

$$MQL = 3.3 \times MDL$$

Upon written approval by the EPA Region 6 NPDES Permits Branch (6WQ-P), the effluent specific MQL may be utilized by the permittee for all future Discharge Monitoring Report (DMR) calculations and reporting requirements.

An example calculation of an MDL follows. This example is for cyanide analysis of a reagent water matrix using the ion chromatographic method. The same calculation steps are used for matrix-specific MDLs.

EXAMPLE - MDL Calculation for Cyanide Analysis by Ion Chromatographic Method

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Matrix:	Reagent Water
Spiked Concentration:	0.00125 mg/L
Sample Number	Measured (mg/L)
1	0.00243
2	0.00158
3	0.00234
4	0.00188
5	0.00184
6	0.00179
7	0.00164
8	0.00143
Standard deviation (s)	0.000353
Student's t value (t)	2.998
Calculated MDL (s x t)	0.001058

In the calculations, there is no rounding until the final MDL is stated. The 0.001058 mg/L result should be rounded to significant figures. In this example, because the measurements have three significant figures, the MDL could be stated with the same number of significant figures (that is, as 0.00106 mg/L). As a practical matter, however, a single significant figure is more common, simpler, and does not overemphasize the precision of the result. It should be understood that rounding to a single significant figure will lose some of the precision associated with the estimate, but in most cases should be acceptable. EPA's draft guidance on approval of alternative methods (see Part III, **References and Acronyms**), rounds the ML (3.18 times the MDL) to a single significant figure.

Thus, if single significant figures are used, the MDL in the above example would be 0.001 mg/L or 1 µg/L. To obtain the minimum level (ML) for the method, the MDL would be multiplied by a factor of 3.18, giving a result of 0.003366 mg/L. Rounded to a single significant figure, the ML would be 0.003 mg/L or 3 µg/L.

Interlaboratory variation in detection and quantification limits can be incorporated into the matrix-specific MDL and ML for an analyte by performing the matrix-specific MDL study at two or more laboratories and then statistically combining the results. The statistics involved in developing the interlaboratory MDL are quite simple (see Chapter 9, **Statistical Calculations** for the equations and example). The biggest drawback is simply that one must be willing to pay for independent studies at two or more laboratories.

There is considerable ongoing controversy concerning the appropriate definitions and calculation methods for detection and quantification limits. Strong technical arguments have been presented to EPA by an industry coalition showing that the current EPA definitions of the MDL and ML are not statistically correct and/or consistent, do not sufficiently characterize interlaboratory uncertainty, and require definitions that are more scientifically rigorous. Although there are ongoing discussions between regulated stakeholders (industry, municipalities) and EPA, there are no currently approved alternatives to the MDL and its related quantification limits.

NOTE
It is very important to remember that the MDL is the only definition of a detection limit that is specifically adopted by the NPDES program, and therefore it, and the quantification limits derived from it (the ML, MQL, PQL), must be used for NPDES compliance reporting and permit applications unless the permit (or an NPDES-authorized state policy or regulation) specifies an alternate method of reporting.

In the case of demonstrating compliance with wastewater permit limits, it is always wise for a permittee to identify a detection limit or quantification limit constraint before the permit is issued so that it can be dealt with during the permit drafting process. Negotiations after the fact, particularly when they are done under the threat of an enforcement action, should be avoided. Obviously, the time to address detection and quantification limit issues with respect to NPDES permit compliance is when the permit is being issued, amended, or renewed. Most permitting agencies are well aware of these issues, but not

many of them routinely incorporate detection or quantification limits and related provisions into permits. If a permit will establish limits for pollutants where these will be an issue, the permittee should work with the permit writer to be sure that such provisions are included in the permit.

Regulatory agencies, other than EPA, do not have the staffs or budgets to develop MDLs and quantification limits for specific wastewater matrices. Even EPA has its own budget constraints and has not developed interlaboratory MDLs for its approved analytical methods. Therefore, it falls on the person who is being regulated to evaluate if and when a matrix-specific MDL or quantification limit is needed, and to conduct the necessary studies.

EPA's policy in its "Technical Support Document for Water Quality-based Toxics Control" (TSD) is that compliance with an NPDES permit limit should be determined using measured values above the quantification limit (see Part III, **References and Acronyms**). EPA's reasoning for this policy is described in the TSD as:

> "EPA is not recommending use of the method detection level because quantification at the method detection level is not as precise as at ML."
> (TSD, page 111)

EPA also states that:

> "The permitting authority may choose to specify another level at which compliance determinations are made. Where the permitting authority so chooses, the authority must be assured that the level is quantifiable, defensible, and as close as possible to the permit level."
> (TSD, page 112)

NOTE
One of the most important aspects of the development of an NPDES permit is to assure that quantification limits, not detection limits, are defined in the permit as the basis for compliance determinations.

It is essential that the MDL or any similar detection limit not be identified in the permit as the basis for making compliance determinations. The use of a detection limit as the basis for determining compliance with an NPDES permit limit results in an unacceptably high probability of false positive reports (the analyte reported as present, but is not actually present).

Unless the permitting agency is provided with an effluent-specific MDL and ML study for a specific analyte, typically it will use the values published by EPA as the basis for complying with the permit limit. In some cases, permitting agencies will have their own quantification and detection limits developed from studies conducted under their auspices, based on experience,

or based on a policy such as the PQL methodology used in the EPA drinking water program. Below is an example of a PQL study conducted by the state of New Jersey.

EXAMPLE - Example PQL Study by Regulatory Agency

In 1987 the New Jersey Department of Environmental Protection (NJDEP) conducted an interlaboratory PQL study in which all environmental laboratories certified by the state were requested to participate. In this study, the target analytes were organic chemicals in drinking water samples. Based on the results of this interlaboratory study, the NJDEP determined that the MDL to PQL multiplier had a range of 3 to 12, and an average of 5.3. The NJDEP then established a multiplier of 5 to calculate the PQL from an MDL for a specific analyte and analytical method for drinking water, ground water, surface water, and effluent samples.

The permitting agency does have the authority, under the NPDES permitting regulations, to establish required compliance reporting limits in each permit. These can be either some form of quantification limit (PQL, ML, MAL) or a detection limit (MDL, LOD). Obviously, from the permittee's perspective it is important that a quantification limit rather than a detection limit be used for a compliance limit. Therefore, during the permit development process it is extremely important for the permittee to make every effort to assure that compliance will be determined using quantification levels rather than detection limits.

When a permittee believes that compliance with a standard detection or quantification limit used by the permitting agency is likely to be an analytical problem, it is prudent to collect the necessary data to document the problem and to provide the basis for an effluent-specific compliance limit. This may be an effluent-specific MDL development study (40 CFR 136, Appendix B) or an even more rigorous analysis of the effluent matrix. It is important, however, that the steps to obtain better sensitivity for the analysis be completed before trying to develop matrix-specific detection and quantification limits. A permit agency is unlikely to approve matrix-specific limits if there is a more sensitive EPA approved analytical method that may be suitable. The need for a matrix-specific limit usually can be identified when the effluent is sampled for the permit application. When the permit is to be for a future discharge, the actual wastestream cannot be sampled. One approach is to sample and analyze the effluent from a facility that is expected to have a similar matrix. If this is not possible, it is important to try to obtain in the permit a provision that will allow development of an effluent-specific detection or quantification limit.

If the permit authority issues a proposed permit limit set at a detection limit or quantification limit that is too low to be reliable, the permittee may challenge this permit condition through the administrative appeals process provided for by the NPDES regulations (40 CFR 125). Because these appeals are a complicated and costly process, they should not be considered unless the permittee is quite certain that the proposed limit will result in a compliance problem. Most permittees find that compliance levels based upon EPA's ML values for organic chemicals or MQLs and PQLs calculated as a multiple of published MDLs, are acceptable and do not pose too high a risk of false positives, which represent permit exceedances.

Whether or not to appeal a final NPDES permit because of an inappropriate permit limit based on a detection or quantification limit obviously requires the permittee to have a good understanding of the potential extent of the problem. This usually requires sufficient testing and analysis of the actual effluent matrix to demonstrate that the detection or quantification limit set in the permit is inappropriate. These data should be collected before or during the permit negotiation period, because typically they would have to be filed as comments on the proposed NPDES permit, in order to serve as the basis for the administrative appeal.

Chapter 6

Quality Assurance/Quality Control

QA/QC procedures are established to produce accurate and reliable data. Quality control procedures are sometimes specified in individual analytical methods or general method references. The laboratory may add its own quality control procedures and will also develop a quality assurance program to *assure* that quality control is implemented properly. Specific regulatory activities will have their own QA/QC requirements. Therefore, when developing a sampling and analysis plan or reviewing a laboratory report, it is important to know what QA/QC procedures are followed by the laboratory and how these compare to what is needed for a particular project.

This chapter discusses common QA/QC terms and QA/QC requirements specified in analytical methods and laboratory QA/QC programs.

Common Terms

This section discusses how spikes, duplicates, replicates, blanks, and standards are used in the QA/QC of laboratory analyses. Examples are given of how each is found and used in laboratory reports.

Spikes

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

A spiked sample is used to calculate the recovery of an analyte (see Chapter 9, **Statistical Calculations**). 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. The different types of sample spikes are discussed in the following sections.

Standard Solutions

Standard solutions are prepared by spiking an analyte(s) into reagent water. Laboratory control samples are made from these standard solutions and analyzed to generate data for laboratory control limits and to demonstrate that on any given day, laboratory procedures are in control. An example of control sample spike recovery data from a laboratory report follows.

EXAMPLE - Control Sample Spike Recovery Data

Category:	Volatiles
Matrix:	Leachate
QC Lot:	18 Feb 94-E
Units:	mg/L

Analyte	Spike	Measured	Recovery	Control Limits
1,1-Dichloroethene	0.250	0.232	93%	56-138%
Trichloroethene	0.250	0.266	106%	76-109%
Benzene	0.250	0.266	106%	78-119%
Toluene	0.250	0.249	100%	82-114%
Chlorobenzene	0.250	0.257	103%	84-117%

Matrix Spike

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.

Matrix spikes are used to assess method performance and to judge whether the analysis is appropriate for the matrix and is within control limits. The recoveries of matrix spikes are used to identify unusual matrix effects, analytical errors, or other problems. Matrix spike duplicates also are run to assess precision.

Matrix spikes are added to the sample before analytical extraction or processing. Analytes that are typically used for matrix spikes are shown in Table 6-1 for volatile organics, semivolatile organics (base/neutral and acid), and pesticides. An example follows of matrix spike recovery data from a laboratory report.

EXAMPLE - Matrix Spike Recovery Data

Category:	Volatiles					
Matrix:	Aqueous					
Sample ID:	088017-0001					
Units:	µg/L					
Analyte	Unspiked Sample		Spike Added		Spiked Sample	Recovery
1,1-Dichloroethene	ND		250		240	96%
Trichloroethene	ND	250		250	100%	
Benzene	100		250		340	96%
Toluene	120		250		340	88%
Chlorobenzene	ND		250		250	100%

Table 6-1. Example of Analytes Used for Matrix Spikes for Organic Analyses

Volatile Organics
- 1,1-Dichloroethene
- Trichloroethene
- Chlorobenzene
- Toluene
- Benzene

Base/Neutral Organics
- 1,2,4-Trichlorobenzene
- Acenaphthene
- 2,4-Dinitrotoluene
- Pyrene
- N-Nitroso-di-n-propylamine
- 1,4-Dichlorobenzene

Acid Organics
- Pentachlorophenol
- Phenol
- 2-Chlorophenol
- 4-Chloro-3-methylphenol
- 4-Nitrophenol

Pesticides
- Lindane
- Heptachlor
- Aldrin
- Dieldrin
- Endrin
- 4,4'-DDT

Surrogate Spike

Surrogate spikes are used to identify unusual matrix effects, analytical errors, or other problems. Constituents used for surrogates are supposed to be chemically inert and are not expected to occur in the sample being analyzed so that they can be distinguished from the target analyte. Surrogates are added to the sample before analytical extraction or processing. Therefore, surrogates are spiked at the same point as matrix spikes. Analytes that are typically used for surrogate spikes are shown in Table 6-2 for volatile organics, semivolatile organics (base/neutral and acid), and pesticides. An example of surrogate spike recovery data from a laboratory report follows.

Table 6-2. Example of Analytes Used for Surrogate Spikes for Organic Analyses

Volatile Organics
- p-Bromofluorobenzene
- 1,2-Dichloroethane-d4
- Toluene-d8

Base/Neutral Organics
- 2-Fluorobiphenyl
- Nitrobenzene-d5
- Terphenyl-d14

Acid Organics
- 2-Fluorophenol
- 2,4,6-Tribromophenol
- Phenol-d6

Organochlorine Pesticides
- Dibutylchlorendate (DBC)
- 2,4,5,6-Tetrachloro-meta-xylene (TCMX)

EXAMPLE - Surrogate Spike Recovery Data

Client Sample ID:	GW-2		
Lab Sample ID:	B7252109		
Sample Date:	6/30/96		
Analysis:	volatile organics		
Units:	%		
Analyte		Recovery	Control Limits
Toluene-d8		99	88-110
p-Bromofluorobenzene		96	86-115
1,2-Dichloroethane-d4		107	76-114

Internal Standard Spike

The recoveries of internal standards are used to calibrate the analytical instrument for volatile and semivolatile organic analyses. Internal standards are added to the sample just prior to measurement by the analytical instrument. For semivolatiles, this is after the extraction and cleanup steps. Because there are no extraction or cleanup steps for volatile analyses, internal standards for volatiles are added at the same point as matrix and surrogate spikes. Analytes that are typically used for surrogate spikes are shown in Table 6-3 for volatile and semivolatile organics. An example of internal spike recovery data from a laboratory report follows.

Table 6-3. Example of Analytes Used for Internal Standard Spikes for Organic Analyses

Volatile Organics
Bromochloromethane
1,4-Difluorobenzene
Chlorobenzene-d5
Semivolatile Organics
1,4-Dichlorobenzene-d4
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12

EXAMPLE - Internal Standard Spike Recovery Data

Client Sample ID:	GW-1
Lab Sample ID:	X001963-A
Sample Date:	7/17/97
Units:	%

Analyte	Recovery	Control Limits
Chlorobenzene-d5	91	50-200
1,4-Difluorobenzene	94	50-200
1,4-Dichlorobenzene-d4	84	50-200

Isotope Dilution Spike

Isotope dilution uses an isotopically labeled analog of the target analyte (for example, benzene-d6 for benzene) for organic analyses. The isotope is spiked into the sample and its recovery is used to calculate the concentration of the target analyte. For organics requiring an extraction step such as semivolatiles, the isotopes are spiked before extraction. For volatile organics analysis which does not include an extraction step, the isotopes are spiked just prior to analysis (at the same point as matrix spikes, internal standards, and surrogate standards for volatiles).

Method of Standard Addition Spike

The method of standard addition is used in metals analysis. This method uses progressive spiking of the sample to correct for matrix effects on recovery. The spikes are added to the sample after the sample has been digested. In contrast, a matrix spike for metals analysis would be added before digestion.

Recovery Correction

Recovery correction refers to the adjustment of a value by the recovery percentage or fraction. For example, if recovery is 80% and the value found is 80 µg/L, the recovery-corrected value would be 100 µg/L (80 µg/L ÷ 0.8).

Some analytical methods include recovery correction as an intrinsic part of the method and do not need further correction. Examples of these methods are those based on isotope dilution (volatile and semivolatile organics) and purge and trap (volatile organics). In these methods the isotope and internal standard spikes are added at the beginning of the analysis and therefore, their recoveries are supposed to reflect all the effects of the different analytical steps. Applying matrix spike recoveries to these analyses would be incorrect because it would be correcting for recovery twice.

Recovery data from quality control samples and matrix and surrogate spikes are normally used to monitor analytical performance, rather than recovery correct analytical results. Quality control samples are used to judge if the analytical system performance is under control. Matrix and surrogate spikes are used to indicate matrix effects and sample processing problems.

Recovery correction using matrix or surrogate spikes may be specified by a regulatory agency or in an analytical method. An example of an analytical method requiring matrix spike recovery correction was the 1990 version of EPA's TCLP; the method has since been revised to remove the recovery correction requirement.

With analytical methods that include recovery correction directly, additional recovery correction is not correct and should not be done. In other methods, recovery correction with matrix or surrogate spikes presents some special concerns.

One issue with recovery correction is decreased precision. Statistically, recovery correction introduces one more variable into the calculation of the analytical result, which decreases its precision. This decrease in precision can be significant, making the benefit of recovery correction questionable.

Another issue is whether the sample used for the matrix spike is representative of the sample being recovery corrected. With matrix spikes, the laboratory does not spike every sample being analyzed, rather one sample in an analytical batch is selected for spiking. Recovery correction for all the samples in the set would then be based on the one matrix spike. Although the spiked sample is supposed to represent the same matrix as the others, it cannot have all their characteristics that affect the analytical result. There also is a question of whether matrix spikes themselves are representative of the original sample from which they are taken. When matrix spikes are prepared, a second portion of the sample is spiked. The recovery from this second sample may not be representative of the first because normal variability in analyst technique, instrumentation, method efficiency, and sample homogeneity will result in a different recovery value.

Duplicates

The meaning of the term duplicate is self-explanatory; however, 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 or it could be only the analytical step that is duplicated on the same sample.

A duplicate sample is a second sample collected as close as possible to the same point in space and time as the first. It is used to evaluate sample variance or precision, including the variability associated with splitting the initial sample or collecting a separate second sample. A duplicate sample may be called a field duplicate because it is prepared while in the "field."

A duplicate measurement is a second measurement made in the laboratory on the identical sample, useful in evaluating measurement variance or precision. A laboratory duplicate may be called a matrix duplicate when the field sample is split into subsamples in the laboratory. Duplicate control samples (spiked reagent water) are another type of laboratory duplicate. With duplicate measurements, it is very important to know which analytical steps are

included in the duplication. For example, a duplicate measurement may be made for semivolatile analyses before or after the extraction step.

The term duplicate is apt to be used very loosely by the general public. 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.

Replicates

Replicates refer to more than one sample or sample measurement. Duplicates are a special case where the number of items is two. The discussion about duplicates in the preceding subsection applies also to the general case of replicates.

Blanks

A blank is a sample that is not supposed to contain the target analyte(s). Typically, reagent or distilled water is used to prepare blanks for wastewater or other aqueous samples. 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.

Laboratory blanks include instrument blanks, calibration blanks, and method blanks. An instrument blank is not an actual sample, rather it is the baseline response of a instrument in the absence of a sample. An instrument blank, also referred to as a system blank, is used to identify system contamination, carry over from high concentration samples, and instrument memory effects.

A calibration blank, also referred to as a solvent blank, is used to identify contamination introduced by the solvent and to zero the instrument signal.

A method blank is prepared in the laboratory. The blank is supposed to contain none of the target analytes and is carried through the complete sample preparation and analytical procedures, including the addition of reagents.

Therefore, a method blank also may be referred to as a reagent blank. The method blank is the type of laboratory blank that typically is included in the laboratory report.

Field and trip blanks are terms that are sometimes used interchangeably, but they are not necessarily the same. Because different sampling programs may define these samples differently, it is important to understand how these samples are prepared and handled in a given situation. Therefore, the following discussion of field and trip blanks should not be taken as formal definitions, but rather examples of common usage. Again, it is important that in a given situation, the meaning of field and trip blanks should be well-defined and understood.

Trip blanks for aqueous samples are samples of reagent or distilled water prepared in the laboratory or in the field. When prepared in the laboratory, the trip blank goes with the other sampling equipment in the field and returns to the laboratory unopened. When prepared in the field, the blank water is poured into the sample container and sent with the other samples to the laboratory. A trip blank sample is not run through the sampling equipment, but merely poured into the container. Trip blanks are useful in identifying contamination of volatile organic samples.

A trip blank may be considered one type of field blank where exposure is limited to the ambient environment. Other types of field blanks will include exposure to sampling equipment such as filters, bailers, pumps, and containers. Such samples may be referred to as equipment blanks. Samples of water after equipment decontamination steps also may be referred to as equipment rinsate blanks.

Requirements in Analytical Methods

QA/QC requirements may be found in the text of the analytical methods themselves or in the QA/QC section of the general reference source for the methods. Table 6-4 contains examples from 40 CFR 136, SW-846, and *Standard Methods*.

The QA/QC requirements in the analytical methods may be used as a general outline of the procedures that a laboratory should follow. As a practical matter, however, the laboratory client will not be researching the analytical methods to determine what the laboratory should do. If regulatory activities specify certain QA/QC requirements, these will be given priority. If there are no specific regulatory requirements, QA/QC requirements will depend on what the laboratory can provide and what the client needs for a particular project. These topics are discussed in the following section.

Table 6-4. Example QA/QC Requirements in Analytical Methods

Standard Methods, 18th ed., Section 1020 B. "Quality Control"

- Recovery of known additions plus duplicates - 10% of samples
- Analysis of externally supplied standards - once a day
- Reagent blanks - 5% of sample load
- Duplicates - 5% of samples

SW-846, Chapter 1, "Quality Control"

- Field duplicate - one per day per matrix type
- Equipment rinsate blank - one per day per matrix type
- Trip blank - for volatile organic sampling, one per day
- Matrix spike - one per batch, or 1 per 20 samples of each matrix
- Matrix duplicate or matrix spike duplicate - one per batch
- Chain of custody records
- Analytical control limits
- Control samples - one per sample batch
- Method blank - one per sample batch

40 CFR 136

Method 601 Purgeable Halocarbons

Method 602 Purgeable Aromatics

- Quality control check samples - 10% of samples
- Matrix spikes - 10% of samples
- Method blank - once per day
- Surrogate spikes - each sample, standard, and blank

Method 624 Purgeables

- Method blank - one per day
- Quality control check samples - 5% of samples
- Matrix spikes - 5% of samples
- Surrogate spikes - all samples

Method 625 Base/Neutrals and Acids

- Method blank - before processing any samples and each time sample set extracted or reagents changed
- Quality control check samples - 5% of samples
- Matrix spikes - 5% of samples
- Surrogate spikes - all samples

Method 1624 Volatile Organic Compounds by Isotope Dilution

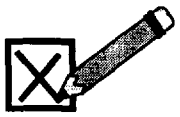
Method 1625 Semivolatile Organic Compounds by Isotope Dilution

- Method blank - one per sample lot (8-hour shift)
- Isotope spike - all samples
- Aqueous performance standard - one per sample lot, at beginning of 8-hour shift

Laboratory Requirements

A competent laboratory will have an effective QA/QC program and include QA/QC data in the analytical report. A good QA/QC program is comprehensive and covers many activities that are not reported with the analytical results, such as those listed in Table 6-5.

Minimum QA/QC information that should be provided by the laboratory is listed in Table 6-6. Additional QA/QC specifications that may be needed for a particular project are listed in Table 6-7. The QA/QC items in these two tables have also been made into a Checklist, **QA/QC Data in Laboratory Report**, located in Part IV.



See the checklist in Part IV, **QA/QC Data in Laboratory Report.**

Table 6-5. Example Elements of QA/QC 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
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

Table 6-6. Recommended Minimum QA/QC Information

Chain of custody form with documentation of sample receipt by laboratory
Spiked standards or laboratory control samples
Laboratory control sample duplicates/replicates
Indication of results outside allowable limits
Indication of any problems encountered with analysis or unusual results
Method blanks
Identification and signature of reviewers

Table 6-7. Additional QA/QC Specifications to Consider

Recovery results
Matrix spikes
Surrogate spikes
Isotope spikes
Internal standard spikes
Precision results
Duplicates/replicates of client samples
Matrix spike duplicates
Blind duplicates
Sample Blanks
Field blanks
Trip blanks
Equipment blanks

Checking Performance with QA/QC Criteria

Recovery and precision are the two main performance criteria for laboratory analyses. Laboratory reports that include control limits for recovery and precision data make it easier for the client to evaluate laboratory performance

and identify any problem in analyses. Making this performance check is easy—if the result is within control limits, it means the laboratory technique is under control and its results should be reliable. It does not mean, however, that the results are the most precise, the most accurate, and completely unbiased; but under normal circumstances, the results should be acceptable.

How is performance evaluated when control limits are not included in the laboratory report or when particular performance criteria must be used? In the latter case, when a project requires specific criteria, these criteria can be used to review the laboratory data. When no particular criteria are specified in the laboratory report or project requirements, the performance data available in the analytical method may be used.

Performance data for the "600 series" of analytical methods for volatile and semivolatile organics at 40 CFR 136, Appendix A are presented as equations. These equations were based on interlaboratory studies performed on aqueous samples, using the 600-series methods. The 600 series equations have since been incorporated into the corresponding SW-846 methods. Performance data for metals analyses using the "200 series" methods at 40 CFR 136, Appendices C and D also are in equation form, developed from interlaboratory studies. Performance data in equation form are also available for some methods from other references such as *Standard Methods*. Examples of analytical performance equations for selected analytes and analytical methods are listed in Table 6-8.

The two examples that follow illustrate how to use these equations to evaluate QA/QC data in a laboratory report for a quality control check sample and a matrix spike.

Table 6-8. Analytical Method Performance Equations for Selected Analytes

	Method	Accuracy (µg/L)	Overall Precision (µg/L)
BOD5	SM 5210 B	X=0.658(C)+0.280	S=0.100(C)+0.547
Cyanide	SM 4500-CN E	—	S=0.06(X)+0.003
Metals			
Arsenic	EPA 206.2	X=0.9652(C)+2.112	S=0.1411(X)+1.873
Copper	EPA 220.2	X=0.9253(C)+0.010	S=0.2735(X)-0.058
Zinc	EPA 289.2	X=1.6710(C)+1.485	S=0.6740(X)-0.342
Volatiles (40 CFR 136, Method 624 and SW 846, Method 8240)			
Benzene		X=0.93(C)+2.00	S=0.25(X)-1.33
Ethylbenzene		X=0.98(C)+2.48	S=0.26(X)-1.72
Toluene		X=0.98(C)+2.03	S=0.22(X)-1.71

Semivolatiles (40 CFR 136, Method 625 and SW 846, Method 8270)		
Benzo(a)pyrene	X=0.90(C)-0.13	S=0.32(X)+1.35
2,4-Dimethylphenol	X=0.71(C)+4.41	S=0.22(X)+1.31
Phenol	X=0.43(C)+1.26	S=0.35(X)+0.58

C - True value for the concentration, µg/L
X - mean recovery, µg/L
S - Overall precision (standard deviation), µg/L
SM - *Standard Methods*, 18th ed.

EXAMPLE - Checking Quality Control Sample Using Analytical Method Performance Equations

---

Data in laboratory report:

Analyte:	benzene
Method:	EPA 624
QC Lot:	25 AUG 94 - 1A
Units:	µg/L
Spiked Value:	50
Sample 1:	46.9
Sample 2:	47.1

Average recovery concentration of Sample 1 and Sample 2:

$$X = \frac{46.9 + 47.1}{2} = 47.0\ \mu g/L$$

Average recovery calculated with method performance equation:

$$X = 0.93C + 2.00$$
$$= 0.93(50) + 2.00$$
$$= 48.5\ \mu g/L$$

Overall precision calculated with method performance equation:

$$S = 0.25X - 1.33$$
$$= 0.25(48.5) - 1.33$$
$$= 10.795\ \mu g/L$$

The recovery range in concentration units (µg/L) is calculated using a factor of 2 for the standard deviation, which is a simplified factor for a 95% tolerance interval (tolerance interval factors actually depend on significance level and number of measurements).

Recovery range:

$$R = X \pm 2(S)$$

Therefore, the lower and upper recovery limits are, respectively:

$R = 48.5 - 2(10.795) = 26.91\ \mu g/L$

$R = 48.5 + 2(10.795) = 70.09\ \mu g/L$

Because the laboratory recovery falls within this range, it would be considered acceptable.

EXAMPLE - Checking Matrix Spike Using Analytical Method Performance Equations

---

Category: Volatiles
Matrix: Aqueous
Sample ID: 088017-0001
Units: µg/L

Analyte	Unspiked Sample	Spike Added	Spiked Sample	Recovery
Toluene	120	250	340	88%

$$\left[\text{Note}: \frac{340 - 120}{250} \times 100\,\% = 88\,\%\right]$$

Recovery of spike calculated with method performance equation:

$X = 0.98(C) + 2.03$
$= 0.98(250) + 2.03$
$= 247.03\ \mu g/L$

Calculated recovery as a percentage:

$$P = \frac{247.03}{250} \times 100\% = 98.8\%$$

Overall precision calculated with method performance equation:

$S = 0.22X - 1.71$
$= 0.22(247.03) - 1.7$
$= 52.6366\ \mu g/L$

The recovery range as a percent:

$$R = \frac{X \pm 2(S)}{C} \times 100\ \%$$

Therefore, the lower and upper recovery percentage limits are, respectively:

$$R = \frac{247.03 - 2(52.6366)}{250} \times 100\% = 56.7\%$$

$$R = \frac{247.03 + 2(52.6366)}{250} \times 100\% = 140.9\%$$

Because the laboratory recovery falls within this range, it would be considered acceptable.

If an analytical method does not include performance equations, it will usually have in the text of the method some precision and accuracy data summarized from studies. These data may be used to get a general idea of what is acceptable method performance. Examples follow for ammonia and oil and grease analyses.

EXAMPLE - Checking Method Performance for Ammonia

Data in laboratory report:

Analyte:	ammonia-nitrogen
Method:	*Standard Methods* (18th ed.) 4500-NH3 F
Sample Type:	wastewater effluent
Analysis Date:	18 FEB 96
Units:	mg/L
Sample Results:	18.2
Duplicate Results:	17.6

Average of sample and duplicate:

$$X = \frac{18.2 + 17.6}{2} = 17.9 \text{ mg/L}$$

Precision expressed as standard deviation (see **Standard Deviation**, in Chapter 9):

$$s = |18.2 - 17.6| \times \sqrt{0.5} = 0.4243 \ \mu g/L$$

Precision expressed as relative standard deviation (RSD):

$$s = \frac{0.4243}{17.9} \times 100\% = 2.4\%$$

Performance data given in method: Method 4500-NH3 F is the selective electrode method. Performance data for this method are given in Table 4500-NH3:I of *Standard Methods*. In this table, a concentration of 20 mg/L is closest to the sample results. Listed precision and bias data for this concentration in effluent water are: 95% mean recovery, 3 mg/L overall standard deviation, and 2 mg/L single operator standard deviation. Because the samples were not spiked, mean recovery is not calculated for the samples. Because a single analyst performed the duplicate analyses, the single

operator precision rather than the multiple operator (overall) precision from the method is used to compare to the laboratory results.

Method single operator precision calculated as RSD:

$$RSD = \frac{2}{20} \times 100\% = 10\%$$

The precision of the duplicate samples is less than the method precision, indicating that the analytical results are acceptable.

EXAMPLE - Checking Method Performance for Oil and Grease

Data in laboratory report:

Analyte:	oil and grease
Method:	EPA Method 1664, HEM (1994 version)
QC Lot:	18 FEB 96-2A
Units:	mg/L
Spike Level:	10
QC Sample 1:	7.8
QC Sample 2:	8.5

Average recovery concentration of Sample 1 and 2:

$$X = \frac{7.8 + 8.5}{2} = 8.15 \text{ mg/L}$$

Average recovery as percent:

$$X = \frac{8.15}{10} \times 100\% = 81.5\%$$

Performance data given in method:

Method 1664, HEM is the oil and grease method based on n-hexane extractable material (HEM). Performance data for this method are given in Table 1 of EPA report number EPA-821-B-94-004. In this table, recovery limits for ongoing performance in a laboratory are 79-114%. Because the laboratory recovery is within this range, the oil and grease results would be considered acceptable.

Chapter 7

Method References

This chapter describes the references for analytical methods for the NPDES program and EPA's analytical manual, SW-846, which is used primarily for non-NPDES analyses.

NPDES Method References

All EPA approved methods for analyses to demonstrate compliance with NPDES permit limits and to supply information for NPDES permit applications are listed at 40 CFR 136. The analytical methods shown in the regulation are the only federally approved methods that can be used for the analytes that are listed. These analytical methods must be used for demonstrating NPDES permit compliance irrespective of whether the permit is issued by an authorized state or by an EPA regional office. States and EPA regions may specify, in permits or application forms, analyses by methods not shown in 40 CFR 136, but only if this is determined to be necessary because there is not an approved method available for an analyte or because increased sensitivity of analysis is needed.

Analytical methods approved for the NPDES program at 40 CFR 136 include not only EPA methods, but methods from several other sources. Although the most commonly used references for NPDES analyses are the EPA methods and those from *Standard Methods*, a laboratory may use any one of the approved methods from any of the reference sources at 40 CFR 136 without consulting EPA or the state. The method references for methods approved for NPDES analyses are described in the following sections. The complete reference for these methods are included in Part III, **References and Acronyms**.

U.S. Environmental Protection Agency

The reference for the EPA analytical methods listed at 40 CFR 136 is "Methods for Chemical Analysis of Water and Wastes," revised March 1983 and 1979. Methods in this reference cover physical properties such as pH, residue (TSS), and hardness; metals; inorganics such as chlorides, cyanide, and ammonia; and organics such as BOD, COD, and oil and grease.

American Public Health Association

Standard Methods for the Examination of Water and Wastewater, which is published by the American Public Health Association in cooperation with the Water Environment Federation and American Society of Civil Engineers, is probably the most widely used reference manual for wastewater analysis in the U.S. At the time of this writing, it is in its 19th edition. An analytical procedure is included in *Standard Methods* for almost every corresponding EPA analyte and method. In fact, for one parameter, carbonaceous five-day biochemical oxygen demand (CBOD), the only EPA-approved method is from *Standard Methods*.

One note of caution must be given when Standard Me*thods* is used as the principal methods reference in a laboratory. The listing of approved analytical procedures in 40 CFR 136 often lags the most recent edition of *Standard Methods*. For example, as of July 1998, 40 CFR 136 cites analytical methods from the 18th edition of *Standard Methods* as approved, even though the 19th edition was published in 1992. In fact, even older versions of *Standard Methods* are listed for a few specific analytes such as sulfates (turbidimetric, 15th edition) and total phenols (14th edition). Therefore, for NPDES analyses, the laboratory must reference and use the procedures from the approved edition rather than the updated procedures in the 19th edition.

American Society for Testing and Materials

ASTM publishes a number of approved analytical methods for wastewater in its *Annual Book of ASTM Standards, Water and Environmental Technology*. Most of the approved ASTM methods are for analytes listed at 40 CFR 136 in Table IB, "List of Approved Inorganic Test Procedures," and Table ID, "List of Approved Test Procedures for Pesticides."

Association of Official Analytical Chemists

The AOAC publishes a number of analytical procedures that are approved for NPDES analyses or inorganic analytes. The reference for these methods is "Official Methods of Analysis of the Association of Official Analytical Chemists."

U.S. Geological Survey

The USGS methods listed at 40 CFR 136 are primarily for what EPA identifies as inorganic chemical analytes. Other USGS methods include those for bacteria and radiological tests. The USGS references at 40 CFR 136 are:

- "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples,"
- "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments,"
- "Methods for the Determination of Organic Substances in Water and Fluvial Sediments,"
- "Water Temperature—Influential Factors, Field Measurement and Data Presentation," and
- "Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters."

Proprietary Methods

Included in 40 CFR 136 are several proprietary analytical methods for analyzing wastewater samples for specific analytes. Most of these proprietary methods are from the Hach Chemical Company and many are widely used. In fact, Hach's micro-COD test may be more widely used than the EPA or *Standard Methods* procedure because of its speed, simplicity, and small amounts of sample and reagents required.

A number of proprietary methods using specific instrumental analyses are also included at 40 CFR 136. These include the Oceanography International Corporation COD method, the direct current plasma (DCP) optical emission spectrometric methods for trace metals analysis marketed by Fison Instruments Inc., and several automated analysis methods for inorganic analytes by Bran & Luebbe (Technicon).

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, when the sample is not taken for NPDES monitoring or sampling, 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 (TCLP). SW-846 is available in paper or CD-ROM. SW-846 is divided into four volumes:

- Volume IA for inorganic analytes;
- Volume IB for organic analytes;
- Volume IC for "miscellaneous" analytes such as cyanide, oil and grease, sulfate, phenolics, hazardous waste characteristics; and
- Volume II for field activities such as sampling and monitoring.

Chapter 8

Method-Defined Analytes

There are certain commonly used analytical methods in which the analyte is defined by the actual procedures of the method. These methods do not analyze for individual chemicals such as chromium or benzene, rather they analyze chemical groups or chemical properties as a whole. Examples of method-defined analytes are BOD, TSS, COD, TOC, oil and grease, and TPH. Some of these method-defined analytes are often reasonably well correlated, especially in a specific wastewater matrix. It is important for a reviewer and user of laboratory data to understand what the method-defined analytes actually represent, and how the results of one method relate to another. The most common of the method-defined analytes for wastewater, and their relationships, are discussed in this chapter. Method references that are cited in the discussion may be found in Part III, **References and Acronyms**.

Biochemical Oxygen Demand

The BOD test is a measure of the biologically oxidizable substances in an aqueous sample. The amount of biodegradable substances is expressed as the amount of oxygen consumed during biological oxidation of these substances over a given time period. Of the methods listed at 40 CFR 136 for BOD, the most common are EPA 405.1 and Standard Methods 5210 B. These methods test for BOD over a 5-day period at a constant incubation temperature of 20 °C. The analyte is often referred to as BOD5, BOD_5, 5-day BOD, or simply as BOD. Care should be taken when reviewing data reported as "BOD" without reference to the time period. Although 40 CFR 136 methods for BOD contain procedures specific to the 5-day BOD test, the test period can be extended to measure total or ultimate BOD (where the test period is usually 20 days or longer). Five-day BOD is commonly used in wastewater permits.

The reliability of the BOD test result is dependent upon the ability of the bacterial seed to biodegrade the substances. Bacterial seed from domestic sewage or commercial seed preparations may not provide reliable BOD measurements on certain industrial wastewaters, especially untreated process wastes. In this case, to obtain reliable and reproducible BOD results, the bacterial seed must be acclimated to the wastewater. Standard Methods describes how to develop an acclimated seed.

The BOD test measures biodegradable carbon compounds and, if nitrifying bacteria are present in the bacterial seed used in the test, the test will include ammonia and related reduced nitrogen compounds. If only carbonaceous BOD (CBOD) is to be measured, a chemical is added to suppress nitrification. If the nitrogen oxygen demand is significant in a sample, CBOD results naturally will be less than BOD results. In cases where limits or regulatory requirements stipulate the BOD test, the CBOD test cannot be used as a substitute. Only when the limit or requirement is stated in terms of CBOD can the CBOD test be used.

Chemical Oxygen Demand

The COD test measures the amount of all substances in an aqueous sample that can be oxidized by a strong solution of chromic acid at high temperature in the presence of a silver catalyst. Of the methods listed at 40 CFR 136 for COD, the most common are EPA 410.1, 2, 3, and 4 and Standard Methods 5220 C and D. The amount of oxidizable substances is expressed as the oxygen that would be required to achieve the degree of oxidation measured in the test. Most, but not all, organic chemicals are completely oxidized by the standard COD test. Reduced nitrogen compounds (ammonia and amines) are not oxidized in the COD test, but sulfides and chlorides are oxidized. Chloride concentrations greater than 1,000 to 2,000 mg/L interfere with the test, giving false positive results (biased on the high side). Therefore, samples containing high concentrations of chlorides are not appropriate for COD analysis.

It should be noted that wastewater effluent limitations and guidelines for petroleum refineries at 40 CFR 419 recognize the chloride interference and allow substitution of TOC for COD as a permit parameter. To obtain this substitution, the permit applicant must show that the chloride concentration is greater than 1,000 mg/L.

Because the COD test completely oxidizes almost all organic chemicals, the COD results for most samples should be greater than the BOD results. If a sample has a high ammonia concentration compared to its organic carbon composition, and there are nitrifying bacteria in the BOD seed, then this relationship may not be true. However, once a BOD:COD ratio is established for a particular wastewater, it should not change significantly unless there is a change in its composition.

In some countries, oxidizing chemicals other than chromic acid, such as potassium permanganate, are used in the COD test. These other oxidants are often not as aggressive as chromic acid and thus will oxidize fewer organic substances or oxidize them incompletely. Therefore, the relationship between COD and BOD described above for the standard chromic acid test procedure may not apply to these alternate COD methods.

Total Organic Carbon

The amount of total organic carbon (TOC) in an aqueous sample is measured by furnace combustion of the organic compounds to carbon dioxide. The TOC instrument subtracts out the carbon dioxide generated by the decomposition of inorganic carbon chemicals. Of the methods listed at 40 CFR 136 for TOC, the most common are EPA 415.1 and Standard Methods 5310 B, C, and D. Because TOC results are reported as organic carbon, they should always be lower than COD results, unless most of the organic compounds are resistant to chromic acid oxidation (which in most situations, is highly unlikely).

Oil and Grease

The two method references for oil and grease (O&G) listed at 40 CFR 136 are EPA 413.1 and Standard Methods 5520 B. A more recent method is EPA 1664, which has not yet been listed at 40 CFR 136, but can be used in NPDES permit monitoring if specifically included in the permit.

In O&G methods, a solvent is used to extract fatty-type materials from the sample. Older methods for O&G, including EPA 413.1, use Freon-113® as the solvent. Newer methods are using other solvents because of the international ban on chlorinated fluorocarbons (CFCs) (the Montreal ozone protocols). For example, Standard Methods 5520 B allows use of either Freon-113® or a mixture of n-hexane and methyl-tert-butyl ether (MTBE), and EPA 1664 uses n-hexane. To distinguish EPA Method 1664 from the Freon-113®-based methods, the Method 1664 analyte is not referred to as oil and grease, but as "n-hexane extractable material (HEM)."

The O&G and HEM methods extract any substances that are more soluble in the solvent than in water. Extraction efficiency, and thus, the analytical result, depends on the hydrophobicity (water-hating) and oleophilicity (fat-loving) of the extracted substances. In addition to aliphatic hydrocarbons, extracted materials may include vegetable oils, animal fats, and some nonpolar organic chemicals such as chlorophyll. Long-chain hydrocarbon molecules that are found in heavy fuel oils or crude petroleum may not be extracted.

After extraction the solvent is evaporated and the residue left behind is measured as O&G or HEM. These methods do not measure volatile hydrocarbons that are driven off when the solvent is evaporated.

Total Petroleum Hydrocarbons

Methods for total petroleum hydrocarbons (TPH) measure petroleum hydrocarbons extractable by an organic solvent. There are no methods listed at 40 CFR 136 for TPH and it is not a common parameter in NPDES permits. If it is included in an NPDES permit, the permit should state which analytical method(s) is acceptable. Common method references for TPH include EPA 418.1 and a variation of EPA 1664. EPA 418.1 uses Freon-113® as the extraction solvent, and the EPA 1664 TPH option, referred to as "silica gel treated n-hexane extractable material (SGT-HEM)," uses n-hexane.

TPH and SGT-HEM are not synonymous with O&G and HEM. O&G and HEM extract and measure biodegradable animal greases and vegetable oils along with relatively non-biodegradable mineral oils. TPH and SGT-HEM measure the relatively non-biodegradable mineral oils alone. TPH methods are very similar to O&G methods, except TPH methods introduce silica gel to the sample, to remove animal and vegetable fatty materials. Thus, one would expect TPH results to be always less than or equal to O&G results; however, this is not always the case.

The older method for TPH, EPA 418.1, does not evaporate the extraction solvent. Rather, it uses infrared analysis of the solvent/analyte mixture, thereby measuring some of the volatile compounds that would be lost through evaporation. If a sample contains mostly petroleum hydrocarbons (and little animal/vegetable oils), TPH results with EPA 418.1 may be higher than O&G results with EPA 413.1. This situation should not occur if the HEM and HEM-SGT methods are used, because solvent evaporation is used in both tests.

Phenols

Methods for total recoverable phenolics measure a wide range of OH-derivatives of benzene and its condensed nuclei, including phenol, ortho- and meta-substituted phenols, and para-substituted phenols when the substitution is a carboxyl, halogen, methoxyl, or sulfonic acid group. They will not measure para-substituted phenols with substitution by other groups, such as those with alkyl or aryl groups; for example, para-cresol, which is found in some industrial wastewaters.

The two method references for phenols listed at 40 CFR 136 are EPA 420.1 and 2, which are manual and automated colorimetric methods, respectively. The colorimetric method uses the specific chemical phenol as the color standard to quantify phenolic compounds. Because color development with this test is not the same for all of the hydroxy-substituted benzene and benzene

derivatives that are measured by this test, and because substitution generally reduces the color response, the results should be considered an indication of the minimum amount of phenolic substances in a sample.

The results of the phenols test generally cannot be correlated closely with measurements of specific phenolic substances unless the sample contains only a few phenolic compounds that produce color in the test to the same degree and at the same wavelength. Thus, for many wastewater samples it is fruitless to try to compare the sum of the concentrations of individual phenolic chemicals in a sample to the concentration reported in the phenols test.

Total Solids

Total solids (TS) are also known as total residue. Of the methods listed at 40 CFR 136 for TS, the most common are EPA 160.3 and Standard Methods 2540 B. In the test, the sample is dried at 103° to 105° C and the remaining residue is weighed.

Total Suspended Solids

Total suspended solids (TSS) are also known as nonfilterable residue, that is, the solids that do not pass through the test filter. Of the methods listed at 40 CFR 136 for TSS, the most common are EPA 160.2 and Standard Methods 2540 D. TSS is defined by the type of filter (glass fiber) and the drying temperature (103° to 105° C) used. The method allows removal of certain large solids from the filter before drying and weighing. TSS is a portion of the total solids in a sample.

Total Dissolved Solids

Total dissolved solids (TDS) are also known as filterable residue, that is, the dissolved solids that pass through the test filter. Of the methods listed at 40 CFR 136 for TDS, the most common are EPA 160.1 and Standard Methods 2540 C. The test involves filtering a sample through a glass fiber filter, evaporating the filtrate (what passes through the filter) to constant dryness at 180 °C, and weighing the residue. TDS is a portion of the total residue in a sample. The sum of TDS and TSS, which is also part of the total solids, is not equal to the total solids concentration because different drying temperatures are used in the tests. Although the sum of TSS and TDS is often close to the total solids concentration, one cannot use these two analyses to calculate a total solids concentration for NPDES analyses. The total solids test must be performed as a separate analysis.

Surfactants

Surfactants, also sometimes known as methylene blue active substances (MBAS), are measured by a colorimetric procedure based on the production of color by the reaction of certain anionic surface active agents with methylene blue. Through this reaction, methylene blue is transferred to a chloroform phase for colorimetric measurement. The method is specific to anionic substances that will react with methylene blue, but weakly anionic soaps are not measured. There are a number of positive interferences by anionic substances (for example, phenols, sulfates, nitrates, chlorides) that are not surface active agents, but can transport methylene blue into the chloroform phase. A subsequent water wash step of the chloroform extract will remove many of these interferences, but because these interfering compounds are present in many wastewater samples, strict adherence to the chloroform:sample ratio and the backwash procedure is required to achieve reliable results with this method. Of the methods listed at 40 CFR 136 for surfactants, the most common are EPA 425.1 and Standard Methods 5540C.

Whole Effluent Toxicity

Although not strictly an analytical method, the whole effluent toxicity (WET) test deserves some discussion as a method-defined parameter. The WET test exposes either fresh water or salt water aquatic organisms (vertebrates, invertebrates, and plants) to mixtures of wastewater effluent and surface water, surface water alone, or effluent alone. Fresh water WET tests are used for discharges to fresh water streams, and salt water WET tests are typically used for discharges to estaurine or salt water bodies (even if the effluent itself is freshwater).

WET tests are either acute (short term impacts, typically lethality) or chronic (an estimate of longer term impacts, typically but not always sublethal). The test measures include survival, growth in weight, and reproduction. The test measures all physical and chemical components of an aqueous matrix that can cause an adverse effect on the test species and includes interactive effects of different chemicals and physical properties of the samples (synergism, antagonism) — hence, the name "whole" effluent toxicity. The method references for aquatic toxicity listed at 40 CFR 136 are, for acute toxicity, Section 9 in EPA/600/4-90/027F (EPA 1993b), and for chronic toxicity, EPA 1000.0-1009.0 (EPA 1994a, 1994b).

There are two general types of WET tests that are widely used in NPDES permits and applications: (1) the static acute toxicity test for 24 to 96 hours, where the endpoint of the test is organism survival; and (2) the short-term

static renewal chronic test for 7 days, where the test endpoint may be survival, growth, and/or reproductive success. These tests are termed static because the test organisms are exposed to the effluent:dilution water mixture in a chamber, which is manually filled at the start of the test. The static renewal test involves replacing the water in the test chambers several times during the exposure period.

Most WET tests are run using what are known as serial dilutions of effluent and dilution water, for example, 10%, 20%, 30%, and so on. The serial dilutions are designed to estimate statistically what effluent dilution will be lethal to or will inhibit growth or reproduction of the test organisms. When lethality is tested, the term "lethal concentration" or LC is used. An LC_{50} is the concentration (dilution) of effluent which results in death of 50% of the organisms. When inhibition of biological processes such as growth or reproduction is tested, the term "inhibition concentration" or IC is used. For example, an IC_{25} for reproduction is the effluent concentration which causes a 25% decrease in reproduction.

A control consisting of 100% receiving water or synthetic dilution water is run with every dilution series. The dilution of effluent and receiving water (or synthetic dilution water) used in the WET tests is typically established based on the allowable mixing zone dilution. Receiving water usually is the dilution water; typically, synthetic dilution water is used only when the receiving water exhibits toxicity to the test organisms and cannot be used as a test control.

The WET test procedures, including sample collection and preservation requirements, are described in several EPA manuals that are referenced in 40 CFR 136. These manuals are:

- "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms," 4th edition, EPA/600/4/90/027F, Office of Research and Development, Washington, D.C., 1993.

- "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms," 3rd edition, EPA-600-4-91-002, Office of Research and Development, Washington, D.C., 1994.

- "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine Organisms," 3rd edition, EPA-600-4-91-003, Office of Research and Development, Washington, D.C., 1994.

These manuals contain laboratory procedures for the WET tests as well as the sample collection and preservation methods. EPA will allow laboratories flexibility in WET test conditions, as long as the conditions are within the acceptable ranges specified in the methods. For example, in one case study, a discharger with a high salinity effluent found it necessary to culture the test organism (mysid shrimp) at the maximum salinity allowed in the test method in order to obtain reproducible and accurate WET test results.

In addition to these static and static renewal WET tests, there are protocols for continuous flow-through aquatic toxicity tests, which can also be used to determine effluent toxicity. These continuous flow-through tests mix effluent and dilution water at a series of dilutions in multiple test chambers containing the test species. Because the flow-through tests are more representative of a flowing water body, and reflect variations in effluent and receiving water quality, they provide more accurate measurements of effluent toxicity potential. However, they are very labor-intensive and expensive compared to the static and static renewal tests, and are not conducive to large-scale testing of multiple effluents such as required for the NPDES program. Therefore, this type of WET test is not routinely conducted for permit applications or permit compliance monitoring, although some states do require such testing for certain effluents and discharge locations. Such testing is more likely if the receiving water is considered to be very sensitive.

Chapter 9

Statistical Calculations

This chapter discusses typical statistical terms and calculations likely to be encountered in environmental sample analyses and laboratory reports. It begins with an introduction to data distributions. Three of the most common statistical terms in laboratory analyses are discussed next—precision, bias, and accuracy. A discussion of outliers, nondetects (censored data), and EPA's method detection limit calculations follows.

Data Distributions

How values in a data set are distributed—for example, bell-shaped (normal curve), skewed to one extreme or the other, bimodal—define what statistical parameters will be calculated and what statistical tests are valid. The most common data distributions used with environmental data are the normal and lognormal distribution.

The normal distribution has a classic bell shape as shown in Figure 9-1. When data fitting a normal distribution are plotted on a probability plot, the data will appear as a fairly straight line as shown in Figure 9-2. Some deviation from the line is typical and acceptable; however, extreme "bending" of the line near the upper or lower end (or both) indicates that the normal distribution may not be a good fit.

Data sets that do not fit a normal distribution may be "transformed" into one that does. The most common transformation is to take the logarithm of each value, typically the natural (base e) logarithm. Data sets that are "normalized" in this way are called lognormal. A quick way of checking if a data set is lognormal is to plot the data on a probability plot with the vertical axis on log 10-scale (Figure 9-3). With the vertical axis on log-scale, no transformation of the values is necessary for the plot; however, statistical calculations must be based either directly or indirectly on the transformed data.

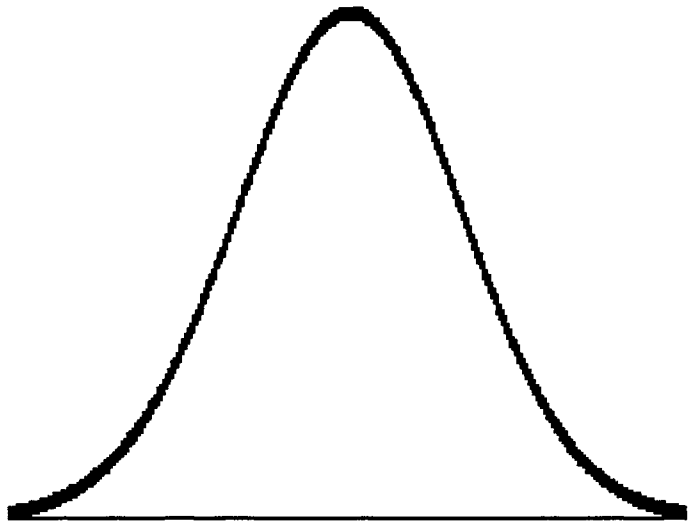


Figure 9-1. Bell-Shaped Normal Distribution

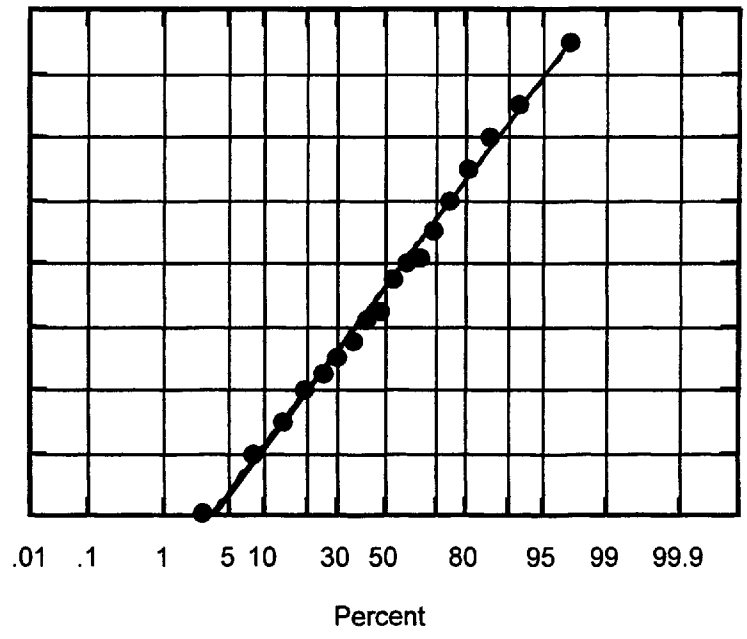


Figure 9-2. Probability Plot (Normal Scale)

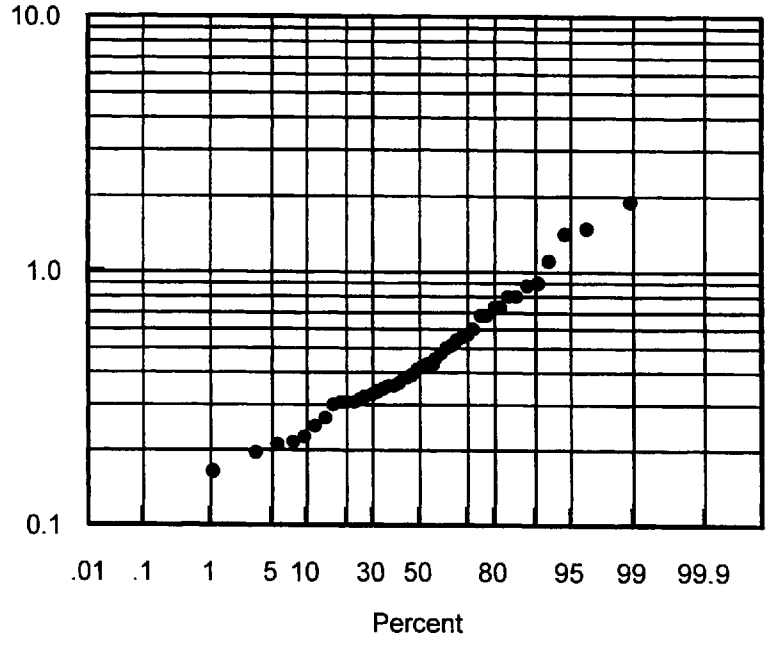


Figure 9-3. Probability Plot (Log Scale)

Precision

NOTE
Being precise is not the same as being accurate!

Precision reflects the difference in repeated measurements and represents random error. A distinction must be carefully drawn between precision and accuracy. In analytical terms *being precise is not the same as being accurate!* For example, a laboratory may have great precision and get essentially the same value with repeated measurements of the same sample. However, if this value is only half of what the true value is, the laboratory is not very accurate.

Two sets of data from two different laboratories are plotted in Figure 9-4. The set of data from Laboratory A on the left side of the figure shows more scatter compared to the data on the right side from Laboratory B. Laboratory A's precision is not as good as Laboratory B's.

There are different ways to express precision. Precision may be reported as a standard deviation, relative standard deviation, relative percent difference, or control limits (tolerance limit or confidence limit). Sometimes precision is only reported as the range in duplicate analyses or the duplicate analyses are reported merely as individual values.

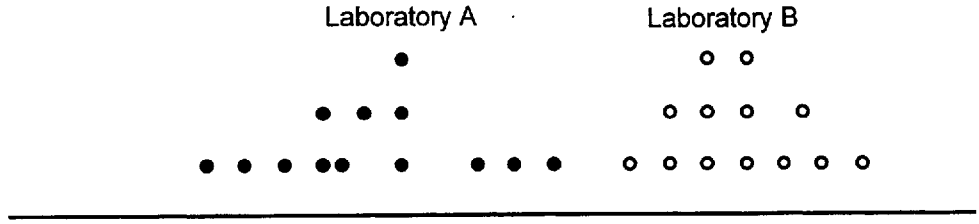


Figure 9-4. Comparing Precision of Data Sets from Two Different Laboratories

Standard Deviation

The standard deviation is a measure of the difference in multiple values compared to the average of all the values. In equation form, the standard deviation, s, is:

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

where: $\bar{x}$ = mean of all values
x_i = individual values from i = 1...n

or when n = 2,

$$s = \frac{|x_1 - x_2|}{\sqrt{2}}$$

where: x_1 = first data value
x_2 = second data value

Precision statements in laboratory reports are usually based on duplicate samples, so that n = 2.

Coefficient of Variation

The coefficient of variation (COV) is a way of expressing the standard deviation. The COV is the standard deviation divided by the mean:

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

The COV is a useful way of expressing the standard deviation when the magnitude of the standard deviation changes with the mean. For example, the standard deviation at concentration levels near 10 mg/L might be 2 mg/L and at concentration levels near 100 mg/L, it might be 20 mg/L. In this example, the ratio of the standard deviation to the mean, or the COV, remains constant over the concentration range (COV equals 0.2).

Relative Standard Deviation

The relative standard deviation (RSD) is the standard deviation divided by the mean, expressed as a percentage.

$$RSD = \frac{s}{\bar{x}} \times 100\%$$

The RSD and COV are similar expressions of the standard deviation and in common usage these two terms often are used interchangeably.

Relative Percent Difference

The relative percent difference or RPD is the difference between two duplicate values divided by the average, expressed as a percentage:

$$RPD = \frac{|x_1 - x_2|}{(x_1 + x_2)/2} \times 100\%$$

Tolerance Limit

A tolerance limit is a control limit on an *individual* value. It is different from a confidence limit, which is a control limit on the *mean* value. Control limits have both upper and lower bounds.

To determine if precision is acceptable, control limits are placed on the RPD. In placing control limits on RPD, however, the lower value is not a concern, because as the RPD approaches zero, precision only improves. Thus, only the upper limit need be calculated.

Tolerance limits for RPDs may be set as both warning limits and action limits. The upper warning limit (WL) is typically calculated as the mean value plus two standard deviations. The upper action limit (AL) is typically calculated as the mean value plus three standard deviations. In equation form, these limits are:

$$WL = \bar{x} + 2s$$

$$AL = \bar{x} + 3s$$

The tolerance limit for precision, if given in the laboratory report, will not include the data used to calculate it. The following example is given to illustrate how a tolerance limit would be calculated for precision.

EXAMPLE - Precision Tolerance Limit

Analyte: benzene
Method: EPA 624

Relative percent differences for most recent quality control set (%):

5	6	2	3	8	9	8
10	4	1	6	5	4	9

Calculated average: 5.714
Standard deviation: 2.785

Upper action control limit:

AL=5.714+(3)(2.785)=14.069%

Confidence Limit

A confidence limit is a control limit on a mean value. It is different from a tolerance limit, which is a control limit on an individual value. As with tolerance limits, confidence limits for mean values may be set as both warning and action limits. The difference between the calculation of a tolerance limit and a confidence limit is in the standard deviation. In a confidence limit the standard deviation is adjusted to reflect a distribution of means. Equations for the WL and AL for confidence limits are:

$$WL = \bar{x} + 2\frac{s}{\sqrt{n}}$$

$$AL = \bar{x} + 3\frac{s}{\sqrt{n}}$$

The following example is given to illustrate how a confidence limit would be calculated for precision.

EXAMPLE - Precision Confidence Limit

Analyte: benzene
Method: EPA 624

Long-term average RPD:	5.0%
Standard deviation estimated from 20 individual samples:	2.9%

Upper action control limit on mean RPD:

$$AL = 5.0 + 3 \times \frac{2.9}{\sqrt{20}} = 6.945\%$$

Precision Statements

The following is an example of how precision may be expressed in a laboratory report and how these calculations are made.

EXAMPLE - Precision Calculations

Data in laboratory report:

Analyte:	benzene
Method:	EPA 624
QC Lot:	25 AUG 94 - 1A
Units:	µg/L
Spiked Value:	50
Sample 1:	46.9
Sample 2:	47.1

Average of Sample 1 and Sample 2:

$$\bar{x} = \frac{46.9 + 47.1}{2} = 47.0 \quad g/L$$

Precision expressed as range in measured values:

46.9 - 47.1 µg/L

Precision expressed as relative percent difference (RPD):

$$RPD = \frac{|46.9 - 47.1|}{47.0} \times 100\% = 0.4\%$$

EXAMPLE - Precision Calculations, *continued*

Precision expressed as standard deviation:

$$s = |46.9 - 47.1| \times \sqrt{0.5} = 0.1414 \quad g/L$$

Action control limit for RPD (stated without data used to calculate it):

14.0%

Bias

Bias in laboratory analyses is what it sounds like—it is a systematic error in measurement that produces results that are persistently too high or too low with respect to the true value. When bias produces results that are too high, it is called positive bias. When the results are too low, the bias is negative.

Either type of bias can be a problem. For example, wastewater effluent monitoring data that are biased high may indicate false exceedances of wastewater discharge permit limits. Conversely, if a wastewater discharge permit limit were based on wastewater characterization data that were biased

too low, once the bias is discovered and removed, the permit limit may prove too restrictive and exceedances may then be observed.

Bias in sample analyses can arise from many different sources. Examples of these sources are listed in Table 9-1.

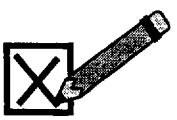
NOTE
Bias is more likely to be discovered when multiple samples, routine monitoring, or multiple laboratories are involved.

Table 9-1. Examples of Sources of Bias in Sample Measurement

Process inefficiencies (chemical reactions, extractions, cleanup)
Analytical interferences
Analyst techniques (operator bias)
Matrix effects
Method calibration
Persistent sample contamination
No correction for method blanks
Shifts in instrument response or operation
Tolerance adjustments of equipment
Theoretical basis for method

Bias in a single sample may be hard to recognize because there is no trend in the data to indicate a persistent problem. Bias is more likely to be discovered when multiple samples, routine monitoring, or multiple laboratories are involved. For example, suppose oil and grease values from routine wastewater effluent monitoring suddenly increase and persist during a time when there is no apparent change in wastewater treatment performance. When sampling techniques are investigated, it is discovered that the sample bottles were not being cleaned properly, and the bottles contaminated the samples.

Possible sources of bias should be investigated and corrected so that sample analyses are as accurate as possible. Bias in sample analyses may be indicated by events or conditions noted in Table 9-2. It is important to remember that the situations listed in the table may only suggest that bias is present. If the situation does not *persist*, it reflects random error, not systematic error, which is bias. Part IV also contains a Checklist based on this table, **Indications of Analytical Bias**. This Checklist can be used as an initial check for analytical results that are consistently too high or too low.



See the checklist in Part IV, **Indications of Analytical Bias.**

Table 9-2. Situations that May Indicate Sample Analysis Bias

Shift in results with no apparent change in sample characteristics
Significant difference in results in split samples sent to different laboratories
Significant difference in results when a different laboratory begins to analyze samples
Recovery QA/QC data submitted with laboratory report uniformly high or low with particular type of analysis
Shift in results with change in analytical method

Bias can be relative (proportional) or constant. For example, if results consistently average 80% of the true value, the bias is proportional. If results are offset from the true value by a constant amount, the bias is constant. Both types of bias can be present in sample analysis. The data shown in Figure 9-5 illustrate the combined effects of relative and constant bias. The figure is a plot of measured versus true values. The slope of the data line reflects relative bias and the intercept reflects constant bias. Constant bias is of concern with trace and low-level measurement because its effects can be large in this region. Relative bias is of more concern when concentrations are higher.

Accuracy is another term that is related to bias; however, bias and accuracy are not the same and care should be taken not to confuse them. Accuracy and its related term, recovery, are discussed in the next section.

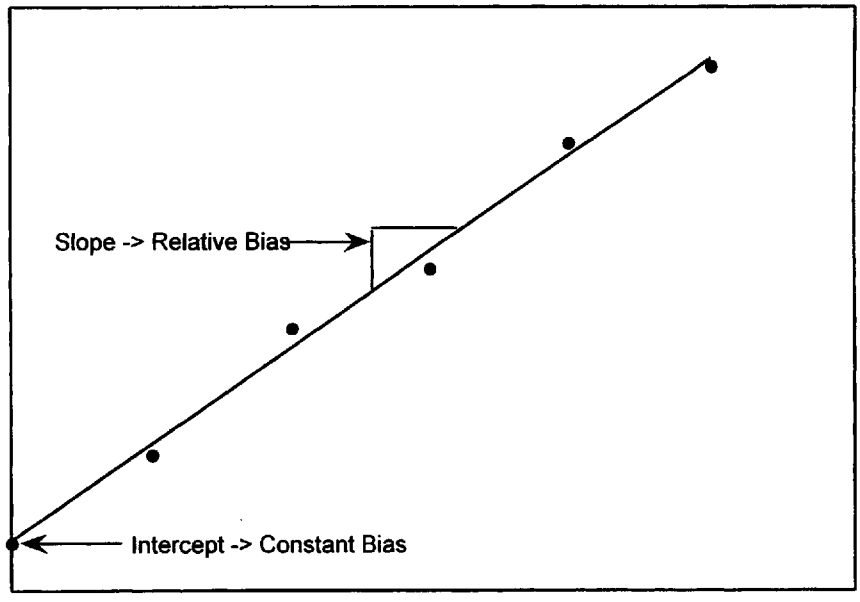


Figure 9-5. Relative and Constant Bias in Sample Analyses

Accuracy and Recovery

Accuracy and recovery are used interchangeably in laboratory reports. Recovery reflects how much of the material was found or recovered compared to what is contained or added. Recovery is calculated for spiked samples. A spiked sample can be a standard solution, which is prepared by spiking (adding) a known amount of a particular analyte to reagent water. A spiked matrix sample is one in which the spike is either added to the sample being analyzed, or to another sample with similar characteristics. When an unspiked sample does not contain the analyte, recovery as a percentage, R, is calculated for a spiked sample as:

$$R = \frac{x}{S} \times 100\%$$

where:

x = measured concentration
S = spiked concentration

When the unspiked sample contains the analyte initially, recovery is calculated by taking the difference between the spiked, x_2, and unspiked value, x_1:

$$R = \frac{x_2 - x_1}{S} \times 100\%$$

The following example shows both types of recovery calculations.

EXAMPLE - Recovery Calculations

Data in laboratory report:

Analyte:	chromium
Method:	ICP-AT
QC Lot:	25 AUG 94 - T
Units:	mg/L
QC Spike:	0.20
QC Sample 1 Result:	0.193
QC Sample 2 Result:	0.192
Matrix Sample:	0.362
Spiked Matrix Sample:	0.549

Average recovery of QC samples:

QC Sample 1

$$R_1 = \frac{0.193}{0.20} \times 100\% = 96.5\%$$

QC Sample 2

$$R_2 = \frac{0.192}{0.20} \times 100\% = 96.0\%$$

Average of Samples 1 and 2

$$\frac{96.5\% + 96.0\%}{2} = 96.25\% \text{ (rounded to 96\% in report)}$$

Recovery of matrix spiked sample:

$$R = \frac{0.549 - 0.362}{0.20} \times 100\% = 93.5\%$$

Accuracy is not the same as bias. As discussed in **Bias**, bias is systematic error. Accuracy is affected by both systematic and *random* error. The relationship between accuracy and bias and how they also relate to precision is explained in the next section.

Relationships Among Precision, Bias, and Accuracy

NOTE
Bias and accuracy are related, but different terms and should not be confused. Accuracy is the combined effect of bias and imprecision.

To be able to evaluate the quality of laboratory data properly, it is important to understand the relationship and differences among precision, bias, and accuracy. For example, a laboratory can be very precise, but very inaccurate, when its recoveries are consistently very low. Another laboratory can be very accurate in the long-term, but its individual results are so variable (imprecise) that they are not reliable.

Accuracy is how close a measured value compares with the true value. Accuracy is the combined effect of precision and bias. Because precision (or really imprecision) is random error and bias is systematic error, accuracy is the combined effect of random and systematic error. A simple example may illustrate the point. If the long-term recovery associated with a particular metals analysis is 95% because of process inefficiencies in chemical reactions, the method is biased low. On any given day, the laboratory equipment is subject to some random error in adjustment. Thus, when an individual sample is analyzed, the accuracy of its result is affected by the inherent bias in the method and the randomness of other error sources that day.

By definition, random errors are unpredictable and vary in their deviation from the true value, that is, making the measured result high or low compared to the true value. Over the long-term, random errors average out, such that their long term effect is zero. Thus, the long-term recovery performance of a method calculated from a large data set is a measure of the bias of the method.

Figure 9-6 shows four data sets that have different combinations of precision, accuracy, and bias. These are not all the possible combinations, but are given here to help explain the relationship among the three terms. Data Set 1 in Figure 9-6 is what everyone strives for—very precise measurements that are also very close to the true value. Data Set 2 is the other extreme—very inaccurate with poor repeatability in measurement (poor precision or a great deal of imprecision). Data Set 3 is a different combination—fairly good precision and little bias, which is shown by the small deviation of the average from the true value. Data Set 4 also shows fairly good precision, but its results are more biased, producing less accurate individual measurements than Data Set 3.

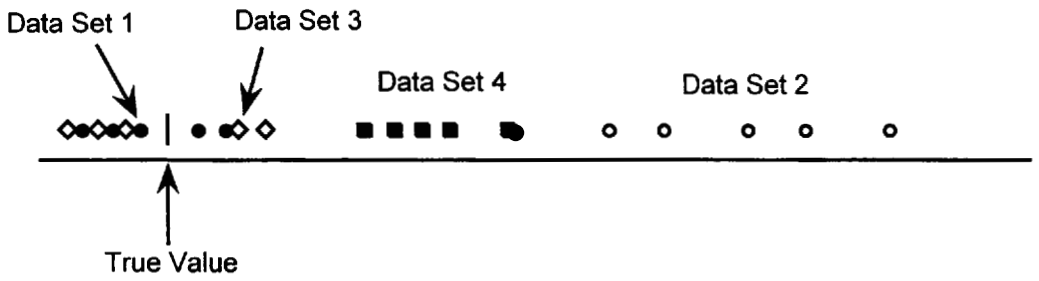
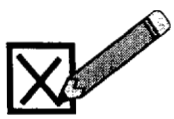


Figure 9-6. Relationships Among Precision, Accuracy, and Bias

Outliers

Outliers are values that appear to "lie outside" the normal range of expected values. Outliers may be truly valid results representing unusual, but real conditions affecting a sample, or they may result from errors that can and should be corrected when possible. An example of a real condition may be a rapid increase in organic load on a wastewater treatment facility that causes a large increase in effluent BOD concentration. Examples of errors, not all of which may be correctable, are shown in Table 9-3. This table has also been converted to a Checklist in Part IV, **Errors That Can Result in Outliers.**



See the checklist in Part IV, **Errors That Can Result in Outliers.**

Table 9-3. Examples of Errors that Can Result in Outliers

Calculation errors (dilution factor, wrong number entered)
Transcription errors (transposition, wrong entry, decimal misplaced)
Sample contamination
Wrong sample analyzed or reported
Different analytical method used
Wrong reading of instrument
Analytical step left out or done improperly
Incorrect method calibration

When an outlier appears in a data set, a decision must be made whether it stays or is omitted from certain data analyses. Careful consideration should be given on this point and never should a value be deleted merely on the basis of statistical tests or "gut feeling." Suspect values should be investigated by reviewing possible sources of error in sample collection, handling, and analysis. The discussion in Section 4, **Problems Requiring Immediate Response** and **Are the Results Reasonable?** provides more specific guidance on investigating possible outliers.

NOTE
Deletion of outliers must be considered carefully. Suspect values should be investigated by reviewing possible sources of error in sample collection, handling, and analysis.

Outliers can be identified by simple comparison with the normal, or expected range in values. There are also a number of statistical tests and methods available to identify outliers (see Part IV, **References and Acronyms**). Examples of these tests are:

- Grubbs' *T* Test
- Dixon's Test
- Youden's Rank Test for Laboratories (comparing split samples from multiple laboratories).

Nondetects and Censored Data

Analyses of environmental samples at very low or trace concentrations often result in *nondetectable* or *less than values*, for example, "ND," "BDL," or <0.0002 mg/L. Data sets that include nondetectable data are referred to as *censored.* Because statistical parameters, even something as simple as the mean, cannot be calculated directly when some of the data are NDs or less than values, special statistical techniques must be used. The better of these techniques are somewhat complicated and therefore will not be discussed in detail here; however, interested readers can find sources in Part IV, **References and Acronyms**. Two of the more common techniques that have been used by EPA are Cohen's method and the modified delta-lognormal distribution.

These and a few other techniques are described briefly in the following sections.

Substitution

The simplest technique for handling "less than values" in data calculations is to substitute the censored data with either zero or one-half the reported limit. For example, if there are two less-than values in a data set of 10 analyses (<5 and <10), both values may be substituted by zero, or <5 may be substituted by 2.5 and <10 may be substituted by 5. This simple technique does have drawbacks. When a large portion of a data set is censored, this form of substitution can seriously distort the mean and variance. EPA suggests that substitution with one-half of the reporting limit not be used with data sets where more than 15% of the values are censored (EPA 1989). One study of censored data techniques concluded that substitution should not be used to calculate variances on which probabilistic statements are made, such as confidence intervals (NCASI 1991). As a general rule, if the data set is very large, say more than 100 values, and only one or two results are censored, substitution should be acceptable.

Median

The median of a censored data set can be used to estimate its mean if less than half of the results are censored and the data are expected to be normally distributed or symmetric around the mean. A disadvantage of this technique is that it does not provide an estimate of the variance of the data set.

Modified Delta-Lognormal Distribution

The modified delta-lognormal distribution technique is a way of estimating the mean and variance of a censored data set. The calculations are based on the fraction of data that is censored and the assumption that the rest of the data, the noncensored part, follows a lognormal distribution. This technique was used by EPA to develop effluent guideline limitations for the chemical and pesticide industries. The original version of the technique was limited to data sets that had the same censored values, for example, all the NDs were <25. A later version of the technique allowed different censored values, for example, <5, <10, <25 (EPA 1995).

Cohen's Method

Cohen's method for estimating the mean and variance of a censored data set assumes that the data are normally distributed (Cohen 1959, 1961). In its original form, it is limited to data sets that have the same censored values. With data sets that have different reporting limits or censored values, one can use the highest of the reporting limits in the calculations. Doing so reduces somewhat the accuracy of the data set, but if there are few censored data or the reporting limits are similar, this modification should be acceptable. Cohen's method involves simple calculations, but is complicated by multiple steps and lookup tables.

EPA Method Detection Limit

EPA's technique for calculating an MDL is given in Appendix B at 40 CFR 136. The calculations are simple. First the standard deviation, S, of the n sample results is calculated. Then the MDL is calculated by the following equation.

$$MDL = t_{(n-1,1-\alpha=0.99)}S$$

where $t_{(n-1,1-\alpha=0.99)}$ = the Students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

EPA's Appendix B provides values of Students' t for selected values of n (number of samples).

This calculation produces an MDL for a single laboratory (intralaboratory MDL). If one wants to estimate an interlaboratory MDL representing the overall performance of a group of laboratories, the above equation can be used after substituting the single laboratory standard deviation with the "pooled" standard deviation from the group of laboratories. A pooled standard deviation, S_p, is calculated by the following equation.

$$S_p = \sqrt{\frac{\sum_{i=1}^{m}(n_i - 1)S_i^2}{\sum_{i=1}^{m}(n_i - 1)}}$$

where m = number of laboratories and
n_i = number of samples from laboratory i

The MDL calculations are shown in the following example.

EXAMPLE - MDL Calculations

MDL for Individual Laboratory

Analyte: benzene
Method: EPA 602
Method MDL: 0.2 µg/L
Matrix: Effluent from wastewater biological treatment plant

Sample results: 0.23, 0.36, 0.44, 0.35, 0.55, 0.38, 0.41 µg/L

Standard deviation: 0.09720 µg/L
Students' t: 3.143
Matrix-specific MDL: 3.143(0.09720)=0.3 µg/L

MDL for Group of Laboratories

Laboratory Number	Number of Samples	Standard Deviation (µg/L)
1	7	0.0972
2	8	0.1129
3	7	0.0845

Pooled Standard Deviation:

$$S_p = \left[\frac{6(0.09720)^2 + 7(0.1129)^2 + 6(0.0845)^2}{6+7+6}\right]^{0.5}$$

$= 0.09967$

Students' t for 19 degrees of freedom is 2.539

Interlaboratory matrix-specific MDL:

MDL=2.539(0.09967)=0.25 µg/L

The interlaboratory MDL is lower than the MDL for Laboratory 1 because it is based on a much larger number of samples and the Students' t value is thus, smaller. As

shown by the next data set, the interlaboratory MDL can be greater than the intralaboratory (single laboratory) MDL when the pooled standard deviation is much larger than the single analyst standard deviation.

Laboratory Number	Number of Samples	Standard Deviation (µg/L)
1	7	0.0972
4	8	0.2146
5	7	0.1542

Pooled Standard Deviation:

$$S_p = \left[\frac{6(0.09720)^2 + 7(0.2146)^2 + 6(0.1542)^2}{6+7+6}\right]$$

Students' t for 19 degrees of freedom is 2.539

Interlaboratory matrix-specific MDL:

MDL=2.539(0.1657)=0.42 µg/L

Part III
References and Acronyms

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Acronyms and Abbreviations

ACS	American Chemical Society
AOAC	Association of Official Analytical Chemists
APHA	American Public Health Association
ASCE	American Society of Civil Engineers
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene, xylenes
BOD	Biochemical oxygen demand
CBOD	Carbonaceous biochemical oxygen demand
CD	Conventional detector
CFC	Chlorinated fluorocarbon
CFR	Code of Federal Regulations
COD	Chemical oxygen demand
COV	Coefficient of variation
CRDL	Contract required detection limit
DBC	Dibutylchlorendate
DCP	Direct current plasma
DCS	Duplicate control sample
DMR	Discharge monitoring report
DQO	Data quality objectives
EPA	Environmental Protection Agency
FR	Federal Register
GC	Gas chromatography
GFAA	Graphite furnace atomic absorption
HCl	Hydrochloric acid
HEM	Hexane extractable material
HPLC	High performance liquid chromatography
H_3PO_4	Phosphoric acid
H_2SO_4	Sulfuric acid
IC	Ion chromatography
ICP/AES	Inductively coupled plasma/atomic emission spectrometry
IDL	Instrument detection limit
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of detection
LOQ	Limit of quantitation
MBAS	Methylene blue active substances
MTBE	Methyl-tert-butyl ether
MAL	Minimum analytical level
MDL	Method detection limit
mg/L	Milligrams per liter
ML	Minimum level

MQL	Minimum quantification level
MS	Mass spectrometry
NaOH	Sodium hydroxide
$Na_2S_2O_3$	Sodium thiosulfite
ND	Not detected
NPDES	National Pollutant Discharge Elimination System
O&G	Oil and grease
OH	Hydroxy
PQL	Practical quantitation limit
QA/QC	Quality assurance/quality control
QC	Quality control
RCRA	Resource Conservation and Recovery Act
RPD	Relative percent difference
RSD	Relative standard deviation
SGT-HEM	Silica gel treated n-hexane extractable material
TCMX	2,4,5,6-Tetrachloro-meta-xylene
TCLP	Toxic Characteristic Leaching Procedure
TDS	Total dissolved solids
THC	Thin layer chromatography
TIC	Tentatively identified compounds
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
TS	Total solids
TSD	Technical support document
TSS	Total suspended solids
µg/L	Micrograms per liter
USGS	U.S. Geological Survey
WEF	Water Environment Federation
WET	Whole effluent toxicity

Part IV
Checklists

Checklist

Initial Review of Laboratory Report

Use this checklist to review a laboratory report initially, to see if there are any immediate problems that require followup with the laboratory or resampling. Although laboratory reports may look different, this checklist covers items that most reports will or should have.

Sample Information

- ❑ Do all sample descriptions and identification codes match information on the chain of custody form?
- ❑ Do all sample dates and times match information on the chain of custody form?
- ❑ Were all samples received within required/recommended holding times?
- ❑ Were all samples analyzed as requested?

Analyses

- ❑ Are all sample preparation dates within required/recommended holding times?
- ❑ Are all sample analysis dates within required/recommended holding times?
- ❑ Were all samples analyzed with appropriate/approved methods?
- ❑ Do all analytical methods match those that were specified?
- ❑ Are all requested analytes reported?
- ❑ Are all analyte forms clear (total/dissolved, wet/dry weight, as "N," as "P," etc.)?
- ❑ Are all measurement units clear and appropriate for the sample types (mg/L, mg/kg, etc.)?
- ❑ Do all detection/analytical limits meet specifications?

Quality Control and Quality Assurance

- ❑ Are all chain of custody forms included, completed properly, and signed by laboratory personnel?
- ❑ Are QA/QC data included?
- ❑ DO QA/QC data meet performance criteria?
- ❑ If there were QA/QC problems, were they resolved?

Checklist

QA/QC Items for Initial Discussion with Laboratory

Use this checklist to review with a laboratory which QA/QC procedures are normally used, whether any additional QA/QC work is required for a particular project, and what it will cost.

Type of QA/QC Samples

- ❑ Matrix spikes and matrix spike duplicates. Frequency?_____
- ❑ Duplicate laboratory control samples (QC standards). Frequency?_____
- ❑ Sample duplicates. Frequency?_____
- ❑ Blank samples. Frequency?_____

Detection and Reporting Limits

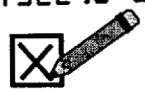
- ❑ Can laboratory provide list of detection/reporting limits for requested analytes?
- ❑ Does laboratory preview list of analytes and required detection/reporting limits, and inform client when certain limits cannot be achieved?
- ❑ Does laboratory have procedures to try to eliminate matrix interference when detection/reporting limits cannot be met?

Problem Resolution

- ❑ If sample container is received broken or damaged, is client contacted immediately?
- ❑ If sample holding time is exceeded, is client contacted immediately?
- ❑ If detection/reporting limits cannot be met because of matrix interference, is client contacted immediately?
- ❑ If there is a QA/QC problem, is client contacted immediately?

Costs

- ❑ When laboratory errors occur, is sample reanalyzed at no additional cost?
- ❑ If agreed upon QA/QC requirements are not met, is payment for that particular analysis required?
- ❑ When additional QA/QC is required for a particular project, how is the additional cost determined?

Checklist 

QA/QC Data in Laboratory Report

Use this checklist before you send samples to the laboratory to identify which QA/QC data are to be included in the laboratory report. After the laboratory report is received, use the checklist to verify that all of the requested QA/QC data are included in the report.

This checklist contains a recommended "minimum" QA/QC list, as well as additional QA/QC that may be needed for a particular project.

Recommended Minimum QA/QC Information

- ❑ Chain of custody form with documentation of sample receipt by laboratory
- ❑ Spiked standards or laboratory control samples
- ❑ Laboratory control sample duplicates/replicates
- ❑ Method blanks
- ❑ Indication of QA/QC results outside allowable limits
- ❑ Identification and signature of reviewers

Additional QA/QC Information

- ❑ Recovery results
  - __ Matrix spikes __Surrogate spikes
  - __Internal standard spikes __Isotope spikes
- ❑ Precision results
  - __Duplicates/replicates of client samples
  - __Matrix spike duplicates __Blind duplicates
- ❑ Sample blank results
  - __Field blanks __Trip blanks __Equipment blanks

Checklist

Data Quality Objectives

This checklist can be used to outline simple Data Quality Objectives (DQOs) for a project. A simple DQO plan would be an analytical schedule for samples in a table format, showing analytes, minimum analytical limits, and reasons for analysis (wastewater permit application, ground water monitoring, etc.). A narrative description of project objectives and activities can also be included in the DQO plan. The DQO plan can then be given to the laboratory to help it understand the project analytical requirements.

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.

Checklist

Selecting a Laboratory

Use this checklist to help in selecting a laboratory. The checklist can also be used to identify a "short list" of laboratories for potential work.

Required Analyses (also see Checklist, **Developing an Analytical Schedule**)

- ❑ Can the laboratory perform all required analyses in-house or will certain analyses be performed by subcontractor or "sister" laboratories?
- ❑ If a subcontract laboratory is used, does the original laboratory inform the client prior to having the analyses performed by the subcontractor?

Staffing

- ❑ Does the laboratory staff include degreed chemists (PhD, MS, BS)?
- ❑ If analysts are not degreed chemists, do they have degrees in related or technical fields?
- ❑ Does the number of analysts appear sufficient for the laboratory's size?
- ❑ Does the laboratory have a dedicated supervisor or manager?
- ❑ Is there an onsite QA/QC manager?

Support Services

- ❑ Can the laboratory provide sample bottles, sample preservatives, chain of custody forms, shipping containers, local pickup/delivery?
- ❑ Can the laboratory provide field personnel to collect samples?

Recordkeeping and Reporting

- ❑ Do laboratory reports appear neat, well-organized, easy-to-read, and complete?
- ❑ Do laboratory reports include at least the usual level of detail (also see Checklists, **Initial Review of Laboratory Report** and **QA/QC Data in Laboratory Report**)?
- ❑ Can the laboratory prepare customized reports, for example, with additional QA/QC data?
- ❑ Does the laboratory's recordkeeping system appear neat, well-organized, and complete (also see Checklist, **Evaluating Laboratory Recordkeeping**)?
- ❑ Does the laboratory have a sample storage/archiving system?

Checklist

Selecting a Laboratory, *continued*

Reputation and Size

- ❑ Can the laboratory provide client references?
- ❑ Are the laboratory's client references satisfied with its work?
- ❑ Has the laboratory been in business long enough to appear stable?
- ❑ If the laboratory is small, does it have the capabilities to perform the analyses?
- ❑ If the laboratory is part of a larger organization, does the larger organization have a good reputation and is it financially sound?

Costs

- ❑ Are the analytical costs within the normal range of other laboratories?
- ❑ Will the laboratory negotiate cost discounts for a large number of analyses or guaranteed, periodic analyses?

Checklist

Developing an Analytical Schedule

Use this checklist to set up an analytical schedule (analytes, detection limits, number of samples, etc.). This schedule will help you make sure that all analyses are identified and whether there are any problems with sampling or analysis. This schedule can also be given to the laboratory to ensure that the correct analyses are performed.

Analytes

- ❑ List all analytes required for:
  - ❑ NPDES/state wastewater permit compliance monitoring.
  - ❑ NPDES/state wastewater permit application.
  - ❑ Other regulatory program/permit.
  - ❑ Material/waste characterization, for example, those affecting handling or treatment.

Number of Samples and Sample Frequency

- ❑ Identify total number of samples and sampling frequency required for:
  - ❑ NPDES/state wastewater permit compliance monitoring.
  - ❑ NPDES/state wastewater permit application.
  - ❑ Other regulatory program/permit.
  - ❑ Material/waste characterization.

Sample Containers and Preservation

- ❑ Identify sample container requirements (plastic, glass) for each analyte.
- ❑ Identify preservation requirements for each analyte, particularly chemical preservatives.

Sample Type

- ❑ Identify sample type (grab, composite) for each type
- ❑ Identify any of the following analytes that normally require grab samples:
  - ❑ pH, temperature, dissolved oxygen, chlorine, volatile organics, oil and grease, coliforms, total phenols, sulfites, sulfides, and hexavalent chromium

Checklist

Developing an Analytical Schedule, *continued*

Sample Holding Times

- ❑ Identify sample holding times for each analyte.
- ❑ Identify any of the following analytes that have relatively short holding times:
  - ❑ pH, coliforms, aquatic toxicity, chlorine, hexavalent chromium, nitrate (not nitrate and nitrite combined), dissolved oxygen, sulfite, surfactants, turbidity

Detection/Quantification Limits

- ❑ Identify most restrictive detection/quantification limits among all analytical requirements (permit compliance monitoring, permit application, etc.).
- ❑ Send laboratory detection limit requirements for review.
- ❑ Can laboratory meet required detection limits?

Analytical Methods

- ❑ Identify any analytical methods specified by regulations, permit, or project.
- ❑ For each analyte for NPDES monitoring and for which there is no analytical method specified in the permit, identify approved methods at 40 CFR 136.
- ❑ Identify appropriate methods for nonNPDES analyses.
- ❑ Select one or more analytical methods for each analyte, based on knowledge of the waste matrix and the required quantification/detection limits. Preliminary screening sample may be needed to define matrix characteristics.

Checklist

Identifying Parts of a Laboratory Report

Use this checklist to review the general contents of a laboratory report or to list what information you want in a laboratory report. If you are evaluating a group of laboratories for potential work, this checklist can also be used to compare each laboratory's level of detail.

Client Identification

- ❑ Mark which of the following items are included as client identification:
  - ❑ Client name, client address, client phone number, client contact, project title or description, facility site address

Sample Information

- ❑ Sample description
- ❑ Sample matrix type
- ❑ Sample identification code given by client
- ❑ Sample identification code given by laboratory
- ❑ Sample collection date and time
- ❑ Date of receipt in laboratory

Analyses

- ❑ Method reference codes and descriptions
- ❑ Dates of sample preparation steps
- ❑ Date of analysis
- ❑ Analyte or parameter name
- ❑ Analytical result
- ❑ Analytical units
- ❑ Detection, quantification, or reporting limit
- ❑ Analytical notes and explanations with key codes
- ❑ Identity of analyst

Checklist

Identifying Parts of a Laboratory Report, *continued*

Quality Control and Quality Assurance

- ❑ Chain of custody form
- ❑ Recovery/accuracy results and allowable ranges
  - ❑ Spiked standards or control samples
  - ❑ Matrix spikes
  - ❑ Surrogates in volatile and semivolatile analyses
- ❑ Precision results and allowable ranges
  - ❑ Laboratory control sample duplicates/replicates
  - ❑ Client sample duplicates/replicates
- ❑ Indication of results outside allowable limits
- ❑ Method blanks
- ❑ Identification and signature of reviewers

Checklist

Problems Requiring Immediate Response

Use this checklist to help you respond quickly to problems indicated by a laboratory report. This checklist includes suggestions on how to handle certain problems; however, every situation is unique and may require different actions. It is also important to check any requirements of regulatory agencies and those of your own company before taking action.

Regulatory Permit Limit Exceeded

- ❑ Does any result exceed a regulatory permit limit (for example, an NPDES permit)?
  - ❑ Verify that sample was correctly collected, preserved, and analyzed.
  - ❑ If report indicates problems with sampling or analysis, contact laboratory to determine if analytical result is valid.
  - ❑ If result is valid, consider resampling to determine whether exceedance condition persists or was incidental.
  - ❑ If result is questionable or invalid, consider resampling to obtain valid result.

Wrong Analytical Method

- ❑ Was the wrong analytical method used (for example, method not listed at 40 CFR 136 used for NPDES analyses)?
  - ❑ Does permit or other regulatory requirement allow alternate method?
  - ❑ Contact laboratory to ask if actual analytical steps conform to required method and if so, if report can be reissued with correct method reference.
  - ❑ If holding time not exceeded, reanalyze sample.
  - ❑ If holding time exceeded or original sample not available for reanalysis, resample.

Checklist

Problems Requiring Immediate Response, *continued*

Holding Time Exceeded

- ❑ Was holding time exceeded?
  - ❑ Resample.
  - ❑ Where timing is a problem with sample collection, modify steps to meet holding time requirement.
    - ❑ Measure analyte at point of collection (for example, pH).
    - ❑ Arrange for quicker transport to laboratory.

Improper Preservative or Container

- ❑ Was improper preservative or container used?
  - ❑ Resample.
  - ❑ Determine if using improper preservative changed analyte (for example, total versus dissolved metals), but produced other valid data that could be used.
  - ❑ Determine if despite bias (low or high result) caused by improper preservative or container, analytical result is still useful (for example, total metal result that is greater than a cleanup standard for the dissolved metal).

Wrong Reporting Limits

- ❑ Does reporting limit not meet requirements of permit, other regulatory program, or other project needs?
  - ❑ Ask laboratory, based on data associated with analysis, if lower limit can be reported without reanalysis. If so, ask for revised report.
  - ❑ If holding time not exceeded, reanalyze sample.
  - ❑ If holding time exceeded or original sample not available for reanalysis, resample.

Checklist

Problems Requiring Immediate Response, *continued*

Holding Time Exceeded

- ❑ Was holding time exceeded?
  - ❑ Resample.
  - ❑ Where timing is a problem with sample collection, modify steps to meet holding time requirement.
    - ❑ Measure analyte at point of collection (for example, pH).
    - ❑ Arrange for quicker transport to laboratory.

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  - ❑ Determine if using improper preservative changed analyte (for example, total versus dissolved metals), but produced other valid data that could be used.
  - ❑ Determine if despite bias (low or high result) caused by improper preservative or container, analytical result is still useful (for example, total metal result that is greater than a cleanup standard for the dissolved metal).

Wrong Reporting Limits

- ❑ Does reporting limit not meet requirements of permit, other regulatory program, or other project needs?
  - ❑ Ask laboratory, based on data associated with analysis, if lower limit can be reported without reanalysis. If so, ask for revised report.
  - ❑ If holding time not exceeded, reanalyze sample.
  - ❑ If holding time exceeded or original sample not available for reanalysis, resample.

Checklist

Problems Requiring Immediate Response, *continued*

Examples of Alternate Names for Some Common Wastewater Analytes

IUPAC Name	Alternate Name
Bromodichloromethane, Dibromochloromethane, Tribromomethane, and Trichloromethane	Trihalomethanes
2-Butanone	Methyl ethyl ketone, MEK
Chloroethene	Vinyl chloride
Dichloromethane	Methylene chloride
1,2-Dimethylbenzene	o-Xylene
1,3-Dimethylbenzene	m-Xylene
1,4-Dimethylbenzene	p-Xylene
2-Methylphenol	o-Cresol
3-Methylphenol	m-Cresol
4-Methylphenol	p-Cresol
4-Methyl-2-pentanone	Methyl isobutyl ketone (MIBK)
2-Propanone	Acetone
Tetrachlorethene	Perchloroethylene, PERC, PCE
Tribromomethane	Bromoform
Trichloroethene	Trichloroethylene, TCE
Trichloromethane	Chloroform

Checklist

Checking If Results Are Reasonable

Use this checklist to check if analytical results in a laboratory report seem reasonable. This checklist addresses only a few, obvious problems. Thus, it should not be considered an in-depth and complete review of analytical data. Any questionable value should be discussed with the laboratory to see if it is the result of an error. If the value is not in error, then further investigation, and possibly resampling, may be needed.

Presence of Analyte Not Expected

- ❑ Is an analyte that is not expected to be in the sample measured above the laboratory's detection limit?

Relationship Among Parameters Unlikely

- ❑ Is the relationship among parameters unlikely?

  Examples

  - ❑ COD less than TOC
  - ❑ O&G less than TPH when EPA 1664 used for both

Analytical Notations

- ❑ Do any of the analytical results have notes or flags that indicate problems with the analysis?
  - ❑ High detection limits from sample dilutions needed to resolve matrix interference
  - ❑ Difficulty in resolving gas chromatograph peaks for analyte identification
  - ❑ Blank sample contamination
  - ❑ QA/QC criteria not met
  - ❑ Other

Result Outside Normal Range

- ❑ Is an analytical result outside its normal range?

Report Errors

- ❑ Are there many obvious typographical errors in the laboratory report, raising questions about the overall quality of the laboratory work?

Checklist

Resolving Detection/Quantification Limit Problems

This checklist outlines the steps that are normally taken to address problems in achieving a detection or quantification limit. If you suspect that you will have a detection/quantification limit problem, you should try to resolve it prior to submitting analytical data with a regulatory application or accepting a permit with unachievable analytical limits.

Sample Cleanup

- ❑ Ask the laboratory if it has tried alternate clean up steps allowed by the method.

More Sensitive Method

- ❑ If alternate clean up procedures cannot achieve the required sensitivity, ask the laboratory if a more sensitive method is available.

Matrix-Specific Limit

- ❑ If none of the methods or clean up procedures can achieve the required sensitivity, consider developing a matrix-specific detection/quantification limit. Regulatory approval of such is required for NPDES permits and likely for other regulatory programs as well.

Checklist

Indications of Analytical Bias (Too High or Too Low)

Use this checklist to indicate if a laboratory has a possible significant analytical bias (results that are too high or too low). Bias is not a single high or low result, but rather a pattern that persists. When there are only a few analyses, it is important to remember that the items in this checklist may only suggest that bias is present. Bias is more likely to be discovered when multiple samples, routine monitoring, or multiple laboratories are involved.

Shift in Analytical Results

- ❑ Shift in results with no apparent change in sample characteristics
- ❑ Shift in results with change in analytical method

Results with Different Laboratories

- ❑ Significant difference in results in split samples sent to different laboratories
- ❑ Significant difference in results when a different laboratory begins to analyze samples

Pattern in QA/QC Data

- ❑ Recovery QA/QC data uniformly high or low with particular analysis

Checklist

Errors That Can Result in Outliers

Use this checklist when you have an unusual analytical result that you suspect may not be valid. The checklist suggests possible errors that could have caused the outlier. Some of these errors are correctable; others may require reanalysis.

- ❑ Calculation errors (dilution factor, wrong number entered)
- ❑ Transcription errors (transposition, wrong entry, decimal misplaced)
- ❑ Sample contamination
- ❑ Wrong sample analyzed or reported
- ❑ Different analytical method used
- ❑ Wrong reading of instrument
- ❑ Analytical step left out or done improperly
- ❑ Incorrect method calibration

Checklist

Selecting the Right Analytical Method

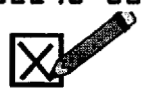
Use this checklist to help you identify which analytical methods will meet your project requirements. Even if you give the laboratory primary responsibility for selecting the methods, you should be aware of any special regulatory requirements (such as 40 CFR 136 methods for NPDES analyses) so that you can review them with the laboratory. This checklist will help you identify those special requirements.

NPDES Analyses

- ❑ Depending on whether the NPDES analyses are for a permit application or for permit monitoring, identify every analyte that must be measured.
- ❑ Identify any required analytical detection or quantification limits.
- ❑ If detection/quantification limits are not specifically identified by the permit agency, select limits that are sensitive enough to demonstrate compliance with any applicable permit effluent limit.
- ❑ Identify any analytical methods specified in the permit (Be sure to check footnotes in the "effluent limits and monitoring" section and "other conditions" section of the permit).
- ❑ For each analyte, if there is no specific method identified in the permit, identify approved methods at 40 CFR 136.
- ❑ Select the method that will meet the required detection/quantification limit, if applicable, and any other special project requirement.
- ❑ If no method is specified in the permit or listed at 40 CFR 136, select a method from SW-846 or work with the laboratory on selecting/developing an acceptable method.

Other Regulatory Programs

- ❑ Identify every analyte that must be measured.
- ❑ Identify any required analytical detection or quantification limits.
- ❑ If detection/quantification limits are not specifically identified by the regulatory agency, select limits that are sensitive enough to meet project objectives (such as a clean up level).
- ❑ Identify any analytical methods specified in permits or other regulatory requirements.
- ❑ For each analyte, if there is no particular method specified by the regulatory agency, identify methods from 40 CFR 136, SW-846, and EPA's "Methods for Chemical Analysis of Water and Wastes" (1979). If there is no method for the analyte in any of these references, work with the laboratory on selecting/developing an acceptable method.
- ❑ Select the method that will meet the required detection/quantification limit, if applicable, and any other special project requirement.

Checklist 

Elements of a Good Laboratory Recordkeeping System

Use this checklist to evaluate a laboratory's recordkeeping system. This checklist identifies elements that are generally considered part of a good recordkeeping system. The checklist is simple and does not include detailed questions that would be asked during an onsite audit. However, if the checklist is reviewed with the laboratory, it will give you an initial idea about the quality of the laboratory's recordkeeping system.

Sample Management

- ❑ Chain of custody documentation of sample collection, transport, and delivery to laboratory.
- ❑ Tracking system for initial sample receipt, sample delivery to analysts, sample holding times, and sample storage after analysis.

Analytical Worksheets and Data Records

- ❑ Handwritten records by individual analysts kept in bound notebook.
- ❑ Handwritten records made in ink, data corrected by crossing out and initialing instead of erasure.
- ❑ All necessary analytical information is completed.
- ❑ Samples clearly identified and traceable to chain of custody records.
- ❑ Times are recorded as necessary at each analytical step.
- ❑ Each analyst signs or initials his or her analyses.
- ❑ Results recorded in central reporting system in a timely manner.

Files

- ❑ Well organized system for maintaining and archiving worksheets, notebooks, chain of custody forms, equipment maintenance records, and other items of laboratory operation.
- ❑ Well organized computer data system, including routine data backups.
- ❑ System for archiving files and identifying files no longer needed so that they can be destroyed.

Checklist

Items for Onsite Laboratory Evaluation

Use this checklist to outline the items that should be included during an onsite laboratory evaluation or audit.

General Conditions

- ❑ Cleanliness
- ❑ Organization
- ❑ Storage of chemicals
- ❑ Condition of work surfaces and areas
- ❑ Safety equipment

Staffing

- ❑ Number of degreed chemists (PhD, MS, BS)
- ❑ Number of non-chemistry degreed analysts
- ❑ Number of supervisors and qualifications
- ❑ QA/QC manager onsite

Equipment

- ❑ Equipment appropriate to each type of analysis
- ❑ Utility equipment such as refrigerators, ovens, balances, incubators
- ❑ Cleanliness and routine maintenance

Manuals

- ❑ Analytical reference manuals
- ❑ Standard operating procedures
- ❑ QA/QC procedures
- ❑ Equipment manuals

Records

- ❑ Sample chain of custody
- ❑ Analytical worksheets, logbooks, or computer printouts
- ❑ Equipment calibration and maintenance

Reports

- ❑ Organization and clarity of standard analytical report
- ❑ Contents of standard analytical report
- ❑ Detail of standard analytical report
- ❑ Other data that can be reported if requested

Regulatory Requirements

- ❑ General knowledge of regulatory programs requirements (NPDES, etc.)
- ❑ Knowledge of analytical requirements for regulatory programs

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