Tier I Data Validation Manual

For the

Ohio EPA

Division of Hazardous Waste Management

June 13, 2011

Revision Summary

Revision	Date Effective	Summary
Revision 2.0	July 17, 2003	Chapter 11-pH was added. TCLP and Flashpoint chapters were renumbered. The checklist examples were updated to match the most current Tier I Data Validation Checklists.
Revision 2.5	April 1, 2004	Lists of common laboratory contaminants found in Chapter 6 and in Appendix II were modified. Toluene was dropped from the lists and cyclohexane was added. This modification was necessary to be consistent with federal guidance (U.S. EPA National Functional Guidelines for Organic Data Review (OSWER 9240.1-05A-P, EPA540/R-99/008, October 1999).
Revision 3.0	January 9, 2006	The changes increase information about DV responsibilities in Chapter 1; introduce a tracking system (Chapter 1), and introduce a new chapter (Chapter 14) on summarizing data validation information.
Revision 4.0	February 1, 2006	Updating the portions of the Tier I Data Validation Checklist in the manual to match the most current version.
Revision 5.0		Chapter 1 was updated to better define the role of inspectors in the data validation process; a new chapter was added that explain data validation for hexavalent chromium and cyanide analyses (Chapter 14; the former Chapter 14 was re-numbered to Chapter 15)

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Introduction To The Data Validation Manual

1.0 Introduction

The Ohio Environmental Protection Agency (Ohio EPA) uses environmental data from a number of sources to support its decision-making processes. This manual outlines a process called **Data Validation** that will enable Ohio EPA staff to review analytical data for consistency, quality and relevance before using it as a basis for making decisions that will affect closure and corrective action sites. In addition, the validity of analytical data is important because it serves as a basis for evaluating compliance with the hazardous waste rules and for Ohio EPA's enforcement actions. This chapter will discuss the importance of valid analytical data, the concept of data validation, the role of the Division of Hazardous Waste Management's (DHWM) inspectors and Division of Drinking and Ground Waters' (DDAGW) geologists, the levels of validation, and the tools provided to aid in the process.

This manual will serve as a compendium for data validation methods and examples, and as a tool to improve the Data Validator's ability to evaluate data reports. It is not intended to be an exhaustive reference, but will provide the fundamental information necessary to evaluate laboratory data commonly received by DHWM. Therefore, the procedures discussed in this manual will be confined to common SW-846 analytical methods reviewed by DHWM. This manual concentrates on SW-846 methods 1311 (Toxicity Characteristic Leaching Procedure (TCLP)), 8260B (Volatile Organic Compounds (VOCs)), 8270D (Semi-Volatile Organic Compounds (SVOCs)), 6010C (metals and trace elements using ICP), 6020A (metals using ICP/MS), 9040C (pH determinations for corrosivity) and 1010A (flashpoint determination for ignitability). SW-846 Method 1010A is actually a summary of ASTM Method D93 which contains the specific procedures this manual references.

It should be noted that while data validation is a key component of the data assessment process; this manual will not serve as guidance for data assessment. We must point out this distinction because data assessment is the process used to determine whether or not the data quality objectives for a project are met. Therefore, there are many criteria beyond data validation that may determine the relevance of analytical data. Data assessment activities may concentrate on, among other topics, the age of the data, the sample collection techniques, or the use of appropriate SW-846 test methods to analyze the samples. Data assessment is important because the data quality objectives, or the certainty regulators place in the data, will affect the final management decisions at regulated sites. The manual discusses this subject in Chapter 15 which is titled Data Summary. DHWM training procedures also incorporate the need to summarize the uncertainty in data and determine its usefulness.

In general, data validation is the process of evaluating the completeness, correctness, consistency, and compliance of a data package against a standard or against project-specific criteria. Data validation will identify laboratory and analytical errors that are associated with a data set. In addition, the data validation process may identify potential sampling errors, such as preservation and sample handling methods, which are out of conformance with the sampling plan's data quality objectives.

In most cases, the standards that will be used in this manual are those described in U.S. EPA's SW-846 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (1986) and the National Functional Guidelines for Organic and Inorganic Data Review (2010, 2009, 2008, 2007, 2002, 2001, 1996, 1994). Other criteria for data validation will be consistent with the U.S. Army Corps of Engineers (USACE) data validation process and with the requirements of rules and regulations that DHWM is authorized to administer.

1.1 The Tiered Approach

Data validation will be conducted by Ohio EPA in a tiered approach. Tier I Data Validation will include a general review of sample receipt, analysis, and the ability of the instruments to recover the elements or compounds that were analyzed. The main components of a Tier I Data Validation include: assessing the technical holding times, surrogate recoveries, matrix spike/matrix spike duplicates, laboratory control samples, and method blanks. The following items are to be evaluated during a Tier I Data Validation review:

Tier I Review Components:

VOCs (8260B), SVOCs (8270D), and Metals (6010C):

- Chain of Custody;
- Case narrative;
- Field and sample identifications (IDs) cross reference;
- Holding times;
- Preservation and cooler receipt;
- Surrogate recoveries (for organics only);
- Laboratory blank data (method blanks, preparation blanks);
- Spike data (including MS/MSD);
- Laboratory Control Samples (LCS).

Flash Point (ASTM Standard D-93):

- Chain of Custody;
- Case narrative;
- Field and sample identifications (IDs) cross reference;
- Holding times;
- Preservation and cooler receipt;
- ASTM test method;
- LCS;
- Heating protocols (initial temperature, final temperature, time intervals between flame application);
- Duplicate samples (criteria for duplicates specified in the method);
- Rate of temperature increase information;
- Temperature corrected for ambient barometric pressure;
- Viscosity information, p-xylene information, stirring rate information.

TCLP (1311):

- Chain of Custody;
- Case narrative;
- Field and sample identifications (IDs) cross reference;
- Holding times;
- Preservation and cooler receipt;
- Percent solids;
- TCLP blank;
- Extraction fluid information (pre-test information, extraction fluid type, pH, volume);
- Spike recoveries for metals;
- Tumbler rate, tumbling time, and room temperature.

Tier II Data Validation will include all of the parameters assessed during the Tier I Data Validation as well as the parameters listed below. These parameters primarily deal with instrument calibration and analysis sensitivity. Additionally, Tier II Data Validation includes several methods that are not, or are only generally, addressed in the Tier I Data Validation Checklist.

Tier II Review Components:

VOCs (8260B) / SVOCs (8270D):

- Mass spectrograph tuning;
- Initial calibration;
- Continuing calibration;
- Internal standards;
- Target compound identification.

Tentatively Identified Compounds (TICs): TICs will only be addressed in Tier II Data Validations and are generally evaluated only for ground water recovery results.

Metals (6010C and 6020A):

- Initial and continuing calibration;
- Duplicates;
- Metals spikes and LCS recovery;
- Assessment of Interferences;
- Mass tuning (6020A).

Cold Vapor Atomic Absorption (AA) for Mercury (7470A/7471B):

- Holding times/preservation;
- Calibration/instrument run QC;
- Sample results;
- Preparation/matrix QC;
- Method blank;
- Spikes;
- Addition of Potassium Permanganate (KmnO4).

1.2 Inspector/Geologist Involvement and Validation Requirements

It is generally accepted that data generated pursuant to the hazardous waste rules and regulations need to be viewed with an idea of its quality and validity. Clearly then, any data used for waste determination, site characterization and compliance evaluation should be subject to validation. Consequently, DHWM inspectors and DDAGW geologists must be familiar with data validation precepts. Inspectors and geologists will be expected to conduct Tier I Data Validations on data that they receive as part of their work activities. DHWM inspectors will perform Tier I Data Validations on waste, surface water and soil data, while the DDAGW geologists will complete Tier I Data Validations on ground water data. While district staff are expected to validate their own data, each district will have at least one staff member who can provide guidance on Tier I procedures and be able to perform a Tier II Data Validation upon request.

DHWM inspectors are expected to validate any data that is used to make regulatory decisions. However, there may be cases where validation is not necessary. One example may be when a parameter being analyzed does not have quality assurance data associated with it. This is sometimes the case with older compliance data from hazardous waste generators. Another case may be where data has been generated for a period of time for a particular waste stream. If it has been repeatedly validated and found to be acceptable, then the inspector may not need to perform data validation. If these and other instances arise, then the inspector should consult his/her supervisor and provide written justification in the facility's file that states the reasons that data validation is not necessary. There are data for specific purposes that should invariably be focused on. For example, data that will be used in enforcement cases or data with obvious errors noted in the laboratory's Quality Control (QC) documentation. To support this effort, inspectors need to ask for copies of associated QC documents when samples are analyzed for waste determination. This type of request is least expensive and most successful when it is made prior to, or along with, submittal of samples to the lab. In addition, they need to insist that generators keep QC information on file with the analytical results.

DHWM expects that at least ten percent of data submitted for a facility as part of RCRA Supplemental Annual Ground Water Monitoring Reports be reviewed by DDAGW staff at the Tier I Data Validation level. If problems are encountered or the data appears questionable, then good practices would imply that a greater percentage of the data be validated and/or the validation proceed to a Tier II Data Validation.

DHWM expects that at least 10 percent of data submitted in support of a Resource Conservation and Recovery Act (RCRA) closure be validated through a Tier I Data Validation. The DHWM inspector should strongly consider insisting that a facility or its laboratory validate its own data prior to submittal to the Agency. The burden of providing accurate and valid data is the responsibility of the regulated facility. To aid this effort, DHWM has made publically available this manual and the data validation checklists on its internet site. If problems are encountered or if the data appears questionable, a greater percentage may need to be validated and/or subjected to a Tier II Data Validation.

In addition to RCRA closure, U.S. EPA recognizes that corrective action sites must develop data quality objectives the Data Quality Objective (DQO) process. Data validation is an important aspect of this process. It is important to consider data validation procedures and requirements when a facility's corrective action work plan is being developed. The facility should be required to perform a certain level of data validation on all media types and parameters that are being evaluated. Presumably, the facility should evaluate the performance of its laboratory early in the data acquisition phase of the RCRA Facility Investigation (RFI). If problems are encountered, then measures can be taken to correct any laboratory deficiency before a large amount of samples are acquired. DHWM recommends, as part of its oversight role, that at least ten percent of data submitted in support of a RCRA corrective action be reviewed. It is highly recommended that if problems are encountered or the data appears questionable, then good oversight practices would imply that a greater percentage of the data be validated.

Corrective action and closure situations often require prompt data validation. For example, rapid validation is essential for data that are being used for confirmation of adequate excavation or other remediation. These areas are often backfilled and paved as part of the site's post-remediation land use. Planning ahead to allow for timely data validation before the excavation is backfilled will save cost and effort for all involved parties.

1.3 Tier II Data Validation Responsibilities

A Tier II Data Validation may be automatically performed, based on the usage of the data in question (*e.g.*, closure of a hazardous waste unit, corrective action, or data for an enforcement case), or it may become necessary, as when triggered by problems found with data during a Tier I Data Validation. One example of a data set that may be elevated from Tier I to a Tier II Data Validation would be one where both the matrix spike/matrix spike duplicate (MS/MSD) and the surrogates were found to be outside of accepted QC criteria. The MS/MSD indicates the ability of the lab to evaluate the target analytes in the matrix submitted, while the surrogates indicate the ability of the lab to evaluate analytes similar to target analytes. When both measures are outside of accepted QC parameters, it may indicate that severe matrix problems exist which can hamper the ability of the laboratory to accurately quantify the sample results. In such a case, a Tier II Validator should be consulted. The DHWM or DDAGW Tier I Data Validator will use the Tier I Data Validation Checklist to make this determination in consultation with their District Office Tier II Data Validator and the Tier I Validator's supervisor.

Regardless of what triggers a Tier II Data Validation, the process is designed so that a Tier I Data Validation would be first completed by the person(s) primarily responsible for the site. In most cases, once this review is completed, a Tier II Data Validator would be contacted for the subsequent review. In some cases, such as where it is known a Tier II Data Validation will be performed, the Tier I and Tier II Data Validators may choose to work together from the beginning in completing the necessary data validation procedures.

1.4 Resources

Resources, such as Tier I and Tier II Checklists, division-wide Tier I Data Validation training and this manual, are provided to help Data Validators review data generated at their sites. The purpose of these resources is to both aid Data Validators in the validation process and to provide consistency in practice among the various districts and divisions. These data validation resources are discussed on the following page:

1.4.1 Tier I Data Validation Checklist

The Tier I Data Validation Checklist ensures that all Tier I Data Validations are consistent and address the same QC criteria. It provides a step-by-step guide that begins by helping Data Validators identify necessary components of a data package. It examines quality control criteria, and judges whether data should be accepted, estimated, or rejected. At each step, the checklist will instruct Data Validators on how to find information in the QC package, contact the lab if it is missing or incomplete, evaluate the information against set standards and gauge the quality of the data.

1.4.2 Tier I Data Validation Training

Training events will introduce new personnel to the concepts of data validation and provide a hands-on review of the Tier I Data Validation Checklist for current employees. Training will be repeated as the checklists are updated or changes in validation procedures become evident or when warranted by employee needs. In addition to Tier I training, DHWM and DDAGW will each have at least one Tier II Data Validator, per district, which will be responsible for conducting a Tier II Data Validation. These staff will act as a resource for their district/division, answer data validation questions, be their district's representative on the Data Validation Committee and provide Tier II Data Validation services upon request.

1.4.3 Tier I Data Validation Manual

The manual provides an in-depth compilation of decision criteria and examples. It contains basic information about sample extraction, preservation and analysis criteria as it applies to the quality of data. It also provides several examples to help Data Validators interpret site-specific QC data and apply consistent data qualifiers. This should enhance the usability of the checklist. Many chapters in the manual, with the exception of these introductory chapters, contain worked Tier I Data Validation Checklist questions that will instruct the Data Validators in the proper way to answer each question. In addition, Appendix III contains a fictitious Data Report and completed Tier I Data Validation.

1.4.4 Tier I Data Validation Tracking System

A data validation tracking system for DHWM has been devised. This database system serves as a means to review the amount of data validation performed by each district as well as to provide additional information to Data Validators. This last item may be the most useful for DHWM and DDAGW. Data Validators may view the validation summary data from a particular laboratory (e.g., to note particular problem areas for that lab) or matrix. In addition, this database can be used to find other districts or validators who may have worked on similar data types, examine solutions to similar validation problems, or to identify problem areas for laboratory analyses in general. Data that will be included in the database will be entered primarily by district office personnel or conveyed to the district's Tier II Data Validator. This information will be conveyed from the district to the Tier II Data Validators in Central Office for incorporation into an excel spreadsheet. Access to information can be made by submitting inquiries either to the district's Tier II representative or the Central Office Tier II Data Validator.

1.5 Final Data Usability and Satisfaction of Data Quality Objectives

Although the Data Validation tools listed above are helpful in qualifying data, first the data must be qualified in the context in which it was taken - in full consideration of the Data Quality Objectives under which the analysis was requested. Data that may be deemed acceptable (given a particular set of laboratory QC results, such as spike and surrogate recoveries) in one situation may be unacceptable for another. While some aspects of this evaluation may go beyond what is traditionally thought of as data validation, it is inappropriate to ignore these other factors and validate data in a "vacuum." Such decisions can result in consequences such as ignoring likely exceedances of regulatory levels or risk levels due to contamination remaining at a site. A new chapter, Chapter 14, has been added to this manual to provide a discussion of sample usability by analytical method. This section is meant to provide a thorough analysis of whether the data has satisfied the DQOs that triggered the sampling and to provide a space for summarizing that analysis.

Additionally, data usability can also be impacted by bias in the data. An assessment must be made, by method, matrix, and even laboratory batch, of whether there is a directional bias associated with a data set. Typically, we are most concerned about a low bias to results, but a high bias can also be a factor in data usability. While the validator can evaluate the possible presence of bias throughout the process, a summary of any potential bias should be made at the completion of a data validation and included at the end of the checklist.

1.6 References

The above resources are based, in part, on information from the following references. These references are provided as additional tools for Data Validators to utilize during the data validation process. The web links included may prove particularly useful as the information is easily available and pertinent to data validation questions.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm

The U.S. EPA publication SW-846 is the Office of Solid Waste's official compendium of analytical and sampling methods evaluated and approved for use in complying with the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements.

U.S. EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review

OSWER 9240.1-48, USEPA-540-R-08-01, June 2008

http://www.epa.gov/superfund/programs/clp/download/somnfg.pdf

This document is designed to offer guidance on CLP organic analytical data evaluation and review. It is intended to assist in the technical review of data generated through the CLP.

U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review

EPA-540/R-04-004 (OSWER 9240.1-45) October 2004

This document is designed to offer guidance on CLP inorganic analytical data evaluation and review. It is intended to assist in the technical review of analytical data generated through the CLP.

U.S. EPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review

EPA-540-R-00-006 June 2001

http://www.epa.gov/superfund/programs/clp/guidance.htm

This document is designed to offer guidance on contract laboratory program (CLP) low concentration organic analytical data evaluation and review. It is intended to assist in the technical review of analytical data generated through the CLP.

U.S. EPA Region I Tiered Data Validation Program

U.S. EPA Region I, EPA-New England Data Validation Functional Guidelines for evaluating Environmental Analyses, Office of Environmental Measurement and Evaluation, Revised December 1996.

http://www.epa.gov/region1/oeme/DVMANUAL.pdf

U.S. EPA Region II Data Validation Checklists

U.S. EPA Region II, SOP No. HW-7, Revision 3, TCLP Checklist

U.S. EPA Region II, Evaluation of Metals Data for Contract Laboratory Program, Statement of Work 3-90, SOP Revision XI, Checklist

U.S. EPA Region III Guidance

U.S. EPA Region III Modifications to National Functional Guidelines for Organic Data Review Multi-Media, Multi-Concentration (OLMO1.0-OLMO1.9), Central Regional Laboratory, Quality Assurance Branch, 201 Defense Highway, Suite 200, Annapolis MD. 21401. September 1994.

U.S. EPA, Region III Innovative Approaches for Data Validation of Organic and Inorganic Data-Standard Operating Procedures, Analytical Services and Quality Assurance Branch, 201 Defense Highway, Suite 200, Annapolis, MD. 21401. June 1995.

U.S. EPA Region IV Guidance

Data Validation Standard Operating Procedures for Contract Laboratory Program Routine Analytical Services, Revision 2.1, July 1999, Office of Quality Assurance U.S. EPA Region IV, Environmental Services Division (ESD), Athens, Georgia.

http://www.epa.gov/region4/sesd/oqa/rassop.html

The purpose of this document is to promote uniformity of data review is to help clarify and augment the review guidance of the National Functional Guidelines, to give guidance for areas of data review that require considerable professional judgment, and to specify procedures that are unique to the needs of U.S. EPA Region IV.

1.7 Summary

Data validation is an important tool that is not only being used by U.S. EPA and other state agencies but also by other entities in industry and environmental consulting to evaluate the precision and accuracy of data. Accurate data validation will help both Ohio EPA and Ohio EPA-regulated entities make appropriate decisions.

It is essential that inspectors communicate to owners and operators the importance of data validation during the planning phase of closures and corrective actions. Likewise, when requiring analytical waste evaluations, inspectors need to communicate the importance of requesting laboratory Quality Assurance/Quality Control documents with all sample results. Through communication at the outset of all sampling events, data validation will become a routine and logical addition to Ohio EPA's RCRA review process.

Chapter 2
Common Analytical Methods

2.0 Introduction

In order to understand the data validation process, it is helpful to understand how data is generated when a sample is analyzed. The data validation process is complicated by the fact that environmental data is generated from numerous analytical methods and different types of equipment. A discussion of quantitative analytical chemistry is outside of the scope of this manual; however, this chapter will examine the Inductively Coupled Plasma Spectroscopy (ICP), ICP/Mass Spectrometry (MS), and the Gas Chromatography-Mass Spectroscopy (GC/MS) methods. These analytical methods are the most widely used to analyze samples for metals or for organic compounds. This chapter will focus on the data generation process, and later chapters will discuss data validation issues with the methods that use these types of instruments to analyze data.

No matter what method is being used, or what parameters are being analyzed, the first step in generating analytical data is the preparation of the raw sample into a form that will be introduced to the analytical instrument. The preparatory method can significantly impact the sample results. Therefore, it is critical that the Tier I Data Validator understand which preparatory procedures are being used by a laboratory. The typical SW-846 preparatory methods used to prepare environmental samples are shown in Table 2.1.

Table 2.1 Table of Common Analytical Preparatory Methods and Associated Analytical Methods Described in SW-846, Update III

SW-846 Analytical Method	SW-846 Preparatory Method	Description
8260B-Volatile Organics	5021	Head space preparatory method for solid material
8260B-Volatile Organics	5030B	Purge and trap preparatory method for aqueous samples and some solids
8260B-Volatile Organics	5035	Preparatory method for soil, sediment and sludge
8270D-Semi Volatiles	3510C	Separatory funnel method for liquids
8270D-Semi Volatiles	3520C	Continuous liquid-liquid extraction
8270D-Semi Volatiles	3540C	Soxhlet extraction for soils and other solids
8270D-Semi Volatiles	3541	Automated Soxhlet extraction for solids
8270D-Semi Volatiles	3550C	Ultrasonic extraction for solids
8270D-Semi Volatiles	3580A	Solvent dilution and extraction for wastes
6010C or 6020A-Metals	3010A	Strong acid digestion for aqueous and solid samples
6010C or 6020A-Metals	3050B	Microwave assisted digestion for wastes
6010C or 6020A-Metals	3052	Microwave assisted digestion for silicates
7470A - Mercury	7470A	Mercury in liquid waste (Cold Vapor)
7471B - Mercury	7471B	Mercury in solid waste (Cold Vapor)

2.1 Sample Preparation

Many of the procedures described in Table 2.1 are known as either extraction procedures (associated with organic analysis) or digestion procedures (associated with metals analysis). The use of a particular preparatory method will depend upon the type of analysis to be performed, the analytical instrument chosen and the type of sample to be prepared. Common extraction and digestion procedures are discussed in the following sections.

2.1.1 Extraction Procedures for Organic Compounds

Extraction procedures rely chiefly on the chemical affinity of organic pollutants with a solvent. The old adage, "like dissolves like," basically describes this chemical phenomena. When a soil or water sample is mixed with organic solvent, chemicals may be released from the sample and dissolve, or be "extracted" into the solvent. For semi-volatile organic compounds (SVOCs), the extraction solvent may preferentially solvate either base/neutral, or acid compounds. Each class of compounds will have a designated set of quality control compounds used in data validation. In certain cases, the sampler may request only the "base-extractable" compounds instead of the entire analyte list of the method. Most preparatory procedures facilitate the extraction process by heating or shaking the samples. After the extraction process is finished, the solvent can then be prepared for analysis.

Volatile organic compounds (VOCs) represent a special set of organic compounds. Many preparatory methods do not call for solvent extraction due to these compounds' natural tendencies to partition from the solid or liquid phase to the air. Preparatory Methods 5021 and 5030B take advantage of this partitioning effect by drawing in a portion of a gaseous sample either from the head space of the sample or by bubbling an inert gas through the sample and then trapping the volatile compounds. These compounds can then be analyzed. Method 5035 for VOCs in solid samples also requires the addition of a solvent to the sample. However, this solvent is primarily required for preservation, not for extraction. Consult SW-846 for preparatory methods for special matrices or analyses.

2.1.2 Digestion Procedures for Inorganic Compounds

Digestion procedures for solid and aqueous samples primarily use strong acids, such as nitric and hydrochloric acids, to remove metals from solids or to keep metals in a solution. The procedures listed in Table 2.1 also require heating the sample either through applied heat or by a microwave oven technique. It should be emphasized that most of the procedures listed in SW-846 are not total digestion. This means that the entire matrix of a solid sample may not be taken into solution. If a total digestion is required, preparatory Method 3052 is recommended. In addition, there are special preparatory methods for certain metals that are either volatile or are easily oxidized or reduced during the sample preparation step, such as mercury and arsenic. Refer to SW-846 for these methods and any special requirements associated with them.

2.2 Instrumental Analysis

The samples must be analyzed once they have been properly prepared. Two common quantitative methods used for VOCs/SVOCs and metals are gas chromatography and emission spectroscopy, respectively. These techniques form the basis for the Gas Chromatography/ Mass spectroscopy (GC/MS, SW-846 Methods 8260B and 8270D) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, SW-846 Method 6010C). This section will briefly explain the basics of each analytical system. The Data Validator is invited to gain a more in-depth understanding of these systems by reviewing general college texts on instrumental analysis. Additionally, be aware that the two analytical systems discussed in the following sections are not the only systems of analysis listed in U.S. EPA's SW-846. Many environmental samples for metals are still analyzed by atomic absorption spectroscopy. For example, newer methods utilizing mass spectroscopy and isotope dilution techniques are gaining wide acceptance throughout the environmental community.

2.2.1 Chromatography

Chromatography has been used as a separation technique for organic compounds since early in the twentieth century. The technique usually employs a two phase system, where compounds in a mobile phase interact with an immobile or stationary phase. In practical terms, the organic chemicals from a prepared environmental sample will be partially trapped by material (solid sorbent) in a column. The sorbent is carefully chosen so that it only retains the compounds but does not fully immobilize them. The result is that the chemicals moving through the chromatography column will begin to separate from one another. The degree of separation is a function of a particular chemical's affinity for the material in the column. The amount of time that a chemical will be retained by the column is known as its retention time. Retention times will vary by the length of the column, the sorbent material chosen, the type of solvent used, and the chemical undergoing separation. A diagram of this process is shown in Figure 2.1.

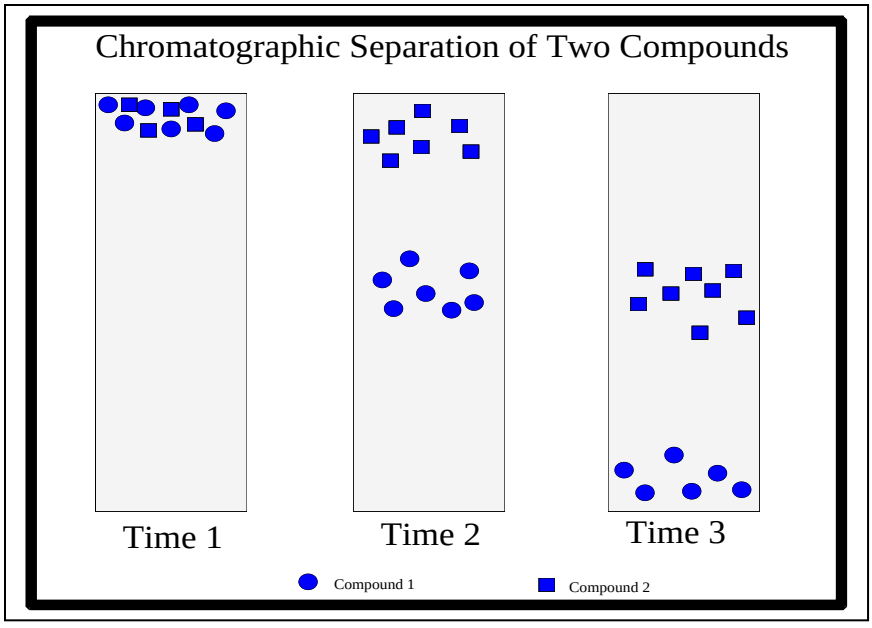


Figure 2.1 The Chromatographic Separation of Two Compounds

Gas chromatography, more correctly called gas-liquid chromatography, is one of the most common analytical techniques used to quantify organic materials in environmental samples. A gas chromatograph is typically constructed as shown in Figure 2.2.

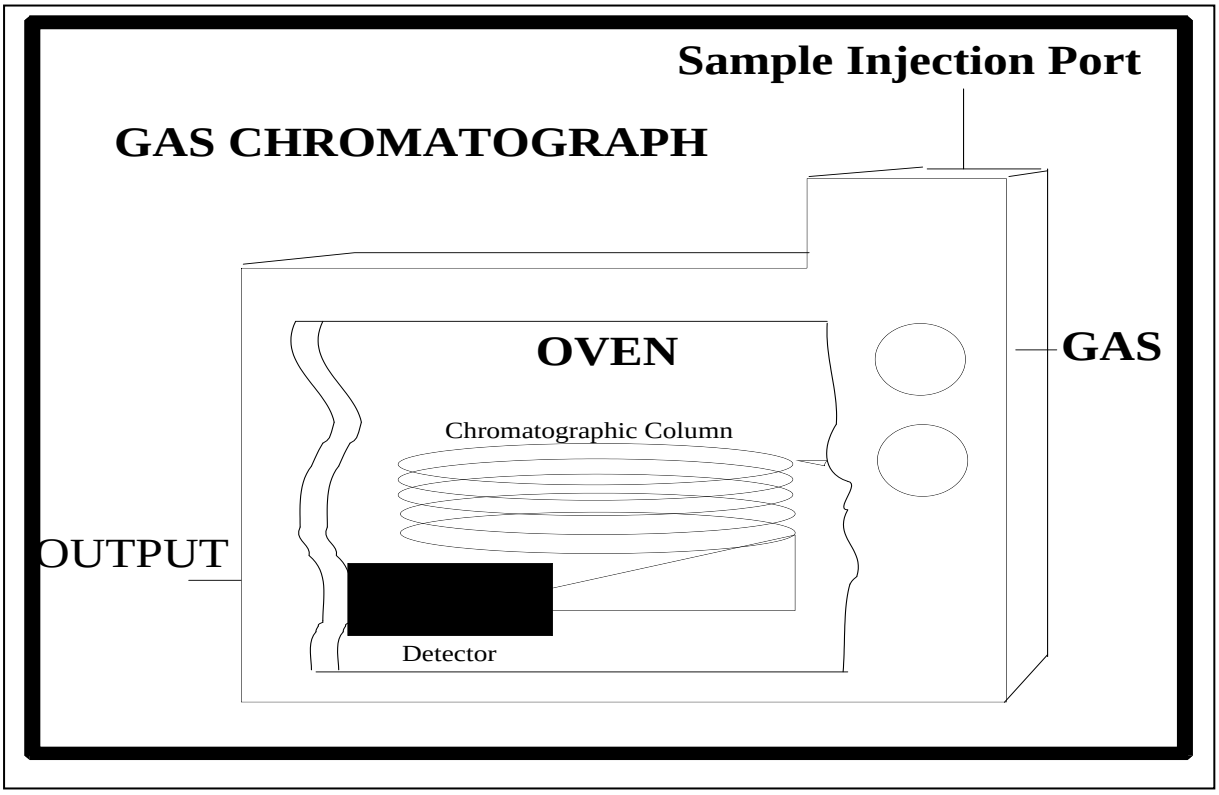


Figure 2.2 A Typical Gas Chromatograph Used for Environmental Samples

A gas chromatograph consists of a carrier-gas supply, sample injection port, chromatography column, oven, detector, and some sort of integrator/recording device to manipulate raw data and save the results of the analysis.

The carrier gas is used to transport the organic chemicals from the injection port, through the column, and finally to the detector. Carrier gases are inert and do not chemically interact with the compounds in the samples. Typically, carrier gases are high purity nitrogen or helium. The injector port is where the prepared extract is introduced to the chromatograph. If a liquid sample extract (typically 1 to 10 µL) is directly injected onto the column, the carrier gas will sweep it through the column separating individual compounds along the path. Other methods can also be used to introduce the sample into the chromatograph. For example, VOC analysis from aqueous samples (5 to 25 mL samples, SW-846 Methods 5030B and 8260B) commonly uses a purge and trap technique where carrier gas passes through the liquid sample, liberating the volatile compounds which are then separated on the instrument's column.

The column is housed within an oven where the temperature can be raised or lowered or maintained throughout an analysis. The variable temperature options allow an analyst to program the instrument so that it is very efficient in liberating and separating organic compounds.

The detector is one of the most important devices found on a gas chromatograph. There are many types of detectors, including: flame ionization detectors (FID) and mass spectrographs (MS). These detection systems are integral to many of the commonly used methods in SW-846, and are briefly discussed in the following paragraphs.

The FID mixes hydrogen gas and air to produce a very hot (2100°C) flame. FIDs are equipped with a collector electrode, placed above the flame that measures its conductivity. When compounds exiting the chromatograph's column encounter the flame, the organic compounds are ionized (i.e., become charged by losing or gaining electrons). As the compounds are ionized, they create changes in the conductivity of the flame, which can be measured. The relative change in conductivity is associated with a compound's concentration in a sample.

Mass spectroscopy utilizes the mass of organic compounds to identify and quantify the amount of a chemical present in a sample. In GC/MS, effluent from the gas chromatograph is pumped under high vacuum into the mass spectrograph. The organic compounds are bombarded by a high energy electron beam, producing fragments of the original compounds. These fragments are typically charged. These fragments are accelerated through a voltage potential into the center of four parallel rods, called a quadrupole filter. The quadrupole arrangement separates the fragments by their mass to charge ratios. Compounds fragment according to well defined patterns which allows for identification of parent compounds. The quadrupole arrangement separates the fragments by their mass to charge ratios. The number of fragments for a given mass to charge ratio is related to the concentration of the original compound.

2.2.2 Emission Spectroscopy

Emission spectroscopy refers to light emitted and detected from elements as they de-excite from an ionized state. The process usually is described as a solution containing the elements of interest being passed through an energy source. The elements are stripped of one or more of their outer shell electrons and ionized. The ions are in a highly excited state, and will de-excite to a more stable state by giving off energy. This energy is a part of the electromagnetic spectrum, and may be thought of as light. The light is given off by each element with a wavelength that is characteristic for that element. The detection of characteristic wavelengths of light allows the analyst to identify each element present in a sample. In addition, the intensity of the light can also be measured. The light intensity is a function of the amount of the element in a sample, which can then be used to determine the element's concentration. The type of emission spectroscopy most commonly used for environmental samples involves a plasma, and is termed Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and is the basis for SW-846, Methods 6010C and 6020A. A typical ICP is shown in Figure 2.3.

The sample is introduced to a nebulizer which turns the sample into a fine spray. This spray is then introduced into a plasma. The plasma ionizes the elements initially, then as they cool they de-excite by emitting light at a characteristic wavelength. The light and its intensity are detected, and the amount of an element is quantified.

In a typical ICP, a plasma is formed by radio-frequency heating of argon (Ar) gas. A plasma is a gaseous mixture of ions. Extremely high temperatures can be reached in the plasma of an ICP, usually on the order of 6,000 to 10,000°K (6,273-10,273°C or 11,323.4-18,523.4°F). The extreme temperature instantly vaporizes the nebulized sample solution. Almost as rapidly, outer shell electrons will be stripped from elements contained in the solution.

This produces ions that, in turn, will produce a characteristic spectrum when they de-excite. The detection system used by ICP spectroscopy varies, but many modern instruments utilize detectors built upon the sample principle as in video cameras. These charged-coupled devices (CCDs) record the entire spectrum of light that is generated from an analyzed sample. This type of detector allows the user to select alternate wavelengths for the detection of elements when interferences are a problem. In addition, background light emissions can be removed by careful examination of the sample's spectrum.

Emission spectroscopy does have its limitations. For example, the plasma will generate an emission spectrum itself that may interfere with the emission of another element. Another source of background radiation is the emission of light from molecular species, for example, FeO. In addition, elements may ionize into a variety of states, such as Fe(0) and Fe(I). These ions will produce their own characteristic emission radiation.

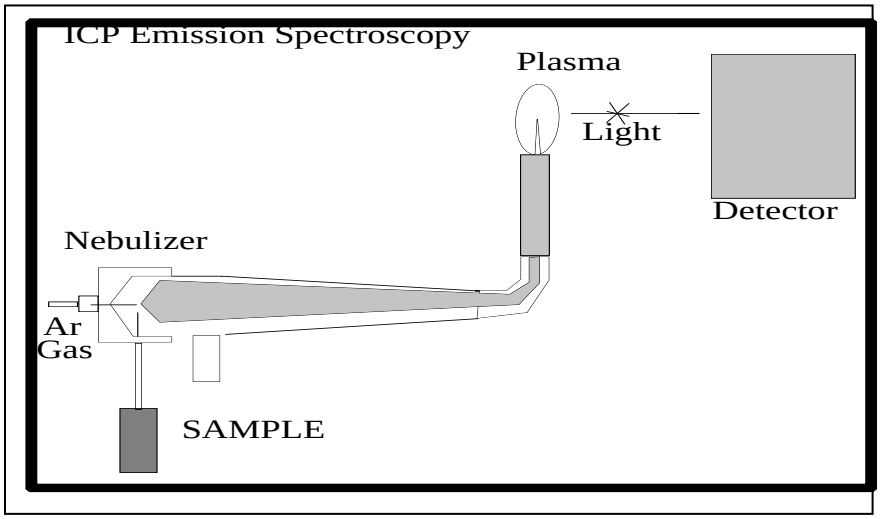


Figure 2.3 A Typical ICP-AES System

Finally, ions commonly will have multiple energy states when they are ionized by the plasma. The de-excitation process usually proceeds through multiple energy states and consequently produces light of varying wavelengths and intensities. Therefore, each element may produce not a single characteristic wavelength, but an entire spectrum of light. Analytical chemists refer to this as "stray light" which may add to the characteristic wavelength of another element. If this stray light is not corrected, a positive bias or interference may result. To further complicate matters, light from emitting ions can produce a negative bias, termed a negative interference, due to sorption by other ions in the spectrum. Both Method 6010C and 6020A contain a procedure to attempt to compensate for these interferences. A set of standards collectively called the Interference Correction Standard (ICS) is used to compensate or identify when interferences are a problem. The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with solution A, for all wavelengths used for each analyte reported by ICP. The results of these standards are used to determine whether the instrument and its software can overcome potential biases due to sample matrix.

Method 6020A is a newer analytical technique that is being applied to the analysis of metals in soil and aqueous matrices. This method combines the emission spectroscopy techniques of ICP-AES with mass spectroscopy to overcome potential matrix interferences. The method starts by first passing a nebulized sample into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

Chapter 3
Accuracy And Precision

3.0 Introduction

The goals for sampling a site may vary considerably from one project to the next, however, most data quality objectives will require that measures of accuracy and precision be incorporated into the analysis plan. **Accuracy** and **precision** in analytical measurements are prime concerns of data validation. Ideally, analytical systems are both accurate and precise; in reality, however, this is not always the case. Analytical systems may be capable of good accuracy, but may not be able to repeat the measurement on a sample through time. Conversely, the analytical system may be able to repeatedly acquire the same result, but the result is inaccurate. Tier I Validators must verify that measures of accuracy and precision fall within acceptable ranges as specified in the sampling and analysis plan or by the lab's quality assurance project plan (QAPP).

3.1 Accuracy

Accuracy can be defined in numerous ways. One definition by Taylor (1987) defines analytical accuracy as "the degree of agreement of a measured value with the true...value." This definition implies that analytical measurements are really estimates of the true concentration of a chemical in a sample. Since the goal is to determine the concentration of a compound or element in a sample, how can a determination be made as to whether the estimate is indeed accurate without knowing the true concentration? In addition, what degree of difference is acceptable between the estimated concentration and the true concentration?

The analytical process devised by U.S. EPA and codified in SW-846, Test Methods for Evaluating Solid Waste (1986) attempts to provide measures of accuracy within the analytical process. This is accomplished in two ways. First, every testing procedure requires calibration. Calibration is the act of determining the analytical instrument's response to standards which contain compounds at known concentrations. The calibration response curve is then used to establish the concentration of compounds in the samples submitted to the laboratory. Most analytical procedures described in SW-846 and other guidance requires that the lab check the validity of the calibration curve at regular intervals or re-calibrate the instrument each working day. These calibration checks are then used to assure whether the instrument is responding in a proper manner when samples are analyzed over a given period of time. The review of initial and continuing calibration data, instrument response through time, internal standard response, and retention time of internal standard compounds are important aspects of data validation. However, the review of calibration data is a subject left for DHWM's Tier II Data Validation process.

The second approach to determining accuracy is through the use of spikes and system monitoring compounds or surrogate compounds. Surrogate compounds, discussed in detail in Chapter 8, are organic compounds that are not expected to occur in environmental samples, but which behave similarly to target compounds. Surrogate compounds are usually brominated or deuterated (labeled with a "heavy" hydrogen atom in a specific position indicated with a number in the name of the surrogate), making them easy to distinguish from target compounds.

Because surrogate compounds are spiked into each sample extract at known concentrations, a measure of accuracy can be determined based upon a comparison of the measured concentration of the surrogate compound to the actual amount spiked into a sample.

This comparison is usually represented by the Percent Recovery (%R) of a spiked compound. The general formula for the percent recovery is given in the following equation:

Equation 3.1

$$\%R = \frac{SSR}{C_s} X\,100$$

Where:

%R	=	Percent Recovery
SSR	=	Spiked Sample Result
C_s	=	Concentration of the Spike Added

This equation implies that as the measured concentration (SSR) from an analysis approaches the spiked concentration from a standard (C_s), the %R approaches 100 percent.

Surrogate compound analysis gives the Tier I Data Validator important information on what effect the sample material may have on the measurement of a compound in a sample. Therefore the Validator may also be able to determine whether the accuracy of the measurement may be adversely biased.

Measures of accuracy, such as the % R, are rarely equal to 100%. Usually there is a range of %R values centered around 100 percent. If variability is expected, what %R is acceptable such that the measurements may be considered accurate enough for the goals of the sampling project? The answer to this question is generally predicated on the project's data quality objectives (DQOs). In addition, each laboratory specifies its own quality control acceptance level. It is, therefore, important for the Tier I Data Validator to assess the laboratory's quality control acceptance criteria for surrogate recovery ranges prior to analysis in order to determine whether they meet the project-specific DQOs. In general, for volatile organic compound analysis, the acceptance criteria %R is 100 +/- 25 %. Surrogate recoveries outside of this range are qualified based upon the magnitude of the exceedances.

3.2 Precision

Precision can be defined as the amount of agreement between repeated measurements of a sample or a set of samples. Because of fluctuations in the analytical process, repeated measurements of a sample will commonly differ. If enough measurements are made, the distribution of data points should approximately conform to a standard normal distribution, where data points are distributed about a mean value. In general, the range of scatter in the distribution is a measure of the precision of the analytical process.

Unfortunately, the acquisition of sufficient replicates is beyond the scope and budget of most environmental sampling projects. If this is so, how may a determination be made as to whether the analytical process is precise enough to be acceptable?

U.S. EPA has devised a quality control check on analytical precision by requiring the analysis of spiked and spiked duplicate samples (please see Chapter 7 for more information on matrix spike and spike duplicates). The measure of precision is expressed as the relative percent difference (RPD) between the spiked and the spiked duplicate sample results. Most methods in U.S. EPA SW-846 require that a matrix spike (MS) and matrix spike duplicate (MSD) sample be analyzed and evaluated for precision. The formula that is used to calculate the RPD between a spike and its duplicate is given below.

Equation 3.2

$$RPD = \left| \frac{C_1 - C_2}{\frac{C_1 - C_2}{2}} \right| X\,100$$

Where:

C_1 = The higher of the spike or spike duplicate results (concentration)
C_2 = The lower of the spike or spike duplicate results (concentration)

It is important to note that the spike and spike duplicate result concentrations be used in equation 3.2 and not the recoveries for the spike or spike duplicate results. The concentrations are in ug/l, while the recoveries are a percentage.

Equation 3.2 implies that as the results of the spike and spike duplicate begin to deviate from each other, the value of the RPD increases from 0%. Like accuracy, the quality control criteria for precision data must be either required in the work plan, in a contract with a laboratory, or the Tier I Data Validator must know the acceptance level for precision set by the laboratory performing the analyses. In general, the data quality objective for precision in laboratory analyses is an RPD of 20% or less for volatile organic data. Individual analytes and other methods may have different criteria.

Chapter 4
Dilution And Detection Limits

4.0 Introduction

Data validation procedures are used to assess the accuracy and precision of a dataset. Most of these procedures evaluate the recovery and reproducibility of spikes. However, another important aspect of data assessment must also be considered in reviewing data. The detection or quantitation limits can have a bearing on successfully meeting a sampling project's data quality objectives (DQOs). For example, if the detection limits are above risk-based remediation goals, then few or no decisions may be made concerning whether a site has met its closure performance standards. Interferences from the sample matrix may also act to raise the detection limits of a sample. This chapter will briefly discuss one factor in raised detection limits, namely, dilution. This chapter will also examine the different types of dilution and quantitation limits often associated with environmental data.

4.1 Definitions

Dilution: The act of adding distilled water and/or other preparation reagents to a sample extract or digestate to overcome an interferent or to bring the concentration of a target analyte back into the working calibration range of the instrument.

Dilution Factor: The total number of volumes, including the sample volume, in which the sample will be dissolved.

Dilution Ratio: The number of volumes of sample as compared to the dilution factor.

Serial Dilution: A sample aliquot that is subjected to a multiple or series of dilution steps. Serial dilution is usually performed on new or difficult matrices that may display significant matrix interference.

4.2 Dilution Factors

Dilution is the act of adding distilled water and/or other preparation reagents to a sample extract or digestate to overcome an interferent or to bring the concentration of a target analyte back into the working calibration range (determined by the concentration range of calibration standards used to develop a response factor ratio for that instrument) of the instrument. Dilution may be thought of as combining a unit volume of a sample with an appropriate volume of a solvent liquid to achieve the desired concentration. The dilution factor is the total number of volumes, including the sample volume, in which the sample will be dissolved. For example, a dilution factor of four (4), or a 1:4 dilution ratio, means combining one volume of diluent (the material to be diluted) + three equal volumes of the solvent medium. The dilution ratio is stated more generally in the following equation:

Equation 4.1

$$\text{Dilution Ratio} = \frac{\text{volume of sample aliquot}}{\text{volume of sample aliquot + dilution volume}}$$

For example, a can of soup concentrate is usually diluted with one additional can of water (the dilution solvent) giving a dilution factor of two. The soup concentrate represents one unit volume to which has been added one can (same unit volume) of water. Therefore, the soup concentrate is now distributed through two unit volumes. This would be called a 1:2 dilution ratio, and the soup is now ½ as concentrated as it was originally. As an exercise, evaluate the dilution factor for the following situation:

Example 1

What is the dilution factor, if 500 µl (micro liters) of a sample have been added to a volume of 5 ml (milliliters) of distilled water?

Step 1 (Dimensional Analysis):

In order to complete the exercise, the units of volume must be the same. For this example,

5 ml = 5000 µl

and 500 µl = 0.5 ml (on a micro liter basis).

Step 2 (Dilution Ratio):

Use Equation 4.1 to determine the dilution ratio.

$$\frac{500\ \mu l}{(500\ \mu l + 5000\ \mu l)} = \text{1 to 11 ratio}$$

Step 3 (Dilution Factor):

The dilution factor in this case is 11.

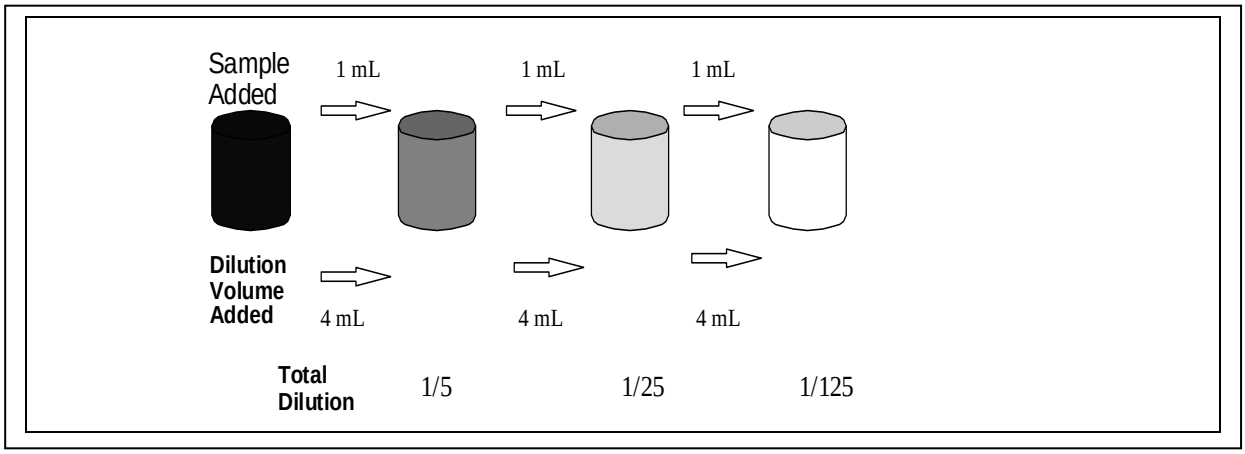
Example 2

Care should be taken in determining the dilution factors for volumetric data from laboratory bench sheets. For example, if a 500 µl aliquot of a sample is to be part of a total volume of 5 ml then:

$$\text{Dilution Ratio} = \frac{500\ \mu l}{5000\ \mu l} = \text{1 to 10 ratio and the dilution factor is 10}$$

Another type of dilution that is associated with environmental sample analysis identification is serial dilution. Certain methods like SW-846, Method 6020A require that serial dilutions be performed if the Quality Control data (matrix spikes) suggest that significant matrix interference exists. As the name implies, a serial dilution is just a series of dilutions. The source of dilution material for each step comes from the diluted material of the previous. In a serial dilution, the total dilution factor at any point is the product of the individual dilution factors in each step up to it. Figure 4.1 shows a set of samples where serial dilution has been performed.

Equation 4.2 Total Dilution Factor (DF) = DF1 x DF2 x DF3, etc.



The figure above shows the effect of serial dilution. Each dilution step is made by adding an aliquot from the previous step to a fixed volume of solvent material. The total dilution factor for the serial dilution is determined by multiplying the dilution factor from each step.

4.3 Identifying Dilution

An essential task of data validation is to identify whether a sample or a set of samples have been diluted. This task may be easy, as most laboratories will list the dilution factor used for a sample. However, some data reports may not clearly define the dilution factor. If this is the case, the Tier I Data Validator will have to establish the dilution factor by consulting the laboratory and requesting the information. If this is not possible, the Tier I Data Validator may be able to calculate the dilution factor if sufficient information is present in a data report. If method blank data is present, a comparison of the method detection limits listed with the blank data and the method detection limits listed with the sample results can be used to determine the dilution factor. In this case, the dilution factor is simply the ratio of the two method detection limits. Care must be exercised in using this method. The Tier I Data Validator must not compare method detection limits (MDLs) with reporting or quantitation limits. Comparing detection limits to quantitation limits will greatly exaggerate the dilution factor.

4.4 Consequences of Dilution

As mentioned previously, a laboratory may be forced to dilute a sample for a variety of reasons. Commonly, a sample may contain a constituent of concern at concentrations that are well above the analytical instrument's calibration range. If this is identified, the laboratory will dilute the sample in order to bring the concentration back into the range of calibration.

Dilution may have several undesirable effects. First, the detection limit will be raised proportionally to the amount of dilution. Secondly, dilution may lessen the signal from other constituents of concern in the sample to the point that they are no longer identified. The consequence is that the sample results may be interpreted as not containing these compounds and the false negative results may bias the sampling effort. Additionally, for organic analyses, surrogates standards that are added to each sample prior to analysis may be diluted to the point that recovery suffers or is non-existent. If this is the case, the Tier I Data Validator will not be able to use the quality control information and the data will be flagged. Consequently, dilution may hinder the validation of a dataset.

Dilution must also be factored into certain data validation calculations. Most notably, the evaluation of blank data requires that the dilution factor be known. Chapter 6 - Blanks covers the evaluation of blank data and how to use the dilution factors to accurately assess the significance of blank contamination. If dilution is not accounted for, erroneous conclusions concerning laboratory contamination may result.

4.5 Detection Limits - Introduction

The majority of data validation in DHWM's Tier I process is concerned with evaluating the results of quality control samples. However, the Tier I Data Validator is also confronted with issues dealing with the detection limit of analyses. The evaluation of detection limits is important. For example, if dilution of the sample is necessary, the detection limits are raised proportionately to the amount of dilution. If the detection limits are raised above a regulatory or risk level, then the usability of the data is debatable. In addition, there is general confusion concerning the myriad of ways that detection and quantitation limits are reported. This chapter will describe the commonly used detection and quantitation limits and discuss the effect of dilution. This chapter will not present methods of data evaluation concerning raised detection limits and data usability. However, these issues should be discussed in terms of the overall process for a project.

4.6 Types of Detection Limits

Environmental data may be reported with a variety of detection or quantitation limits. Detection and quantitation limits are not the same. The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated as an exact value. The detection limit is based more upon the sensitivity of an analytical instrument and will only rarely account for the full range of matrix effects that are normally encountered with environmental samples. Various detection limits associated with environmental samples are discussed below. Quantitation limits will be discussed in Section 4.7.

4.6.1 Method Detection Limit (MDL)

The Method Detection Limit (MDL) is commonly found in environmental data reports. The procedure for determining the MDL is defined in the United States Code of Federal Regulations (40 FR part 136, Appendix B). The MDL is a statistically defined number based upon the standard deviation of seven replicate analyses of a standard that is analyzed over multiple-day time-period. The MDL is the minimum concentration of an analyte that can be determined with 99 percent confidence that the true value is greater than zero.

4.6.2 Instrument Detection Limit (IDL)

The Instrument Detection Limit (IDL) is the lowest concentration that can be detected by an instrument without correction for the effects of sample matrix or method-specific parameters such as sample preparation. IDLs are statistically determined based upon direct measurements. The IDL is defined as three times the standard deviation of the mean noise level. This represents a 99% confidence that the signal is not random noise. The inorganic methods in SW-846 give typical IDLs, but laboratory-derived IDLs (adjusted for sample size, dilution, and % moisture) are also commonly reported. The IDL does not account for matrix effects or for sample preparation.

4.6.3 Estimated Detection Limit (EDL)

The Estimated Detection Limit (EDL) is the minimum concentration required to produce a specified signal-to-noise (S/N) ratio. EDLs are not common. However, SW-846, Method 8290A for dioxins/furans requires that EDLs be used for reporting limits. Each analyte in each sample will have an explicitly determined EDL. EDLs are determined by accounting for the noise in the vicinity of an analyte, then multiplying that number by a S/N ratio of 2.5.

4.7 Quantitation Limits

The quantitation limit is the lowest amount of an analyte in a sample which can be quantitatively determined with suitable precision and accuracy. The quantitation limit differs from the detection limit in that it takes into account sample matrix effects. Unfortunately, like detection limits, there are a variety of quantitation limits that are reported with environmental data. Common quantitation limits are discussed in the following paragraphs.

4.7.1 Minimum Level of Quantitation (ML)

The **Minimum Level of Quantitation** (ML) is defined by U.S. EPA as the "lowest level at which an analytical system is expected to give a recognizable signal and acceptable calibration point." The minimum level value is determined by multiplying the MDL by 3.18 and rounding this value to the nearest number in the series (1, 2, or 5) x 10n , where n is an integer.

4.7.2 Estimated Quantitation Limit (EQL)

The Estimated Quantitation Limit (EQL) is the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. EQLs are reported in SW-846 for most organic methods. Most organic SW-846 methods give EQLs which are often set at some multiple of typical MDLs for reagent water.

Equation 4.3

EQL = [Method Detection Limit] X [Factor]

Multiplying factors, given for various matrices such as ground water, wastewater, soil and sludge, are also listed with each SW-846 method. In general, EQLs are approximately 5 to 10 times the MDL. It should be noted that EQLs listed for soil/sediment are typically reported on a wet-weight basis. Normally data are reported on a dry-weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample. It is always appropriate to discuss with laboratory if a reported EQL was determined on a dry or wet-weight basis and what specific weighting factors were used in calculating the EQL.

4.7.3 Practical Quantitation Limit (PQL)

A Practical Quantitation Limit (PQL) is generally the same as an EQL. However, since 1994SW-846 no longer uses PQLs. PQLs are still listed in regulatory and guidance documents, and good sampling practices imply that the Tier I Data Validator receive full documentation on the origin of a PQL listed in a data report. Unlike EQLs, PQLs do not have method or matrix-specific factors.

4.7.4 Sample Quantitation Limit (SQL)

The Sample Quantitation Limit (SQL) is, in general, like the PQL. It is not specifically mentioned in SW-846, but it is commonly found in data reports. Like the PQL, it does not have a specific definition, but is generally 5 to 10 times the MDL. The SQL represents a quantitation limit adjusted to reflect sample-specific actions, such as dilution or use of smaller aliquot sizes, or to report results on a dry-weight basis.

Chapter 5
Sample Report Completeness and Technical Holding Times

5.0 Introduction

The first step in conducting a data validation is ensuring that the sample data report, or laboratory data package, received from a laboratory or regulated facility is complete. Checking for **completeness** ensures that the sample report has all of the components necessary to evaluate the data. The Tier I Data Validator must examine the documents and, if necessary, ask for missing information from the facility and/or the laboratory. In order to determine if sufficient information is present, it is convenient to assume that a typical data report can be divided into three parts: 1) supporting documents, 2) analytical results and 3) quality assurance/quality control (QA/QC) information.

The following information comprises the components of a basic (Tier I) data package:

- Supporting Documents:
    - Chain of custody;
    - Case narrative;
    - Statements of quality assurance/data validity;
    - Sample receipt form.
- Analytical Results:
    - Sample results package;
    - Detection limits.
- QA/QC Sample Results:
    - Method blanks;
    - Matrix spike/ matrix spike duplicates;
    - Laboratory control samples;
    - Surrogate recoveries.

5.1 Supporting Documents

Most data reports will include information that can be used in conjunction with other applicable QA/QC information. In some cases, such as with the Chain of Custody or the statement of quality assurance, documentation is mandatory, because it is needed for litigation purposes. Other important information that can aid the Tier I Data Validator in validating data is found in the case narrative. Case narratives should summarize any quality control problems that were encountered by the laboratory during the analysis of a client's samples, and what steps the laboratory took to rectify these issues. By following the case narrative, the Tier I Data Validator may be able to focus on significant data problems or areas of concern within a data set. The Chain of Custody, case narrative, statement of quality assurance, and sample receipt form will be discussed in the following sections.

5.1.1 Chain of Custody

The Chain of Custody (COC) can be strictly defined as a record of all persons who handled the samples prior to relinquishing them to the laboratory for analysis. Figure 5.1 shows an example of a COC form. For the Tier I Data Validator, the COC also provides a valuable means of checking whether all the sample analyses that were requested were actually performed by the laboratory and whether the analyses were performed by the requested SW-846 method (if specified on that particular COC). It can also indicate any special handling procedures that were requested by the samplers. For instance, the Chain of Custody may specify that only a sub-set of parameters are to be analyzed for specific samples instead of the SW-846 analytical method's full target analyte list.

The COC should contain the following information:

- Sample field ID numbers;
- Date and time for each sample collected;
- List of requested parameters and/or SW-846 test methods;
- Preservatives used, if any;
- Sampler name(s);
- Special handling instructions;
- Signatures of people with control of the samples, including the person relinquishing the samples to the lab and the person from the laboratory receiving the samples;
- Date and time that samples were relinquished to the lab.

Note: Anytime control of the sample(s) is being relinquished, the individual relinquishing and accepting control of the sample(s) should mark the Chain of Custody with the date and time of transfer. However, it is the policy of some carriers to not sign off on the Chain of Custody for sample transfer.

The Tier I Data Validator will use the COC to determine if there is missing information in the sample data report. The COC stipulates the time and date each sample was collected and can be used as an independent check on **technical holding times**. The COC also should indicate the preservatives used for each parameter. This information can be cross checked with the sample receipt form to evaluate whether the proper preservatives were used for each sample. Other important information contained on the form includes identification of the sampler~~,~~ and signatures recording transference of sample custody. If the laboratory has an internal COC, it should also be included with the data package sample receipt form.

OHIO EPA - Division of Hazardous Waste Management	Name of Facility:
1800 Water Mark Dr. , Columbus, OH 43216 (614) 644-2917 Attn.	Facility and Sample locations:
Split Samples Offered ( ) Accepted ( ) Declined	

Sample ID.	Date	Time	COMP.	GRAB	ANALYSIS REQUIRED	NO. of CONTAINERS	STATION DESCI

Transferred By: Time/Date Received By:

Figure 5.1 Example Chain of Custody Record

5.1.2 Case Narrative

The case narrative is generated by the laboratory and states whether any problems were encountered between sample receipt and analysis. The case narrative must be signed by the laboratory's QA Officer or the Laboratory Manager, include certification that all analyses were performed by SW-846 or other approved methods, and meet any required standards. The case narrative often includes a discussion of general QA/QC procedures and any anomalies, such as QA/QC sample results that did not meet acceptable limits. The client's name, associated sample ID numbers, U.S. EPA SW-846 method numbers, an evaluation of technical holding times and a discussion of potential QA/QC sample concerns should also be included.

5.1.3 Statement of Quality Assurance

A statement of quality assurance by the laboratory is required by Ohio EPA's DHWM before an analytical report is accepted for data validation. Ohio EPA's RCRA Program regards a statement of quality assurance as a legal means of assuring that acceptable and uniform laboratory methods and QA/QC practices were followed by the laboratory. The Tier I Data Validator should review the data package for a statement attesting that all analytical methods were performed using acceptable methods, and that the QA/QC procedures stipulated in these methods were followed. Usually, this statement is signed by an officer of the company such as the quality assurance officer or laboratory manager. If this statement is missing from a report, the Tier I Data Validator should contact the facility or the laboratory and new report should be submitted to the Agency with the required statement of quality assurance.

5.1.4 Sample Receipt Form

A sample receipt form, or cooler receipt form, documents the condition of the samples as they are received by the laboratory. Information recorded on this form should include the temperature of the cooler and the condition of the sample containers. Temperature is an important measurement because many analytical parameters require cooling to 4°C. Information typically found on a Sample Receipt Form includes the following:

- Client name;
- Project name and number;
- Lab project manager's name and project number;
- Date received;
- Turn Around Time (TAT);
- Temperature of the samples within the cooler(s), and/or internal temperature of the cooler(s) upon receipt;
- Sample condition (i.e., are all containers intact?);
- Sample preservation methods utilized;
- Presence and condition of custody seals;
- Indication that sample labels and COC agree;
- Any damaged samples or the presence of air bubbles for volatile samples.

5.2 Analytical Results Package

Each data report should contain a complete set of results for analyses that were requested on the Chain of Custody form. The Tier I Data Validator should use information, such as the Chain of Custody and/or the provisions required in the approved closure plan, to assure that all the required analyses were performed. In addition, the Tier I Data Validator should review the submittal for obvious clerical mistakes that may affect interpretation of the data. Finally, if the data quality objectives for the set of sample analyses indicate that the data may be used in a risk assessment, it is important to review whether the data is reported using the proper detection or quantitation limits. If inconsistencies in the data set are noted, the Tier I Data Validator should request further information from the facility or laboratory.

5.2.1 Sample Results Package

The sample results must contain enough information to determine whether technical holding times were met, the proper analytical methods were used, and all the parameters that were requested were analyzed. In addition to the raw data, the sample results package normally contains the facility or site name, the field sample ID numbers, the laboratory ID numbers, the analytical method numbers, the date of receipt, the date(s) of extraction, and the date(s) of analysis. Additionally, the analysts' ID number or initials may be included with the data package.

5.2.2 Detection Limits

The analytical report must contain detection limits or acceptable reporting limits (which must be presented with dilution factor information). DHWM recommends that either the Method Detection Limit (MDL) or the Estimated Quantitation Limit (EQL), as defined by 50 FR 46906, be reported with the data set. See Chapter 4 for a discussion of detection and quantitation limits.

5.3 Quality Assurance and Quality Control Sample Results

Quality assurance and quality control (QA/QC) data that supports whether the analyses were performed in an acceptable manner, according to the analytical method, and within acceptable criteria for precision and accuracy, must be included in every analytical report. The type and amount of QA/QC information will be dependent upon the analytical method and data quality objectives for which the samples were taken. Most SW-846 methods detail the necessary QA/QC procedures that must be followed.

In general, to complete a Tier I Data Validation for common organic and inorganic analyses, a summary of quality control results for method blanks, matrix spikes/duplicates, laboratory control samples and surrogate recoveries (organic analyses only) should be included with the data package. Each of the quality control data is noted briefly in the following sections and discussed in detail in subsequent chapters.

5.3.1 Method Blanks

Method blanks, or preparation blanks, are used to determine whether laboratory contamination is present and, if so, whether it can significantly bias the analytical results. Method blanks consist of all the reagents that are used in preparing a sample for analysis, including internal standards and surrogate compounds. The data validation procedures for method blanks are given in Chapter 6.

5.3.2 Matrix Spike/Matrix Spike Duplicates (MS/MSD)

A matrix spike sample is an aliquot of either soil, water or other material (i.e., the matrix) that is spiked with known amounts of target analytes. Matrix spikes are analyzed with each analytical batch of samples of a given matrix. Matrix spikes are used to assess the effect or bias of the sample matrix on the analytical results.

Matrix spike duplicates are performed on a second aliquot of the same matrix as the matrix spike. The results of the matrix duplicate are compared to the matrix spike results and can give an indication of precision. Criteria for Matrix Spike/Matrix Spike Duplicate data validation are given in Chapter 7.

5.3.3 Laboratory Control Samples (LCS)

Laboratory control samples are blanks spiked with a representative set of target analytes (usually the same analytes and the same concentrations as with matrix spike samples). The performance of an analytical instrument is largely measured with the LCS results. If an analytical instrument does not perform adequately on the LCS sample, the ability of the analytical instrument to accurately analyze non-QC samples is questionable. Immediate corrective action by the laboratory should be performed. The LCS data validation criteria are found in Chapter 8.

5.3.4 Surrogate Compound Analysis

Surrogate compounds, or system monitoring compounds, are spikes of brominated or deuterated compounds incorporated into samples for organic analyses. These analytes have similar characteristics to target analytes but are not commonly found outside the laboratory setting.

Therefore, the recovery of the surrogate compounds is used as a measure of accuracy and to judge the effect of sample matrix on the recovery of target analytes. Surrogate compound data validation procedures are given in Chapter 9.

5.3.5 Regulatory Tests

Regulatory tests including the Toxicity Characteristic Leaching Procedure (TCLP), flashpoint and corrosivity (pH) tests have specified procedures that must be performed by the laboratory. For example, the TCLP requires a minimum of 100 grams for proper extraction of metals and SVOCs in a solid waste sample. These specific method requirements have been the primary reasons for DHWM rejecting data to this point in time. The tests and the requirements for these tests are outlined in Chapters 11 through 13.

5.4 Data Report Organization

Individual laboratories format their data reports in a variety of different ways. For instance, DHWM's former contract laboratory had five different reporting packages differentiated by level of QC data presented. However, most laboratories divide their data packages into sections of inorganic, volatile organic, and semi-volatile organic data. It is recommended that the Tier I Data Validator organize the data report into separate analytical batches (usually identified by a specific batch number) based on the analytical methods, matrices, and laboratory analytical methods or parameters of interest. By doing this, it is possible to associate the pertinent analytical QA/QC data with each batch.

1. Separate the laboratory data into the following report sections:
   - Chain of custody form(s);
   - Narrative summary;
   - Sample results;
   - Quality control data.

2. Separate sample results by matrix:
   - Water samples (ground water, surface water, etc.);
   - Solid and waste samples (soils, sediments, sludges, solid and liquid wastes, leachate, etc.).

3. Separate sample results in water and solid/waste matrices by specific analytical methods:
   - Example: The parameters received include Volatile Organic Compounds (VOCs) in Ground water, Base Neutral and Acid (BNA) Semi-Volatile Organic Compounds (SVOCs) in ground water, and benzene/toluene/ethylene/xylene (BTEX) compounds in soil. The data package can be arranged in the following way:
   - Place all VOC results by SW-846, Method 8260B together
   - Place all BNA results by SW-846, Method 8270D together
   - Place all BTEX results by SW-846, Method 8021B together

4. Arrange all sample results for each SW-846 method and matrix in chronological order according to the date of analysis:
   - Based on the number of analyses requested for each sample, there will be one or more groups of sample results placed in chronological order and separated by SW-846 method and sample matrix.

5. Separate the QA/QC data by matrix/method/date (i.e., batch), and combine this information with the appropriate sample results:
   - Laboratories normally state which samples are associated with each QA/QC data sheet. If the data report package is not clear as to which analytical samples are associated with each QA/QC sample/batch, contact the laboratory for clarification.

6. Proceed to Tier I Checklist:

5.5 Technical Holding Times

Technical holding time is the time, usually measured in days, in which a sample must be processed through the steps of collection, preservation, laboratory preparation, and analysis. Technical holding time varies according to the analytical method used and the matrix being evaluated. Each party involved with a given sample, whether it is collection, packaging, shipping, receiving, or analytical processing, should perform their duties in a manner which ensures that technical holding times are met. This would include the sampler promptly shipping samples with short technical holding times and notifying the laboratory of their time critical nature, as well as the laboratory promptly contacting sampling representatives if questions exist as to the analytical request. Furthermore, each party should have standard operating procedures in place which detail the way their respective duties will be carried out.

5.6 Definitions

Technical Holding Time: The time, measured in days, in which a sample must be processed - through the steps of collection, preservation, laboratory preparation, and analysis as specified by the analytical method and sample matrix.

5.7 Specific Information

Evaluation of whether a sample's technical holding time has been met is an essential component of the data validation process. If the technical holding time is not met, it may cause the analytical results to be rejected or qualified as estimated. Technical holding times range from as short as 15 minutes for pH analysis of ground water samples and 48 hours for Method 5035 extraction (EnCore™ samplers), to as long as six months for Method 1311, metals extraction. Personnel involved in development of sampling and analysis plans (SAPs) must be aware of these considerations to ensure that their responsibilities for technical holding times are met.

When a technical holding time has been exceeded, it may cause the Tier I Data Validator to qualify the data as “J,” estimated, as “UJ,” estimated undetected, or as “R,” rejected. It does not mean that all of the data is unusable. Detected results which are qualified as “J-” should be considered biased low. The reason for, and length of, the technical holding time exceedance in conjunction with the DQOs for that sample will help the sampler or other personnel requesting the analysis to determine whether the data is of value. Additionally, a sample with an exceeded technical holding time may be considered a candidate for re-sampling based on initial results, regulatory or data quality objectives, and sampler and/or program discretion. Furthermore, a sample qualified as “UJ,” estimated undetected, may, in fact, contain constituents of concern above the detection or regulatory limit that remained undetected due only to improper preservation or technical holding time exceedance(s). Such results may be considered unusable, or a candidate for re-sampling, based on the end use of the data and the best professional judgment of the Tier I Data Validator.

Particular attention must be paid to the technical holding time when an extraction or preparation step is performed as part of the analysis. It is not sufficient to evaluate only the time elapsed between sampling and analysis. If a technical holding time is established for the steps of extraction and/or preparation, and these holding times are not met, then the data must be qualified per the Tier I Data Validation Checklist and the sampling DQOs.

5.8 Checklist

The technical holding times for the most common hazardous waste methods are listed on the following page in Table 5.1.

Table 5.1 (Table 2 from the Tier I Checklist) Technical Holding Times for Volatile, Semi-Volatile, Metals and pH Samples

Method	Preserved*(see note below)	From field collection to extraction	From extraction to preparation	From extraction to analysis	Max Holding Times	Common preservative
VOCs (8260B) (aqueous)	Yes	NA	NA	14 days	14 days	Cool to 4+/-2 ◦c, HCl
VOCs (8260B) (aqueous)	No	NA	NA	7 days	7 days	Cool to 4+/-2 ◦C
VOCs (8260B) (liquid waste)	No	NA	NA	14 days	14 days	Cool to 4+/-2 ◦C
VOCs (8260B) (solid/soil/waste)	No	NA	NA	NA	14 days	Cool to 4+/-2 ◦C or no preservative
VOCs (EnCore) (5035/8260B) (solid/soil/waste)	Yes	2 days	NA	12 days	14 days	Encore Sampler or pre-preserved VOA vial
SVOC (8270D)	Yes	7 days	NA	40 days	47 days	Cool to 4+/-2 ◦C
Total Metals (6010C/7000B)	Yes	NA	NA	180 days	180 days	Aqueous: HNO3 (pH<2); Solids: 4+/-2 ◦C
Mercury (7470A, 7471A)	Yes	NA	NA	28 days	28 days	Aqueous: HNO3 (pH<2); Solids: 4+/-2 ◦C
TCLP VOCs (1311/8260B)	No	14 days	NA	14 days	28 days	no preservative
TCLP SVOCs (1311/8270D)	No	14 days	7 days	40 days	61 days	no preservative
TCLP Metals (except mercury) (1311/6010C)	No	180 days	NA	180 days	360 days	no preservative
TCLP mercury (1311/7470A)	No	28 days	NA	28 days	56 days	no preservative
pH (9040C)	No	NA	NA	24 hours	1 day	no preservative

The Tier I Data Validator should enter all pertinent data in Table 1 of the Tier I Data Validation Checklist or use Table 5.2. In order to facilitate this evaluation, the following documents should be consulted: Chain of Custody, cooler receipt form, sample run log(s), extraction log(s), and bench sheet(s). If the necessary information is not present, the laboratory should be contacted for additional deliverables.

Table 5.2 Technical Holding Times

2.0 Technical Holding Times						
Sample ID	**Sample Matrix**	**Preserved? Y/N**	**Date Sampled**	**Date Lab Received**	**Date Extracted**	**Date Analyzed**

While data sets with limited samples or parameters may not contain extensive technical holding time information, multi-media events typically will. All technical holding time information should be evaluated. While this step of the Tier I Data Validation process is not particularly technical, it may be confusing and present organizational difficulties. Since a review of the completed table may cause analytical data to be qualified or rejected, care and time is required in completing this section. Additional copies of Table 1 (Completeness and Technical Holding Times found in the Tier I Data Validation Checklist) may need to be printed to record all technical holding times.

The following information is a completed table for the technical holding times for the “Dirty Drum Corporation” sampling event.

Table 5.3 Dirty Drum Corporation Completeness and Technical Holding Times Example

(Example uses Table 1 from the Tier I Data Validation Checklist)

TABLE 1 - Completeness and Technical Holding Times										
Sample ID	**Lab ID**	**Matrix**	**Sample Date**	**Date Received by the Lab**	**Parameter**	**Extraction Date**	**Preparation Date**	**Analysis Date**	**QA/QC Data Present ?**	**Batch ID#**
Waste Pit 1	51101 -9386	solid	5/10/01	5/11/01	Total VOCs 8260B	-	5/22/01	5/22/01	Yes	501522
Waste Pit 1		solid	5/10/01	5/11/01	TCLP VOCs 8260B	5/17/01	5/29/01	5/31/01	Yes	501208
Waste Pit 1		solid	5/10/01	5/11/01	TCLP SVOCs 8270D	5/17/01	5/24/01	5/29/01	Yes	501184
Waste Pit 1		solid	5/10/01	5/11/01	Total Metals 6010C	-	-	5/29/01	Yes	
Waste Pit 1		solid	5/10/01	5/11/01	Total Hg 7471B	-	6/1/01	6/2/01	Yes	
Waste Pit 1		solid	5/10/01	5/11/01	TCLP Metals 1311/6010 C	5/17/01	6/1/01	6/4/01	Yes	
Waste Pit 1		solid	5/10/01	5/11/01	TCLP Hg 1311/ 7471B	5/17/01	6/1/01	6/12/01	Yes	
Drum 54		liquid	5/10/01	5/11/01	Total VOCs 8260B	-	5/23/01	5/26/01	Yes	
Drum 54		liquid	5/10/01	5/11/01	TCLP VOCs 8260B	5/17/01	5/23/01	5/26/01	Yes	
Drum 54		liquid	5/10/01	5/11/01	TCLP SVOCs 8270D	5/17/01	6/1/01	6/6/01	Yes	
Drum 54		liquid	5/10/01	5/11/01	flash-point ASTM	-	-	5/30/01	Yes	

1.2 Technical Holding Times - Volatile Organic Compounds

1.2.1 Are samples properly preserved? Check preservation requirements, chain of custody, and sample receipt form for discrepancies. *Action: Note improprieties and use the information to qualify results.*	List impropriety(-ies): No preservatives were listed on the COC for either sample. Contacted facility rep., who stated that no preservatives, other than ice, were used. All samples were correctly preserved as they were waste samples.
1.2.2 If samples were improperly preserved, or unpreserved, and the technical holding times were exceeded, qualify all positive results for affected samples as "J-" and all non-detected results as "UJ."	List sample ID(s): Waste Pit: All VOC analyses were within holding times. Drum 54: Total VOC technical holding time was exceeded from sampling to analysis (16 days instead of the 14 days specified). **Results must be qualified as per the criteria**.
1.2.3 If technical holding times are greatly exceeded (> 2x the time requirement) upon analysis or re-analysis then the Validator may use professional judgment to qualify all non-detected compounds as "J" or "R" based upon professional judgment and on DQOs.	List sample ID(s): NA

In this example, the COC does not indicate the presence of preservatives in the sample containers. However, neither the sample narrative nor the cooler receipt form indicates any deviations. The Tier I Data Validator should contact the sampler and/or laboratory to determine if proper sample preservatives were used. In this case, the sampler was contacted and confirmed that no preservatives, other than ice, were used due to the sample matrix being waste. This should have been reported on the COC to alert the laboratory to the need for potentially expedited action(s) based on technical holding times for unpreserved samples.

In this example, technical holding times were not met for two of the analyses. For Drum 54, VOCs (SW-846, Method 8260B), the analysis was performed in 16 days instead of the method-specified 14 days. Also, for Drum 54, TCLP SVOCs (SW-846, Methods1311/8270D), the step from extraction to preparation was performed in 15 days instead of the method-specified 7 days. For this reason, these analyses must be qualified.

1.2 Technical Holding Times - Semi-Volatile Organic Compounds

1.2.4 If technical holding times are exceeded (Table 1), qualify all positive results for affected samples as "J-" and all non-detected results as "UJ."	List sample ID(s): Waste Pit: TCLP SVOC technical holding times were not exceeded. Drum 54: TCLP SVOC technical holding times were exceeded for the extraction to SVOC preparation interval (15 days instead of the 7 days specified). **Results must be qualified as per the criteria**.
1.2.5 If technical holding times are greatly exceeded (> 2x the time requirement), based on the project's DQOs, the data Validator may use professional judgment to qualify all non-detected compounds as "R" and all positive results as "J-."	List sample ID(s): Waste Pit: TCLP SVOC technical holding times were not exceeded. Drum 54: TCLP SVOC technical holding times were exceeded by greater than 2x for the extraction to SVOC preparation interval (15 days instead of the 7 days specified). **Results must be qualified as per the criteria**.

1.2 Technical Holding Times - Inorganic Compounds

1.2.6 Are samples properly preserved (4C for solids; acid preservation for aqueous samples)? Check preservation requirements, chain of custody, and sample receipt form for discrepancies. *Action: Note any impropriety and use the information to qualify results.*	List impropriety(-ies): Drum 54: No preservatives were listed on the COC for either sample. Contacted facility rep., who stated that no preservatives, other than ice, were used. All samples were correctly preserved as they were waste samples. Based on the Case Narrative and the Sample/Cooler Receipt form, the sample was received at 5°C. However, qualification for temperature is not necessary as this is a waste sample.

1.2.7 If samples were improperly preserved or properly preserved and the technical holding times were exceeded (Table 1), qualify all positive results for affected samples as estimated ("J-") and all non-detected results as "UJ" or rejected ("R") depending on DQOs.	List sample ID(s): NA
1.2.8 If technical holding times are greatly exceeded (> 2x the time requirement), the Validator may use professional judgment and the project's DQOs to qualify all non-detected compounds as "R" and all positive results as "J-" or "R" depending on DQOs.	List sample ID(s): NA

According to the cooler receipt form, the samples were received at 5°C which is acceptable since the preservation requirement is 4+/-2°C. Furthermore, as these samples were waste material, they should not be acid preserved, but chilling the samples is acceptable.

When evaluating technical holding times, special attention should be given to the actual method(s) used to analyze individual analytes, as several methods may be used to analyze a set of target compounds or elements for a sample. Each method may have different technical holding time requirements. A common example of this is the use of SW-846, Method 7471B for mercury analysis in conjunction with SW-846 Methods 6010C and 6020A for the remainder of the RCRA 8 metals (see technical holding times for these methods in Table 2). SW-846 Methods 6010C and 6020A are not appropriate for the analysis of mercury. Another reason that laboratories may use other methods to analyze elements in a given sample is to achieve lower detection limits for individual analytes (e.g., using SW-846, Method 6020A for arsenic, cadmium and lead). Finally, if pH data were presented, the following excerpt from the Tier I Data Validation Checklist can be used to evaluate data.

1.2 Technical Holding Times - pH

1.2.9 If technical holding times are exceeded, the Validator may use professional judgment and DQOs to qualify data as "R" or "J-." **Note:** For ground water samples, pH should be evaluated in the field within 15 minutes of sampling. For waste samples, the technical holding time is more flexible and requires an examination of the type of waste and the project's DQOs. If technical holding times exceed 24 hours, consider qualification. If wastes exhibit the characteristic of corrosivity (i.e., <pH 2 or > pH of 12.5), samples should not be qualified.	List sample ID(s):

This data report did not include pH analyses, so this section is not evaluated in this example.

The Data Validator should note that no guidance currently exists for technical holding times for flashpoint analysis. The data validator should consult ASTM Standard D-93 and Chapter 12 of this manual for details on flashpoint evaluation.

5.9 Questions

Q: What if a particular sample or analyte is repeatedly qualified as "J," estimated, or "UJ," estimated undetected, based on Tier I Data Validation Checklist criteria?

A: If Tier I Data Validation results in an analyte being repeatedly qualified, it may point to greater problems with the procedure or analysis. There is no specific guidance for accepting or rejecting ("R") such data. However, the Tier I Data Validator has the discretion, based on best professional judgment, to accept or reject this data. This decision is best made considering the original DQOs for the sample (see Chapter 14 for additional discussion of this topic). It is recommended that the Tier II Data Validator be consulted if there is a question regarding how to best qualify such data.

Q: What if a technical holding time exceedance is due to error on behalf of the party requesting the analysis (such as delay in shipment of EnCore or pH samples, or "add on" requests for analysis made to the laboratory after the samples have been received)?

A: If technical holding times are exceeded, regardless of the reason, data should be qualified or rejected using the Tier I Data Validation Checklist and in consideration of DQOs. How this data will be used and other potential measures to be taken, such as re-sampling, will be at the discretion of the sampler and program.

Q: What if a technical holding time is exceeded due to the sampler not field preserving a sample or due to ambiguity as to sample preservation on the COC?

A: The results should still follow the Tier I Data Validation Checklist and receive the appropriate qualifiers in regard to sample DQOs. However, it should be a standard operating procedure of the laboratory to contact the sampler to clarify any questions or discrepancies that may arise.

Q: What are the technical holding times for pesticides, herbicides, and radiological samples for aqueous matrices?

A: Pesticides and herbicides have holding times of 7 days from sampling until extraction and 40 days from extraction to analysis for a total of 47 days. Most radiological parameters have a holding time of 6 months. However, individual radiological parameter holding times should be checked with the analytical method to verify whether an analysis was performed within holding times.

Chapter 6
Blanks

6.0 Introduction

Blanks are used throughout the analytical process to verify that the analytical equipment, reagents, internal standards, surrogates and handling procedures do not introduce constituents of concern into the samples at unacceptable levels. For SW-846 methods, blanks are required for both metals and organic compound analysis. The three most common types of blanks found in a Tier I data package are calibration blanks, instrument blanks and method blanks. Other types of blanks that may be encountered are field blanks, rinsate blanks and trip blanks. These important quality control samples are used to assess whether sampling practices at a field site have imparted an undue bias to the unknown samples. These quality control samples are evaluated with many of the same criteria that are presented in this manual. However, for a Tier I Data Validation, the principle emphasis is on evaluating method blanks.

6.1 Definitions

Batch: A batch is a group of samples that behave similarly, with respect to the analytical procedures being employed, and are processed as a unit. Most SW-846 methods define a batch as twenty total samples, which include quality control samples and "client/field samples." For Quality Control (QC) purposes, twenty is the maximum number of samples in a batch (as sample groups of greater than twenty must be split into multiple batches for laboratory QC purposes).

Field Blanks: Usually an organic or aqueous solution (as free of analytes as possible) that is transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. This serves as a check on reagent and environmental contamination. Generally, one field blank is analyzed with each analytical batch or every twenty samples, whichever is more frequent.

Instrument Blanks: Blanks that are analyzed after any sample that has high concentrations of analytes. The instrument blank assesses whether residual contaminants in the analytical system could be carried over to other samples.

Method Blanks: Blanks that are prepared using the same techniques and reagents as field samples. Method blanks are used to assess whether a positive bias has been imparted to the results through the analytical procedures or materials used by the laboratory. Method blanks are also referred to as analytical blanks or preparation blanks.

Rinsate Blanks: Usually an organic or aqueous solution that is analyte-free and transferred to the site, opened in the field, and poured over or through the decontaminated sample collection device, collected in a sample container, and returned to the laboratory. Generally, one equipment blank is analyzed with each analytical batch or every 20 samples, whichever is more frequent. The results of analysis are used to demonstrate adequate cleanliness and, or decontamination of the sample equipment. Rinsate samples may not be necessary if dedicated equipment is used for each sample collection (i.e., disposable bailers).

Trip Blanks: A sample of analyte-free media taken from the laboratory to the sample site and returned to the laboratory, unopened. A trip blank is used to document contamination attributable to shipping and field-handling procedures. This type of blank is useful in documenting contamination of samples analyzed for volatile organic compounds (VOCs). The trip blank must accompany sample containers to and from the field when analysis for VOCs is being requested.

6.2 Method Blanks

Data from the method blank is used to verify that the reagents and preparation procedures do not impart an unacceptable bias on the sample results. Under optimum conditions, no constituents of concern are measured in the method blank above the Method Detection Limit (MDL). However, it is common to find some target analytes above the detection limits. This is often due to impurities, such as solvents or acids (or impurities found in solvents/acids), which are commonly used in laboratories, contaminating reagents, or cross contamination from other highly contaminated samples.

Method blanks consist of reagent grade water or other matrix that is treated in the same manner as a sample. Though method blanks are created in the lab, they are extracted and/or digested in the same manner as a sample collected in the field. Method blanks are analyzed at least every twelve hours or at a rate of one method blank per every twenty samples. Most SW-846 methods define a batch as twenty total samples, which include quality control samples and samples of interest. The sequence of method blank analysis is also important. A method blank is analyzed just after each calibration verification sample in each batch.

If samples of interest are divided into different analytical batches, results for more than one method blank should be included with a sample report. In this case, it is important to note which specific sample results are associated with each method blank. Consequently, a method blank will be analyzed for each matrix type and for each SW-846 method. If no information is given that allows for correlation of sample results with a particular method blank, then either the laboratory or the facility must be consulted and the information provided. Please refer to the boilerplate letter found in Appendix I to simplify requesting more information from a laboratory.

6.3 Data Requirements for Blank Validation

The Data Validator must examine a data package for the following information:

- Batch ID: This information will relate the sample batch QA/QC results to the correct samples;
- Sample identification;
- Instrument identification;
- Date and time of analysis;
- Results of blanks analysis;
- Sample results;
- Dilution factors;
- Detection limits;
- Which samples of interest, Laboratory Control Samples (LCS), and Matrix Spikes/Matrix Spike Duplicates (MS/MSD) are associated with this blank.

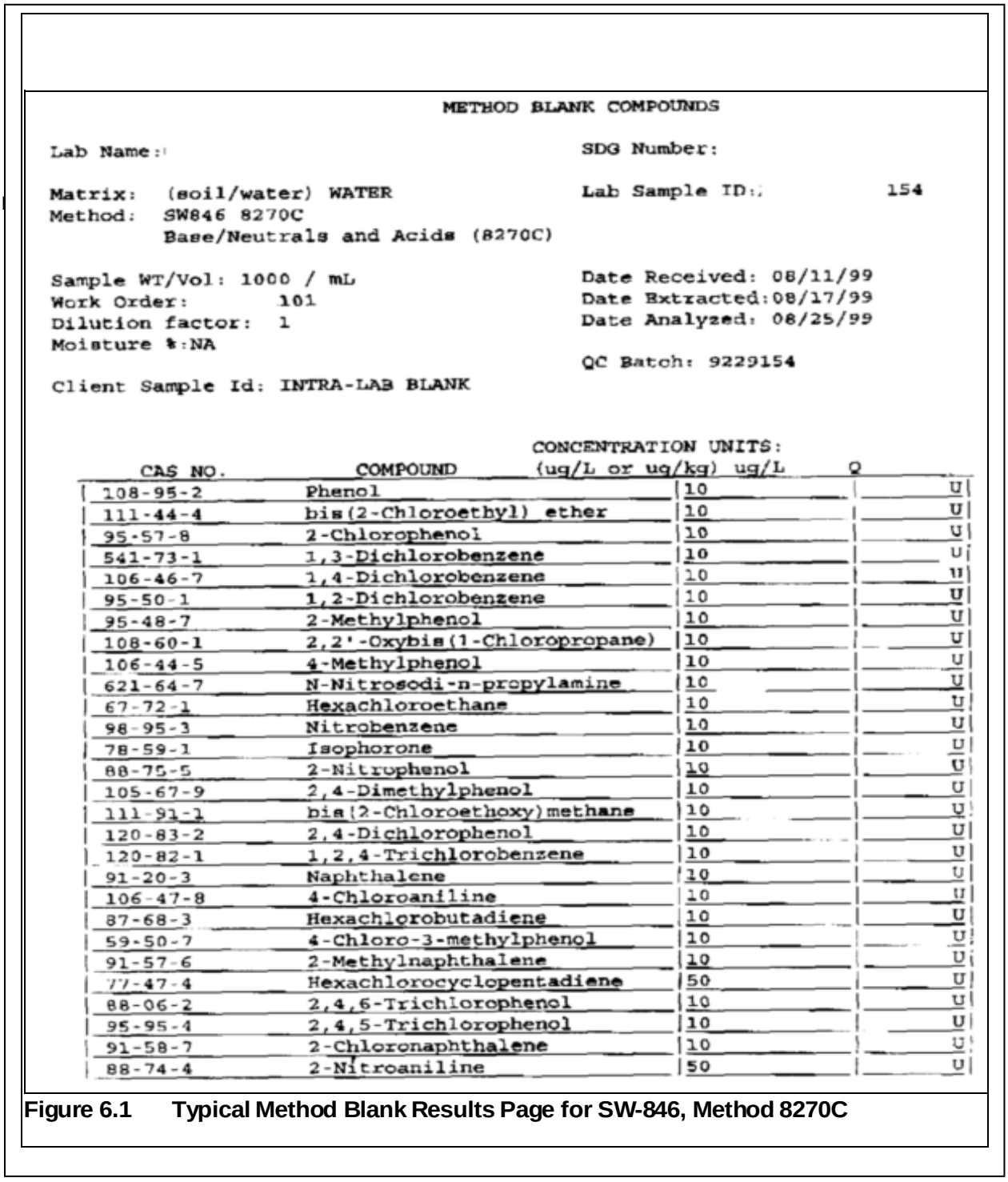
Figure 6.1 shows a typical method blank data summary page. The method blank report has a variety of information that may prove useful. This information includes the date the samples were extracted and analyzed, the detection limit and dilution factor. In this example, analytes, matrix type (water here - but could be solid, liquid, or waste), and SW-846 method number (8270C) are also listed. A list of samples associated with the method blank is useful information that is not present in this example. This information is especially important when analytes are detected in the method blank. If these same analytes were detected in the samples of interest, then blank evaluation would be necessary. If no analytes were detected in the samples, blank valuation would not be necessary. Laboratories usually summarize most of the required data for their clients.

The QC batch number will enable the Data Validator to associate the sample results, MS/MSD, surrogate and LCS results with this particular method blank. This can be extremely important if there are numerous samples of different matrices that are spread among different analytical batches. There will be one method blank associated with each batch of samples of a particular matrix. For example, if soil and water samples were analyzed by SW-846, Method 8260B, then at least two method blanks will be associated with the sample results (one for each matrix). Additional SW-846 methods will also have associated method blanks. Finally, if there are sufficient samples that the laboratory has to split them into multiple analytical batches, then each additional batch will have method blank data. The laboratory run log can also be helpful in associating samples with the appropriate method blank (batch QA/QC).

One way to simplify the evaluation of blanks is to separate the sample results and the associated Quality Assurance/Quality Control (QA/QC) data from a data report by matrix. If necessary, the data can be further subdivided by batch. In this manner, large, complicated data sets can be made more manageable.

If any of the required data is missing, the Data Validator must either consult with the laboratory or ask the facility to supply the necessary information. In addition, the Tier I Data Validator may consult with their district's Tier II Data Validator.

Figure 6.1 Typical Method Blank Results Page for SW-846, Method 8270



METHOD BLANK COMPOUNDS

Lab Name:

SDG Number:

Matrix: (soil/water) WATER
Method: SW846 8270C
Base/Neutrals and Acids (8270C)

Lab Sample ID: 154

Sample WT/Vol: 1000 / mL
Work Order: 101
Dilution factor: 1
Moisture %:NA

Date Received: 08/11/99
Date Extracted:08/17/99
Date Analyzed: 08/25/99

QC Batch: 9229154

Client Sample Id: INTRA-LAB BLANK

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/kg) ug/L	Q
108-95-2	Phenol	10	U
111-44-4	bis(2-Chloroethyl) ether	10	U
95-57-8	2-Chlorophenol	10	U
541-73-1	1,3-Dichlorobenzene	10	U
106-46-7	1,4-Dichlorobenzene	10	U
95-50-1	1,2-Dichlorobenzene	10	U
95-48-7	2-Methylphenol	10	U
108-60-1	2,2'-Oxybis(1-Chloropropane)	10	U
106-44-5	4-Methylphenol	10	U
621-64-7	N-Nitrosodi-n-propylamine	10	U
67-72-1	Hexachloroethane	10	U
98-95-3	Nitrobenzene	10	U
78-59-1	Isophorone	10	U
88-75-5	2-Nitrophenol	10	U
105-67-9	2,4-Dimethylphenol	10	U
111-91-1	bis(2-Chloroethoxy)methane	10	U
120-83-2	2,4-Dichlorophenol	10	U
120-82-1	1,2,4-Trichlorobenzene	10	U
91-20-3	Naphthalene	10	U
106-47-8	4-Chloroaniline	10	U
87-68-3	Hexachlorobutadiene	10	U
59-50-7	4-Chloro-3-methylphenol	10	U
91-57-6	2-Methylnaphthalene	10	U
77-47-4	Hexachlorocyclopentadiene	50	U
88-06-2	2,4,6-Trichlorophenol	10	U
95-95-4	2,4,5-Trichlorophenol	10	U
91-58-7	2-Chloronaphthalene	10	U
88-74-4	2-Nitroaniline	50	U

Figure 6.1 Typical Method Blank Results Page for SW-846, Method 8270C

6.4 Data Evaluation

Method blank data is evaluated similarly for both organic compound analysis and metals analysis. Ideally, method blank data will not contain any analytes of interest above the detection limit of the instrument. However, when the method blank does contain analytes of interest above the detection limit, the Data Validator must assess whether a positive bias has been imparted to the sample results. This is done by comparing the analytes identified in the method blank with results from the associated samples. Method blanks may be assessed as follows:

- If the method blank does not contain target analytes above the detection limit, no further action or qualification is necessary.

- If the method blank has target analytes above the detection limit, but these same analytes were not identified in the sample results, then no further qualification is necessary.

- If the method blank has target analytes above the detection limit and positive results for these same analytes are reported in the sample results, then blank contamination must be assessed and the data qualified, if necessary. In this case, the Data Validator must make sure that correct sample results are associated with the correct method blank (i.e., from the same batch), and there are sufficient data to proceed with the validation.

6.4.1 The 5X and 10X Rules

Please refer to section 6.5.1 for more explanation about the 5X and 10X Rules. The 5X and 10X Rules will be applied if the evaluation shows that:

- The sample result(s) are less than 5X or 10X the concentration of the detected target analytes in the blank. If so, the sample results will be qualified as “U,” undetected.

- The sample result(s) are more than 5X or 10X the concentration of the detected target analytes in the blanks. If so, the results will not be qualified.

6.4.2 MS/MSD

The Data Validator will also examine the MS/MSD data for potential positive bias associated with blank contamination.

6.5 Blanks Associated with Organic Compound Analysis

The principal criteria used to evaluate blank data is that no target compounds are found in a blank above the Method Detection Limit (MDL). If contaminants are detected in the blanks, but not observed in samples, then generally no action is required. This is easily applied to a data report. However, concern also exists as to how to qualify data when blank contamination is present and positive results are observed. U.S. EPA recognized this fact and developed a concept known as the 5X and 10X Rules for organic compound analysis (SW-846, Methods 8260B and 8270D).

The 5X Rule applies to every organic compound found in a blank except for a select few where the 10X Rule applies. These select compounds are common laboratory solvents and are often observed contaminating blanks.

10X Rule
Common Laboratory Contaminants

- Methylene Chloride (8260B)
- Acetone (8260B)
- 2-butanone or methyl ethyl ketone (8260B)
- Cyclohexane (8260B*)
- Phthalate esters (8270D)

Note: Cyclohexane is not normally included on the 8260B target analyte list.

Using the 5X and 10X Rules is simple. The rule is designed to gauge if contamination found in a blank could account for apparent contaminant(s) present in a field sample. If a target compound is found in a blank and also detected in a sample, but it is not one of the common laboratory contaminants listed above, and if the sample value(s) is less than 5 times the blank concentration (5X Rule), then positive results are qualified "U," undetected. If one of the common laboratory contaminants is detected in both the blank and a sample, and if it is less than 10 times the blank concentration (10X Rule), then the sample result is qualified "U," undetected. If the concentration of a sample is greater than 5 or 10 times the blank concentration, then no qualification is necessary. In other words, the bias imparted by either the contaminated reagents or analytical system is negligible, and the results in the sample can be viewed as representative. The following examples will be useful in illustrating how to apply the 5X and 10X Rules.

Example 6.1 will illustrate that dilution of a sample may be a key factor in evaluating blank contamination. When a sample is diluted, the detection limit is effectively raised by the dilution factor. In order to evaluate whether blank contamination is significant, blank and sample results must be compared on the same basis (the amount "seen" by the instrument's detector). In other words, the dilution factor must be taken into account in order to correctly apply the 5X or 10X Rules. Example 6.2 illustrates how to account for dilution, and Example 6.3 illustrates a common problem with detection limits and blank contamination.

Example 6.1 Is the Methylene Chloride in the sample "real" or is it a laboratory contaminant?

Sample	Parameter	Result	Method Detection Limits (MDL)
Soil Sample	Methylene Chloride	40	5 mg/L
Method Blank	Methylene Chloride	10	5 mg/L

1. What is the dilution factor? The dilution factor is usually listed with the results. If it is not, the Data Validator may evaluate whether the sample was diluted by examining the detection limits of the sample and the blank. The dilution factor is the multiplier between the detection limit of the sample and that of the blank. In this example, the detection limits are the same. Therefore, the dilution factor is equal to the sample detection limit divided by the blank detection limit. ~~Which,~~ In this case, it is equal to 1.

2. Do the 5X or 10X Rules apply? Methylene chloride is one of the common laboratory contaminants. Therefore, the 10X Rule applies.

3. Apply the 10X Rule: The 10X Rule states that sample results less than 10 times the blank concentration must be qualified. In this example, the blank concentration is 10 mg/L. Therefore:

   10 mg/L (blank) X 10 (10X Rule) = 100 mg/L

   Since 100 mg/L is larger than the sample result of 40 mg/L, the sample result may be the due to laboratory contamination and the sample result will be qualified as "U," undetected.

Sample	Parameter	Results	Method Detection Limits	Qualifier
Soil Sample	Methylene Chloride	40	5 mg/L	U*
Method Blank	Methylene Chloride	10	5 mg/L	

*The qualifier "U" is used to indicate that the sample result is "undetected."

Example 6.2 Is the Benzene in the sample "real" or a laboratory contaminant?

Sample	Parameter	Results	Method Detection Limits (mg/L)
Soil	Benzene	200	10
Method Blank	Benzene	10	1

Steps to evaluate the problem:

1. What is the dilution factor? The MDL is elevated in the sample results as compared to the blank. The dilution factor can be calculated by dividing the MDL of the sample results by the MDL of the blank.

   Dilution Factor = 10 mg/L (sample MDL) ÷ 1 mg/L (blank MDL) = 10
   The dilution factor must be taken into account in order to use the 5X or 10X Rules.

2. Do the 5X or 10X Rules apply? Benzene is not one of the common laboratory contaminants. Therefore, the 5X Rule applies.

3. Dilution Evaluation: The dilution factor must be taken into account. Either divide the sample concentration by the dilution factor or multiply the blank concentration by the dilution factor before applying the 5X Rule. If dividing the sample result by the dilution factor then:

   200 mg/L ÷ 10 = 20 mg/L (concentration actually detected by the instrument)

4. Apply the 5X Rule

   10 mg/L (blank result) X 5 (5X Rule) = 50 mg/L

   Since 50 mg/L is greater than 20 mg/L (sample result corrected for dilution), the results can be attributed to blank contamination. Therefore:

Sample	Parameter	Results	Method Detection Limit	Qualifier
Soil Sample	Benzene	200	10	U

Example 6.3 Is the 2-butanone in the sample real or laboratory contamination?

Note: This example uses a slightly different method than above. Here the amount detected in the blank is multiplied by 5X or 10X (instead of dividing the sample result) but the end result is the same.

Sample	Parameter	Results	Reporting Limit (mg/L)
Soil Sample	2-butanone	300	20
Method Blank	2-butanone	25	20

Steps to evaluate the problem:

1. What is the dilution factor? Apparently, the dilution factor is 1:

   Dilution factor = 20 (sample reporting limit) ÷ 20 (blank reporting limit) = 1

   However, the report does not list the method detection limit, but rather a reporting limit. Reporting limits are not the same as a method detection limit, but rather a value that the laboratory can reliably achieve for most matrices that it receives. Therefore, if the dilution factor is not listed in the report, it is not possible to determine whether a dilution factor will be accounted for in the blank contamination procedure. At this point either proceed with the calculations or consult the facility or the laboratory for method detection limit information or information on dilution. If proceeding, then:

2. Do the 5X or 10X Rules apply? 2-butanone is a common laboratory contaminant, so the 10X Rule applies.

   25 mg/L (method blank concentration) X 10 (10X Rule) = 250 mg/L

3. Dilution Evaluation The sample result was 300 mg/L of 2-butanone, which is greater than the value of the blank multiplied by 10. Therefore, the amount of 2-butanone observed in the sample is considered “real” and the result is unqualified.

Sample	Parameter	Results	Reporting Limits (mg/L)	Qualifier
Soil Sample	2-butanone	300	20	
Method Blank	2-butanone	25	20	

Remember, the interpretation of the results is predicated on the sample not being diluted. Additional information may change the interpretation entirely. As an exercise, the Data Validator is encouraged to re-evaluate exercise 6.3 with a dilution factor of 2.

Note: When evaluating method blank contamination for solid samples reported in mg/kg, ug/kg, consideration must be given for sample preparation and difference in units (ug/L – ug/kg). As stated above, referral to the raw data from the sample can be of valued assistance.

6.6 Tier I Checklist Example

The Tier I Checklist for blank contamination is found in Appendix II. An example on how to fill out the Checklist is given in the following sections.

6.6.1 Example Data Report and QA/QC Summary

A data report and QA/QC summary report are submitted for evaluation. The data report and QA/QC summary are given in Figure 6.2. This figure shows an abbreviated list of volatile organic compounds that are typically analyzed in SW-846, Method 8260B. Are there sufficient data to assess whether blank contamination has biased the sample results? It would appear that there is sufficient information to continue with the evaluation if the sample results and the QA/QC data are examined, and the following information is included in the data package:

- Date and time of analysis
- Batch ID
- Dilution factor
- Sample results
- Blank results
- Detection limit

Figure 6.2 Example Data Report and QC Summary

ANY LABORATORIES, INC. - EPA SW-846, Method 8260B

Project:	Big Site
Project #:	IOQI3
Report Date/Time:	10/11/01; 16:58
Prepared & Analyzed:	09/27/01
Dilution:	1
Batch #:	2802
SAMPLE ID:	X102

Analyte(s)	Result	RDL	Units	Flag
Dichlorodifluoromethane	ND	10.0	µg/L	
Chloromethane	ND	10.0	µg/L	
Vinyl chloride	57.5	10.0	µg/L	
Bromomethane	ND	10.0	µg/L	

ANY LABORATORIES, INC.

Project:	Big Site
Project #:	IOQI3
Report Date/Time:	10/11/01; 16:58
Prepared & Analyzed:	09/27/01
Dilution:	1
Batch #:	2802
SAMPLE ID:	X102

EPA SW-846, Method 8260B

Analyte(s)	Result	*RDL	Units	Flag
Dichlorodiflоromethane	ND	10.0	µg/L	
Chloromethane	ND	10.0	µg/L	
Vinyl chloride	57.5	10.0	µg/L	U
Bromomethane	ND	10.0	µg/L	
Chloroethane	ND	10.0	µg/L	
Trichlorofluoromethane	ND	5.0	µg/L	
Acrolein	ND	10.0	µg/L	
Acetone	ND	10.0	µg/L	
1,1-Dichloroethene	ND	5.0	µg/L	
Methylene chloride	ND	5.0	µg/L	

The Tier I Data Validator may question whether the Report Detection Limit (RDL) is really the method detection limit. Note that the RDL for the blank and the sample results are the same. In addition, the dilution factor is reported as 1, which corresponds with the data presented for the RDL in the sample results and in the QA/QC results. For the sake of this example, assume that the RDL is the method detection limit. When there is doubt about the detection limit, it is always appropriate to request clarification or additional information from the laboratory.

The results in Figure 6.2 indicate that there is a compound detected in the method blank and also in the sample; therefore, evaluate whether to qualify the data.

6.6.2 Tier I Checklist for Organic Blank Evaluation

The Tier I Checklist is designed to look at blank data, and was developed with U.S. EPA National Functional Guidelines (NFGs) as the general reference. Ohio EPA - Division of Hazardous Waste (DHWM) is well aware that the NFGs were designed to evaluate data from U.S. EPA's Contract Laboratory Program (CLP). The designers of the Tier I Checklist endeavored to keep the assumptions in the Checklist as generic as possible. The Data Validator will inevitably find a laboratory data package that includes method blank data that does not resemble the forms listed in the NFGs (or in this guidance). However, if sufficient data is given in the package, then validation practices will not be hindered and the data can be successfully evaluated. The Data Validator is therefore encouraged to thoroughly examine a data package for the required information and pay less attention to the form of the data presentation.

Note: For brevity, answers to the VOC questions from the following portions of the Tier I Checklist have been combined with those from the Semi-Volatile Compounds (SVOC) section. The questions are identical.

2.1 Blank Data Summary Review - Volatile Organic Compounds

Blank Data	
Laboratory blanks are used to assess whether contamination from the laboratory, reagents, or other samples exists and whether this contamination can bias sample results. The qualification of sample results will depend upon the magnitude of blank contamination.	
2.1.1 Is the method blank data present for each batch (matrix and sample number dependent), including TCLP? *Action: If not present, request information from the facility or laboratory. If the required method blank(s) was not analyzed, sample results may be qualified as estimated ("J," for positive results and "UJ," for non-detected compounds) based upon the validator's judgment. Additional qualification may be warranted based upon other QA/QC information.*	Yes, the method blank summary is present. The information necessary to evaluate blank contamination is also present. This data includes a batch ID that can be used to associate sample data with the appropriate blank, detection limit, sample results, blank results and dilution factor.

The method blank summary is present as are the results. The Data Validator will want to pay particular attention to the detection limits listed for the method blank and the sample results. It is commonly observed that blank analyses are reported with the detection limit, but sample results are reported with a reporting limit. If this is the case, the Data Validator must obtain the detection limit data from the laboratory. This information is necessary to understand whether the reported dilution factor is correct and whether to apply the 5X and 10X Rules.

2.1.2 Is there an indication that the samples associated with that blank were diluted? **Note:** The dilution factor can be found in the data report (a dilution factor of 1 indicates no dilution).	**List the dilution factor(s):** The dilution factor is 1. Verify this by dividing the detection limit listed for the sample results by the detection limit listed with the method blank.

2.1.3 Do any method/field/trip/rinsate blanks have any positive results for any volatile target analytes? Were the same target compounds found in the samples? List those analytes and the results that are both found in the blanks and samples. These analytes are subject to qualification. **Note:** A list of samples associated with each of the contaminated blanks should be prepared. Trip blanks are used to qualify samples based on potential contamination during shipment, and are not required for non-aqueous matrices. *Action: Follow the directions in question 2.1.4 using the criteria in the table below to qualify sample results due to blank contamination. Use the largest value from all of the associated blanks. If any blanks are grossly contaminated, all associated data may be qualified as "R," based upon professional judgment and the project's DQOs.*	Field, trip, or rinsate blanks were not taken. **Action:** Follow the directions in the table below to qualify sample results due to blank contamination. Use the largest value from all of the associated blanks. If any blanks are grossly contaminated, all data associated may be qualified as "R", based upon professional judgment and the project's DQOs.

Question 2.1.3 asks the Data Validator to evaluate other blanks that are associated with the sample results. The blanks include field, trip, and rinsate blanks. The sample results are compared to these blanks in the same way as with the method blank. The 5X and 10X Rules also apply. Therefore, if the data set includes these types of blanks, examine the blank results, detection limits, dilution factors and other required data just as with the method blank examples that have been previously presented.

2.1.4 For those analytes identified in question 2.1.3 follow the directions in the following table. **Note:** If analytes are detected in a blank but not in the sample of interest, then qualification of those analytes is not necessary. Use the information from 2.1.2 to determine whether a dilution factor should be used to determine qualification. When a dilution is applied to samples, the contaminant concentration in the samples is divided by the dilution factor, then use the criteria listed in the following table to qualify blanks and sample data.	Yes, vinyl chloride is detected in both the sample and in the method blank. Use the steps to evaluate blank data shown previously to evaluate how the data will be qualified (See Example 6.4).

Table 3 VOC Blank Contamination Decision Table

When a dilution factor is applied to sample data, the results of the samples are divided by the dilution factor, then the criteria listed in Table 3 are used to qualify the results.

For Common Volatile Contaminants: methylene chloride, acetone, 2-butanone, cyclohexane (for SVOCs: Phthalate esters)	For Other Contaminants:	Action:
Sample Conc. > Detection Limit but < 10x Blank Result	Sample Conc. > Detection Limit but < 5x Blank Result	Identify the sample result "U," undetected
Sample Conc. < Detection Limit & < 10x Blank Result	Sample Conc. < Detection Limit & < 5x Blank Result	Report the detection limit and qualify result as "UJ," estimated undetected
Sample Conc. > Detection Limit & > 10x Blank Result	Sample Conc. > Detection Limit & > 5x Blank Result	No qualification is necessary

Example 6.4

The steps to evaluate this problem have been demonstrated in previous sections. This problem may be evaluated as follows:

1. What is the dilution factor? **The dilution factor is 1**

2. Do the 5X or 10X Rules apply? **Vinyl chloride is not a common laboratory contaminant. Therefore, the 5X Rule applies: 5X (5X Rule) X 12.5 = <u>62.5 µg/L</u>**

3. Evaluate whether blank contamination is significant and qualify data

   Since 62.5 µg/L is greater than the sample result of 57.5 µg/L, it can be concluded that blank contamination is significant and the sample data must be qualified as "U," undetected. The data report, after completing validation, is shown in Figure 6.4.

ANY LABORATORIES, INC.

Project:	Big Site
Project #:	IOQI3
Report Date/Time:	10/11/01; 16:58
Prepared & Analyzed:	09/27/01
Dilution:	1
Batch #:	2802
SAMPLE ID:	X102

EPA SW-846, Method 8260B

Analyte(s)	Result	*RDL	Units	Flag
Dichlorodiftuoromethane	ND	10.0	µg/L	
Chloromethane	ND	10.0	µg/L	
Vinyl chloride	57.5	10.0	µg/L	U
Bromomethane	ND	10.0	µg/L	
Chloroethane	ND	10.0	µg/L	
Trichlorofluoromethane	ND	5.0	µg/L	
Acrolein	ND	10.0	µg/L	
Acetone	ND	10.0	µg/L	
1,1-Dichloroethene	ND	5.0	µg/L	
Methylene chloride	ND	5.0	µg/L	

6.6.3 Tier I Checklist for Inorganic Blanks Evaluation

Blank evaluation is also important for metals. The procedures for evaluating metals results are the same as for organic compounds except that the 10X Rule applies only to mercury. All metals blank results are based upon the 5X Rule. The following portions of the Tier I Checklist are used for metals analyses.

4.1.1 Is the method/prep blank summary data present for each batch (generally separated by method and matrix), including TCLP? *Action: If not present, request information from the facility. If the required method blanks were not analyzed, sample results <u>may</u> be qualified as "J" for positive results and "UJ" for non-detected compounds. Qualification should take into account other QA/QC information and the DQOs.*	
4.1.2 Were any samples diluted? *Action: Record the sample ID and dilution factor(s).*	

4.1.3 If metals are detected in the blank, check the sample results and record all analytes and the results detected in both the blank and sample. **Note:** Use the information from 4.1.2 to determine whether a dilution factor should be used to determine qualification. When a dilution factor is applied to samples, the contaminant concentration in the samples is divided by the dilution factor. The criteria discussed below is used to qualify sample results. *Action: Positive sample results that are greater than the detection limit but less than 5 X the blank results (after dilution is accounted for) should be qualified as estimated and flagged with a "U." Sample results greater that 5X the blank results (after accounting for dilution) should not be qualified.*	

For mercury analysis, the following part of the Tier I Checklist is used to evaluate blank quality control data. The data validator is reminded that mercury evaluations use the 10X rule.

4.1.4 Was a method/preparation blank included with each batch of samples? *Action: Consult the lab and if possible have the data submitted. If the data is not available, the data validator may apply best professional judgment to qualify the sample results.*	
4.1.5 Did the method blank contain mercury above detectable levels? Was mercury also detected in the sample results? If so, these results are subject to qualification. **Note:** If mercury is discovered in the method blank above the detection limit, the lowest concentration of any sample in that batch must be 10 times the method blank concentration (after dilution is accounted for). If this is not the case, all samples in that batch should have been re-digested and re-analyzed. *Action: Review the blank data. If the sample results are positive but less than 10 times the concentration in the blank, the results should be qualified as "U."*	

Chapter 7
Matrix Spikes And Matrix Spike Duplicates

7.0 Introduction

The **Matrix Spike** (MS) and **Matrix Spike Duplicate** (MSD) are quality control samples that are associated with both organic and inorganic analyte analysis. Data for MS/MSD samples are generated to determine long-term precision and accuracy of the analytical SW-846 method on various matrices and to demonstrate acceptable analyte recovery by the laboratory at the time of sample analysis. MS/MSD data alone cannot normally be used to evaluate the precision and accuracy of individual samples (particularly others in the batch that were not subjected to MS spiking). However, when used in conjunction with other available quality control (QC) information, the MS/MSD recoveries provide a strong indication of the laboratory's ability to measure the target analytes in the sample media. A MS/MSD is included with every batch of samples that is analyzed.

The MS is used to evaluate the effect of the sample matrix on the analysis. MS samples are prepared by spiking known amounts of specific analytes into a sample. The effect of the matrix on the analyte recovery is then evaluated by comparing the recoveries of the added spike with the actual spike value. For example, if 1 mg/kg of chlorobenzene was added as a spike, and the results indicated 1 mg/kg was detected during the analysis, then 100 percent of the spike was recovered. This result would indicate that the matrix had little effect on the ability of the analytical instrument to analyze the analyte.

Matrix spikes are used to provide a measure of accuracy for a batch of samples of the same matrix, such as soil. Due to the inherent heterogeneity of samples from different locations, however, the matrix effects seen in one sample may not be representative of the matrix effects throughout the batch. As a result, the MS/MSD samples provide an indicator of the potential for matrix interferences, but for the purpose of flagging data, the results from one sample cannot be used to flag other samples in the batch without corroboration from other QA/QC data. In addition, if the MS/MSD analysis was not performed on a sample of interest, the Tier I Validator can assume little information regarding accuracy.

The MSD is a spike added to a second aliquot of the same sample used for the matrix spike. The MSD provides a measure of precision of the analysis. The duplicate is evaluated through the relative percent difference (RPD), or deviation, of the spike recoveries between the two samples. If, after analysis, the matrix spike and the matrix spike duplicate have similar results, then the relative percent difference would be low and the effect of the sample matrix on reproducibility of analyses would be assumed negligible.

7.1 Definitions

Aliquot: A fraction of a whole; as in aliquots of a sample used for testing or analysis.

Batch: A group of 10 to 20 samples prepared and analyzed identically, run consecutively on the same equipment and associated with the same QA/QC samples.

Bias: The deviation due to matrix effects of the measured value from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike).

Control Limits: Established to evaluate lab precision and bias based on the analysis of control samples. Typically, control limits for bias are based on historical mean recovery plus or minus three standard deviation units. Control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units.

Interference: Additions or detractions from a signal generated by analytical instruments. Interferences can either add to the signal received by the instrument producing a positive bias, or detract from a signal producing a negative bias. QA samples such as Matrix Spikes, Matrix Spike Duplicates, and Laboratory Control Samples may be used to assess and overcome interferences.

Laboratory Control Sample (LCS): A blank is spiked with analytes representative of the target analytes used to document laboratory performance prior to the preparation step. An LCS monitors the efficiency of the preparation procedures for analysis, providing the best idea of whether poor analytical results are matrix dependent or a result of an analytical problem. The LCS should be analyzed for each sample matrix (soil and water) using the same preparation procedures and analytical methods as the actual samples. Spiked compounds and concentrations are generally the same for LCS and MS/MSD samples.

Matrix Spike: The introduction of a known concentration of analyte(s) into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology. Matrix spikes are used to provide an indication of bias due to matrix effects and a measure of accuracy of associated results.

Matrix Spike Blank: The introduction of a known concentration of analyte(s) into a blank. It provides a measure of whether the spiking analytes are appropriate for a specific batch of samples.

Matrix Spike Duplicate: Analysis of spiked duplicates is used to provide a measure of the precision in the analytical process. Matrix spikes are evaluated by criteria based upon the relative percent difference of the duplicates.

Percent Recovery (%R): Percent recovery of the spike analyte. Used for organics and inorganics. The spike percent recovery and the spike provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. The spike recovery must be within established limits given on the QA/QC sheets provided by the laboratory (i.e., 75-125%).

Pre-digestion Spike: (Same as Matrix Spike)

Relative Percent Difference (RPD): Relative percent difference is used for organics and inorganics when comparing the duplicate sample results to the original sample results. Analytical results within 20% of each other indicate that the laboratory followed their Quality Assurance Program Plan (QAPP). See formula in Equation 7.2 below.

Spike: A known analyte and volume added to a sample to verify QA/QC results.

7.2 Quality Assurance/Quality Control Specific Information

The MS/MSD are batch specific QA/QC samples. When analyzing by SW-846 methods, the MS/MSD are required for every batch of samples of similar matrix that are analyzed using SW-846, Methods 8260B, 6010C, and 8270D. If the samples in question are spread among different batches, MS/MSD information will be available for each batch. The Tier I Data Validator must be able to relate the correct MS/MSD results to each sample.

The MS/MSD results are evaluated using results from a specific unspiked sample in a batch, the results from the same sample that have been spiked (matrix spike), and the results from a second spiked aliquot of the same sample (matrix spike duplicate).

The matrix spike is evaluated using the percent recovery of the spike. The percent recovery can be determined from the following formula:

Equation 7.1		$\%R = \frac{(S - U)}{C_{SA}} * 100$
Where:		
%R	=	percent recovery of the spike analyte
S	=	measured concentration of an analyte in the matrix spike sample result
U	=	measured concentration of an analyte in the unspiked sample (0 if undetected)
C_{SA}	=	actual concentration of the spike added

For example, an analysis determined that 5 mg/kg of TCE (U) was present in a sample. If 1 mg/kg spike (C_{SA}) was added to an aliquot of this sample (matrix spike) and the analysis indicated that 5.9 mg/kg (S) of TCE was present in this spike sample, the percent recovery can be determined from equation 7.1 to be:

%R = (5.9 mg/kg - 5.0 mg/kg)/(1 mg/kg) X 100 = 90 % recovery

The matrix spike duplicate is evaluated by the Relative Percent Difference (RPD) between the matrix spike results and the matrix spike duplicate results. The RPD can be evaluated using the following equation:

Equation 7.2		$RPD = \left\| C1 - C2 \right\| \Big/ \frac{(C1 + C2)}{2} \times 100$
Where:		
RPD	=	Relative Percent Difference
C1	=	The larger value of either the matrix spike or matrix spike duplicate (measured concentration of a spike analyte)
C2	=	The smaller value of either the matrix spike or matrix spike duplicate

For example, if the result for a matrix spike is 7 mg/kg of TCE and result for the matrix spike duplicate is 6 mg/kg, the relative percent difference may be calculated using equation 7.2.

$$RPD = (7\ mg/kg - 6\ mg/kg) \div [(7\ mg/kg + 6\ mg/kg)/2] \times 100 = \underline{2\ \%}$$

7.3 Information Necessary to Validate MS/MSD Data

The following information is required to complete a review of matrix spike/matrix spike duplicate data:

- Batch ID: This information will relate the sample batch QA/QC results to the correct samples;
- Dilution factor of the sample;
- Matrix spike recoveries;
- Matrix spike duplicate recoveries;
- Relative percent differences between the matrix spike and matrix spike duplicate;
- Quality control criteria;
- Detection limit;
- Run log;
- Results of blank analysis;
- Spike concentrations;
- Post-digestion spike information, if applicable (spiked sample result, sample result, spiking solution, %R and control limits).

7.4 Data Validation Criteria

Samples are not normally qualified using MS/MSD results alone. The Tier I Data Validator should first try to determine to what extent the results of the MS/MSD indicate that the associated data is affected by matrix interferences. In instances where it may be determined from other QA/QC sample data that the results of the MS/MSD affect only the spiked sample, then qualification would be limited to that sample alone. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes which is affecting all associated samples. The Tier I Data Validator must use professional judgment, in conjunction with other QC criteria to determine the need for qualification of positive results of non-spiked analytes. These criteria should be clearly stated on the Tier I Data Validation Checklist.

The criteria that a specific laboratory uses to evaluate MS/MSD data must be presented in the data report or obtained from the laboratory. Percent recovery criteria usually are 100% +/- 20%. Reproducibility data are usually considered adequate if the RPD is equal to 20% or less.

The Tier I Data Validator must verify that MS and MSD samples were analyzed at the SW-846 required frequency and that results were provided for each sample matrix. If possible, the Tier I Validator must verify that the calculations were performed correctly by using raw data from the laboratory report to verify calculations using equations 7.1 and 7.2.

At least one spiked sample (pre-distillation/pre-digestion) must be prepared and analyzed from each group of samples with a similar matrix type (e.g., solids or water) and concentration (e.g., low, medium) or for each Sample Delivery Group (SDG). A SDG may be either a case of field samples, each set of twenty field samples in a case, or each 14-day calendar period during which a case of field samples are received, beginning with receipt of the first sample.

If two different SW-846 analytical methods are used for the same parameter (i.e., metals analysis) within the same SDG, spiked samples must be run with each SW-846 method. If more than one spiked sample recovery result per matrix and concentration, per analytical SW-846 method, per sample delivery group, is not within control criteria, all the samples of the same matrix, level, and SW-846 method in the sample delivery group would be flagged.

Determination of bias (% recovery) requires a minimum of two matrix spikes. Good sampling practices mandate that a determination of precision be made using a minimum of eight matrix spikes with analyte concentrations within range of the level of interest. These samples are site specific and contain the target analyte at or near the concentration level expected.

The Tier I Data Validator must verify that the field blank samples were not used for the spiked sample analysis. If a lab uses the field blank for spike analysis, then all other data must be carefully checked as to whether it is acceptable. If the field blank was used, it must be noted in the Tier I Data Validation Checklist.

In Flame Atomic Absorption (AA), Inductively Coupled Plasma Spectroscopy (ICP), and Cyanide (CN) analysis, if the pre-distillation/pre-digestion metal spike recovery is outside of the control limits, and the sample result does not exceed 4 times the spike added, good sampling practices for all SW-846 methods (except furnace AA) mandate a post-digestion/post-distillation spike be run for all parameters not meeting the specified criteria (with the exception of Ag and Hg). The data from post-spikes is NOT to be used to qualify sample results. If this post-digestion data has been used to qualify data, the Tier I Data Validator must note this on the Tier I Checklist. The spike concentration is 2 times the indigenous level or 2 times the contract required detection limit, whichever is greater.

Spike %R must be within the established control limits, however, verification must be made that no action was taken to qualify results based on matrix spike alone. If other batch data is outside of specification, spike data can be used to additionally justify qualifying data as estimated, “J,” or rejected, “R.” If sample concentrations exceed the spike concentration by a factor of four or more, the data would not be qualified even if the %R does not meet the control limits.

If the spike sample analysis was run on the sample chosen for duplicate analysis, good sampling practices mandate that all spike calculations be run on the results from the “original” sample. The average of duplicate results may not be used to determine %R.

7.5 Worked Example

The results page for a water sample from Boring B12 is listed in Table 7.1.

Table 7.1 Sample Results from Boring B12

Report Date:	Oct. 22, 1999			
Sample Delivery Group:	C1986			
Client Name:	Ohio EPA			
Client Address:	122 S. Front St. , Columbus, OH 43216			
Batch ID:	C9567	**Lab Sample ID**:	C0009184-23	
Method:	8260B	**Extraction Date**:	Sept. 22, 1999	
Matrix:	SOLID	**Analysis Date**:	Sept. 22, 1999	
Sample ID:	B12			
Batch Id: C9567		**Lab Sample ID:**	C0009184-23	
Method: 8260B		**Extraction Date:**	Sept. 22, 1999	
Matrix: SOLID		**Analysis Date:**	Sept. 22, 1999	
Sample ID: B12				
Analytes	**Result: Dry Weight (µg/Kg)**		**RDL (µg/Kg)**	
1,1-Dichloroethene	<5.0		5.0	
Benzene	<5.0		5.0	
N-Hexane	8.1		5.0	
Toluene	7.4		5.0	
Chlorobenzene	<5.0		5.0	

QA/QC data that accompanied this report included the information presented in Tables 7.2 and 7.3. The Tier I Data Validator must note that not all target analytes are analyzed in the MS/MSD samples. In addition, the matrix spike duplicate used a different spiking level compared to the matrix spike (55.6 µg/Kg for the MSD compared to 64.7 µg/Kg for the MS). While different spiking levels are not expressly forbidden, an explanation from the laboratory is warranted. In general, the spike concentrations should be at the same level as the Laboratory Control Sample (LCS).

Table 7.2 Matrix Spike QA/QC Summary Data						
Batch ID:			C9567			
QC Sample ID:			C0009184-23MS			
Sample Affected:			C0009184-23			
Analytes	**Result (µg/Kg)**	**% Recovery**	**QC Limits**	**Spike Level (µg/Kg)**	**RPD**	**RPD Limits**
1,1-dichloroethene	75.6	117	70-130	64.7		
Benzene	50.6	74.0	70-130	64.7		
N-hexane	36.9	44.5	70-130	64.7		
Toluene	55.0	73.6	70-130	64.7		
Chlorobenzene	39.3	60.7	70-130	64.7		

Table 7.3 Matrix Spike Duplicate QA/QC Summary Data						
Batch ID:			C9567			
QC Sample ID:			C0009184-23MS			
Sample Affected:			C0009184-23			
Analytes	**Result (µg/Kg)**	**% Recovery**	**QC Limits**	**Spike Level (µg/Kg)**	**RPD**	**RPD Limits**
1,1-dichloroethene	55.6	100	70-130	55.6	30.5	0-30
Benzene	46.3	78.4	70-130	55.6	8.88	0-30
N-hexane	38.0	53.8	70-130	55.6	2.94	0-30
Toluene	47.7	72.5	70-130	55.6	14.2	0-30
Chlorobenzene	31.5	56.7	70-130	55.6	22.0	0-30

Note: For brevity, the Tier I Data validation checklist VOC questions have been combined with those for the SVOCs. The questions are identical.

Question 2.3.1

The first Tier I Data Validation Checklist question asks the Tier I Validator to determine whether sufficient information exists to review MS/MSD data. One MS/MSD must be run per batch of 20 or fewer samples for each matrix for each SW-846 analytical method. Verification must also be made that the field blank samples were not used for spiked sample analysis.

2.3.1 Is the matrix spike/matrix spike duplicate recovery data present? *Action: If matrix spike data is missing, the laboratory should be contacted for re-submittal.*	Yes, there is sufficient information to relate the batch QA/QC samples to each specific sample. Spike concentrations, percent recovery and relative percent difference information are also present.

Question 2.3.2

The second question asks the Tier I Validator to determine whether any recoveries are outside of the quality control criteria. In this example, the laboratory has conveniently summarized the information in Table 7.2 and 7.3. The Tier I Validator should note whether %R data is present for both the matrix spike and the matrix spike duplicate. However, RPD is only recorded for the matrix spike duplicate. The question does not specify which spike, the MS, or the MSD, is being referred to. The Tier I Validator must note any %R data from either spike sample that is outside of the quality control criteria.

2.3.2 How many VOC spike recoveries are outside of the QC limits?	Record spike recovery(ies) and control limits. MS: 2 spike recoveries for N-hexane (44.5%) and chlorobenzene (60.7%) are outside of the 100% $\pm$ 30% percent recovery criteria for batch C9567 which affects sample C0009184-23 MSD: 2 spike recoveries for N-hexane (58.8%) and chlorobenzene (56.7%) are outside of the 100% $\pm$ 30% percent recovery criteria for batch C9567 which affects sample C0009184-23.

If discrepancies from the QA/QC criteria are found, it is appropriate to determine if transcription or calculation errors may be responsible. If the MS/MSD produces low recoveries, it may be due to matrix effects, SW-846 method failure, inadequate background correction or inadequate clean up, improper spiking, degraded spiking solution or a failed spiking device [High MS/MSD recoveries may result from some of the same causes with the addition of possible use of contaminated reagents, gases or glassware]. Equations 7.1 and 7.2 can help determine whether recording errors are a possibility. Using the data for N-hexane as an example, the following information was provided in the laboratory report.

	Result (µg/Kg)	
Sample result (Table 7.1)	8.1	Unspiked concentration (U)
MS concentration (Table 7.2)	64.7	Conc. of Spike added (C_{sa})
MS result (Table 7.1)	36.9	Spiked sample result (S)
%R = (S-U)/(C_{sa}) X 100 Equation 7.1		
%R = (36.9 µg/Kg – 8.1 µg/Kg)/(64.7 µg/Kg) X 100 = **44.5%**		

The result determined through use of equation 7.1, 44.5% is the same as reported in Table 7.1. The Tier I Validator can therefore assume that calculations and transcription errors are minimal.

Question 2.3.3

The last question asks the Tier I Data Validator to check the relative percent difference quality control criteria between the MS and MSD. The data to answer this question is found in Table 7.3. According to quality control criteria listed in the table, RPDs must be below 20%.

2.3.3 How many RPDs for matrix spike and matrix spike duplicate recoveries are outside the QC limits for VOC? **Note:** The MS/MSD results may be used in conjunction with other QC criteria to determine the need for data qualification. Outliers should be identified.	Record the recovery data out of criteria and control limits. Review surrogate recovery and LCS data to determine if qualifiers are necessary. 1,1-dichloroethene is outside of the control limit with and RPD of 30.5. This result affects batch C9567 and sample C0009184-23.

The data can also be used to recalculate a relative percent difference from MS/MSD data. Using the data for N-hexane again as an example, the following information has been provided in the laboratory report.

	Result (µg/Kg)
MS Result (Table 7.2)	36.9
MSD Result (Table 7.3)	38.0
RPD = (C_1-C_2)/[(C_1 + C_2)/2] X 100 (Eq. 7.2)	
RPD = (38 µg/Kg – 36.9 µg/Kg)/[36.9 µg/Kg+38 µg/Kg/2] X 100 = **2.94**	

This result is the same as reported in Table 7.3. The Data Validator can assume that transcription or calculation errors are minimal. However, based upon the different spiking levels for the MS/MSD, the relative percent difference results indicate little about reproducibility.

Based upon the matrix spike/matrix spike duplicate analysis, should the data be qualified? The answer is no, unless significant deviations are found in associated quality control data such as Laboratory Control Sample (LCS) results, or surrogate recoveries. However, it may be determined that the matrix of the spiked sample and its duplicate affected the recovery of particular analytes. The deviations should be noted in the data narrative. In addition, the different spike concentration levels are questionable.

If the spike was performed on a sample of interest, such as one the Validator submitted to the laboratory, the potential negative bias seen in the samples should be noted. To allay any concerns, the Tier I Data Validator may request matrix spike/matrix spike duplicate information on batches with a similar matrix that were analyzed over a period of time that included the affected MS/MSD. If a trend is apparent, then data quality may be suspect. The results of the MS/MSD may not result in qualification of data, but it may lead the Tier I Data Validator to assess whether the data quality objectives of the sampling event were met.

7.6 Metal Spike Recovery Checklist

An example Tier I Checklist Metal Spike Recovery section has been completed based on the following information:

Matrix Spike Analyte	DL (µg/L)	Sample Conc. (µg/L)	Spike Added (µg/L)	MS Conc. (µg/L)	MS % Rec.	% Rec. Limits	Data Qualifier
Barium	20	ND	1000	990	99	75-125	J
Cadmium	5	33	1000	896	86.3	75-125	
Chromium	70	519	620	1300	126	75-125	J
Selenium	20	67	1000	905	89.9	75-125	R
Lead - Soil	10	35	5000	5134	102	75-125	

Matrix Spike Analyte Duplicate	DL (µg/L)	MSD Conc. (µg/L)	Spike Added (µg/L)	MS % Rec. (µg/L)	% RPD	QC Limits RPD	LCS	LCS Limits	% Rec.	Data Qualifier
Barium	20	1350	1000	135	30.7	0 - 20	1208	80-120	121	J
Cadmium	5	862	1000	82.9	4	0 - 20	789	80-120	79	J
Chromium	70	1100	620	93.7	29.4	0 - 20	616	80-120	99.3	J
Selenium	20	862	1000	79.5	5.3	0 - 20	490	80-120	49	R
Lead - Soil	10	5215	5000	103.6	1.6	0 - 20	5176	80-120	103.5	

4.2.1 Confirm that at least one pre-digestion spiked sample was analyzed per batch, matrix type or sample delivery group. *Action: If not present, contact the facility for re-submittal.*	Yes, at least one spiked sample was analyzed per batch.

At least one spiked sample (pre-distillation/pre-digestion) will be prepared and analyzed from each group of samples with a similar matrix type (e.g., soil and water) and concentration (e.g., low, medium) for each SDG. The SDG may be either a case of field samples (set of twenty field samples in a case) or each 14-day calendar period during which a case of field samples are received, beginning with receipt of the first sample [if there is more than one spiked sample result per matrix, concentration level, sample delivery group, and individual SW-846 analytical method; if one of those spiked sample recovery results is not within control limit criteria, then flag all of the samples of the same matrix, level and SW-846 method in the sample delivery group]. The following worked example does not include all the questions contained in the checklist, but it will serve to illustrate the data validation process for metals data.

4.2.2 Are all spike recoveries (except Hg and Ag) within control limits (e.g., 75% to 125%). **Note:** When the spike sample result is less than the instrument detection limit, the percent recovery calculation should use a value of zero (not the detection limit) for the sample result. *Action: Is the sample concentrations $\geq$ 4 times the spiked concentration? If yes, disregard the spike recoveries for analytes whose concentrations in samples are >4 times the spike added. If no, circle those analytes whose concentration is <4 times the spike added.*	List those elements out of control: No. Chromium had a spike recovery of 126% in the MS ad Barium had 135% in the MSD. The spike concentration for Cr is 620 µg/L. The sample concentration is 519 µg/L. Since the sample concentration is NOT > 4X the spike concentration, this information should be noted in the data narrative and the analyte should be circled. Likewise, barium was not detected and should be circled.
4.2.3 Based on the results of 4.2.2, if the sample results were < 4 times the spike amount and the spike recoveries were out of criteria, a post-digestion spike should be analyzed. **Note:** Post-digestion spikes are not required for Ag or Hg; however, these spikes are usually analyzed if the LCS is out of control limits. The post-digestion spike confirms a matrix interference problem and should not be used for qualification. *Action: Contact the facility/laboratory for an explanation if the post-digestion spike was not analyzed. If a satisfactory explanation is not forthcoming, us professional judgment to qualify sample results.*	There is no evidence that a post-digestion spike was analyzed. The lab should be contacted for an explanation.

4.2.4 Are any aqueous spike recoveries (pre- and Post- digestion): 1. Less than 30% 2. Between 30% and 74%? 3. Between 126% and 150%? 4. Greater than 150%? **Note:** The TCLP extract should be handled as an aqueous sample. *Action: If <30%, and the sample results are below the detection limit, all data should be qualified as rejected and flagged with an "R."* If between 30% and 74%, qualify all positive data as estimated and flag data with a "J-" qualifier, and qualify all non-detected data as "UJ." If between 126% and 150%, qualify all positive data as estimated-positive and flag this data with a "J+" qualifier. All undetected analytes are acceptable. If > 150% note for possible positive system bias. The Validator may qualify data as rejected (flagged with an "R") based upon professional judgment and the eventual use of the data.	No spike recoveries are less than 30%. No spike recoveries are between 30 and 70%. One spike recovery is 126% and one is 135%. No spike recoveries are >150%. Therefore, the Cr and Ba results should be qualified as "J+". Both have high %R values in the MS and MSD and the RPDs above 20%. In addition, Cd is "J" flagged and Se is rejected due to low LCS. recoveries. See also has a low MS %R value.
4.2.5 Are any soil/solid/waste spike recoveries (pre- and post-digestion): 1. Less than 10% 2. Between 10% and 74%? 3. Between 126% and 200%? 4. Greater than 200%? **Note:** the TCLP extract should be handled as an aqueous sample. *Action: If <10%, and the sample results are below the detection limit, all data should be qualified as rejected and flagged with an "R."* *If between 10% and 74%, qualify all positive data as estimated and flag data with a "J-" qualifier, and qualify all non-detected data as "UJ."*	All soil spike recoveries were with the 75% to 125% control limit range.

If between 126% and 200%, qualify all positive data as estimated-positive and flag this data with a "J+" qualifier. All undetected analytes are acceptable. *If > 200% note for possible positive system bias. The Validator should qualify data as rejected (flagged with an "R").*	
4.2.6 If the pre-digestion spike was outside of the quality control limits for Atomic Adsorption furnace analysis (e.g., SW-846 methods in the 7000 series), was a post-spike recoveries within the quality control range (75% TO 125%).	There is no evidence that a post-digestion spike was performed. The laboratory should be contacted.

7.7 Questions:

Q. Were any sample results greater than 110% of the highest calibration standard or blank?

A. If so, results must be flagged as "J", estimated.

Q. Should samples be adjusted for bias?

A. Adjustment of sample value for bias is not recommended. However, bias should be evaluated, depending on the bias direction (+ or -), by adding or subtracting the value (% bias x spike concentration) to or from the sample values. Percent bias is the reciprocal value of % recovery (i.e., for 70% recovery there is a negative 30% bias). Use the average~~5~~ recovery from the total number of matrix spikes analyzed. This adjustment approach assumes a spiking concentration equal to the concentration found in the sample.

Q. If one spiked sample recovery is not within control limits, will that affect how all the other samples are treated?

A. If there is more than one spiked sample per matrix and concentration, per analytical SW-846 method, per sample delivery group, and one spiked sample recovery is not within control limit criteria, then qualify all of the samples of the same matrix, level and SW-846 method in the sample delivery group.

a. If the spike recovery is >125% and the reported sample results are <IDL (instrument detection limit), the data is acceptable for use.
b. If the spike recovery is > 125% or < 75% and the sample results are > than the IDL, good management practices would qualify the as estimated and it would be flagged with a "J".

c. If the spike recovery results fall within the range of 30 to 74% and the sample results are < IDL, the sample results would be qualified as estimated undetected and data flagged with an “UJ”.

e. Whenever possible, the potential effects on the data due to out of control spiked sample results must be noted in the data review narrative.

Q. For Atomic Adsorption Analysis: Are any furnace results flagged with an (E) by the lab to indicate an interference? If yes, was there a post digestion spike analyzed? If so, was the post digestion spike recovery less than 10% for any of the (E) flagged results?

A. If yes, reject (flag with and “R”) all affected data.

7.8 Resources

DOE: Data Quality Objectives – DOE site Applications: http://dqi.pnl.gov/.

Indiana Department of Environmental Management, 2000. Environmental Quality Manual on DQOs and Laboratory Quality Assurance.

Nielsen, David. 1991. Practical handbook of Groundwater Monitoring. Lew Publishers. Michigan.

U.S. EPA, 1990. Office of Emergency and Remedial Response, Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures, Interim Final. EPA 540/G-90/004. OSWER Directive 9360.4-01, April 1990.

U.S. EPA, 1992. USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Multi-Media Multi-Concentration. Document Number ILM05.4.

U.S. EPA Region 9, DRAFT Laboratory Documentation Requirements for Data Validation. July 1997.

U.S. EPA, 2004. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, OSWER 9240.1-45, EPA 540-R-04-004, October 2004.

U.S. EPA, 2005. USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Review, EPA-540-R-05-00. September 2005.

U.S. EPA, 2008. USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review. EPA-540-R-08-01. June 2008 .

U.S. EPA Region 3 Quality Assurance Manual, Chapter 3. October 1997

U.S. EPA: Analytical Methods and Other Information:
http://www.epa.gov/osa/fem/methcollectns.htm

U.S. EPA: Guidance Documents for Data Quality Assurance: http://www.epa.gov/quality/.

Chapter 8
Laboratory Control Sample

8.0 Introduction

A **Laboratory Control Sample** (LCS) is a batch specific quality control sample that is used to assess whether the analytical system can perform adequately for a given matrix. An LCS is sometimes referred to as a blank spike. The LCS consists of an aliquot of a clean matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike, matrix spike duplicate analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

An LCS is required for the common organic analyses (8270D and 8260B) and for most inorganic analysis methods. The LCS for the volatile (8260B) analysis should at a minimum include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The LCS for semi-volatile analysis (8270D) should, at a minimum, include the following compounds:

Base/neutrals	**Acids**
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

Method 6010C requires the analysis of a matrix spike and a matrix spike duplicate to evaluate matrix interference problems. If a problem is encountered, a post-digestion spike may be analyzed. These spikes take the place of an LCS. In fact, many laboratories will report results as LCS/LCSD on quality control reports. The data validator should analyze LCS/LCSD, post digestion spike recoveries using the equations and criteria defined in Chapter 7.

The LCS is used in relation to other quality control data such as the matrix spike/matrix spike duplicate recoveries. The matrix spike and its duplicate should contain the same compounds as the LCS and with the same concentrations. The comparisons between the LCS and MS/MSD can be used to verify that a matrix interference problem exists. For example, if a matrix interference is suspected based on matrix spike/matrix spike duplicate data, adequate recovery of compounds in the LCS will assure the validator that the laboratory can analyze samples with accuracy and precision based upon LCS spike recovery. If results show that compounds in the LCS can be recovered within the quality control criteria, a matrix interference can be confirmed. Conversely, if recovery data for compounds in the LCS fail the QC criteria, then the integrity of the analytical system is suspect and corrective measures may be required.

8.1 Definitions

Aliquot: A fraction of a whole; as in aliquots of a sample for testing or analysis.

Batch: A group of 10 to 20 samples prepared and analyzed identically, run consecutively on the same equipment and associated with the same QA/QC samples.

Control Limits: Established to evaluate lab precision and bias based on the analysis of control samples. Typically, control limits for bias are based on historical mean recovery plus or minus three standard deviation units. Control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units.

Interference: Additions or detractions from a signal generated by analytical instruments. Interferences can either add to the signal received by the instrument producing a positive bias, or detract from a signal producing a negative bias. QA samples such as Matrix Spikes, Matrix Spike Duplicates, and Laboratory Control Samples may be used to assess and overcome interferences.

Laboratory Control Sample (LCS): A blank is spiked with analytes representative of the target analytes used to document laboratory performance prior to the preparation step. An LCS monitors the efficiency of the preparation procedures for analysis, providing the best idea of whether poor analytical results are matrix dependent or a result of an analytical problem. The LCS should be analyzed for each sample matrix (soil and water) using the same preparation procedures and analytical methods as the actual samples.

Matrix Spike: The introduction of a known concentration of an analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology. Matrix spikes are used to provide an indication of bias due to matrix effects and a measure of accuracy of associated results.

Matrix Spike Blank: The introduction of a known concentration of analyte into a blank.

Matrix Spike Duplicate: Analysis of spiked duplicates is used to provide a measure of the precision in the analytical process. Matrix spikes are evaluated by criteria based upon the relative percent difference of the duplicates.

Spike: A known analyte and volume added to a sample to verify QA/QC results**.**

8.2 Quality Assurance/Quality Control Specific Information

The LCS is a batch specific QA/QC sample. When analyzing by SW-846 methods, the LCS is required for every batch of samples of similar matrix that are analyzed using SW-846, Methods 8260B, 6010C, and 8270D. If the samples in question are spread among different batches, LCS information will be available for each batch. The Tier I Data Validator must be able to relate the correct LCS results to each sample.

The LCS is evaluated by **the percent recovery** of the spike. The percent recovery can be determined from the following formula given in equation 8.1.

Equation 8.1

$$\% \text{ Recovery} = \text{LCS Result}/C_{SA} \times 100$$

Where the LCS result is the analyzed concentration from each of the analytes added to the LCS and C_{SA} is the concentration of the added spike.

8.3 Necessary Information Required to Evaluate LCS data

The following information is required to complete a review of LCS data:

- Batch ID: This information will relate the sample batch QA/QC results to the correct samples;
- LCS chemicals and recoveries;
- Quality control criteria;
- Detection limit;
- Spike concentrations;
- Post-digestion spike information, if applicable (spiked sample result, sample result, spiking solution, %R and control limits).

Other information that may be useful in an evaluation of LCS data includes the following:

- Sample dilution factor;
- Run Log;
- Blank analysis results.

8.4 Data Validation Criteria

LCS results are evaluated using the percent recovery data calculated using Equation 8.1. If the LCS recovery criteria are not met, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution.

Professional judgment should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgment to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in performance of the LCS compound to the non-LCS compound. If the LCS recovery is greater than the upper acceptance limit, then positive sample results for the affected compound(s) should be qualified with a “J+.” If the mass spectral criteria are met but the LCS recovery is less than the lower acceptance limit, then the associated detected target compounds should be qualified “J-” and the associated non-detected target compounds should be qualified “R,” If more than half of the compounds in the LCS are not within the recovery criteria, then all of the associated detected target compounds should be qualified “J” and all associated non-detected target compounds should be qualified “R”.

8.5 Worked Example

The following example will illustrate data validation procedures using LCS data. The example is for semi-volatile organic data, but the validator should find it useful for evaluating volatile analytical data.

Figure 8.1 shows an analytical summary report for a soil sample analyzed for semi-volatile compounds. Figure 8.2 shows a summary QC report for the laboratory control sample that was included in the analytical batch.

LABORATORY CONTROL SAMPLE

Login Number:L0108493 Run Date:08/29/2001 Sample ID:WG103297-03
Instrument ID:HPMS5 Run Time:16:50 Method:8270
File ID:5M18197 Analyst:CLK Matrix:SOLID
Blank Workgroup:WG103827 Units:ug/kg

Analytes	Expected	Found	% Rec	LCS Limits	Q
Naphthalene	1670	1210	72.5	10 - 95	
Acenaphthylene	1670	1360	81.4	10 - 109	
Acenaphthene	1670	1360	81.4	10 - 123	
Fluorene	1670	2540	152.0	10 - 122	#
Phenanthrene	1670	1490	89.2	10 - 144	
Anthracene	1670	1530	91.6	10 - 149	
Fluoranthene	1670	1610	96.4	10 - 158	
Pyrene	1670	1600	95.8	10 - 161	
Benzo[a]anthracene	1670	1630	97.6	10 - 159	
Chrysene	1670	1690	101	10 - 153	
Benzo[b]fluoranthene	1670	1640	98.2	10 - 161	
Benzo[k]fluoranthene	1670	1620	97.0	10 - 165	
Benzo[a]pyrene	1670	1650	98.8	10 - 152	
Indeno[1,2,3-cd]pyrene	1670	1740	104	10 - 162	
Dibenz[ah]anthracene	1670	1780	107	10 - 169	
Benzo[ghi]perylene	1670	1760	105	10 - 160	

Figure 8.1 Example summary report for semi-volatile compounds.

RESULTS

Analytical Method : 8270 Preparatory Method: 8270C\3550B [redacted]

[redacted] Matrix: Soil

% Solids: 86 Initial Calibration ID: HPMS5 29-AUG-2001

Date Received: 22-AUG-01 Date Extracted: 22-AUG-01 Date Analyzed: 31-AUG-01 01:32

Concentration Units: ug/kg

Analyte	MDL	RL	Concentration	Dilution	Qualifier
Acenaphthene	959	1900	959	10	ND
Acenaphthylene	959	1900	2700	10	
Anthracene	959	1900	959	10	ND
Benzo(a)anthracene	959	1900	6100	10	
Benzo(a)pyrene	959	1900	7400	10	
Benzo(b)fluoranthene	959	1900	6100	10	
Benzo(g,h,i)perylene	959	1900	5600	10	
Benzo(k)fluoranthene	959	1900	4600	10	
Chrysene	959	1900	6000	10	
Dibenzo(a,h)anthracene	959	1900	959	10	ND
Fluoranthene	959	1900	8900	10	
Fluorene	959	1900	959	10	ND
Indeno(1,2,3-cd)pyrene	959	1900	4400	10	
Naphthalene	959	1900	959	10	ND
Phenanthrene	959	1900	3500	10	
Pyrene	959	1900	11000	10	

Figure 8.2 Figure showing LCS summary data.

The analytical results can be evaluated with the following sections of the Tier I Checklist.

3.2 Semi-Volatile Data Review - Laboratory Control Sample (LCS)

3.2 Semi-Volatile Data Review - Laboratory Control Sample (LCS)	
3.2.1 Was an LCS prepared, extracted, analyzed and reported once per group of 20 samples (per batch)? **Note:** This information should be included in the QA/QC package provided by the laboratory. If not, contact the laboratory and request that the information be submitted to the Agency. *Action: If LCS information is not present, consult the facility for re-submission of the data package. If LCS information is not available, qualify all positive results as "J." If warranted, the Validator may reject all results.*	Yes.
3.2.2 Does the LCS contain the following semi-volatile target compounds in addition to the required surrogates? **Note:** Method 8270D calls for base/neutral compounds to be spiked at 100 µg/L and acid compounds to be spiked at 200 µg/L. However, for waste samples the concentration should be 5 times higher. Other compounds can be spiked into the LCS; however, these compounds should represent the entire range of target analytes. In addition, the compounds in the LCS should be consistent with the compounds included in the matrix spike/matrix spike duplicate. **Base/Neutrals** 1,2,4-Trichlorobenzene Pentachlorophenol Acenaphthene 2,4-Dinitrotoluene Pyrene N-Nitroso-di-n-propylamine 1,4-Dichlorobenzene **Acids** Phenol 2-Chlorophenol 4-Chloro-3-Methylphenol 4-Nitrophenol	No, the compounds in the LCS only contain PAH compounds of interest and not compounds included within the acid fraction. An explanation was sought from the laboratory. The laboratory responded that only base/neutral fraction analysis was being performed for this batch of samples and therefore acid fraction surrogates were not necessary.

3.2.3 Do the percent recoveries (%R) meet the QC limits provided by the lab? **Action***: If the LCS recovery is greater than the upper acceptance limit, then positive sample results for the affected compound(s) should be qualified as "J."* *If the mass spectral criteria are met, but the LCS recovery is less than the lower acceptance limit, then the associated detected target compounds should be qualified as "J," and the associated non-detected target compounds should be qualified as "R."* *If more than half of the compounds in the LCS are not within the recovery criteria, then all of the associated detected target compounds should be qualified as "J," and all associated non-detected compounds should be qualified "R."*	List compounds and sample IDs that do not meet QC limits: *No. The LCS recovery for fluorene (% R = 152) were outside of the acceptance criteria (10-122).* Fluorene was not detected in the sample above the reporting limit, but at the MDL. The LCS recovery was above the criteria. Therefore, no qualification is necessary
3.2.4 Verify the calculations for at least one %R. *%R = found/true X100* **Action:** If the %R is not calculated correctly, verify the other %R calculations and/or contact the lab for re-submission. If the recalculated %R values fall within the QC limits, the Validator should use professional judgment to determine if the lab should be contacted for re-submission or the data should be flagged.	%R for Fluorene: % R = 2540 /1670 = 1.521 X 100 = 152%

Based upon strict conformance with data validation principles, no qualification of the results are necessary. However, the results from the data validation indicate that the laboratory was not in exact conformance with SW-846 Method 8270D for the LCS compounds. If the Data Validator should encounter this problem, a review of the compounds included in the matrix spike/matrix spike duplicate data should be performed. If the compounds are not the same or do not have the same concentrations, the laboratory of the facility should be contacted for an explanation. Without correspondence between these batch QC samples, it will be difficult for the Data Validator to determine whether a matrix interference is present or a system analytical problem exists.

Chapter 9
Surrogate Recovery

9.0 Introduction

Surrogates are used in organic SW-846 analytical methods as a means to evaluate what effect the matrix has on accuracy of individual samples. This is accomplished by measuring the percent recovery of the surrogate compounds added to the sample. Surrogates are organic compounds which are similar to the target analytes in chemical composition and behavior, but which are not expected to be detected in environmental media. Most surrogates are target analytes which have been chemically altered through bromination, fluorination, or isotopic labeling. Surrogate compounds are added to every sample, blank, matrix spike (MS), matrix spike duplicate (MSD), matrix spike blank (MSB) and standard prior to any extraction or analysis procedure.

9.1 Definition

Surrogate Recovery (%R): Amount of a specific surrogate compound recovered during analysis, expressed as a percentage. Surrogate recovery is used to measure accuracy. The percent recovery is determined using the following equation:

Equation 9.1

$$\%R = \frac{\text{Concentration (or Amount Found) of the Spiked Sample}}{\text{Concentration (or Amount Added) of the Spike}} \times 100$$

Surrogate recovery information must be included within the data report. If this information is not included, the facility or the laboratory should be consulted and the necessary information supplied to the Tier I Data Validator. A boilerplate letter (to be used for requesting missing information) is available at the end of this document in Appendix I. In order to assess whether the surrogate recovery is acceptable, the laboratory must also supply surrogate recovery criteria. Good analytical procedures imply that the laboratory provide this information or the individual laboratory's Quality Assurance Program Plan (QAPP) may also be consulted as to its surrogate recovery criteria.

This chapter discusses surrogate recovery procedures for the common organic laboratory SW-846 methods (volatile and semi-volatile analyses).

9.2 Volatile Organic Compound (VOC) Specific Information

The following four surrogate compounds, recommended for SW-846, Method 8260B, are added to all VOC samples and blanks to measure their recovery in environmental samples and blank matrices:

- 1,2-Dichloroethane-d4
- Bromofluorobenzene
- Toluene-d8
- Dibromofluoromethane

Surrogate recoveries in volatile organic samples and blanks must be within the limits specified in the SW-846 method. To find the applicable limits for these surrogate compounds, refer to the laboratory's Standard Operating Procedures (SOP) or QAPP. Typical surrogate recovery ranges may be found in Table 9.1. Internal Standards and their associated surrogates for SW-846, Method 8260B may be found in Table 9.2. Most laboratories report surrogate recovery limits on the sample data and blank results sheets.

Table 9.1 Guidelines For Surrogate Recovery For SW-846, Method 8260B

Surrogate Compound	Water	Soil/Sediment
1,2-Dichloroethane-d_4	80-120	80-120
Toluene-d_8	88-110	81-117
4-Bromofluorobenzene	86-115	74-121
Dibromofluoromethane	86-118	80-120

9.2.1 VOC Data Evaluation

The QA/QC information supplied with a data report must be checked to verify that the surrogate recovery information is present and is within the acceptance criteria set by the laboratory or the projects DQOs. If any of the surrogate compounds are outside of this criteria, these compounds should be marked with an asterisk. According to SW-846, the laboratory should use the method to re-analyze the sample to confirm that the problem is due to sample matrix effects rather than laboratory deficiencies. Often, there is little information presented to indicate that re-analysis was performed. If a surrogate's recovery is outside the acceptance criteria, it is appropriate to confirm that re-analysis was performed with the facility or its laboratory. The data validator may wish to carefully review the data narrative for an indication that re-analysis was performed. It should be noted that upon successful re-analysis, the laboratory is not required to report the initial, failed analysis, since the second analysis is within the acceptance criteria.

The Tier I Data Validation Checklist does not require that individual surrogate recoveries be checked mathematically. As an optional exercise, the Tier I Data Validator may verify that the percent recovery calculations were performed correctly.

Table 9.2 Internal Standards & Their Associated Analytes & Surrogates For SW-846, Method 8260B

Pentafluorobenzene	1,4-Difluorobenzene	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
Dichlorofluoromethane	1,2-Dichloroethane-d4 (Surr.)	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane (SPCC)
Chloromethane (SPCC)	1,1-Dichloropropane	Dibromochloromethane	Isopropylbenzene
Vinyl Chloride (CCC)	1,2-Dichloroethane	Tetrachloroethene	1,2,3-Trichloropropane
Bromomethane	Carbon Tetrachloride	1,2-Dibromomethane	Bromofluorobenzene (Surr.)
Chloroethane	Benzene	Chlorobenzene (SPCC)	Bromobenzene
Trichlorofluoromethane	Trichloroethene	1,1,1,2-Tetrachloroethane	n–Propylbenzene
1,1-Dichloroethene (CCC)	1,2-Dichloropropane (CCC)	Ethylbenezene	2-Chlorotoluene (CCC)
Acrolein	Dibromomethane	m&p-Xylene	4-Chlorotoluene
Methylene Chloride	Bromodichloromethane	Styrene	1,3,5-Trimethylbenzene
trans-1,2-Dichloroethene	2-Chloroethyl vinyl ether	o-Xylene	tert-Butylbenzene
Acrylonitrile	cis-1,3-Dichloropropene	Bromoform (SPCC)	1,2,4-Trimethylbenzene
1,1-Dichloroethane (SPCC)	Toluene-d8 (Surr.)	sec-Butylbenzene	
Methyl ethyl ketone	Toluene (CCC)	1,3-Dichlorobenzene	cis-1,2-Dichloroethene
trans-1,3-Dichloropropene	p-Isopropylbenzene	2,2-Dichloropropane	1,1,2-Trichloroethane
1,4-Dichlorobenzene	Chloroform (CCC)	1,2-Dichlorobenzene	Bromochloromethane
n-Butylbenzene	1,1,1-Trichloroethane	1,2-Dibromo-3-chloropropane	Dibromofluoromethane (Surr.)
1,2,4-Trichlorobenzene	Naphthalene	Hexachlorobutadiene	1,2,3-Trichlorobenzene
Surr. = surrogate CCC = Calibration Check Compound SPCC = System Performance			

Check the sample by using raw data from the laboratory report and verify calculations using the formula listed above or from specific method requirements found in SW-846.

The Tier I Data Validator must check surrogate recoveries associated with the blanks if they are present. If any of this data is out of compliance, it must be reported on the Tier I Data Validation Checklist.

9.2.2 Action

Based on the findings, good data validation procedures imply that VOC data be qualified using the following criteria:

- If a surrogate compound is above the upper control limit, then all positive results would be qualified as "J+", estimated. Results listed as non-detect would not be qualified.
- If any surrogate recovery is less than the lower criteria, but greater than or equal to 10% recovery, then all detected compounds would be qualified as "J-", estimated, and all non-detect compounds would be qualified as "UJ", estimated undetected.
- If any surrogate recovery is less than 10%, then all detected compounds would be qualified as "J-," estimated, and all non-detect compounds as "R", rejected.

An example showing how to validate soil data is presented using Section 2.1 of the Tier I Data Validation Checklist and the following information.

Example 9.1 How would the following VOC data be qualified based on surrogate recovery data?

Volatile Organic Compounds by SW-846, Method 8260B

Analyte(s)	Result	RDL	Unit	SW-846	Method #	Flag
Chlorobenzene	10	6.1	ug/kg dry	SW-846	8260B	
Ethylbenzene	ND	6.1	ug/kg dry	SW-846	8260B	
o-Xylene	ND	6.1	ug/kg dry	SW-846	8260B	

Surrogate: 1,2-Dichloroethane-d_4	*138%*	*(70-130)**
Surrogate: Bromofluorobenzene	*110%*	*(70-130)*
Surrogate: Toluene-d_8	*94%*	*(70-130)*

2.4.1 Are the surrogate recovery data present for each batch (method and matrix), including TCLP? **Note:** Samples may be included in separate sample batches and separate surrogate recoveries should be provided. *Action: If no, contact the laboratory for explanation and re-submittals.*	Yes, surrogate recovery results are present.

2.4.2 Were any outliers marked correctly (based upon the laboratory's criteria)? *Action: Mark, circle or highlight the suspected outliers. List the sample ID(s), matrix(-ces) and parameter(s).*	Yes, the surrogate outlier, 1,2-Dichloroethane-d4, was marked with an asterisk. The surrogate recovery was 138 % which was above the upper quality Control Criteria of 130%.
2.4.3 If any surrogate compound was out of compliance, was re-analysis performed to confirm a matrix interference? **Note:** Check the report narrative for an indication of re-analysis. Additionally, qualification may not be appropriate for TCLP data. Best professional judgment may be used to qualify data. *Action: If a surrogate is above the upper control limit, all positive results should be qualified as "J+." Results listed as non-detected should not be qualified.*	No reanalysis was performed. Since 1,2-Dichloroethane-d4 was above the upper control limit, the positive result (10) for Chlorobenzene should be qualified as "J+".

If any surrogate recovery is less than 10%, all detected compounds should be qualified as "J-" and all non-detected compounds as "R." List sample ID(s) for surrogate compounds out of compliance and criteria:

In the example, there is no indication that re-analysis was performed. For a real sample report, the Tier I Data Validator must check the data narrative for an indication of re-analysis. If no indication of re-analysis can be found, good data validation practices imply that the facility or its laboratory be contacted and confirmation of re-analysis be obtained. If no information is available, the Tier I Data Validator, at his or her discretion, may qualify the affected data using best professional judgment. The Tier I Data Validator is directed to consult with the district Tier II representative for advice.

In the example, 1,2-Dichloroethane-d4, was found to have a percent recovery of 138% which is above the upper bounds of the quality control criteria. In example 9.1, only Chlorobenzene was detected. This value should be flagged with a "J+" as being an estimated quantity. The other parameters were not detected and therefore do not require qualification.

The VOC data indicates that Chlorobenzene was detected at 10 micrograms per kilogram (ug/kg) while Ethylbenzene and o-Xylene were non-detect. The surrogate data shows that 1,2-Cichloroethane-d4 is above the upper control limit while Bromofluorobenzene and o-Xylene were within the specified limits.

Since one surrogate compound was above the upper control limit, good data validation practices imply that Chlorobenzene, which is a positive result, be qualified as "J+," estimated. Ethylbenzene and o-Xylene would not be qualified. The qualified laboratory report for Example 9.1 would resemble the following:

Volatile Organic Compounds by SW-846, Method 8260B

Analyte(s)	Result	RDL	Unit	SW-846	Method #	Flag
Chlorobenzene	10	6.1	ug/kg dry	SW-846	8260B	J+
Ethylbenzene	ND	6.1	ug/kg dry	SW-846	8260B	
o-Xylene	ND	6.1	ug/kg dry	SW-846	8260B	

Surrogate: 1,2-Dichloroethane-d_4	*138%*	*(70-130)**
Surrogate: Bromofluorobenzene	*110%*	*(70-130)*
Surrogate: Toluene-d_8	*94%*	*(70-130)*

9.3 Semi-Volatile Organic Compound (SVOC) Specific Information

Surrogate compounds recommended for SVOC analyses by SW-846, Method 8270D include compounds that can be divided into two fractions: acid compounds and base/neutral compounds. Each class has an assigned set of surrogate compounds. For the base/neutral fraction, the following compounds are recommended as surrogates:

- Nitrobenzene-d5
- 2-Fluorobiphenyl
- p-Terephenyl-d14

For the acid fraction, the following compounds are recommended as surrogates:

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

Similar to volatile organic results, surrogate recoveries for SVOC samples and blanks must be within the limits specified by the laboratory. To find the applicable limits for these surrogate compounds, refer to the laboratory's SOP or QAPP. Typical surrogate ranges can be found in Table 9.3. Internal Standards and their associated analytes and surrogates for SW-846, Method 8270D can be found in Table 9.4. Most laboratories report surrogate recovery limits with the sample data and blank results.

9.3.1 SVOC Data Evaluation

The data report must be checked to verify that the recoveries are within the acceptance criteria. Any surrogate recovery outside of this criteria should be marked with an asterisk. If any two surrogate compounds in either the acid or base/neutral fraction are out of criteria, then re-analysis should be performed to confirm that the problem is due to sample matrix effects rather than laboratory deficiencies. The report narrative must also contain an indication that re-analysis was performed. As an optional exercise, the Tier I Data Validator can verify that the percent recovery calculations were performed correctly by using raw data from the laboratory report and verify calculations using the formulas available in the specific methods found in SW-846.

Table 9.3 Guidelines For Surrogate Recovery For SW-846, Method 8270D

Surrogate Compound	Water	Soil/Sediment
Nitrobenzene-d5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d14	33-141	18-137
Phenol-d6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

Note: Sample extracts with high analyte concentrations may not have surrogate recoveries reported due to sample extract dilution. Re-analysis or re-extraction may not be performed since dilution of the extract is due to high analyte concentration and not matrix interferences.

9.3.2 Action

If any two base/neutral or acid surrogates are out of the acceptance criteria, or if any one base/neutral or acid extractable surrogate has a recovery of less than 10 percent, then re-analysis should be performed to confirm a matrix effect rather than to identify laboratory deficiencies. The report narrative must also be checked for an indication of re-analysis.

Based on this evaluation, semi-volatile analyses are qualified using the following criteria:

- If any two surrogates in a particular class are above the upper control limit, then all positive results in that class would be qualified as “J+,” estimated.

- Results listed as non-detect would not be qualified.

Table 9.4 Internal Standards & Their Associated Analytes &Surrogates For SW-846, Method 8270D

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Aniline	Nitrobenzene-d_5 (Surr.)	1,2,4,5 - Tetrachlorobenzene
2-Fluorophenol (Surr.)	Nitrobenzene	Hexachlorocyclopentadiene
Phenol-d_6 (Surr.)	n-Nitrosopiperdine	2,4,6-Trichlorophenol (CCC)
Phenol (CCC)	Isophorone	2,4,5-Trichlorophenol
Pyridine	2-Nitrophenol (CCC)	2-Fluorobiphenyl (Surr.)
Bis (2-Chloroethyl) ether	2,4-Dimethylphenol	1-Chloronaphthalene
2-Chlorophenol	bis (2-Chloroethoxy)methane	2-Nitroaniline
1,3-Dichlorobenzene	2,4-Dichlorophenol (CCC)	Dimethylphthalate
1,4-Dichlorobenzene (CCC)	1,2,4-Trichlorobenzene	Acenaphthylene
Benzyl alcohol	Benzoic acid	2,6-Dinitrotoluene
1,2-Dichlorobenzene	Naphthalene	3-Nitroaniline
2-Methylphenol	4-Chloroaniline	Acenaphthene (CCC)
bis (2-Chloroisopropyl) ether	Hexachlorobutadiene (CCC)	2,4-Dinitrophenol (SPCC)
Acetophenone	n-Nitroso-di-n-butylamine	4-Nitrophenol (SPCC)
4-Methylphenol	4-Chloro-3-methylphenol	(CCC)Dibenzofuran
n-Nitroso-di-n-propylamine (SPCC)	2-Methylnaphthalene	Pentachlorobenzene
Hexachloroethane		2,4-Dinitrotoluene
		2-Chloronaphthalene
		Diethylphthalate
		Fluorene
		4-Chlorophenyl-phenylether
		4-Nitroaniline

Phenanthrene-d_{10}	**Chyrsene-d_{12}**	**Perylene-d_{12}**
4,6-Dinitro-2-methylphenol	Benzidine	Di-n-octylphthalate (CCC)
n-Nitrosodiphenylamine	Pyrene	Benzo [b] fluoranthene
Diphenylamine (CCC)	Terphenyl-d_{14} (Surr.)	Benzo [k] fluoranthene
2,4,6-Tribromophenol	Dimethylaminoazobenzene	Benzo [a] pyrene (CCC)
4-Bromophenyl-phenylether	Butylbenzylphthalate	3-Methylcholanthracene
Phenacetin	Benzo [a] anthracene	Indeno [1,2,3-cd] pyrene
Hexachlorobenzene	3,3' - Dichlorobenzidine	Dibenz [a,h] anthracene
Pentachlorophenol (CCC)	Chrysene	Benzo [g,h,i] perylene
Pentachloronitrobenzene	Bis (2-ethylhexyl) phthalate	
4-Aminobiphenyl		
Phenanthrene		
Anthracene		
Di-n-butylphthalate		
Fluoranthene (CCC)		

Surrogate = (Surr.)
System Performance Calibration Check = (SPCC)
Continuing Calibration Check = (CCC)

1. If any two surrogates in a particular class have recoveries less than the lower acceptance criteria, but the recovery is greater than or equal to 10%, then all detected compounds would be qualified as "J-," estimated, and all non-detect compounds would be qualified as "UJ," estimated undetected.

2. If any surrogate in a particular class has a recovery less than 10%, then all detected compounds would be qualified as "J-," estimated, and all non-detect compounds as "R," rejected.

The blank data must be checked for surrogate recoveries out of compliance. If any of this data is out of compliance, this must be reported on the Tier I Data Validation Checklist.

An example showing how to validate surrogate data for a ground water sample analyzed for semi-volatile compounds is presented using Section 3.4 of the Tier I Data Validation Checklist and the following information presented in example 9.2.

Example 9.2 How should the following SVOC ground water data be qualified based on the surrogate recovery data?

Semi-Volatile Organic Compounds by SW-846, Method 8270D

Analyte(s)	Result	RDL	Units	SW-846 Method	Flag
Pyridine	ND	0.050	mg/l	SW-846, 8270D	
Nitrobenzene	50	0.050	mg/l	SW-846, 8270D	
Hexachlorobenzene	ND	0.050	mg/l	SW-846, 8270D	

Surrogate:	Nitrobenzene-d_5	2%	(4-140)*
Surrogate:	2-Fluorobiphenyl	9%	(22-160)*
Surrogate:	p-Terephenyl-d_{14}	48%	(18-137)

3.4.1 Are the surrogate recovery data present for each batch (method and matrix), including TCLP? **Note**: Samples may be included in separate sample batches and separate surrogate recoveries should be provided. *Action: If no, contact the laboratory for explanation and re-submittal.*	Yes, surrogate recoveries are present.
3.4.2 Were any outliers marked correctly? Action: Mark, circle or highlight the suspected outliers.	List the sample ID(s), matrix(-ces) and parameter(s): Surrogate recoveries for Nitrobenzene-d5 and p-Terephenyl-d14 were outside of the lower control limit of the quality control criteria. These surrogates were marked with an asterisk.

3.4.3 If any TWO surrogate compounds in either the acid or base/neutral fractions were out of compliance, was re-analysis performed to confirm a matrix interference? **Note:** Check the report narrative for an indication of re-analysis. *Action: Mark, circle or highlight the suspected outliers.* *Action: If no information is present, request information from the facility.*	List the sample ID(s), matrix(-ces) and parameter(s): Surrogate recoveries for Nitrobenzene-d5 and p-Terephenyl-d14 were outside of the lower control limit of the quality control criteria. These surrogates were marked with an asterisk. List sample ID(s) for surrogate compounds out of compliance and criteria. The grouping of surrogates by fraction is as follows: Surrogate Compound — Fraction Phenol-d6 — Acid 2-Fluorophenol — Acid 2,4,6-Tribromophenol — Acid Nitrobenzene-d5 — Base/Neutral 2-Fluorobiphenyl — Base/Neutral p-Terphenyl-d14 — Base/Neutral Both Nitrobenzene-d5 and 2-Fluorobiphenyl are below the lower quality control criteria. There is no indication of re-analysis in the example. For a real sample report, the Tier I Data Validator must check the data narrative for an indication of re-analysis. If no indication of re-analysis can be found, the facility or its laboratory must be contacted and confirmation of re-analysis must be obtained. If no information is available, the Tier I Data Validator, at his or her discretion, may qualify the affected data using best professional judgment. The Tier I Data Validator is directed to consult with the district Tier II Data Validator for advice.

3.4.4 If any ONE surrogate compound has a recovery of less than 10% in either the acid or base/neutral fraction, check for indications that re-analysis was performed to confirm a matrix interference? **Note:** Check the report narrative for an indication of re-analysis.	List sample ID(s) for surrogate compounds out of compliance and criteria: Both Nitrobenzene-d5 and 2-Fluorobiphenyl have less than 10% recovery. See the explanation in Tier I Data Validation Checklist question 3.4.5.
3.4.5 Based on the findings, qualify data in either the acid or base/neutral fraction with the following criteria: **Note:** Qualification may not be appropriate for TCLP data. Best professional judgment may be used to qualify data. *Action: If TWO surrogates in a particular class are above the upper control limit, all positive results, for that fraction, in that fraction should be qualified as "J+." Results listed as non-detected should not be qualified.* *If any TWO surrogates in a particular fraction have recoveries less than the lower criteria, but the recovery is greater than or equal to 10%, all detected compounds, for that fraction, should be qualified as "J-" and all non-detected compounds as "UJ."* *If any surrogates in a particular fraction have recoveries less than 10%, all detected compounds, for that fraction, should be qualified as "J-" and all non-detected compounds as "R."*	List the ID(s) of the affected sample(s): Both Nitrobenzene-d5 and 2-Fluorobiphenyl have less than 10% recoveries. These surrogates are both from the base/neutral fraction. According to the action statements, all detected compounds in base/neutral fraction should be qualified as "J-," estimated, and all non-detect compounds should be rejected and flagged with an "R." For example 2, Nitrobenezene was detected, and therefore, this data should be qualified as estimated and flagged with a "J-."Both Pyridine and Hexachlorobenzene were not detected, and therefore, these data should be rejected and the results flagged with an "R."

The SVOC data indicates that Nitrobenzene was detected at 50 milligrams per liter while Pyridine and Hexachlorobenzene were not detected. The surrogate data show that Nitrobenzene-d5 and 2-Fluorobiphenyl are below the lower QC control limits; and p-Terephenyl is within the specified limits.

Since two surrogate recoveries are below 10% in example 9.2, Nitrobenzene, which is a detected compound, would be qualified as estimated and the data flagged with a "J." Both Pyridine and Hexachlorobenzene were not detected. They would be qualified as rejected and the data flagged with an "R". The lab results would look like this:

Semi-Volatile Organic Compounds by SW-846, Method 8270D

Analyte(s)	Result	RDL	Units	SW-846 Method	Flag
Pyridine	ND	0.050	mg/l	8270D	R
Nitrobenzene	50	0.050	mg/l	8270D	J
Hexachlorobenzene	ND	0.050	mg/l	8270D	R

Surrogate:	Nitrobenzene-d_5	2% (4-140%)*
Surrogate:	2-Fluorobiphenyl	9% (22-160%)
Surrogate:	P-Terephenyl-d_{14}	8% (18-137%)

9.4 Target Analytes By Fraction

The Tier I Data Validation guidance and qualification criteria illustrated in Section 9.3.2 states that target analytes be qualified by either base/neutral or acid fraction. SW-846 does not designate in which fraction each target analyte belongs. In general, acid fraction target analytes will include phenol compounds and other organic acids. The base/neutral fraction will include polynuclear aromatic hydrocarbon (PAH) compounds, such as Pyrene, and chlorinated Benzene compounds. It is important to know to which fraction a target analyte belongs. To aid in the review and correct qualification of data, the following table can be used to assign common semi-volatile compounds to the correct fraction. If a compound is not present in the table, the Tier I Data Validator can consult DHWM's contract laboratory or the facility's laboratory for the fraction to which a target analyte is assigned.

Table 9.5 Common Semi-Volatile Acid Compounds

4-Chloro-3-methylphenol	p-Cresol
2-Chlorophenol	3,5-Dibromo-4- hydroxybenzonitrile
2,4-Dichlorophenol	Hexanoic acid
2,4-Dinitrophenol	2,6-Dichlorophenol
2-Methyl-4,6-dinitrophenol	2,3,4,6-Tetrachlorophenol
2-Nitrophenol	2,3,6-Trichlorophenol
4-Nitrophenol	2,4,5-Trichlorophenol
Pentachlorophenol	2,4,6-Trichlorophenol
Benzoic acid	

Table 9.6 Common Semi-Volatile Base/Neutral Compounds		
Acenaphthene Acenaphthylene Acetophenone 4-Aminobiphenyl Aniline o-Anisidine Anthracene Aramite Benzanthrone 1,3-Benzenediol Benzenethiol Benzidine Benzo(a)anthracene Benzo(k)fluoranthene Benzo(a)pyrene Benzo(ghi)perylene 2,3-Benzofluorene Benzoic acid Benzyl alcohol Biphenyl Bis(2-Chloroethyl) ether Bis(2-Chloroethoxy)methane Bis(2-Chloroisopropyl) ether Bis(2-Ethylhexyl) phthalate 2-Bromochlorobenzene 3-Bromochlorobenzene 4-Bromophenyl phenyl ether Butyl benzyl phthalate Carbazole 4-Chloro-2-nitroaniline 5-Chloro-o-toluidine 4-Chloroaniline 2-Chloronaphthalene 3-Chloronitrobenzene 4-Chlorophenyl phenyl ether 3-Chloropropionitrile Chrysene o-Cresol Crotoxyphos p-Cymene 2,6-Di-tert-butyl-p-benzoquinone Di-n-butyl phthalate 2,4-Diaminotoluene Dibenzo(a,h)anthracene Dibenzofuran Dibenzothiophene 1,2-Dibromo-3-chloropropane 2,6-Dichloro-4-nitroaniline 1,3-Dichloro-2-propanol 2,3-Dichloroaniline 1,2-Dichlorobenzene 1,3-Dichlorobenzene	1,4-Dichlorobenzene 3,3'-Dichlorobenzidine 2,2'-Difluorobiphenyl (int. std.) 2,3-Dichloronitrobenzene 1,2:3,4-Diepoxybutane Diethyl phthalate 3,3'-Dimethoxybenzidine Dimethyl phthalate Dimethyl sulfone p-Dimethylaminoazobenzene 7,12-Dimethylbenz(a)anthracene N,N-Dimethylformamide 3,6-Dimethylphenanthrene 2,4-Dimethylphenol d_3 1,4-Dinitrobenzene 2,4-Dinitrotoluene d3 Di-n-octyl phthalate d_4 Diphenylamine d_{10} Diphenyl ether d_{10} Diphenyldisulfide 1,2-Diphenylhydrazine Ethyl methanesulfonate Ethylenethiourea Ethynylestradiol 3-methyl ether Fluoranthene Fluorene Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Hexachloropropene Indeno(1,2,3-cd)pyrene Isophorone d_8 2-Isopropylnaphthalene Isosafrole Longifolene Malachite green Methapyrilene Methyl methanesulfonate 2-Methylbenzothiazole 3-Methylcholanthrene 4,4'-Methylenebis (2-chloroaniline) 4,5-Methylenephenanthrene 1-Methylfluorene 2-Methylnaphthalene 1-Methylphenanthrene 2-(Methylthio)benzothiazole Naphthalene d_8 1,5-Naphthalenediamine	1,4-Naphthoquinone alpha-Naphthylamine beta-Naphthylamine d_7 5-Nitro-o-toluidine 2-Nitroaniline 3-Nitroaniline 4-Nitroaniline Nitrobenzene d_5 4-Nitrobiphenyl N-Nitrosodi-n-butylamine N-Nitrosodi-n-propylamine N-Nitrosodiethylamine N-Nitrosodimethylamine d_6 N-Nitrosodiphenylamine d_6 N-Nitrosomethylethylamine N-Nitrosomethylphenylamine N-Nitrosomorpholine N-Nitrosopiperidine Pentachlorobenzene Pentachloroethane Pentamethylbenzene Perylene Phenacetin Phenanthrene d_{10} Phenothiazine 1-Phenylnaphthalene 2-Phenylnaphthalene alpha-Picoline d_7 Pronamide Pyrene Pyridine Safrole Squalene Styrene alpha-Terpineol 1,2,4,5-Tetrachlorobenzene Thianaphthene Thioacetamide Thioxanthone o-Toluidine 1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene 1,2,3-Trimethoxybenzene 2,4,5-Trimethylaniline Triphenylene Tripropylene glycol methyl ether 1,3,5-Trithiane

Chapter 10
Batch & Sample QA/QC Summary

10.0 Introduction

The Tier I Data Validation Manual has addressed specific batch and sample quality control (QC) parameters that are used to check the accuracy and precision of environmental data. **Batch specific quality control** results are applied to all the samples contained in a batch. Results from batch specific QC are generally not used on their own to qualify data. One reason for this is that the QC sample(s) analyzed are included in the batch(es) with sample(s) of concern, but may not have been analyzed utilizing sample(s) of concern. Results of this type may indicate problems related to the QC sample's matrix in particular, but may not relate to the actual matrix of the sample(s) of concern. Therefore, **sample specific quality control** results must also be examined when determining whether data should be qualified. Table 10.1 outlines a summary of batch and sample-specific quality control parameters commonly generated with organic and inorganic analyses. This table also indicates the purpose of each QC parameter and what information these samples give the Data Validator concerning the validity of the analytical results.

Table 10.1 Summary of Batch and Sample QA/QC Parameters

QC Parameter Name	Batch, Method or Sample	Performed on Blank or Sample Itself?	Organics or Inorganics	Purpose
Calibration Standard	Per Method & Per Instrument	Sample	Organics	Compound known for eluting from the GC column at a particular time. The elution time is then used to confirm consistent performance of the equipment (compared to previous runs).
Internal Standard	Sample	Blank, Sample	Organics	Used to quantify compounds in a sample, to give an indication of matrix interferences, instrumental control and analyst techniques for individual samples.
LCS (or Blank Spike)	Batch	Blank	Both	Monitors the efficiency of the preparation procedures and methods for each sample matrix using the same procedures and analytical methods as the actual samples. Assessed by % Recovery. Used to document overall lab performance of each step during the analysis, using an ideal “sample.”
Matrix Duplicate	Batch	Sample	Both	Split sample used to document the precision of a method in a given sample matrix.
Matrix Spike	Batch	Sample	Both	Spiking of a sample prior to prep/analysis with a known concentration of target analyte(s). Provides information about the effect of the sample matrix on the digestion and measurement methodology. Used to document the bias of a method in a given sample matrix.
Matrix Spike Duplicate	Batch	Sample	Both	Spike of the same compounds as used in the matrix spike that are added to a second aliquot of the same sample. Intra-lab split samples spiked w/ identical concentration of target analyte(s) prior to prep/analysis. Used to document precision and bias of method in a given sample matrix.
Matrix Spike Blank	Batch	Blank	Both	Provides a measure of whether the spiking compounds are inappropriate for a specific batch of samples. For example, organic acids may react with the sample matrix causing unacceptable MS/MSD reproducibility.
Post-Digestion Spike	Batch	Blank	Inorganics	Addition of a known amount of standard after digestion. Also termed analytical spike. Often used to narrow down source(s) of QC problems found in Pre-Digestion Spike.
Pre-Digestion Spike	Batch	Blank	Inorganics	See Matrix Spike
Prep Spike	Batch	Blank	Inorganics	Spike added at the beginning of a procedure, and therefore subject to preparatory and analytical procedures.
Serial Dilution	Sample	Sample	Both	Sample run at specific dilutions to determine whether any significant chemical or physical interferences exist due to sample matrix effects. (ICP only).
Surrogate	Method	Sample	Organics	Addition of compounds that are similar to target compounds in physical and chemical properties. Provides indications of matrix interference.

Chapter 11
pH

11.0 Introduction

Certain wastes must be evaluated for the characteristic of corrosivity to determine whether they are hazardous wastes (OAC 3745-51-22). By definition, a corrosive hazardous waste is either a) aqueous, and has a pH less than or equal to 2 or greater than or equal to 12.5 as defined by SW-846 method 9040, or b) a non-aqueous liquid, and is shown to be corrosive according to SW-846, Method 1110A, "Corrosivity Toward Steel" (steel coupon test) or equivalent. As Ohio EPA does not routinely receive data for Method 1110, this chapter will address the determination of pH by SW-846, Method 9040C. This chapter discusses **pH** data used to determine corrosivity and the necessary steps for validation of this data.

11.1 Definitions

Aqueous: A solution where at least 20 percent of the solution's composition is water.

Buffer Solution: A stable solution of known pH, used to calibrate a pH electrode. In addition, buffered solutions or buffers will resist a change in pH when small amounts of acid or base are added. Buffered solutions are used to calibrate analytical instruments.

pH: The pH is the negative logarithm of the hydronium ion concentration (moles/L) at a specified temperature and pressure.

The hydronium ion concentration is small in natural water samples and by defining the pH as the negative log of the concentration, we can conveniently establish the pH scale. The usual convention is for the pH scale to extend from 0 to 14. A pH of zero represents very acidic conditions, 7 indicates neutral conditions, and 14 indicates very basic or alkaline conditions.

11.2 QA/QC

The measurement of pH is straightforward and usually can be accomplished without complication. However, there are several important provisions contained within SW-846, Method 9040C that must be observed. This method requires that temperature compensation be made for the final pH determination. Temperature compensation can be either internal, where an instrument uses an automatic temperature compensation (ATC) controller, or external where the temperature is compensated manually. It is important to note that the buffer solution used to calibrate the instrument and the waste pH should be at approximately the same temperature. Method 9040C requires that sample and buffer not differ by more than 2°C without temperature compensation. In addition, the waste temperature should be within the control range of the ATC. For certain wastes, additional information on the instrument's ATC and the temperature of the waste should be obtained in order to evaluate the pH results. For corrosivity characterization, the sample MUST be measured at 25 +/-1°C, if the waste pH is above 12.

The buffer solutions used to calibrate the pH meter must be within their expiration date and must bracket the expected pH of the samples. For a corrosivity determination, at least two pH buffers should be used consisting of a low pH buffer (e.g., 2.0) and/or a high pH buffer (e.g., 12.0), respectively, depending if the sample is acidic or caustic. Other buffers (e.g., 4, 7 and 10) may also be used to establish a pH meter calibration curve.

Samples should be analyzed as soon as possible after collection. Preferably, the analysis would be performed at the same time as waste generation. If this is not possible, analyses should be performed on the same day as sample receipt by the laboratory.

11.3 Information Necessary to Validate pH Data

Most data reports contain little information that may be used to judge the validity of pH measurements. If it becomes apparent that validation of pH data is necessary, the laboratory should be asked to provide the following information:

- Instrument ID;
- Sample ID and laboratory ID;
- Time and date of sampling;
- Time and date of sample receipt;
- Time and date of analysis;
- Last date of NIST (National Institute of Standards and Technology) instrument certification;
- Calibration procedure (daily calibration log, continuing calibration results and criteria);
- Calibration buffers used;
- Calibration standards results;
- Calibration buffer NIST certification or comparable information from a commercial vendor;
- Expiration date of the buffers;
- Temperature of waste and buffers;
- Temperature compensation (manual or ATC);
- Continuing calibration results (if required by the laboratory QAPP or instrument manufacturer).

11.4 Examples Using Checklist

The following example will illustrate the appropriate procedures for validation of pH data used to determine the corrosivity characteristic.

A sample of a liquid waste was split between two laboratories for analysis to determine whether the waste met the regulatory criteria for corrosivity. The analysis from a single contract laboratory determined that the waste pH was 12.1. This pH is slightly below the regulatory criteria for corrosivity. Additional information requested from the laboratory is summarized in Table 11.1 and was used to complete the example pH checklist below.

Table 11.1 pH Calibration and Temperature Information	
Sample Collection Date and Time:	09/27/01; 08:35 hours
Lab Sample Receipt Date and Time:	09/27/01; 16:08 hours
Sample Analysis Date and Time:	09/29/01; 13:47 hours
Calibration Buffers:	4, 7, and 10
Buffer Expiration Date:	11/20/01
Calibrated:	Daily
Certified:	Yearly
Continuing Calibration:	No
Temperature Compensation:	Yes, automatic temperature controller
Temperature of sample:	22.3°C

5.4 pH Determination and Corrosivity Tests

pH

pH is an important parameter used in ambient ground water monitoring and for determining if a waste displays the characteristic of corrosivity. For corrosivity determinations, OAC Rule 3745-51-22 specifies that SW-846, Method 9040C be used as the analytical test.

5.4.1 Were the pH tests performed as soon as practically possible? **Note:** SW-846 Method 9040C does not specify a maximum technical holding time for pH. However, it does state that all tests must be performed as soon as possible. Ohio EPA expects that most laboratories can perform the pH test within 24 hours of sample receipt. *Action: If analyses were performed within 24 hours, no action is necessary. If analyses were performed after 24 hours, but before the end of 7 days after sample receipt, all sample results between a pH of 2.05 and 12.5 will be flagged as "J." If the results are equal to or less than a pH of 2 or greater than or equal to a pH of 12.5, the results will not be flagged.* *If analyses were performed 7 days or more after sample receipt, all sample results between a pH of 2.05 and 12.45 will be flagged as "R." If the results are equal to or less than a pH of 2 or greater than or equal to a pH of 12.5, the results will not be flagged.*	Note time and date of sampling, sample receipt, and analysis for each sample. More than 24 hours elapsed between sample receipt and analysis (09/2701, 16:08 to 09/29/01, 13:47) The sample result of 12.1 should be considered estimated and the results flagged with a "J."
5.4.2 Was a yearly NIST certification of the analytical instrument performed? **Note:** This information must be part of the Laboratory QAPP. Check the QAPP or request information for the facility or laboratory. *Action: If a yearly certification was not performed, flag all results between a pH of 2.05 and 12.5 as "J" All results meeting the regulatory criteria for corrosivity will not be flagged.*	According to information from the lab, the instruments are certified once a year.

5.4 pH Determination and Corrosivity Tests	
5.4.3 Were the calibration buffers within their expiration date? **Note:** The laboratory can provide a photocopy of the expiration date and the buffer batch ID? *Action: If the expiration date is exceeded, flag all results between pH 2.05 or 12.45 as "R." Initially, results meeting the regulatory criteria for corrosivity will not be flagged; however, the Validator may qualify results based upon professional judgment and the DQOs for the data.*	Yes, the calibration buffers are within the expiration date.
5.4.4 Was the instrument calibrated correctly using at least two buffers that bracket the expected pH of the sample? **Note:** For corrosivity determinations, the calibration buffers must include a pH 2 buffer and a pH 12 buffer. Review the calibration log for information or request information from the laboratory. *Action: If an insufficient number of buffers were used (i.e., one) or if the incorrect buffers were used (buffers did not include a pH of 2 or 12 for corrosivity determination), flag all results between a pH of 2.05 and 12.45 as estimated, "J." All results meeting the regulatory criteria for corrosivity will not be flagged. If the pH of the waste is within 1.5 pH units of the regulatory criteria for corrosivity (3.0 or 11.0) and a pH buffer of 12 was not used, the results may be questionable and additional analyses using the correct buffers standards may be necessary*.	The instrument was calibrated using three buffers, 4, 7, and 10. For most water analyses, this buffer set is adequate. However, SW-846, Method 9040C specifies that for corrosivity determinations, calibration buffers of pH 2 and 12 must be used. In this example, these buffers were not used. Since the pH was determined to 12.1, the result should at least be considered estimated and the result flagged, "J." In addition, the result is within 1.0 pH units of the regulatory level. The result is questionable and a second pH determination should be made using the appropriate calibration buffers.

5.4 pH Determination and Corrosivity Tests	
5.4.5 Was continuing calibration performed? **Note:** If continuing calibration was performed, the pH of the continuing calibration buffer must be within 0.5 pH units of the buffer pH. Information on the continuing calibration standard and results must be requested from the laboratory. *Action: If continuing calibration was performed and the results were within 0.5 pH of the calibration buffer, no action is necessary. If continuing calibration was performed, and the results were greater or less than 0.5 pH units of the correct reading for the calibration buffer, then the analysis must have been terminated and the instrument recalibrated. If recalibration was necessary, but not performed, flag all results between a pH of 2.05 and 12.5 as estimated, "J." Initially, results meeting the regulatory criteria for corrosivity will not be flagged; however, the Validator may qualify results based upon professional judgment and the DQOs for the data.*	No, continuing calibration was not performed.
5.4.6 Were the temperature of the sample and the calibration buffers within 2°C of each other? **Note:** Request the information from the laboratory. If the sample and the calibration buffers were not within 2°C, then temperature compensation must have been performed. Request information from the laboratory on manual temperature compensation procedures or whether an automatic temperature compensation was used. *Action: If temperature compensation was required but not performed, flag all results between pH 2.05 or 12.45 as "J." Initially, results meeting the regulatory criteria for corrosivity will not be flagged; however, the Validator may qualify results based upon professional judgment and the DQOs for the data.*	The temperature was controlled with automatic temperature compensation.

5.4 pH Determination and Corrosivity Tests	
5.4.7 If the sample pH was above 12.0, was the temperature of the sample maintained at 25 +/- 1°C? *Action: If the temperature was maintained at 25 +/- 1°C, then no action is necessary. If the temperature was not maintained at 25+/-1°C, but the results meet the regulatory criteria of corrosivity, then the results will not be flagged. If the temperature was not maintained, then reject,"R," all results between 12.0 and 12.5.*	The temperature of the sample was 22.3°C. Temperature was not maintained at 25+/-1°C and therefore, the result should be rejected and the data flagged, "R."

This example illustrates that several QA/QC criteria are more specific for corrosivity determinations than for other pH determinations. For example, the calibration buffer solutions must always include pH 2 and pH 12 and the temperature of the sample must be maintained at 25 +/- 1°C. Because of the added specificity of the corrosivity test, it will most likely be necessary to contact the laboratory to receive information about their procedures. It is always appropriate to determine the exact procedures used by a laboratory when making a waste characterization based on corrosivity.

Chapter 12
Flashpoint

12.0 Introduction

Ohio EPA uses **flashpoint** to assess the characteristic of ignitability. A liquid waste is considered a hazardous waste if its flashpoint is less than 140°F (Ohio Administrative Code (OAC) 3745-51-21). Flashpoint may be assessed by one of two different methods specified in this rule. These methods are "Pensky-Martens Closed Cup Tester" (Association of Standards and Testing Materials (ASTM) Standard D-93-79 or D-93-80) and "Setaflash Closed Cup Tester" (ASTM Standard D-3278-78). The Pensky-Martens Method is used most often since this method is appropriate for materials such as paint wastes and parts cleaner solvents. This method is discussed below.

12.1 Definitions

Flashpoint: the lowest temperature at which application of a test flame appears and instantaneously propagates itself over the surface of the sample.

12.2 Information Necessary to Validate Flashpoint Data

Typically, the initial data package will not contain the information necessary to perform data validation on flashpoint samples. The Tier I Data Validator will need to request bench sheets with this information from the facility or laboratory. A boilerplate letter is available at the end of this document in Appendix I. This letter should help to simplify and standardize Ohio EPA's requests for additional data validation information.

Specific items needed for completing a Tier I Data Validation should be made available by the laboratory. If information is missing or incomplete, use the boilerplate letter to request this information from the facility or laboratory. These items include information for each sample, such as start time and temperature and end time and temperature. Sample results are normally linked by the sample number to information on each sample group. This information may include reference standards evaluated, confirmation that p-xylene was used as a standard, results of any duplicates evaluated, the date the sample group was analyzed, and the name of the person who performed the analysis. If Pensky-Martens Method B is used, sample viscosities (or a description from the lab on how these were assessed) and the barometric pressure (not adjusted for sea level) at the time of the test are also important information to request. The data should reflect any adjustment made to the flashpoint results for Method B. If these items are not available, the laboratory must submit an explanation as to why that is the case (e.g., the barometric pressure was never recorded; a data sheet was misplaced, etc.).

Flashpoint equipment is usually not computerized or automated. Therefore, the supporting documentation the Tier I Data Validator receives from the laboratory will typically be developed by the lab and completed by hand. The sheets will likely be non-standard in format and content. Some labs do not even maintain all records required by the method. The Tier I Data Validator may need to qualify or reject data received due to insufficient documentation. Consult with a Tier II Data Validator in this situation.

12.3 Data Validation Criteria

Pensky-Martens contains two methods, A and B. Choosing the correct method depends on sample viscosity, which is information often not recorded by the laboratory. This can make confirmation of the correct method very difficult. Method A, the basic procedure, is used unless the material being tested is a suspension of solids or a highly viscous material. Those materials require the use of Method B.

According to the Pensky-Martens method, "definite rates of temperature increases ... control the precision of the method." Because of this, one of the main criteria to check during data validation is whether the temperature was raised at the proper rate. The method gives a standard rate of temperature increase. The lab should not vary from the rates given in Method A (5-6℃ or 9-11℉ per minute) or Method B (2-3℉ per minute). The average rate of temperature increase (degrees per minute) needs to be checked based on the starting temperature and time, and the final temperature and time. The rate of increase of temperature is required by the respective method. Raising the temperature too quickly could cause the analyst to miss the flashpoint. Once the flashpoint is exceeded, the atmosphere in the Pensky-Martens cup may become too rich and the sample will not flash. Raising the temperature too slowly could allow more volatile components of a sample to evaporate, artificially elevating the flashpoint of that sample.

A Tier I flashpoint Data Validation may assess the instrument calibration with p-xylene, reproducibility of results, corrections made for barometric pressure readings, and proper thermometer choice. Assessment of much of this information may be triggered by a specific problem or inconsistency (e.g., split samples providing markedly different results).

Method B requires the flashpoint result be adjusted for the barometric pressure at the time of the test. Usually, this correction is not large, but it could affect results near the regulatory threshold if it is run on a day with low barometric pressure.

12.4 Flashpoint Example

Below is an example flashpoint bench sheet and the accompanying Tier I Data Validation Checklist section.

Table 12.1 Example Flashpoint Bench Sheet					
A+ Laboratories, Inc. - ISO 14000 Certified Flashpoint/ Ignitability Bench sheet					
Date: 11-12-01				**Analyst: DF Barometric Pressure: 740.43**	
Sample Number	**Initial Time**	**Initial Temp. °F**	**Final Time**	**Final Temp. °F**	**Comments**
REF	11:20	68°F	11:23	73°F	TV=81°F 90%
Blank	11:40	69°F	11:53	>200°F	
ES-911	12:25	71°F	12:38	>200°F	
MM-666	13:15	70°F	13:20	131°F	
MM-666Dup	13:35	71°F	13:40	136°F	
HS-123	13:55	73°F	14:08	>200°F	
REF	14:50	72°F	14:53	78°F	TV=81°F 96%

5.2 Pensky-Martens (SW-846, Method 1010A) - Procedure A for "Ordinary Liquids"	
5.2.1 Was p-xylene used to calibrate the instrument?	Yes (we're going to say this was by Method A and that information was confirmed by the laboratory).
5.2.2 Was the flashpoint for the calibration standard p-xylene within 81+/- 2°F? **Note:** The method specifies p-xylene with an expected flashpoint of 81°F.	Record the p-xylene calibration flashpoint(s): 73°F and 78°F. 73°F is too low - outside the calibration range. The calibration standard should have been redone after corrective measures were taken.

5.2.3 If the calibration standard was outside of this range (see 5.2.2), was corrective action taken? *Action: If no corrective measures were performed, determine whether a significant bias has been imparted to the samples and qualify the results using professional judgment. If the sample is still available, notify the laboratory. Consult a Tier II Data Validator regarding requests for re-analysis.*	Record sample IDs that are qualified. No evidence of corrective action. A call to the lab confirms no corrective measures. They say this is inside their acceptable range. We would qualify all data. Be particularly concerned about any sample results just below 140^{o}F. Sample MM666 should have been re-analyzed after the calibration problem was corrected. Is there a possibility of low bias based on the low calibration results? Qualify samples as "J," estimated. Possibly reject sample MM-666.
5.2.4 Based on 5.2.3, if corrective measures were taken, was the p-xylene calibration flashpoint within 81+/- 2°F? **Note:** Corrective measures should have continued until this flashpoint calibration range was attained. *Action: If these procedures were not followed and documented, contact the laboratory for an explanation. Lack of an adequate explanation may justify qualifying the data.*	No corrective measures were taken. Data have been qualified. See 5.2.3.
5.2.5 If a sample has an expected flashpoint, based on field/facility information, measurements should begin at least 30-50°F below the expected flashpoint of the material. If the expected flashpoint is unknown, the initial measurements should begin at the ambient temperature of the laboratory. **Note:** Information of the expected flashpoint of a sample should be shared with the laboratory prior to analysis. *Action: If these procedures were not followed and documented, contact the laboratory for an explanation. Lack of an adequate explanation may justify qualifying the data.*	The lab did not begin 30°F below the known standard temperature. We would probably accept the data if this was the only problem. Particularly, if they were getting results consistently close to the known temperature for the p-xylene standard.

5.2.6 Was heat applied so as to raise the temperature of the sample at a rate of 9-11°F per minute? **Note:** Laboratory bench sheets may be required to show the starting temperature, starting time, the flash point (or end) temperature and the time when the flash occurred. These materials should be requested from the laboratory if not present. Documentation of start time is not specifically required per the method but should be adequately demonstrated or explained by the laboratory if not presented. *Action: If these procedures were not followed and documented, contact the laboratory for an explanation. Lack of an adequate explanation may justify qualifying the data.*	Dividing the number of minutes by the time of the test for sample MM-666 and the duplicate gives a rate of temperature change of 12.2°F and 13.0°F. This rate exceeds the prescribed rate of temperature increase. For a result with a flashpoint below 140°F, we would not qualify the data. If the result was a flashpoint over 140°F, or no flashpoint, we would likely reject the data. Raising the temperature too fast makes it easier to miss seeing the flash.

Chapter 13
TCLP Extraction

13.0 Introduction

The toxicity characteristic leaching procedure (TCLP) is used to determine the mobility of selected hazardous constituents in wastes. **TCLP extraction** mimics conditions found in a landfill and attempts to quantify the threat a waste would potentially pose to the environment. Wastes are deemed to be hazardous if they contain extractable levels of constituents at or above certain thresholds, as defined in Ohio Administrative Code (OAC) rule 3745-51-24. TCLP levels for a small number of metals, semi-volatile, and volatile organic compounds are defined in Table 1 of this regulation. The TCLP extraction procedure is defined in SW-846, Method 1311.

TCLP is specifically referred to in the hazardous waste regulations and, therefore, the procedure must be strictly followed. The Tier I Data Validator may have difficulty reviewing TCLP data since most extraction procedure information will be found only in the bench sheets, not in the data report. One of the first steps to completing a data validation of TCLP data may be to request these bench sheets, if they are not provided with the report. Furthermore, the method encompasses not one, but many procedures. The exact procedure used for a sample will depend upon the material extracted, pH of the waste and the analytical parameters.

The Tier I Data Validator must keep in mind that SW-846, Method 1311 is a preparatory procedure, not an analytical procedure. The analytical methods that will accompany TCLP will be the same methods as those used for total constituent analysis, such as SW-846, Method 6010C for metals. Therefore, data validation must include not only the TCLP extraction procedure, but also the QA/QC parameters that are included for each method used to analyze the extract.

13.1 Definitions

Extraction: The removal of solutes from a material by the application of a solvent. In the case of the TCLP, the extraction process is designed to determine the mobility of specific organic and inorganic analytes present in liquid, solid, and multi-phasic wastes.

Type 1 Extraction Fluid: pH equals 4.93 (+/- 0.05). Created by adding 5.7 ml glacial acetic acid (CH3CH2OOH) to 500 ml reagent water, adding 64.3 ml of 1N NaOH and diluting the volume to one liter. Type 1 Extraction Fluid is always used for extraction of samples to be analyzed for VOCs, as well as acidic to slightly basic wastes.

Type 2 Extraction Fluid: pH equals 2.88 (+/- 0.05). Created by diluting 5.7 ml glacial acetic acid (CH3CH2OOH) with reagent water to a volume of one liter. Type 2 Extraction Fluid is used to extract highly alkaline wastes.

Percent Solids: Liquid samples contain less than 0.5 percent solids and can be used as TCLP extract. Solid samples contain less than 0.5 percent liquids and the entire sample must be extracted. Where samples contain between 0.5 and 99.5 percent solids, the solid and liquid component are analyzed separately and the results mathematically recombined. Alternately, the multi-phased components may be physically recombined prior to analysis.

13.2 Method Summary

The first step in the extraction process is to characterize the waste as a liquid, solid or semi-solid. If the waste contains less than 0.5 percent solids, it is deemed a liquid and this liquid is defined as the TCLP extract. If the samples contain greater than 99.5 percent solids, the waste is extracted with the appropriate amount and type of extraction fluid and analyzed by the appropriate analytical method.

If a waste contains more than 0.5 but less than 99.5 percent solids, (i.e., semisolid) the liquid portion is retained for analysis, and the solid portion is placed in extraction fluid equaling 20 times the weight of the solid phase. Next, the solid materials must be examined for particle size and filtered. Particles are measured with a ruler and must be less than 1 cm diameter. The sieve is not used to verify particle size for the volatile sample. Both the solid material extract and liquid portions of the waste are analyzed separately and mathematically recombined. Alternately, the multi-phased components may be physically recombined prior to analysis.

The extraction fluid is made of two different strengths of acetic acid depending upon the alkalinity of the solid material. A test must be performed on each waste sample to make this determination. Type 1 Extraction Fluid (fluid #1) is used for samples to be analyzed for VOCs or waste that is acidic to slightly basic. VOC extraction is performed with a special device known as a Zero Head space Extractor Vessel or a ZHE. Type 2 Extraction Fluid (fluid #2) is used if waste is highly alkaline. Both the solid material extract and liquid portions of the waste are analyzed separately and then mathematically recombined. Alternately, the multi-phased components may be physically recombined prior to analysis. The extraction is performed by placing the extraction vessel in a rotary agitator at 30 +/- 2 rpm for 18 +/- 2 hours. The ambient temperature is maintained at 23 +/- 2°C during agitation. The extracts are defined in more detail below.

13.3 QA/QC Specific Information

The Tier I Validator must pay particular attention to the purpose of TCLP. In addition to waste characterization, TCLP is used to determine if treated wastes meet Land Disposal Restrictions (LDR) (OAC 3745-270). The LDR regulatory levels are very different than the hazardous waste characteristic evaluation. In addition, the Tier I Validator must be aware that there are additional QA/QC requirements for TCLP compared to the normal analytical methods. These tests include:

1. **TCLP Extraction Blanks:** A minimum of one TCLP extraction blank is generated for every 20 extractions processed in a given extraction vessel using the same fluid. Most labs have multiple extraction vessels. The common industry strategy is to generate one TCLP extraction blank for each group of samples processed simultaneously using the same batch of fluid.

2. **Method of Standard Addition:** Four equal-volume, pre-digestion aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot must be 50% of the expected concentration. The concentration of standard added to the second aliquot must be 100% of the expected concentration, and the concentration of standard added to the third aliquot must be 150% of the expected concentration. The volume of the unspiked and spiked standard must be the same.

The Method of Standard Addition is to be used for metallic contaminant determinations if both of the following criteria are met:

- The matrix spike recovery from the TCLP extract is less than 50% and the unpicked sample concentration is less than the regulatory level.
- The contaminant measured in the sample is within 20% of the regulatory level.
- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration: the plot of sample and standards must be linear over the concentration range of concern, and the effect of the interference must not vary as the ratio of the standard added to the sample matrix changes.

3. **Holding Times:** The holding times outlined in Table 13.1 must be met. Sample results must be evaluated for both time-until-extraction and time- until- analysis. Sample data that exceed holding times are not acceptable for verifying that a waste does not exceed regulatory levels. However, if TCLP extract concentrations exceed regulatory action levels, and holding times are exceeded, the data are considered minimum values, and the data are considered valid.

Table 13.1 Technical Holding Information for TCLP Analysis

Analysis	From field collection until TCLP extraction	From TCLP extraction until sample preparation	From preparative extraction to analysis	Total elapsed time
Volatiles	14 days	NA	14 days	28 days
Semi-Volatiles	14 days	7 days	40 days	61 days
Mercury	28 days	NA	28 days	56 days
Metals	180 days	NA	180 days	360 days

13.4 Information Necessary to Validate TCLP Data

The Data Validator will need the following information to complete the Tier I Data Validation Checklist:

- Sampling date;
- TCLP extraction date;
- TCLP extract preparation date (for SVOCs only);
- Percent solids;
- Weight of sample extracted;
- pH of sample after necessary adjustments;
- Type and measured pH of extraction fluid used;
- Amount of extraction fluid used;
- Analyses requested (VOCs, SVOCs, metals, etc.);
- Spike sample results (for metals only).

Contact the facility or the laboratory to request any missing information. A boilerplate letter for requesting additional information is located in Appendix I.

13.5 TCLP Data Validation Criteria

If positive results for TCLP constituents above regulatory levels (OAC rule 3745-51-24; Table1) can be qualified, but not rejected, then it is presumed that waste will be managed as hazardous waste. However, if significant data validation criteria are not within limits, then re-sampling and analysis must be considered. If significant data validation criteria are not within limits and results are non-detect or if positive results are found, but are below the regulatory levels, then qualification or invalidation of sample results must be considered. Rejection of results must be considered if insufficient sample weight is used, if an inappropriate extraction solution was used, or if spike results for metals analysis were below the acceptance criteria.

The criteria that Ohio EPA will use to evaluate TCLP data are as follows:

1. If particle size reduction is required, but not performed, then all non-detected results will be qualified as “R,” rejected, and all positive results will be qualified as “J,” estimated. For results near the regulatory limit, use best professional judgment to decide if the results will be flagged “J,” estimated, or “R,” rejected. Positive results above regulatory levels will not be qualified.

2. If an incorrect extraction fluid was used, all non-detected or positive results below the regulatory limit will be qualified as rejected and flagged “R.” Positive results above regulatory levels will be accepted.

3. If an incorrect amount of sample (less than 100 grams for solids analyzed for metals or SVOCs, or 20 grams for VOCs) was used, then all non-detected compounds or elements will be qualified as “R,” rejected. Furthermore, if less than 30% of the required sample weight is used, then qualify all positive results below the regulatory threshold as “R,” rejected. Positive results above regulatory levels will not be qualified.

4. If the extraction fluid weight is not within +/- 15% of the correct weight (20 times the weight of the sample), then qualify all positive results below the regulatory threshold as “J,” estimated. If the extraction fluid weight is more than +/- 30 percent above or below the correct weight, then qualify all positive results and all non-detects as “R,” rejected. Positive results above the regulatory limit will be accepted.

5. If a TCLP blank was not analyzed per batch of samples, reject all positive data below the regulatory limits. If a blank was included, use the Tier I Data Validation Checklist Method Blanks section to evaluate blank contamination.

6. If technical holding times were exceeded, then reject all positive results below the regulatory limits. Positive results above the regulatory limits will be accepted.

13.6 Example TCLP Data Results

Table 13.2 is an example of a typical bench sheet that a laboratory will use to record method specific information. The Tier I Data Validator will obtain information from the bench sheet to assist in completing Section 5.1 of the Tier I Data Validation Checklist (See section 13.7).

Table 13.2 TCLP Percent Solids

Date	Sample ID	Filter Weight	Container Weight	Sample +	Container Weight (g)	Total Sample Weight	Res-idue +	Filter Weight (g)	Residue Weight (g)	% Solid Comments
6/22/01	JZ101	1.38	10.65	111.67	101.02	89.65	88.27	12.75	87.38	Multi-Phase Waste
6/22/01	JZ102	1.40	10.65	110.76	100.11	1.89	0.49	99.62	0.49	Filtrate is extraction fluid
6/22/01	JZ103	1.38	10.64	111.17	100.53	101.35	99.97	0.56	99.44	

1. Total Sample Weight = (Sample + Container Weight) - (Container Weight)
2. Residue Weight = (Residue Weight + Filter Weight) - (Filter Weight)
3. Filtrate Weight = (Total Sample Weight) - (Residue Weight)
4. % Solids = [(Residue Weight) ÷ (Total Sample Weight)] X 100

If filtrate is over 0.5%, then the waste is multi-phasic. The filtrate is saved as the extract, and the solid material is extracted with twenty times its weight in the proper extraction fluid.

The results for both the original liquid and the extract are mathematically combined using equation 13.1.

$$\text{Final Analyte Concentration} = \frac{(V_1)\,(C_1)\ X\ (V_2)\,(C_2)}{V_1 + V_2} \quad (13.1)$$

Where:
V_1 =the volume of the first phase (L),
C_1= the concentration of the analyte of concern in the first phase (mg/L),
V_2= the volume of the second phase (L), and
C_2= the concentration of the analyte of concern in the second phase (mg/L).

Table 13.3 is an example of a typical TCLP Extraction Log that a laboratory will use to record method specific information. The Tier I Data Validator will obtain information from the extraction log to assist in completing Section 5.1 of the Tier I Data Validation Checklist (See section 13.7).

Table 13.3 TCLP Extraction Log

Date Extr. Started	Sample ID	Sample Weight (g)	Initial pH	pH After HCl	Ext. Fluid #	Ext. Fluid pH	Vol. of Extraction Fluid (ml)	Time On Tumbler (min.)	Time Off Tumbler (min.)	Final pH Before Filtra-tion	Final pH After Filtra-tion
6/22/01	JZ100	100.45	7.18	1.52	1	4.90	2009	5:15	11:00	5.06	5.00
6/22/01	JZ101	12.62	6.78	1.67	1	4.90	252.4	5:15	11:00	5.87	
6/22/01	JZ102	Extraction fluid is direct filtered									
6/22/01	JZ103	100.61	9.45	5.02	2	2.90	2012.2	5:15	11:00	6.88	6.87

Table 13.4 is an example of a typical TCLP ZHE Extraction Log that a laboratory will use to record method-specific information. The Tier I Data Validator will obtain information from the extraction log to assist in completing Section 5.1 of the Tier 1 Data Validation Checklist (See section 13.7).

Table 13.4 ZHE Extraction for Volatile Compounds

Date Extr. Started	Sample ID	Sample Weight (g)	Initial pH	pH After HCl	Ext. Fluid #	Ext. Fluid pH	Vol. of Ext. Fluid (ml)	Time On Tumbler (min.)	Time Off Tumbler (min.)	Final pH Before Filtration	Final pH After Filtration
6/22/01	JZ100	22	ZHE		1	4.90	440	4:15	12:00	5.06	5.00

13.7 Example Tier 1 Data Validation Checklist

The TCLP analytical data validation example below was completed using data from tables 13.2, 13.3 and 13.4.

5.1 TCLP Preparation and TCLP Spike Recovery

Toxicity Characteristic Leaching Procedure

The toxicity characteristic leaching procedure (TCLP) is used to determine whether wastes exhibit the toxicity characteristic or whether Land Disposal Restrictions have been met. The TCLP test is specified in OAC Rule 3745-51-24 and defined in SW-846, Method 1311. TCLP data validation requires specific data concerning extraction preparation in addition to the usual data submitted for organic and inorganic analytical methods. In most cases, a laboratory will have to supply bench sheet data to complete the data validation. The Validator may consult the Tier I Data Validation Manual for specific information and examples.

5.1.1 Did the laboratory calculate TCLP filterable solids? Based on the percent solid calculations, were the correct analytical procedures followed? **Note:** TCLP requires that solid waste, semi-solid waste and liquid wastes be prepared based upon the amount of solids in the waste. For waste that has greater than 99.5% solids, the waste is considered solid and 100 grams of material is extracted with 20 times this weight of extraction fluid. For waste that is equal to or less than 0.5% solids, the waste is considered a liquid, and the liquid itself is considered the extract (no additional extraction fluid or tumbling is necessary). If the waste contains both solids and liquids, the solid portion, trapped by filtering, is extracted with 20 times its weight of extraction fluid and then analyzed. In addition, an aliquot of the liquid is analyzed. The results are then mathematically combined. Alternately, the multi-phase components may be physically recombined prior to analysis. *Action: If percent solids were not calculated, contact the facility for the proper information.* *If, based on the percent solids calculations, the appropriate preparation methods were not used, qualify analytical results using the following criteria: All positive results above the regulatory level should not be qualified.* *All positive results above the detection limits but below the regulatory level should be qualified based on professional judgment and the specific circumstances. The Tier I Data Validator may want to consult the Tier II Validator.* *All non-detected results should be qualified based on professional judgment and the specific circumstances.*	Yes - see Table 13.2, TCLP Percent Solids

5.1.2 Was the proper amount of material extracted? **Note:** For waste samples to be analyzed for metals or SVOCs (in the solid portion), a minimum of 100 grams is required. For waste samples to be analyzed for volatile compounds, approximately 20-25 grams of sample is required. **Note:** Liquid samples are directly analyzed as the TCLP extract, no extraction fluid is added to the sample. *Action: If improper sample mass is used, qualify analytical results using the following criteria:* *All positive results above the regulatory level should not be qualified. All positive results above the detection limits, but below the regulatory level, should initially be qualified as "J" estimated. Based on professional judgment, qualification of data as "R," may be warranted.* *Based on professional judgment, all non-detect results should be qualified as "J" estimated or "R."*	List sample IDs and sample mass(es) used for the extraction. Yes, 100 grams were used for JZ100 and JZ103 which is the correct amount (See Table 13.3, TCLP Extraction Log). Approximately 25 grams of sample were used for JZ100 ZHE extraction (See Table 13.4, ZHE Extraction for Volatile Compounds). For JZ101, 12.62 grams was used for the multiphase sample. Because this is a multiphasic waste, this amount is acceptable (See Table 13.3, TCLP Extraction Log).
5.1.3 Was the correct extraction fluid used? **Notes:** Fluid # 1 is <u>always</u> used for VOC analysis. Fluid #1 should be used if the final pH of the pre-test sample is below 5.0. If the pH is above 5.0, hydrochloric acid should be added to the pre-test sample (refer to the method for specifics). Fluid #2 should be used if the final pH of the pre-test is above 5.0. *Action: Consult with the facility and have the extraction fluid information submitted. If the improper fluid was used, qualify analytical results using the following criteria:* *All positive results above the regulatory level should not be qualified. All positive results above the detection limits but below the regulatory level, should initially be qualified as*	List sample IDs and fluid type(s) used for the extraction: Extraction Fluid #1 was used for all samples. Extraction Fluid #2 should have been used for sample JZ-103 because it's pH after HCL is > 5.0 (5.02 for JZ-103). If metals results were just below regulatory levels, consideration of the proper extraction fluid is very important. A more aggressive extraction fluid (i.e., extraction fluid #2) may have extracted more metals.

"J." Rejection of data may be warranted if other preparatory procedures are outside of criteria. *All non-detected results will be qualified as "R."*	
5.1.4 Did the extraction fluid have the proper pH? Fluid #1 has a pH range of 4.88 to 4.98. Fluid #2 has a pH range of 2.83 to 2.93. *Action: If an improperly prepared extraction fluid is used, qualify analytical results using the following criteria:* *All positive results above the regulatory level should not be qualified.* *All positive results above the detection limits, but below the regulatory level, should initially be qualified as "J." Rejection of data may be warranted if other preparatory procedures are outside of criteria.* *All negative results will be qualified as "R."*	List incorrect fluid pH(s): Only extraction fluid #1 was used and its pH (4.90) was in the proper range. The wrong fluid was used for JZ103. All other sample extraction fluids were acceptable.
5.1.5 Was the correct weight of extraction fluid used? Laboratory bench sheets may be needed to complete this section. *Action: If the extraction fluid weight is not more than +/- 15% of the correct value (2000 grams for metals; 500 grams for VOCs), qualify all results as estimated "J" or "UJ". These values may be re-qualified if additional problems with TCLP preparation exist.* *If the extraction fluid weight is less than 70% of the proper weight, qualify all results as rejected, "R."* *If the extraction fluid weight is more than 30% greater than the proper weight, qualify all non-detect compounds and positive results below the regulatory level, as rejected "R." All positive results above the regulatory limit will not be qualified.*	The correct weights of extraction fluid were used. Yes, the extraction fluid volumes are within 15% of the correct amount (e.g., 20X the sample weight).

5.1.6 Was a TCLP blank analyzed with every batch of samples? **Note:** TCLP blanks should be prepared using the same extraction fluid as is used for the associated sample's extraction. *Action: Contact the facility for submittal of missing data. If no blank was analyzed, qualify all positive results as rejected, "R." If data is available, qualify TCLP data as designated in Section 4.0 Blank Data Summary Review.*	List IDs of affected samples: No information is present.
5.1.7 Was the tumbling time within 18 +/- 2 hours? **Note:** Tumbling time (evaluated based on the day and time tumbling begins/is completed) should be noted on the bench sheets. The laboratory should be contacted if this information isn't present. *Action: If the tumbling time is not within 18 +/- 2 hours, qualify all data as estimated ("J").*	Yes.
5.1.8 Was the tumbler speed within 30 +/- 2 RPM? **Note:** Tumbler speed should be noted on the bench sheets. The laboratory should be contacted if this information isn't present. *Action: If the tumbler speed is not within 30 +/- 2 RPM, qualify all data as estimated ("J").*	No information is present.
5.1.9 Was the room temperature during the extraction 23°C +/-2°C? **Note:** Data would not be rejected using this criterion except in extreme cases (e.g., very cold temperature with detectable TCLP compounds). *Action: Mark as estimated ("J" qualify) data for extractions outside this range or when temperature was not recorded.*	No information is present.

VOC, SVOC and Metals results from the TCLP must meet the sample QA/QC criteria outlined in Sections 1.0 through 4.0.

Chapter 14
Cyanide And Hexavalent Chromium Analysis

14.0 Introduction

DWHM and DDAGW evaluate data from ground water, soil, and waste samples for **cyanide and hexavalent chromium analyses**. These analyses are generally performed in specific instances and are not as common as analyses for other hazardous constituents. Samples for these constituents must be prepared and analyzed in specific ways, and therefore, data validation techniques differ from other data validation activities. Consider cyanide. It can exist in several forms, and there are specific tests that must be used to characterize each cyanide species. It is a component of the Appendix IX (OAC 3745-54-98) list of ground water monitoring constituents, but is not listed with the constituents found in Table 1 of OAC 3745-51-24 for the Toxicity Characteristic. However, DHWM does evaluate cyanide in soil samples for human health risk assessment when it could be a waste constituent at a facility undergoing an investigation. Similarly, hexavalent chromium may be included in ground water monitoring programs at RCRA facilities and may also be evaluated in waste or in soil analyses for human health risks. Facilities have a right to use hexavalent chromium analyses to determine whether a waste is exempt from hazardous waste regulation under OAC 3745-51-04. In this case, wastes which fail the TCLP test because chromium is the sole hazardous constituent can be excluded from hazardous waste management if it can be shown that chromium is primarily trivalent chromium. This chapter will provide an overview of the preparation and analytical methods used to quantify cyanide and hexavalent chromium in solid and liquid matrices. It will also outline those QA/QC requirements that are part of the preparation and analytical methods.

14.1 Definitions

Free Cyanide: Cyanide that in solution is in the anionic state as CN-.

Amenable Cyanide: Cyanide in solution that is capable of reacting with chlorine. Amenable cyanide includes both free cyanide and soluble cyanide complexes.

Total Cyanide: All species of cyanide in a sample including free, soluble complexes and insoluble complexes of cyanide.

Total Chromium: Chromium may exist in a number of oxidation states. Total chromium is the combination of all of these chromium oxidation states in solution or in a sample digestate.

Hexavalent Chromium: Chromium is commonly found in trace concentrations in aqueous solution in different oxidation states as either chromium III or chromium VI. Hexavalent chromium (Cr VI) is the most oxidized form of chromium that commonly exists in nature. Cr VI is more mobile and toxic in the environment.

14.2 Cyanide Methods Summary

Cyanide, in its simplest free-form state, consists of a carbon atom and nitrogen atom that act as an anion in aqueous solution. It can form a variety of complexes depending on other constituents in aqueous solution and the solution's pH and oxidation/reduction state. These complexes can significantly affect the transport and toxicity of cyanide. For example, nearly insoluble metal-cyanide complexes, such as Prussian Blue ($Fe_4(Fe(CN)_6)_3$), can bind cyanide to the soil. In addition, cyanide can sorb into organic matter and be sequestered in the soil column. While cyanide and its complexes can occur naturally, hazardous waste mismanagement, or leachate production from landfills, can notably degrade the environment. Simple, free-form, cyanide (CN^-) is toxic. Generic Cleanup Numbers (GCN) for free cyanide are ~~is~~ listed as 3.03e-1 mg/L for ground water and 1.53e-3 mg/Kg for soil in DHWM's Closure Plan Review Guidance (March, 2008).

Since cyanide can take on so many different forms in the environment, different analytical methods exist to quantify different forms of cyanide. Cyanide is usually measured as 1) free cyanide, 2) amenable cyanide, and 3) total cyanide. Free cyanide is a measure of cyanides in the simplest chemical form such as HCN, NaCN or KCN. These molecular forms are easily soluble, and therefore, can be readily extracted from aqueous or solid matrices. Amenable cyanides refer to cyanides amenable to chlorination, and these tests measure common metal cyanide compounds and complexes except for iron cyanides. Total cyanide is a measure of all cyanides, including iron-cyanide complexes.

SW-846 contains a variety of techniques for analyzing cyanide in soil, ground water and wastes. SW-846 Method 9010C is an acid reflux procedure for water samples that yields total and amenable cyanide concentrations when the extract is analyzed by SW-846 Method 9012B or 9014. For solid samples and wastes, SW-846 Method 9013 (an amendment to 9010C) extracts soluble cyanide from samples, which are then distilled and extracted with 9010C and analyzed by 9012B, 9014 or 9213. In general, a liquid sample is placed in a refluxing chamber with a strong acid. The acid/sample is continuously refluxed which effectively breaks down complexes liberating the cyanide in the form of HCN gas. This gas is swept into an alkaline scrubbing solution which can be analyzed colorimetrically or with an ion-selective electrode. In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reacting with chloramine-T at a pH less than 8 without hydrolyzing to a cyanate. After the reaction is complete, color is formed on the addition of a pyridine-pyrazolone or pyridine-barbituric acid regent. The absorbance is read at 620 nm when using pyridine-pyrazolone and at 578 nm when using pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards. Liquid samples effectively generate either total or amenable cyanide concentrations depending on sub-procedures in Method 9010C. Solid samples will yield primarily free cyanides, since the initial alkaline extraction is not strong enough to break down insoluble complexes from the solid matrix.

14.3 Quality Assurance/Quality Control Specific Information

Since several forms of cyanide may be analyzed, there are a variety of method-specific considerations that must be taken into account when reviewing a data report. These extra considerations are beyond the normal quality assurance and quality control procedures of other methods.

As only a few of these requirements will be discussed here, the reader is referred to the specific SW846 methods: 9010C, 9013, 9012B and 9213 when evaluating cyanide for a specific project. Strict adherence to an extraction method is necessary for full quantification.

Cyanide concentrations can suffer degradation from improper handling and transport. Aqueous samples must be preserved with a 50% sodium hydroxide solution until a sample pH of 12 is achieved. Samples should also be chilled during transport and not exposed to light. If properly preserved, samples may be held for 14 days prior to preparation. Sample distillates should be analyzed as soon as possible after preparation.

Cyanide analyses may be subject to chemical interferences that can bias the sample results. Any oxidizing agent, such as chlorine, must be removed prior to distillation of the sample in order to avoid a negative bias. Methods 9010C and 9013 require that an oxidizer test be performed and that reducing be agents introduced to the sample prior to distillation. KI-starch paper is commonly used as a screening procedure for oxidizers. If the oxidizers are present, then reducing reagents such as ascorbic acid should be added to the sample until the starch paper indicates that reducing conditions are present. It is necessary to document that the KI-starch paper test was performed and the quantity of reducing reagent added to the sample. Conversely, samples with greater than 10 mg/L of nitrites and nitrates must be treated with sulfamic acid prior to distillation to avoid a positive bias. Once again, any sample treatment must be fully documented and discussed in the data narrative of the sample report.

Methods 9010C and 9013 require the following quality control/quality assurance information be provided.

- A reagent blank should be analyzed per analytical batch (every 20 samples). This blank should include all reagents that were used in sample preparation.

- A check standard or Laboratory Control Sample (LCS) should be analyzed per batch and the result should be within 15% of the expected value. If the result is outside of this requirement, the sample should be reanalyzed.

- One sample should be replicated per analytical batch. A replicate is a separate aliquot of a sample that is taken through the preparation and analytical process. The criteria for acceptance listed in SW-846 Method 9010C is that the Coefficient of Variation of the sample and its replicate be within 20%. If this criteria is not met, then the samples should be reanalyzed.

- A matrix spike must be analyzed for every batch of 20 samples. This spike should have a concentration of approximately 40 µg/L. It is expected that matrix spike results should be within +/- 30 percent of the expected value (i.e., 70% - 130% recovery).

- A high and a low standard should be distilled per analytical batch and compared to undistilled standard concentrations. The undistilled standards should be within +/- 10% of the distilled standards. If this was not performed or if the standards were not within +/- 10%, then corrective measures by the laboratory should be initiated before proceeding with cyanide analyses.

- The Method of Standard Additions (MSA) may be used when matrix interferences are suspected (i.e., matrix spike performance).

14.4 Information Necessary to Validate Cyanide Data

The Data Validator will need the following information to complete the Tier I Data Validation Checklist.

- Sampling date;
- Extraction/Preparation date;
- Weight and/or volume of sample extracted;
- pH of sample after necessary adjustments;
- Spike sample results, including LCS and matrix spike data;
- Calibration verification results;
- Blank sample results, including reagent blanks and method blank data;
- Method of Standard Additions information, if necessary.

14.5 Cyanide Data Validation Criteria

The criteria that will be used to evaluate cyanide data is based on the following:

Preservation: The method requires proper preservation of aqueous samples using sodium hydroxide to reach a pH of greater than 12. If samples were not properly preserved, then all detected concentrations will be regarded as estimates (J flagged) and all non-detects may be either judged as estimated (UJ flagged) or rejected (R) based upon the data quality objectives of the project.

Technical Holding Times: The technical holding time requirement for both solid and aqueous samples is 14 days from field preservation to analysis. For detectable quantities of cyanide in samples exceeding 14 days, the results will be considered estimates and data flagged with a J. Samples that exceed the technical holding time and are of non-detectable quantities will be considered estimates (flagged UJ); and if holding times are greatly exceeded (2 times the technical holding time or more), then results may be rejected (R).

LCS Recoveries: The LCS demonstrates that the laboratory instrument is capable of producing accurate results. LCS recoveries within 85% to 115% should not be qualified. If a sample contains a detectable quantity of cyanide, but has an LCS recovery of 50% to 85% or 115% to 150%, then these results should be considered estimated (flagged J). Non-detect samples in these LCS recovery ranges should also be considered as estimated (flagged UJ). Data associated with LCS recovery below 50% or above 150% should be rejected (flagged R).

Replicate Recovery: One replicate should be analyzed for every 20 samples. The coefficient of variation (relative percent difference) for the sample and its replicate should be 20% or less. According to methods 9010C and 9013, if this criteria is not met, then the samples in the batch should be reanalyzed.

High And Low Calibration Standard Verification: The method recommends that a high and low standard be distilled and analyzed per batch of samples. This procedure can be used to validate the calibration curve by comparison to the known concentrations of these standards. It also establishes the linearity of the curve and can be used to confirm the reporting limit used by the laboratory. While the evaluation of two standards is considered optional, the laboratory must confirm the calibration curve with an initial calibration verification (ICV) standard and with continuing calibration verification (CCV) standards. In most cases when a single standard calibration verification test is performed, the standard should have a concentration near the mid-point of the linear range. According to the U.S. EPA's National Functional Guidelines for Inorganic Data Review, initial and continuing calibration verification standards for cyanide should have percent recoveries within +/- 15% of the true value. If the criteria are not met, the laboratory should terminate sample analysis and recalibrate the instrument until acceptable recoveries are verified. If recalibration is not performed, qualification of the samples in the batch is necessary, using the following criteria:

	<70%	**70%<%R>85%**	**85%<%R>115%**	**115%>%R<130%**	**>130%**
Detection	Reject, R	Estimated, J-	Acceptable	Estimated, J+	Reject or estimated*
Non-detection	Reject, R	Estimated, UJ	Acceptable	Acceptable	Acceptable

* Reject data based upon professional judgment or project DQOs.

Blanks. Blanks are required for cyanide analyses. An initial calibration blank should be run just after the calibration sequence but before a verification sample or project samples are analyzed. In addition, a method blank which uses the same reagent and is carried through the distillation process must be analyzed and reported with every batch of samples. Method blanks are evaluated using the "Rule of 5". If target analytes are detected in the blank, then these results are multiplied by 5. This result is compared to the same target analyte results in the sample. If the result of the blank multiplication is higher than the result in the sample, the sample result can be attributed to blank contamination and should be reported as undetected (i.e., the sample result should be flagged U).

14.6 Hexavalent Chromium Method Summary

Chromium can exist in nature in a variety of oxidation states including Cr^{+3} (Cr III), Cr^{+5} (Cr V), and Cr^{+6} (Cr VI or hexavalent chromium). The predominant oxidation state of chromium in the environment is Cr III where it occurs as barely soluble oxides and hydroxide species. Cr VI can also occur naturally, but is commonly associated with releases to the environment from industrial activities or anthropogenic sources. Cr VI is of special concern as this chromium species is soluble and can be transported under natural conditions into ground water where it may be ingested by human and other ecological receptors. Cr VI is the most toxic form of chromium because it mimics sulfur (sulfur in the plus six oxidation state) and can readily enter into cellular membranes.

This increase in toxicity can be readily seen in Ohio EPA's Generic Cleanup Numbers (GCNs) for direct contact in soil. GCNs for Cr III and Cr VI in soil are 9.54e+4 mg/Kg and 2.02e+2 mg/kg respectively which indicate an approximately 100 fold decrease in the allowable concentration of chromium if the dominate species is Cr VI.

In most cases where chromium can be a constituent of concern, knowledge of the oxidation state is not a primary data quality objective. For example, the Maximum Contaminant Level (MCL) for drinking water is based upon a total chromium concentration, not by the relative concentration level of Cr VI. However, in some situations the determination of chromium species can be important. For example, generators that have wastes that fail the toxicity characteristic for chromium can demonstrate, in part, that the waste should be excluded from hazardous waste management if the chromium in the waste is exclusively trivalent (ORC 3745-51-04(B)(6)(a). In addition, some facilities find it desirable to determine the species of chromium present in various media because it may more accurately represent the human health risk.

There are a variety of methods that are available to determine hexavalent chromium in water, soil and waste. The methods for hexavalent chromium in SW-846 are listed in Table 14.1.

Table 14.1 Table of SW-846 Methods for the Preparation And Quantification Hexavalent Chromium

SW-846 Method Number	Method Title
3060A	Alkaline Digestion for Hexavalent Chromium
7195	Chromium, Hexavalent (Co precipitation)
7196A	Chromium, Hexavalent (Colorimetric)
7197	Chromium, Hexavalent (Chelation/Extraction)
7198	Chromium, Hexavalent (Differential Pulse Polarography)
7199	Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography

While all of the methods listed in Table 14.1 are available to Ohio EPA or to a regulated facility, Method 7196A is the most commonly used analytical method for hexavalent chromium. If soil or solid waste is to be analyzed with this method, it must first be extracted with SW-846 method 3060A. Method 3060A must be followed carefully in order to prevent biasing analytical results due to improper handling of the samples. Method 7196A employs colorimetry to quantify hexavalent chromium in aqueous samples or soil and waste extracts. This method is based upon the reaction of hexavalent chromium with diphenylcarbizide in an acid solution, which produces a red-violet product. The absorbance of 450 nm wavelength light is measured photometrically and compared to a calibration curve. The concentration of the sample can then be determined. A detailed summary of the solid extraction procedure and analytical procedures are presented in the following paragraphs.

14.6.1 Method 3060A, Alkaline Digestion Procedure for Soils and Solid Wastes.

Method 3060A is the preferred extraction procedure for soils and solid wastes that can be used in conjunction with methods 7196A and 7199 (listed in Table 14.1). According to the method, "to quantify total Cr VI in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr VI, (2) the conditions of the extraction must not induce reduction of native Cr VI to Cr III, and (3) the method must not cause oxidation of native Cr III contained in

the sample to Cr VI." The method's procedures reliably perform these tasks. The alkaline solution can solubilize hexavalent chromium from a solid matrix and also minimizes oxidation or reduction of chromium. The method also contains testing procedures to determine whether oxidizer components are present in the matrix of the sample and prescribes the addition of an alkaline buffer containing Mg+2 to prevent sample oxidation.

Method 3060A is unique in that it prescribes that the potential for oxidation/reduction is assessed, in part, by measuring additional soil or waste properties, such as Oxidation Reduction Potential (ORP, ASTM Method D 1498-93), pH (SW-846 Method 9045D), ferrous iron (ASTM Method D3872-86), and sulfide (SW-846 Method 9030B). Other indicators may also be used such as chemical oxygen demand and biological oxygen demand. Because of these additional tests, the necessary soil or waste sample volume must be assessed prior to sampling. For soil and solid waste, the measurement of sample specific parameters such as ORP and pH establishes the tendency of Cr VI to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals. If oxidizing conditions are indicated from the testing procedure in Method 3060A, then the addition of Mg+2 is necessary. Section 3.3 of this method goes on to indicate that special precautions are necessary for soils or wastes that contain soluble chromium. Section 3.3 states, for waste materials or soils containing soluble Cr III concentrations greater than four times the laboratory Cr VI reporting limit, Cr VI results obtained using this method may be biased high due to method-induced oxidation. The addition of Mg+2 in a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation. Soluble Cr III can be tested for by performing an extraction using distilled water as the extracting agent.

Maintaining the proper pH through the digestion process is critical. Samples are digested using a sodium carbonate/sodium hydroxide solution that is heated for 60 minutes at 90 degrees centigrade. The efficiency of the procedure to digest both soluble and insoluble chromium is measured through the use of spikes ($K_2Cr_2O_7$ and $PbCrO_4$) that are carried throughout the digestion process.

14.6.2 Method 7196A, Chromium Hexavalent (Colorimetric)

Method 7196A is a colorimetric method that depends upon the reaction of Cr VI with diphenylcarbazide. A calibration curve is developed using stock reagents that are carried through the same digestion procedures as the samples. The calibration curve should be developed daily. Diphenylcarbazide is first added to aqueous samples and soil digestates then acidified to a pH of 2.5 with sulfuric acid. The laboratory should provide proper documentation that this pH was achieved since color development must take place under acidic conditions. Because of some samples' matrices, turbidity may also be a problem. If turbidity is encountered, the laboratory should develop a blank from another portion of the digestate that does not contain diphenylcarbazide.

The absorbance from this blank should be used to correct the reading of the actual sample. Method 7196A is a fairly robust method and not subject to significant interferences. Hexavalent mercury and molybdenum can interfere, but only at significantly high (>200 mg/L) concentrations.

14.7 Hexavalent Chromium Quality Control

Soil and water samples should be collected with non-stainless sampling devices and stored at 4 +/- 2 degrees centigrade until sample extraction (soil or waste) or analysis (aqueous samples).

Aqueous samples should be analyzed within 24 hours of collection. Technical holding times for Cr VI are only established for water, but method (3060A) suggests that soil samples can be stored for up to 30 days prior to digestion, when chilled properly, and then must be analyzed within 7 days after digestion. The QA requirements for solid and water samples vary. The following sections illustrate the requirements for these media.

14.7.1 Quality Control Requirements for Soil and Solid Wastes (Method 3060A)

Method 3060A requires that a preparation blank (method blank) be prepared and analyzed for every batch of samples. The criteria used to evaluate this data are different than for most blanks. The preparation blank must not contain detectable Cr VI (i.e., below the detection limit) or not be greater than 10 percent of the regulatory limit or action limit. If these criteria are not satisfied, then the entire batch must be re-digested.

Soil samples prepared by method 3060A and analyzed by method 7196A should show that the digestate's pH has been adjusted to 7.0 +/- 0.5 units. According to the method (Section 7.7), if this adjustment hasn't been made or if the pH of the digestate is outside of the prescribed range, the digestate should be discarded and a new sample aliquot digested. In addition, soil or waste samples should have one sample in the batch duplicated. This means that a separate aliquot of a sample should be taken, digested and analyzed. The sample and its duplicate should agree within a 20% relative percent difference (RPD). Method 3060A prescribes that both a soluble and insoluble matrix spike be analyzed per batch of samples. The soluble matrix spike should be composed of $K_2Cr_2O_7$ (at least 40 mg of Cr VI added as a spike) and the insoluble matrix spike composed of $PbCrO_4$ (10 to 20 mg added in the spike). These spikes are added to separate aliquots of a sample in the batch and carried through the digestion process. The criteria used to judge the acceptability of these spikes, and therefore the digestion process, is a percent recovery of 85% to 125%. According to section 8.5 of method 3060A, if the matrix spikes have recoveries that are not within the prescribed acceptance criteria, then the entire batch of samples should be discarded and samples re-digested and re-analyzed. If upon reanalysis, the matrix spike is still outside of criteria, but the LCS is within criteria, method 3060A requires that ancillary parameters be evaluated. These ancillary parameters include the determination of field ORP (Eh) and pH. If these parameters were not taken in the field, then the time of analysis should be noted. In addition, analyses for COD, BOD and various redox couples (ferric iron and ferrous iron ratio) may also be made. These parameters can help to interpret whether the matrix is oxidizing or reducing. Eh – pH information should be plotted on Table 2 in SW-846 Method 3060A. The position of data plotted on this diagram will give an indication of a sample's oxidizing or reducing state. If the LCS was within acceptance criteria and the pre-digestion matrix spike recoveries for Cr VI were less than the acceptance range minimum (75%), this indicates that the soil samples reduced Cr VI (e.g., anoxic sediments), and no measurable native Cr VI existed in the unspiked sample.

If the data indicate that the sample is not reducing in nature, but the matrix spike is outside of lower criteria (i.e., less than 75%), then additional ancillary parameters data may be used to indicate the cause of the matrix spike failure. Data may be qualified based upon the percent recovery and the LCS data. Alternately, section 8.5 of Method 3060A states "If a low or zero percent pre-digestion matrix spike recovery is obtained, an alternate approach can be used to determine the potential contribution of the sample matrix to Cr VI reduction. This approach consists of performing a mass balance, whereby total chromium is analyzed (Method 3052) for two samples: (1) a separate unspiked aliquot of the sample previously used for spiking, and (2) the digested solids remaining after the alkaline digestion and filtration of the matrix spike (i.e., the filtered solids from the matrix spike in Section 7.6).

The difference between the total chromium measurements should be approximately equal to the amount of the spike added to the matrix spike. If the LCS met the acceptance criteria and the Cr VI spike is accounted for in the filtered solids as total chromium, it is likely that the reduction of the Cr VI to insoluble Cr III resulted from the reducing matrix of the original sample subjected to Cr VI spiking."

A post-digestion spike per batch is required for soil or other solid wastes. The criteria range for acceptance recommended by Method 3060A is a percent recovery between 85% and 115%. If the acceptance criteria are not met, the laboratory should perform the Method of Standard Additions (MSA). If the MSA technique is applied and no spike is observed from the MSA, then these results indicate that the matrix is incompatible with Cr VI.

14.7.2 Quality Control Requirements for Aqueous Matrix

Water or aqueous waste samples require verification that the sample matrix is not unduly biasing the analytical results. The method allows for samples to be blank corrected and also specifies that analytical results can be corrected for turbidity through the analysis of a turbidity blank (sample aliquot that is prepared as usual, but does not contain diphenylcarbizide).

Verification is required by the method to ensure that neither a reducing environment nor chemical interference is affecting the analytical results. This evaluation is accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr VI. The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 µg of Cr VI/liter. To verify the absence of interference, the spike recovery must be between 85% and 115%. Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0 - 8.5) using 1 N sodium hydroxide and then re-spiking and analyzing the aliquot. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), it can concluded that the analytical method has been verified.

If these criteria are not met, upon verification, an alternate method should be chosen to quantify Cr VI in the sample.

14.8 Quality Assurance and Quality Control Samples

Method 7196A requires the following quality control/quality assurance information be acquired.

- A minimum of one blank should be analyzed per batch of samples.
- A continuing calibration standard should be analyzed every 15 samples. The criteria for verification is 80 to 120% recovery of the standard.
- A matrix spike and/or a replicate sample should be analyzed in every batch.
- The Method of Standard Additions should be used for all extracts and for any samples submitted for delisting petitions.

14.9 Information Necessary to Validate Hexavalent Chromium Data

The Data Validator will need the following information to validate hexavalent chromium data:

- Sampling date;
- Chain of custody;
- Sample receipt log;
- Extraction/Preparation date;
- Analysis date;
- pH of sample after necessary adjustments;
- Spiked sample results, including high/low Cr VI spikes for solid material, LCS and matrix spike data;
- Interference and oxidizing ancillary data;
- Calibration verification results;
- Blank sample results, including reagent blanks and method blank data;
- Method of Standard Additions information, if necessary.

14.10 Data Validation Criteria

The criteria used to validate data are based on whether the sample was solid or aqueous. For solid samples:

1. **Sample Collection and Technical Holding Times.**

   Solid material must be collected using non-metallic sampling devices and placed, without head space, in a glass sampling container with a Teflon lid. Samples should be maintained at 4.0 +/- 2 degrees Centigrade and digested within 30 days. Analysis must occur within 7 days after digestion. If technical holding time criteria are not met, then all positive results should be qualified as estimated (J-) and all non-detections should be qualified as estimated. However, if the holding times are greatly exceeded, then the validator may reject all non-detections based upon professional judgment and the project's data quality objectives. If soil was also collected for soil pH and other ancillary parameters (i.e., ORP, other redox couples), these parameters should be analyzed in the field or with 24 hours.

2. **Preparation.**

   Solid samples must be pretreated/digested prior to analysis. SW-846 7196A/3060A requires that the pH of alkaline digestates of solid samples must be maintained at 7.5 +/- 0.5, as stated in Section 7.7. If the laboratory failed to maintain the pH, the sample should be re-digested. If pH issues are present with the data, the laboratory must be contacted to supply supporting information/explanations. If the laboratory cannot provide the information or if data exists to indicate that the proper pH was not maintained, the sample results should be rejected.

3. Blanks

A preparation blank must be prepared and analyzed with each digestion batch. Detected Cr VI concentrations must be less than the method detection limit or one-tenth the regulatory limit or action level, whichever is greater, or the entire batch must be re-digested. If detectable quantities of Cr VI are found in the blank, then the 10X rule can be applied to determine whether the amount is significant enough to bias sample results. If detectable Cr VI is found in the blank and, upon application of the 10X rule, the result is greater than the Cr VI result in the sample, the sample result should be qualified as undetected and data flagged "UJ". If after application of the 10X rule, the result is below the detected quantity in the sample, the data should be considered valid and not qualified.

4. Laboratory Control Sample

One laboratory control sample (LCS) should be analyzed per batch of samples per matrix. The concentration of Cr VI in the LCS should be near the mid-point of the calibration curve. The criteria for acceptance is a percent recovery between 80 and 120%. If the LCS is outside of the acceptance criteria, the batch of samples should be re-digested and re-analyzed. If the acceptance criteria are not met and the results are reported, the results should be qualified based on the following table:

	<65%	65%<%R>80%	80%<%R>120%	120%>%R<135%	>135%
Detection	Reject, R	Estimated, J-	Acceptable	Estimated, J+	Reject or estimated*
Non-detection	Reject, R	Estimated, UJ	Acceptable	Acceptable	Acceptable

***** Sample results may be rejected based upon professional judgment of the reviewer and the project's data quality objectives.

- **Matrix Spike and Sample Duplicate for Aqueous Samples**

  A matrix spike (mid-level of the calibration curve) or sample duplicate should be analyzed for every 10 samples (method 7196A, section 8.5). The acceptance criteria for spikes should be within 85-115% recovery. Duplicate sample reproducibility is not discussed in the method. If sample duplication is used, the laboratory should establish criteria for validation. If the matrix spike recovery is outside of the criteria, the laboratory should analyze a post-digestion spike to confirm a matrix interference. Alternately, the Method of Standard Additions can be performed to determine the concentration of Cr VI in the sample. Validation of sample results depends on the results of the LCS. If the LCS recovery is outside of its established criteria, then the reviewer may either qualify results as estimated or reject the results based upon the project's data quality objectives.

- **Matrix Spikes (soluble and insoluble) for Solid Matrices**

  According to SW-846 Method 3060A, the analysis of solid matrices requires that both soluble and insoluble pre-digestion matrix spikes be analyzed for every batch of samples. The acceptance range for spike recovery is 75% to 125%. If either spike is outside of control, then re-digestion and re-analysis of the batch should have occurred. If upon re-digestion and re-analysis it is found that the spike recovery(-ies) were still out of control, the LCS results should be reviewed. If the LCS is acceptable, the reviewer should use the following procedure to examine the pre-digestion spike result(s). First, the pH/Eh of the sample should be evaluated using Figure 2 in Method 3060A. Alternatively, the lab can perform a mass balance as described in Section 8.5.2 of SW-846 3060A. If reducing conditions exist, no further action is required. If reducing conditions do not exist, re-analyze the pre-digestion matrix spike(s). If results are acceptable, no further action is required. If matrix spike(s) recovery is between 50 and 74% or >125% and the LCS was in control, no corrective action is required, but samples should be qualified as estimated (J or UJ). If pre-digestion matrix spike(s) recovery is <50% and associated with non-detected results, the non-detected results may be qualified as rejected by the reviewer.

Chapter 15
Data Validation Summary

15.0 Introduction

As illustrated throughout this document, data validation consists of examining quality control information and qualifying sample results based upon pre-defined criteria. By working through the quality control information associated with a method, sample data may be either validated or qualified as estimated or rejected. However, the method of data validation as presented in this manual is limited in its scope. It is meant to acquaint DHWM inspectors and DDAGW hydrogeologists that have little or no background in the subject with elementary methods of validating data. Once a Tier I Checklist has been completed, the reviewer may think that this is the end of the process. This is not the case. Data must be summarized and a final judgment must be made concerning the overall accuracy and precision of the data. Finally, a statement concerning whether the data meets the data quality objectives of the project must be made. This conclusion is not entirely the responsibility of the data validator. Because of the scope of many environmental projects, this final assessment of data usability must be made in consultation with management, risk assessors and field sampling personnel.

The **data validation summary** does not have a strict format. However, it should contain key elements and a summary of the data validation findings. The elements that may be outlined in the summary include the rational for collecting the data, the statement of the data quality objectives, the summary of findings, an analysis of whether the data quality objectives have been met, or whether additional data validation (higher level) is necessary. Finally, data qualifiers, if any, should be assigned to the data in the report. These elements will be discussed in the following sections.

15.1 Facility and Sampling Information

The summary should begin with a simple statement giving the facility name, facility ID number, date of sampling, the number of samples that were taken, and the media that was sampled. Additional information may include the laboratory name, the sampling location name (i.e., “Former Drum Storage Pad”), and a short description of field or sampling conditions that could affect the sample results. Most of this information may be conveniently summarized on the Tier I Checklist and therefore does not need to be repeated if the summary will be attached to checklist as part of the plan review form. However, if the data validation summary will act as a stand-alone document, such as will be used for evidence in a court case, then the required information should be provided to serve as a complete record of the sampling event.

15.2 Sampling Rationale and Data Quality Objectives

A statement should be made describing the regulatory basis for collecting the samples. This may be a simple statement such as “the samples were collected to support the closure of the former drum pad storage area.” Other types of sampling activities that DHWM and DDAGW oversees includes compliance sample data, ground water monitoring data, RCRA Facility Investigations, generator waste analyses, and data derived from complaint investigations.

The statement is not trivial because it tends to form the basis for the data quality objectives of the sampling event. As a reminder, the DQOs are a process that enhances decision making. The DQO process is a seven step process that includes the following (U.S. EPA, *Overview of the EPA Quality System for Environmental Data and Technology*, Nov. 2002. EPA/240/R-02/003):

1) State the Problem
2) Identify the Decision
3) Identify Inputs to the Decision
4) Define the Study Boundaries
5) Develop a Decision Rule
6) Specify Limits on the Decision Errors
7) Optimize the Design

For example, samples may be taken to assure the public that a facility permitted to treat hazardous waste is in compliance with its permit and applicable laws and regulations. The decision (step 2) whether the treatment process is functioning properly will be based upon the results of the compliance samples (step 3, sample results are inputs for the decision). The results must be judged against some criteria. In our example, the criteria may be the LDR requirements for the treated waste or whether the waste displays a characteristic of toxicity. The decision whether the data is useful depends on the quality of the data. If sampling or analytical irregularities are such that the data is rejected, then this data would not be able to serve as input into the decision process. Conversely, data that meets all the data quality criteria would meet this aspect of the DQOs.

15.3 Summary of Findings

A summary of the Quality Control data should be included in the assessment. For the most part, if the Tier I Checklist is used as a tool for validating the data, then this summary is complete. In cases where the checklist was not used or when it is necessary to summarize the findings for a judicial action, then the results for each quality control parameter should be briefly discussed. The best approach is to use the Tier I Checklist as an overall outline of QC parameters to present.

As a general outline, the subjects presented include the following:

1. **Sample/Sample Receipt**. Any problems noted with sampling procedures (improper preservation, etc.) should be noted and a list of qualified sample results.

2. **Batch Specific Quality Control**. Batch specific quality control data may include, laboratory control sample results, matrix spike/matrix spike duplicate results and method blank results.

3. **Sample Specific Quality Control**. Sample specific quality control includes surrogate results for organic compound analytical methods and spike (Method of Standard Additions) results for inorganic methods.

For each quality control section, the problems encountered should be briefly discussed and the qualified sample listed.

15.4 Other Information

The validator should also make a note of several other criteria that can have a significant bearing on the usability of the data. For example, any missing data or QA/QC data should be noted. In addition, an evaluation of whether the reported detection limits or quantitation limits meet the regulatory or risk standards must be made. Finally, any deviations of the method must be noted for evaluation. It is also important to assess whether there is a bias in the data, this can be accomplished by reviewing the qualified data. If the quality control data were generally below or above the quality control criteria, then the validator should suspect a bias and use this knowledge when evaluating the data for usability. More information on bias assessment can be found in Chapter 5 of U. S. EPA's, Data Quality Assessment: A Reviewer's Guide (QA/G-9R), EPA/240/B-06/002, February 2006 (http://www.epa.gov/quality/qs-docs/g9r-final.pdf).

15.5 Data Assessment

Once all the information has been summarized the reviewer must conclude whether the data is of a sufficient quality to be usable. Unfortunately, this may not be as straight forward as presented in the example in Section 15.2. In many instances, professional judgment must be used when assessing the results of the data validation. The reviewer should evaluate all the accumulated data qualifications on a data set and the summary of the findings of the data validation in light of the project's scope and data quality requirements. Thus, if data are qualified as estimated based upon a variety of quality control criteria, it may be deemed unusable for its intended purpose even though the data was not initially rejected. For example, if technical holding times were outside of the acceptance time frame, and batch quality control samples such as the LCS were also below the acceptance criteria, this may indicate that the data does not meet the quality standards necessary to fulfill the project's data quality objectives. This action may also be justified if a bias is found in evaluating the QC data. It must be emphasized that rejection of data or a determination that data is unusable is not an automatic action if data is qualified for multiple reasons. In fact, other actions should also be considered. For example, the reviewer may conclude that additional information may be needed or that a Tier II Data Validation be performed. Another option is to identify if an alternate method can be used to verify the results. This would require that either an additional sample aliquot be analyzed or that the extract be re-analyzed from the original sample. Another option is to consider acquiring additional samples where these extra results can verify the previous sample results. If this action is contemplated, it is crucial to review the necessary changes that must be made by the laboratory to satisfy the project's data quality objects.

6.0 Data Validation Summary	
Data Validation Summary The results of the Tier I Data Validation must be summarized to be useful in making decisions concerning the use of the analytical data. The final decision on whether the data is usable for its intended purpose must be made in conjunction with the project management team and with the stated DQOs for the project. The following items can be used as a general guideline on preparing a data validation summary. More information can be found in Chapter 15 of the Tier I Data Validation Manual.	
6.1 State the regulatory requirement that prompted the samples to be taken.	
6.2 List the DQOs for the sampling.	
6.3 Summarize the findings of each major category of quality assurance data (e.g., blanks, surrogates, spikes, etc.).	
6.4 Assess whether bias is present. **Note:** This can be accomplished qualitatively by reviewing the qualified QA/QC data. If the majority of the QA/QC data are flagged with a "J-then there may be a negative bias present. If the majority of the QA/QC data is flagged with a "J+",– then there may a positive bias. Additional information on the assessment of bias can be found in U.S. EPA's Guidance for Data Quality Assessment: A Reviewer's Guide (QA/G-9R), EPA/240/B-06/002, February 2006.	
6.5 Is the quality of the data sufficient to meet the DQOs of the project?	