

**Validation and Peer Review**  
**of U.S. Environmental Protection Agency**  
**Sampling Methods for Chemical and Radiochemical**  
**Parameters**

*Prepared for:*  
**The EPA Forum on Environmental Measurements (FEM)**

*Prepared by:*  
**The FEM Method Validation Team**

**FEM Document Number 2007-02**  
**December 17, 2007**

**Principal Authors:**

**Kathy Hall**  
National Homeland  
Security Research Center  
Columbus, OH

**Brian Schumacher**  
National Exposure  
Management Center  
Las Vegas, NV

**Erin Silvestri**  
National Homeland  
Security Research Center  
Cincinnati, OH

**Terry Smith**  
Office of Emergency  
Management  
Washington, DC

**Oba Vincent**  
National Homeland  
Security Research Center  
Cincinnati, OH

**Charlena Yoder**  
National Homeland  
Security Research Center  
Cincinnati, OH

**Contributors:**

**Kim Kirkland**  
Office of Solid Waste  
Arlington, VA

**Philip Campagna**  
Environmental Response Team  
Edison, NJ

**Raj Singhvi**  
Environmental Response Team  
Edison, NJ

**Kenna Yarbrough**  
National Enforcement  
Investigations Center  
Denver, CO

**Andy Hess**  
US EPA Region 10  
Port Orchard, WA

**Mike Neill**  
US EPA Region 4  
Athens, GA

**Greg Nagle**  
US EPA Region 9  
Richmond, CA

**Brad Venner**  
National Enforcement  
Investigations Center  
Denver, CO

**Lara Autry**  
Office of Research and Development  
Research Triangle Park, NC

**Shannon Sturgeon**  
Office of Solid Waste  
Arlington, VA

**Teri Schaeffer**  
Versar, Inc.  
Springfield, VA

**Kevin Ashley**  
National Institute of Occupational  
Safety and Health  
Cincinnati, OH

## Disclaimer

This document contains direction developed solely to provide internal guidance to U.S. Environmental Protection Agency (EPA) personnel. EPA retains the discretion to adopt approaches that differ from this guidance on a case-by-case basis. The guidance set forth in this document does not create any rights, substantive or procedural, enforceable at law by a party to litigation with EPA or the United States. The use of mandatory language such as "must" and "require" in this guidance document reflects sound scientific practice and should not be construed to create any legal rights or requirements. The use of non-mandatory language such as "may," "can," or "should" in this guidance does not connote a requirement but does indicate EPA's strongly preferred approach for validating and peer reviewing EPA methods prior to publication for general use.

References within this document to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily imply its endorsement or recommendation by EPA. Neither EPA nor any of its employees, makes any warranty, expressed or implied, nor assumes any legal liability of responsibility for any third party's use, or the results of such use, of any information, apparatus, product, or process disclosed in this manual, nor represents that its use by such third party would not infringe on privately owned rights.

## Foreword

The U.S. EPA Science Policy Council established the Forum on Environmental Measurements (FEM) in April 2003. The FEM is a standing committee of senior EPA managers who provide EPA and the public with a focal point for addressing measurement and methods issues with multiprogram impact. Action teams are commissioned by the FEM to address specific issues. The Method Validation Team was formed in October 2003, and tasked with developing Agency-wide, internal guidance for validating and peer reviewing EPA methods prior to publication for general use.

This document contains guidance for the validation of sampling methods for chemical and radiochemical parameters. It is the third in a series of Agency-wide, method validation guidance documents. Subsequent guidance will be developed for other types of measurement methods (e.g., microbiology, biology, and toxicology).

## Document Review

The US Environmental Protection Agency (i.e., EPA or the Agency) Science Policy Council (SPC) Peer Review Handbook provides Agency-wide requirements and options for document production. All individuals and groups with members are listed below that had the opportunity for review and comment of this work prior to its submission for approval.

### *Individual Reviewers*

Bob Streicher (NIOSH)	Kevin Ashley (NIOSH)	Rick Poeton (R10)
James Mitchell (R5)	George Brozowski (R6)	Gregg Dempsey (OAR)
Bert Coursey (DHS)	John G. Lyon (ORD)	Jane Denne (ORD)
Lawrence Zintek (R5)	John H Zimmerman (ORD)	Terry Smith (OSW)
Dino Mattorano (National Decon Team)		

### *Emergency Response Technical Workgroup (ERTG)*

Andrea Abat (R6)	Anthony Barber (National Decon Team)	Ron Bell (OARM)
Michael Boykin (R10)	Nicolas Brescia (R6)	Philip Campagna (OSW)
Cosmo Caterino (R1)	Margaret Chong (R2)	Jeffery Davidson (OAR)
Dennisses Valdes (OSW)	Will Duncan (R9)	Debra Flagg (OARM)
Benjamin Franco (R4)	Edward Gilbert (OSW)	Kerry Guy (R8)
Scott Hudson (National Decon Team)	Elise Jakabhazy (R1)	Nancy Jones (R6)
Eric Kioglin (NHSCR)	Deborah Kopsick (OAR)	Janice Kroone (R7)
Glen Lapsley (R3)	Dino Mattorano (National Decon Team)	Don Mclaughlin (R3)
James Mitchell (R5)	David Murphy (OARM)	Duane Newell (OSW)
Matt Rees (NEIC)	Jeffry Rodin (R10)	Angel Rodreiguez (R2)
Steve Hawthorn (National Decon Team)	Peter Stevenson (R8)	Daniel Wainberg (R1)
James Webster (R4)	Chris Weis (NEIC)	Dave Williams (OEI)
Dave Wright (R2)	Leonard Zintak (R5)	Donn Zuroski (R9)

*Forum on Environmental Measurement (FEM)*

Michael Shapiro (OW)	Kathy Callahan (R2)	Marty Monell (OPP)
Betsy Grim (OPP)	Diana Love (NEIC)	Barbara Finazzo (R2)
Dennis Wesolowski (R5)	Neilima Senjalia (OIA)	Manisha Patel (OGC)
Walter Kovalick (R5)	Jan Young (OSW)	Mary Smith (OW)
Pamela Barr (OW)	Fred Hauchman (ORD)	Thomas Fontiane (ORD)
Linda Travers (OEI)	Reggie Cheatham (OEI)	Nancy Wentworth (OEI)
Bill Lamason (OAR)	Robin Segall (OAR)	Bonnie Gitlin (OAR)
Lara Autry (ORD)	Steve Knizner (OPP)	Diann Sims (OPP)
Cynthia Doucoure (OPP)	Susan Lawrence (OPP)	Kiran Verma (OPP)
Joseph Ferrario (OPP)	Christian Byrne (OPP)	Elizabeth Flynt (OPP)
Frederic Siegelman (OPP)	Dallas Wright (OPP)	Yaorong Qian (OPP)
Beth Mishalanie (NEIC)	Brad Venner (NEIC)	Richard Reding (OW)
Sherri Umansky (OW)	Greg Carroll (OW)	Dave Munch (OW)
Steve Wendelken (OW)	Pat Fair (OW)	Robin Oshiro (OW)
Sandhya Parshionikar (OW)	Phil Oshida (OW)	Marion Kelly (OW)
David Musick (OAR)	John Griggs (OAR)	Roger Cortesi (ORD)
Norman Birchfield (ORD)	Brian Garges (ORD)	Lynn Bradley (OEI)
Barry Lesnik (OSW)	Mike Johnson (OSW)	Brenda Bettencourt (R9)
Chris Cagurangan (R9)	Marie O'Shea (R2)	Charlie Hooper (R4)
Mike Peyton (R4)	Bruce Means (OSW)	Lek Kadeli (ORD)
Lula Melton (OAR)	Peter Grevatt (OSW)	

## Executive Summary

EPA program offices publish a wide variety of measurement methods for use by EPA personnel, other government agencies, and the private sector. These methods may originate from many sources such as EPA laboratories, EPA contractors, scientific organizations, other government laboratories, and from the private sector. Since these methods may be published as regulations, incorporated by reference in regulations, or published as guidance, they must be thoroughly tested and peer reviewed prior to publication as EPA methods.

This document provides Agency-wide guidance for EPA personnel who will evaluate the performance and suitability of new sampling methods for chemical and radiochemical parameters before EPA publication. The method validation principles contained herein are based on current, international approaches and guidelines for intralaboratory (single laboratory) and interlaboratory (multiple laboratory) method validation studies. Peer review is required for EPA sampling methods for chemical and radiochemical parameters. The EPA Science Policy Council Peer Review Handbook provides Agency-wide requirements and options for that process.

## Table of Contents

<b>Disclaimer</b>		i
<b>Foreword</b>		ii
<b>Executive Summary</b>		iii
<b>1</b>	<b>Introduction</b>	1
	1.1 Purpose	1
	1.2 Intended Audience	1
	1.3 Scope of Guidance	2
	1.4 Terminology	2
<b>2</b>	<b>Planning and Initiating Method Validation Studies</b>	3
<b>3</b>	<b>Method Description</b>	4
	3.1 Procedures Composing a Method	4
	3.2 Method Purpose, Scope, and Applicability	4
<b>4</b>	<b>Critical Method Performance Characteristics</b>	5
	4.1 Selectivity	5
	4.2 Method Uncertainty	6
	4.3 Equipment/Instrument Calibration	7
	4.4 Bias/Trueness	8
	4.5 Detection and Quantification Limits	8
	4.6 Method Ruggedness	9
	4.7 Sample Integrity	9
	4.8 Sample Size	9
<b>5</b>	<b>Sampling Method Validation Reports</b>	11
<b>6</b>	<b>Peer Review</b>	14
<b>7</b>	<b>Terms and Definitions</b>	15
<b>8</b>	<b>References</b>	18
	<b>Appendix A: Sampling Validation Plan</b>	19
 <b>TABLE</b>		
<b>1</b>	<b>Method Validation Report Topic Areas</b>	12

## 1 Introduction

Sampling method validation is the process of demonstrating that a sampling method is suitable for its intended use, and involves conducting a variety of studies to evaluate sampling method performance under defined conditions. Sampling method validation studies may involve a single location or multiple locations. The goal is to demonstrate that sampling procedures of a particular method are fit for an intended purpose. Properly designed and successful sampling method validation studies create confidence in the reliability of a sampling method. Sampling method validation is one of several important quality system components that are designed to ensure the production of scientifically valid and useful data.

EPA's sampling methods are designed for a wide variety of measurement objectives, such as monitoring compliance with environmental regulations, enforcement of environmental regulations, and for information-gathering scientific studies. Because measurement objectives and data quality requirements vary, the technical details and acceptance criteria for conducting method validation studies are contained in existing, program-specific EPA documents rather than in an Agency-wide guidance. Therefore, this guidance document describes fundamental method validation principles and general areas to be addressed when validating sampling methods for chemical and radiochemical parameters. This information is based on current, international approaches and guidelines for single and multiple laboratory method validation studies.

Sampling methods for chemical and radiochemical parameters are used in conjunction with analytical methods, and the importance of adequately validating the sampling method is just as important as validating the analytical method in fulfilling accurate measurement objectives. Any determination of uncertainty or bias of an environmental measurement must be made in relation to both the analytical method and the sampling method for chemical and radiochemical parameters.

Before publication, all sampling methods for chemical and radiochemical parameters also must be peer reviewed. The reader is referred to the most current version of the EPA Science Policy Council's *Peer Review Handbook* (1), an excellent source of information for both internal and external peer review processes.

### 1.1 Purpose

The purpose of this guidance is to describe scientific principles that should be addressed during sampling method validation studies for chemical and radiochemical parameters and to harmonize terms and definitions related to sampling method validation activities. This document provides general guidance for future activities with new and existing sampling methods for chemical and radiochemical parameters; it is not intended to be applied retroactively. This document is intended to address agency-wide guidance, applicable to all Program Offices, for sampling method validation for chemical and radiochemical parameters. This document also lists a number of sampling method guidance documents and procedures that should be reviewed and consulted to determine the level of validation associated with the method.

### 1.2 Intended Audience

This guidance is intended for internal use by EPA personnel who are responsible for sampling methods for chemical and radiochemical parameters, as defined in Section 1.3 of this document, which are to be: (1) published as serially numbered EPA methods, (2) published as regulations, or (3) incorporated by reference in regulations.

### **1.3 Scope of Guidance**

This guidance contains recommendations for validating new sampling methods for collection of radionuclide and chemical parameters, and is intended for use by personnel collecting samples for EPA. These terms are defined as follows:

- “New” means that the method is not currently published as an EPA method or an update of a published EPA method that includes procedural changes that will affect method performance.
- “Sampling Method” is defined as the body of procedures and techniques for performing a collection activity, systematically presented in the order in which they are to be executed.

Due to the nature of the various techniques and tools for sampling when developing, using, or validating a sampling method, the precise procedures of the method must be addressed. It must be indicated whether the method uses a physical sampling or collection tool/technique, such as a split spoon (corer), or whether the method is a field measurement process such as screening or direct reading (i.e., organic vapor analyzer). Conditions must be specified for either type of method.

This document does not address site characterization issues, such as determining the number of samples required to adequately define a site.

### **1.4 Terminology**

Scientific terms and meanings change with time. For many years, national and international standards organizations have attempted to harmonize terminology within scientific disciplines. For the purpose of this guidance, a glossary of terms and definitions is included in Section 7. The entries were compiled from current, authoritative sources, and references are included.

## 2 Planning and Initiating Method Validation Studies

Proper planning is critical for successful method validation studies. A sampling validation plan should be prepared that encompasses all aspects of the validation activity and follows a standardized format similar to that shown in Appendix A. The sampling method is closely tied to the development of the analytical methods and care must be taken to ensure that the new collection method is consistent with the planned analytical methods to be utilized.

Unlike analytical method validation activities, sampling method validation is heavily dependent on the environment in which the sample is collected. Temperature variations, variations in media type and the technique utilized to collect samples (e.g., pressure placed on a surface wipe) can cause great variability in sample collection. Great care must be taken to document and either limit the variables tested or ensure that a range of conditions are included in the test. Additional care must be taken to document the process by which the samples are collected. For example, soil samples can be grab or composite and are typically taken via a mechanical means. Sampling techniques which are simple deviations from existing processes require less rigorous validation (e.g., new size of a split spoon sampler) than a novel sampling technology with little technical basis (e.g., vacuum extraction of organic vapors from soils). The key to any good validation activity is to control and document variability to determine the range for purposeful uses and identify techniques to be utilized when using the sampling technology.

Typically, multiple locations and conditions are recommended to be tested in controlled environments after the initial controlled validation test is conducted. This provides a range of operating criteria and a better understanding of the consistency of the sampling technique. However, this needs to be balanced against the cost of performing sampling method validation studies. Unfortunately, some sampling method difficulties may only be revealed after performing multiple tests, and it may be necessary to troubleshoot and optimize a method after conducting such a study. If procedural changes are required, the changes may affect the method performance characteristics and some or all aspects of the study may need to be repeated.

Safety is a prime consideration in any sampling event. Safety concerns and procedures should be addressed in both the sampling method and the validation plan, including personal protective equipment and first aid. Additional concerns include physical hazards and chemicals that are toxic, corrosive, emit harmful or explosive vapors, or that are incompatible when mixed.

### 3 Method Description

#### 3.1 Procedures Composing a Method

The components of a field sampling technique (i.e., sample collection) or field measurement processes (i.e., screening) that are subject to validation should be clearly described. The matrix being sampled and the purpose of the sampling effort should be defined as they will determine which available techniques/tools will ultimately be used. The general matrices of concern include air, liquids, solids, and surfaces.

Sampling methods for chemical and radiochemical parameters and their validation plans should cover all aspects of the sampling event from sample collection through the delivery of the sample for analysis. For example, the use of a wipe sampling technique should have discussions of procedures for solvent selection as it relates to recovery of the analyte; area to be wiped; wipe handling and sample preservation; and any matrix effects of the material being wiped. In this case, the sampling method validation effort should include an evaluation of all four sampling components combined.

When field measurement processes are to be performed, then all aspects of the equipment/instrument's set-up, calibration, and operation, as well as sample preparation, sample cleanup, and appropriate Quality Assurance/Quality Control (QA/QC) checks should be clearly defined. These processes should be similar to those validated for laboratory-based analytical methods.

#### 3.2 Method Purpose, Scope, and Applicability

The purpose of a sampling method and the intended use of the data must be clearly defined. In addition, method scope and applicability must be well defined and clearly described. This helps minimize misapplications by the user. Method scope and applicability includes the following:

- The sampling or field measurement process components to be validated;
- The nature of the analytes (e.g., semi-volatile organic compounds);
- The matrix to be sampled (i.e., air, liquids, solids, or surfaces) and any inherently unique properties with sampling that matrix (e.g., soil heterogeneity);
- The range of analyte levels for which the method is claimed to be suitable, if field measurement is to be performed;
- A description of any known advantages and limitations of the sampling method;
- A list of the sampling equipment and supplies used to perform the sampling; and
- A description of how the method and analytical parameters chosen meet the data quality objectives for the specific application.

## 4 Critical Method Performance Characteristics

The purpose, scope, and applicability determine the sampling method performance characteristics chosen for study. They will also determine whether the method involves physical collection or direct reading. The accuracy of a method, with respect to the materials and conditions studied during validation, may be evaluated from the performance characteristics. The meaning of the term “accuracy” has changed over the years, and accuracy should be viewed as a quantitative measure that incorporates both precision and bias. Accuracy is defined as the closeness of agreement between a measured value and either a true or accepted reference value.

The performance characteristics that should be evaluated include, but are not limited to the following:

- Selectivity
- Method Uncertainty
- Equipment/Instrument Calibration
- Bias/Trueness
- Detection and Quantitation Limits
- Method Ruggedness
- Sample Integrity
- Sample Size

“Sensitivity” is not listed in this guidance as a method performance characteristic. The scientific literature reflects different meanings and uses for this term. It is used to describe a performance characteristic of a detector, instrument, or an analytical method. However, it is possible to evaluate any of these sensitivity parameters from data and information obtained by studying the performance characteristics listed in this section.

### 4.1 Selectivity

Selectivity refers to the ability to correctly identify the analyte(s) of interest in the presence of expected chemical/physical interferences. Selectivity may be evaluated by sampling an appropriate environmental media both with and without the expected interferences. It is critical that during the development of the sampling validation plan interferences are identified and addressed. For example, a soil sampling technique may be impacted by the amount of gravel contained in the sample environment. In that case, multiple environments should be sampled that contain varying (and measured) amounts of gravel to allow for comparison and evaluation.

In addition, sampling method selectivity should address chemical sampling devices versus physical sampling devices, as applicable. The choice of sampling equipment can be crucial to the task of collecting a sample appropriate for the intended use. For example, ASTM D 6232 (2) lists the following characteristics to consider when selecting sampling equipment and methods:

- Material compatibility (gloves, mixing pans, knives, sample containers, etc.)
- Chemical compatibility
- Sample volume capabilities
- Physical requirements
- Ease of operation
- Decontamination

Method selectivity is typically expressed qualitatively. A qualitative selectivity statement includes a description of known interferences, interference effects, and the nature of the impact of the interference.

## 4.2 Method Uncertainty

The International Standards Organization (ISO) defines measurement uncertainty as a “parameter, associated with the result of a measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand”. Measurand refers to the particular quantity (such as concentration) subject to measurement.

In the case of an analytical test result(s) from an environmental sample containing an unknown concentration of a particular analyte, the measurand is the “true” concentration of that analyte in the sample, and the uncertainty is some representation of the extent of deviation that the test result has from that true value. Uncertainty should not be confused with accuracy, even though accuracy is certainly a constituent of the total uncertainty of a measurement. Accuracy is simply how far off the analytical result is from the true value. This is, in many cases, impossible to determine. Total uncertainty must also represent aspects of precision and bias, as well as an aspect of confidence, i.e. confident that uncertainty is truly represented 80% of the time, or 95% of the time, etc.

To adequately represent the total uncertainty associated with an environmental measurement, two general, but separate sources of uncertainty must be considered. The first consideration involves the uncertainties involved with the actual analytical measurement of the sample. This involves consideration of such parameters as analytical instrumental sensitivity, instrument calibration, analytical duplicate analysis, spike sample analysis, method bias (including sample preparation and instrumental analyses), matrix interferences, etc. The second consideration involves uncertainties involved in collection of the sample in the field. This involves consideration of such parameters as taking an adequate number of field samples to adequately portray environmental conditions at the sampling site, consideration of spatial homogeneity issues, adequate preservation of samples (chemical and temperature preservation), sampling equipment and techniques, etc. The extent of how in-depth one looks at each of these considerations is dependent upon the actual use of the measurement. If an analytical test result is to be used for gaining only a general understanding of the local environmental conditions, then a precise representation of total uncertainty in the result may not be needed. An example would be a situation in which a field analyst uses a portable field meter at a site to measure VOCs in ambient air. In this case, uncertainties represented by the meter manufacturer’s accuracy specifications (e.g. +/- 10 % of the instrument reading) could suffice. In situations involving regulatory action levels, public scrutiny of data results, or inspection audits, representation of

uncertainty must be more detailed and precise. The decision of how in-depth uncertainty is to be determined must be planned in advance before samples are collected in the field. This planning is made based upon data quality objectives (DQOs) that are developed for each environmental site.

### 4.3 Equipment/Instrument Calibration

Sampling method procedures will include a section on equipment/instrument calibration. The section should address the following requirements:

- All equipment that is used to measure or analyze samples in the field requires calibration, routine maintenance, and at least annual standardization. This equipment is calibrated following procedures included in the manufacturer's users manual or performed in the laboratory. Equipment used to obtain volumetric sample measurements must be certified to appropriate volume specifications.
- Instruments that are routinely used in the field and require calibration and standardization or certification to ensure measured sample weights and volumes are accurate include, but are not limited to:
  - Balances or scales
  - Air sampler flow rate meters and totalizers
  - Water pumps
  - Automatic samplers
  - SUMMA<sup>®</sup> canisters
  - Passive/active filters
  - Vacuums
  - Bladder pumps
  - Peristaltic pumps
  - Centrifugal submersible pumps
  - Displacement pumps
  - Multi-gas monitors
  - Particulate monitors
  - Multi RAE
  - Photoionization detector (PID)/Flame ionization detector (FID)
  - Single point monitors
  - Ludlum monitors
  - Personal sampling kits
- Instruments that are routinely used in the field, whose certification or standardization should be provided by manufacturers:
  - Volumetric pipettes, beakers, graduated cylinders, volumetric jars/containers
  - Lapel air samplers
  - Split spoons/corers
  - Syringes

- Draeger tubes
  - Colorimetric pumps/chips
  - Chemical agent detectors
  - Advanced portable detector (APD) chemical agent monitors
  - Flame ionization detectors
  - M8 paper
- Analytical equipment that may be used in the field that require calibration to ensure sample analyses are accurate include, but are not limited to:
    - pH meters
    - Turbidimeters
    - Dissolved oxygen and/or conductivity meters

#### **4.4 Bias/Trueness**

Bias refers to the overall magnitude of known systematic (determinate) errors associated with the use of a sampling method. The presence of systematic errors can only be determined by comparison of the average of many results with a reliable, accepted reference value. Method bias may be estimated by measuring materials whose composition is reasonably well known, such as reference materials, by comparing results to those from at least one alternate method or procedure, or by analyzing spiked materials.

#### **4.5 Detection and Quantitation Limits**

The term “detection limit” is used to describe the lowest analyte level that can be confidently identified. There are many specific definitions for this term, and it is used to describe the detection capabilities of detectors, instruments, and analytical methods. The term “detection limit” must be defined, and a description of how it was evaluated during method validation must be provided. Limits derived from mathematical definitions or statistical models must be verified by testing materials containing the analyte at the claimed detection level. Detection limit, as it applies to instrument detection capability, must also be addressed.

It should be noted that with field screening or detection equipment that requires establishment of a calibration curve, typical detection limits claimed by the manufacturer are not always achievable in the field due to environmental conditions, sample type, etc. Some types of field equipment also refer to resolution rather than detection limits.

As it applies to analytical procedures, quantitation range is used to describe the span of analyte levels, as contained in a sample matrix. For sampling procedures, an appropriate quantity of sample is needed to perform the analysis accurately and appropriately. The sample amount is the minimum amount of sample that should be collected to support analysis of a single sample, and is related to the analytical method and required detection levels, or specific quantitation requirements. Volume and weight requirements depend on the target analyte(s), the analytical method that will be used, and the data requirements. It should be noted that quantitation limits only apply to screening or direct reading methods.

#### 4.6 Method Ruggedness

Ruggedness refers to the extent to which a sampling method remains unaffected by minor variations in operating conditions. Ruggedness testing involves experimental designs for examining method performance when minor changes are made in operating or environmental conditions. The changes should reflect expected, reasonable variations that are likely to be encountered in different field settings or environments.

#### 4.7 Sample Integrity

Sample integrity refers to the unimpaired chemical composition of a test sample upon the extraction of a test sample for analysis. Preserving the integrity of the sample ensures that each sample arrives at the laboratory for analysis in the same condition that it was collected in the field. These field and transportation measures protect the sample from physical contamination, loss of volume, chemical reactions, volatilization, or temperature change.

Aspects of the sample integrity that must be evaluated include, but are not limited to, the following:

- Temperature control
- Preservation chemicals
- Storage
- Container compatibility
- Labeling/seals
- Logbooks
- Chain of Custody
- Transportation regulations

For direct measurements made in the field, sample integrity involves getting the sample quantitatively to the detector. Methods of this type must include appropriate QC steps that verify this (e.g., for air samplers, a gas of known value is typically introduced, along with sample gas matrix, and recovery is observed).

#### 4.8 Sample Size

Especially for solid matrices, sample size may be a major factor in influencing the magnitude of sample collection error. Sample size is defined as the "Number of items or the quantity of material constituting a sample" (ISO 11074-2, 1998) (3). The appropriate sample size may result from extensive mixing of sub-samples to form one sample or may be a grab sample collected with a device with minimal sample size.

Variability in the measurement process also arises from the heterogeneity of the material throughout the measurement process. Sampling method validation studies for any new sampling technologies should take into account the routine sample size typically collected and submitted

to the laboratory, especially in cases where a composite sample is not feasible. Most documents on sampling methodologies stress the importance of collecting a representative sample; otherwise, the analysis and interpretation of the data are of no or limited value. A sampling method validation study should discuss the difference between collecting large numbers of potentially non-representative, heterogeneous samples using limited sampling mass or volume and collecting less of larger well-mixed samples.

## 5 Sampling Method Validation Reports

A specific sampling method should have documentary evidence that the method has been appropriately validated. The validity of a sampling method should be established and verified by field studies, and documentation of successful completion of such studies should be provided in the sampling method validation report. General and specific Standard Operating Procedures (SOPs) and good record keeping are an essential part of a validated sampling method.

A sampling method validation report, suitable for placing in the public docket, should be prepared. The report should address the sampling method validation topics outlined in this guidance document (summarized in Table 1), and provide: (a) background information on sampling method development, (b) a description of the actual sampling method validation techniques, (c) any changes made to the sampling method as a result of the validation studies, and (d) any recommendations for future work. At the minimum, the sampling method validation report must address the information contained in Table 1 below.

**Table 1**  
**Method Validation Report Topic Areas**

Topic	Explanation
<b>Summary</b>	This section should provide an overall summary of the validation report.
<b>Introduction</b>	The introduction should provide background information on sampling method development and state the purpose of the method. The purpose of the method is a clear and concise description of the measurement objectives and the intended use of the data.
<b>Methodology</b>	<p>The methodology should consist of:</p> <ol style="list-style-type: none"> <li>1) A thorough description of the sampling method validation technique/experimental design including a description of the test method/procedure and details of equipment/locations used with calibration status.</li> <li>2) A discussion of how the sampling method scope and applicability served to define the range of method performance. Method scope and applicability topic areas could include the following: <ul style="list-style-type: none"> <li>• The sampling or field measurement process components to be validated.</li> <li>• The nature of the analytes (e.g., semi-volatile organic compounds).</li> <li>• The matrix to be sampled (i.e., air, liquids, soil, or surfaces) and any inherently unique properties with sampling that matrix (e.g., soil heterogeneity).</li> <li>• The range of analyte levels for which the method is claimed to be suitable, if field measurement is to be performed.</li> <li>• A description of any known advantages and limitations of the sampling method.</li> <li>• A list of the sampling equipment and supplies used to perform the sampling.</li> <li>• A description of how the method and analytical parameters chosen meet the data quality objectives for the specific application.</li> </ul> </li> </ol>
<b>Sampling Method Characteristics</b>	<p>This section can include, but is not limited to, the characteristics listed in this document, such as:</p> <ol style="list-style-type: none"> <li>1) <b>Selectivity:</b> Include a discussion of how selectivity was evaluated through the sampling of appropriate environmental media both with and without expected interferences. A statement of how the sampling plan identified and addressed interferences should be included.</li> <li>2) <b>Uncertainty:</b> Include a statement describing the decision of how in-depth uncertainty was determined and what planning took place in advance of samples being collected in the field. In addition, include a discussion of data quality objectives (DQOs) that were developed for the sampling method.</li> <li>3) <b>Equipment Calibration:</b> Include a statement focusing on the equipment that is used to measure or analyze samples in the field and how the required calibration, routine maintenance, and annual standardization are accomplished.</li> <li>4) <b>Bias/Trueness:</b> Include a discussion of how systematic errors were accounted for in the sampling plan through measurements of reasonably well known composition material, results comparisons to alternative methods or procedures, or using analyzed spikes.</li> <li>5) <b>Ruggedness:</b> Include a discussion of sampling method performance after minor changes are experienced in operating or environmental conditions.</li> <li>6) <b>Sample Integrity:</b> Include a discussion of preserving the collected samples' physical and chemical properties and security from the collection site to the analytical laboratory.</li> <li>7) <b>Detection and Quantitation Limits:</b> Include a discussion of how the sampling method determined the appropriate quantity of sample to be taken to support analysis. A discussion of how the detection limit was defined in the method and a description of how it was evaluated during method validation must be provided. Provide a discussion of how limits derived from mathematical definitions or statistical models were verified. Discuss how detection limit, as it applies to instrument detection capability, was addressed in the method.</li> <li>8) <b>Sample Size:</b> Include a discussion of the number or items or the quantity constituting a sample, as appropriate for the method, whether the samples are composites or grab.</li> </ol>
<b>Safety Considerations</b>	A discussion of safety concerns and procedures should be addressed, including personal protective equipment and first aid. Additional concerns include physical hazards and chemicals that are toxic, corrosive, emit harmful or explosive vapors, or that are incompatible when mixed.

**Table 1**  
**Method Validation Report Topic Areas**

<b>Topic</b>	<b>Explanation</b>
<b>Quality Control/Quality Assurance</b>	Provide a discussion of the defined quality control/quality assurance (QA/QC) checks and guidances.
<b>Discussion</b>	<ol style="list-style-type: none"><li>1) Discuss method development.</li><li>2) Discuss results of the validation testing and an evaluation including comparison with the reference substances and preparations, acceptance criteria and recommendations.</li><li>3) Note any changes made to the sampling method as a result of the validation studies.</li></ol>
<b>Conclusions</b>	<ol style="list-style-type: none"><li>1) Discuss formal acceptance/rejection of work.</li><li>2) Provide recommendations for future work.</li></ol>

## 6 Peer Review

Before publication, EPA sampling methods for chemical and radiochemical parameters are peer reviewed in accordance with the information provided in the most current version of the EPA Science Policy Council's *Peer Review Handbook* (1). The *Peer Review Handbook* provides Agency-wide guidance for the consistent implementation of peer review, and Program Offices have the flexibility to design peer reviews to suit their specific needs. The Handbook is the source of detailed information about which Agency work products are subject to peer review. In addition, there is information about selecting peer review mechanisms (internal and external), planning a peer review process, conducting a peer review, and preparing a peer review record.

## 7 Terms and Definitions

Terms and definitions were obtained from the following authoritative sources:

- *Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*, International Organization for Standardization, ISO 5725-1, 1994-12-15 (ISO 5725-1).
- American Filtration & Separations Society: *Filtration & Separation Glossary of Terminology* (AFSS).
- *NIOSH Manual of Analytical Methods* (NMAM).
- ISO VIM (DGUIDE 99999) *International vocabulary of basic and general terms in metrology* [Revision of the 1993 edition] (2004) (VIM).
- Office of Research and Development: *Guidance for Quality Assurance Project Plans* (QA/G-5), EPA/600/R-98/018. (ORD/QAPP).
- *American National Standards Specification and Guidelines for Quality Systems for Environmental Technology Programs*, Annex A (2004) (ANSI/ASQ).
- International Union of Pure and Applied Chemistry, Chemistry and the Environment Division, Commission on Atmospheric Chemistry. *Glossary of Atmospheric Chemistry Terms*, Revision 2000 (GACT).
- *Soil Quality -- Vocabulary – Part 2: Terms and definitions relating to sampling*, International Organization for Standardization, ISO 11074-2: 1998 (ISO 11074-2).
- Chronolab AG Switzerland. *The Quality of Diagnostic Samples, Section 8: Analyte Stability in Sample Matrix*. <http://www.diagnosticsample.com/introduction-text.php?id=31&lang=en> (QDS).
- *ASTM Dictionary of Science and Engineering*, 10<sup>th</sup> edition (2005) (ASTM)
- Bell, S. *A Beginner's Guide to Uncertainty of Measurement*. Measurement .Good Practice Guide No. 11 (Issue 2). 1999 (BGUM).

For each term and definition, the specific reference is indicated in parentheses. The numbering of the notes from ISO 5725-1 is the same as the numbering in the original ISO document.

**accuracy:** the closeness of agreement between a test result and the accepted reference value (ISO 5725-1).

NOTE

- 2 The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component.

**bias:** the difference between the expectation of the test results and an accepted reference value (ISO 5725-1).

NOTE

- 5 Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.

**breakthrough potential:** 1. used to describe the passing of solids through the cake buildup of a

filter medium. Also called breakpoint (AFSS). 2. elution of substance being sampled from the exit end of a sorbent bed during the process of sampling air (NMAM).

**calibration:** set of operations that establishes, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards (VIM).

NOTES

- 1 The result of a calibration permits either the assignment of values of measurands to the indications or the determination of corrections with respect to indications.
- 2 A calibration may also determine other metrological properties such as the effect of influence quantities.
- 3 The result of a calibration may be recorded in a document, sometimes called a **calibration certificate** or a **calibration report**.

**compatibility:** the capability in which one data set can be reconciled or integrated with another, often expressed as a statistical measure (ORD/QAPP).

**measurand:** quantity intended to be measured (VIM).

NOTES

- 1 The measurement can change the phenomenon, body, or substance under study such that the quantity that is actually measured differs from the measurand.  
EXAMPLE: The potential difference between the terminals of a battery may decrease when using a voltmeter with a significant internal conductance to perform the measurement. The open-circuit potential difference can be calculated from the internal resistances of the battery and the voltmeter.
- 2 Observe that this definition differs from that in VIM, 2<sup>nd</sup> Edition, and some other vocabularies, that define the measurand as the quantity subject to measurement.
- 3 The description of a measurand requires specification of the state of the phenomenon, body, or substance under study.

**measurement procedure:** set of operations, described specifically, used in the performance of particular measurements according to a given method (VIM).

NOTE A measurement procedure is usually recorded in a document that is sometimes itself called a “measurement procedure” (or a **measurement method**) and is usually in sufficient detail to enable an operator to carry out a measurement without additional information.

**method:** a body of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, quantification) systematically presented in the order in which they are to be executed (ANSI/ASQ).

**precision:** the closeness of agreement between independent test results obtained under stipulated conditions (ISO 5725-1).

## NOTES

- 9 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.
- 10 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results. Less precision is reflected by a larger standard deviation.
- 11 “Independent test results” means results obtained in a manner not influenced by any previous result on the same or similar test object. Quantitative measures of precision depend critically on the stipulated conditions.

**procedure:** a specified way to carry out an activity or process (ANSI/ASQ).

**retention efficiency:** in particle separation, the ratio of the quantity of particles retained by a separator to the quantity entering it (generally expressed as a percentage). Ability of a filter to retain particles suspended in a gas or liquid (GACT).

**sample size:** number of items or the quantity of material constituting a sample (ISO 11074-2).

**sample stability:** the capability of a sample material to retain the initial property of a measured constituent for a period of time within specified limits when the sample is stored under defined conditions (QDS).

**standardization:** the process of adjusting instrument output to a previously established calibration; the experimental establishment of the concentration of a reagent solution; correlation of an instrument response to a standard of known accuracy (ASTM).

**systematic error:** mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions minus a true value of the measurand (VIM)

## NOTES

- 1 Systematic error is equal to error minus random error.
- 2 Like true value, systematic error and its causes cannot be completely known.
- 3 For a measuring instrument, see “bias” (VIM).

**trueness:** the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value (ISO 5725-1).

## NOTES

- 3 The measure of trueness is usually expressed in terms of bias.
- 4 Trueness has been referred to as “accuracy of the mean”. This usage is not recommended.

**uncertainty:** a parameter, associated with the result of a measurement, which characterizes the

dispersion of the values that could reasonably be attributed to the measurand (BGUM).

## 8 References

### Cited

1. EPA Science Policy Council, *Peer Review Handbook*, 3<sup>rd</sup> ed.; EPA/100/B-06/002; U.S. Environmental Protection Agency, Office of Science Policy, Office of Research and Development, Washington, DC, December 2006.
2. ASTM D 6232-00. Standard Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Activities, *Annual Book of ASTM Standards*. 2002, (11.04), 456-464.
3. International Organization for Standardization (ISO). *Soil quality - Vocabulary – Part 2: Terms and definition relating to sampling*; ISO 11074-2: 1998, Geneva Switzerland, 1998.

### General

1. Bell, S. *A Beginner's Guide to Uncertainty of Measurement*. Measurement Good Practice Guide No. 11 (Issue 2). 1999.
2. Birch, K. *Estimating Uncertainties in Testing*. Measurement Good Practice Guide No. 36. 2001.

## Appendix A

### Sampling Validation Plan

The sampling validation plan is an integral part of the sampling method and planning documents, and should be included as a section within the plan or as a stand-alone document attached as an appendix. It should integrate the contributions and requirements of all stakeholders and present this information in a clear, concise format. To achieve this goal, validation planning should be part of initial planning (e.g., directed planning process) to assure that the data will be validated efficiently to determine its reliability and technical defensibility in an appropriate context and to an appropriate degree. The information and documentation identified in the validation plans should be communicated to the laboratory as part of the Statement of Work (SOW).

The sampling validation plan must address, but is not limited to, the following information:

1. Purpose of Validation
2. Sampling Procedure, including:
  - a. Description of the main principle of the test method
  - b. Description of test procedures and test conditions (including precautions, reagents, reference and preparation substances)
  - c. Details of equipment and facilities to be used (including measuring/recording equipment) with calibration status
  - d. Variables to be monitored
  - e. Samples to be taken – where, when, how, how many
  - f. Extraction efficiency
  - g. Collection efficiency
  - h. Retention efficiency
  - i. Field and Laboratory QC, including:
    - i. Blanks, equipment rinsate samples, and field duplicates
    - ii. Sample integrity (sample labels, logs, preservation, holding times, sample containers, transportation, etc.)
    - iii. Chain of Custody forms
    - iv. Laboratory QC sample
3. Field Variances
4. Data Validation
5. Performance Characteristics, as listed in this document:
  - a. Selectivity
  - b. Method Uncertainty
  - c. Equipment/Instrument Calibration
  - d. Bias/Trueness
  - e. Detection Capability/Limits
  - f. Method Ruggedness
  - g. Sample Integrity
  - h. Sample Size
6. Time schedules
7. Safety considerations
8. Personnel responsibilities
9. Details of methods for recording and evaluating results, including statistical analysis