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Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments, and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director
National Risk Management Research Laboratory

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ABSTRACT

The U.S. Environmental Protection Agency Office of Resource Conservation and Recovery has initiated the review and validation process for four leaching tests under consideration for inclusion into SW-846:

Method 1313[*] "Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure"

Method 1314[*] "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure"

Method 1315[*] "Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure"

Method 1316[*] "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure"

[*] Method identification numbers are subject to change.

These protocols are derived from published leaching methods contained in the Leaching Environmental Assessment Framework (LEAF), an integrated set of testing methods, data management tools, and report support utilities that can be used to support a wide range of environmental management decisions. The methods comprise a suite of available leaching tests, including batch, column and tank tests, which may be interpreted individually or integrated to provide characteristic leaching behavior of a solid material over a range of potential release scenarios. LEAF also includes tools for visualizing leaching data and significantly facilitating data management through the LeachXS Lite^{TM} expert leaching system software program.

LEAF represents a considerable shift in leaching assessment methodology from current approaches which are typically based on single-point pH tests and not necessarily reflective of management conditions. Thus, this document provides the required background necessary to understand the development, application, and use of these four test methods. The document includes sections on an overview of the leaching process, selection of test parameters, and estimates of the time, material and costs required.

Subsequent reports in this series will focus on (i) the inter-laboratory validation of the LEAF test methods, (ii) the relationship between LEAF testing results and field leaching observations, and (iii) applications of the LEAF testing approach for evaluating use and disposal options of coal combustion residues.

ABBREVIATIONS

CEN	European Committee for Standardization
COPC	Constituent of Potential Concern
DOC	Dissolve Organic Carbon
EC	Electrical Conductivity [mS/cm]
ECN	Energy research Centre of the Netherlands
EPA	United States Environmental Protection Agency
FNU	Formazin Nephelometric Unit
ISO	International Standardization Organization
LEAF	Leaching Environmental Assessment Framework
L/S	Liquid-to-Solid Ratio [mL/g, dry mass basis]
L/A	Liquid-to-Surface Area Ratio [mL/cm^2, geometric surface area basis]
LSP	Liquid-Solid Partitioning
MC	Moisture Content [g water/g wet mass basis]
ORP	Oxidation/Reduction Potential [mV]
PAH	Polycyclic Aromatic Hydrocarbon
pD	Diffusivity [m^2/s] in terms of the negative logarithm (-log[m^2/s])
POM	Particulate Organic Matter
PTFE	Polytetrafloroethylene
RCF	Relative Centrifugal Force
SAB	Science Advisory Board
SC	Solids Content
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total Organic Carbon

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1 INTRODUCTION

The U.S. Environmental Protection Agency (U.S. EPA) Office of Resource Conservation and Recovery has initiated the review and validation process for four leaching tests under consideration for inclusion in its analytical chemistry guidance, SW-846.[1] These protocols are derived from published leaching methods (Kosson et al. 2002) and international standards in various states of development and validation on wastes (CEN/TS 14405 2004; CEN/TS 14429 2005; CEN/TS 14997 2005; CEN/TS 15863 2009), construction products (CEN/TS-2 2009; CEN/TS-3 2009), and soils (ISO/TS 21268-3 2007; ISO/TS 21268-4 2007; ISO/DIS 12782 parts 1-5 2010) with further collaborative development between Vanderbilt University, the Energy research Centre of the Netherlands (ECN) and DHI in Denmark.

The four test methods supported in this document provide the required materials leaching information for the Leaching Environmental Assessment Framework (LEAF). These methods have been used as the basis for evaluation of process variables in the leaching of coal combustion residues (Sanchez et al. 2006; Sanchez et al. 2008; Kosson et al. 2009; Thorneloe et al. 2010); however, broader application of these test methods can be used to estimate constituent leaching from a wide range of solid materials in the context of disposal, beneficial use in construction applications, and evaluation of treatment effectiveness.

LEAF is an integrated set of testing methods, data management and visualization tools, and report support utilities that can be used to support a wide range of environmental management decisions. Within the framework, testing characterizes the leaching behavior of a material under equilibrium and dynamic conditions through the use of a suite of four broad-based test methods including batch, column and tank tests. The results of these tests may be interpreted individually or integrated to provide characteristic leaching behavior of a solid material over a range of potential release scenarios. The methods are applicable to a wide range of solid materials, including combustion residues, soils, sediments, construction materials, industrial process residues, for estimation of constituent release, with a focus to date on inorganics, in the context of disposal, beneficial use in construction applications, and evaluation of treatment effectiveness, and remediation. Data management, comparison of test results to previously characterized materials and report output support is greatly facilitated by the LeachXS Lite™ expert leaching system software program.[2]

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[1] These methods have not been incorporated into, nor endorsed by, SW-846 to date but are in the review and evaluation process.

[2] The development of LeachXS™ Lite is the result of collaboration between EPA, Vanderbilt University, the Energy research Centre of the Netherlands and DHI (Denmark). The LeachXS Lite program, LEAF test methods and data management templates are available free of charge at www.vanderbilt.edu/leaching.

Due to the shift in leaching assessment methodology that these methods represent, this document is intended to provide the background necessary to understand the development basis for the four preliminary versions of methods under consideration for adoption into SW-846. The document includes sections on the selection of test parameters and estimates of the time, materials and costs associated with conducting a full characterization of a solid material.

Preliminary versions of the methods are provided in separate appendices as follows:

Appendix A –*Method 1313*[*] "Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure"

Appendix B – *Method 1314*[*] "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure"

Appendix C – *Method 1315*[*] "Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure"

Appendix D – *Method 1316*[*] "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure"

[*] Method identification numbers are subject to change.

Each test method includes an optional Excel® template for data collection and data transfer into LeachXS Lite.

This report is the first in a series documenting the development, validation and implementation of the four LEAF leaching test methods for providing a source term for the next generation of environmental assessment methodologies. Subsequent reports will focus on (i) the inter-laboratory validation of the LEAF test methods, (ii) the relationship between LEAF testing results and field leaching observations, and (iii) applications of the LEAF testing approach for evaluating use and disposal options of coal combustion residues.

2 LEACHING OVERVIEW

Leaching in an environmental context is the process of constituent transfer from a solid material to a contacting liquid or aqueous phase. The release of constituents is governed by a combination of chemical processes and mass transfer mechanisms based on the chemical composition and physical properties of the solid material along with the pH, redox and composition (i.e., dissolved constituents) of the contacting liquid. Constituents of potential concern (COPCs) may include major mineral components, highly soluble salts, and environmental contaminants. In general, the term "leachability" is used to describe either the extent of leaching or time-dependence of release. In environmental applications, leaching represents the source term for release of potentially hazardous substances. Additionally, leachability also can provide an indication of material durability based on the dissolution and transport of the constituents that comprise the solid matrix.

Figure 1 shows the internal and external factors that influence the extent and rate of leaching in a generic release scenario (Garrabrants and Kosson 2005). Transport of constituents within the material is controlled by physical parameters such as porosity and permeability as well as the mass transport characteristics and equilibrium between the pore solution and solid mineral phases. Although Figure 1 depicts the influences on the leaching behavior of a monolithic product, the same basic principles apply to finer-grained materials in which groundwater contact and leaching occur according to a percolation model.

Equilibrium in the pore solution is determined by the pH of the pore water (primarily for inorganic species), the available content of the constituent in the material, and a series of chemical reactions (e.g., sorption/desorption, precipitation/dissolution, complexation) that are also influenced by redox potential and ionic strength. For many cases, the kinetics of these chemical processes are fast relative to the rate of mass transport (Dijkstra et al. 2006). Therefore, the assumption of local equilibrium is a reasonable approximation of leaching in granular materials or the pore concentration within the core of a monolithic material.

Typically, equilibrium, or liquid-solid partitioning (LSP), is determined on the basis of constituent concentrations as a function of pH or liquid-to-solid ratio; however, equilibrium data may also be reported in terms of the mass of constituent release per unit mass of solid material. The mass transport of species through the pore structure to the bulk solid-liquid interface often is controlled by a combination of local equilibrium and diffusion properties. The rate of mass transport may be reported as mass release per unit surface area of bulk interface with respect to time. Characterization of equilibrium and mass transport properties as leaching parameters provides a fundamental behavioral pattern of the solid material regardless of the release scenario.

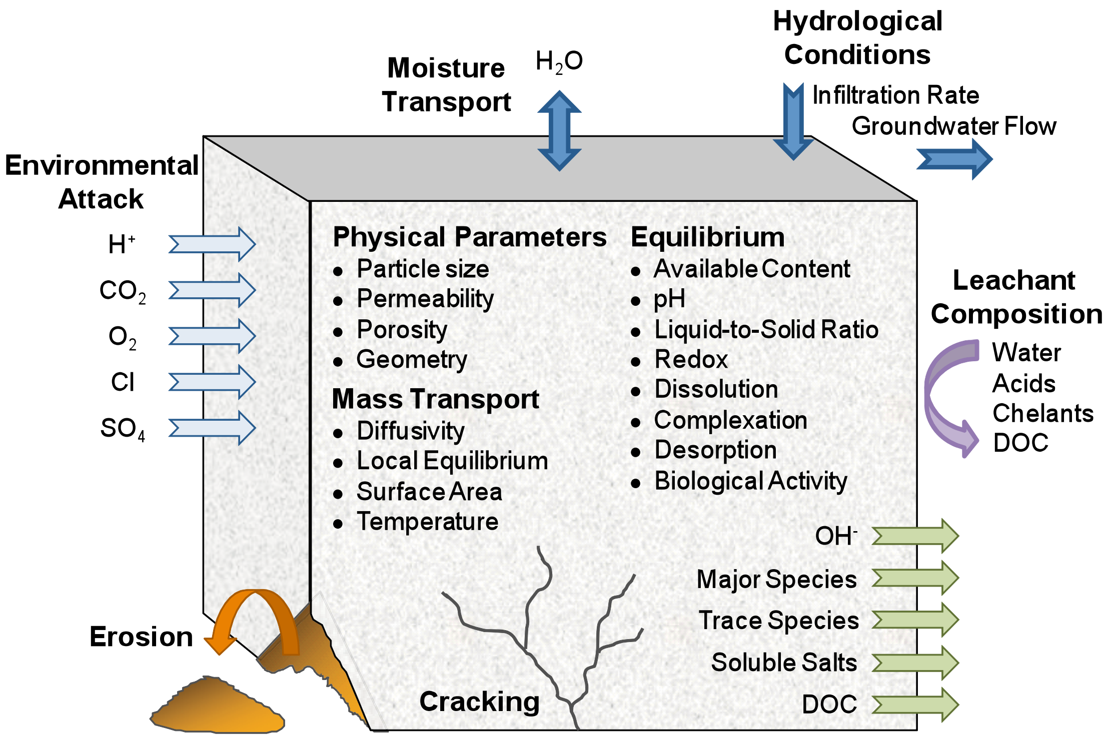

Figure 1. Internal and external factors influencing the leaching process (modified from Garrabrants and Kosson, 2005).

At the material interface, interaction of the solid materials with the surroundings can lead to alteration of the material release behavior. In some cases, reactions with components of the groundwater or subsurface atmosphere may increase release (e.g., through acid attack, erosion, chelation or complexation reactions), while in other cases, release may be reduced (e.g., via precipitates which form boundary layers with reduced transport properties). Many of these external stresses affect both the leaching properties and durability of the material. For example, the composition of the contacting solution, or leachant, has some influence on leaching response. Acids and chelants can interact with the inherent chemistry of the solid phase and alter the LSP of the resultant leachate.

In this document, “solid material” is used as a generic reference to the matrix of concern, regardless of its nature (e.g., monolithic, granular) in the field. “Leachant” and “leachate” are reserved to describe, respectively, the contacting liquid in the natural environment before and after contact with the solid. The associated terms for the contacting fluids used in the laboratory to characterize the release of constituents from solid materials are referred to as “eluent” (before contact) and “eluate” (after contact), respectively. This distinction is made to avoid confusion with field samples during lab-to-field comparisons. Thus, eluents are the liquid phase specified in leaching tests (e.g., *Method 1313* uses dilute acid or base as an eluent) while the eluates that result from a leaching test are processed for chemical analysis.

3 LEACHING ASSESSMENT FRAMEWORK

The leaching test methods presented under LEAF were developed to be part of a tiered assessment methodology that is a more robust, yet flexible, evaluation approach for estimating environmental release, particularly in applications where current regulatory tests are not required (e.g., beneficial use determinations, waste delisting, treatability evaluations, etc.). Under the current regulatory approach, environmental assessment is based on the simulation of release in a defined "mismanagement" or near-surface disposal scenario (U.S. EPA 1988; U.S. EPA 1999a). The source term used in this assessment is described by release estimates for selected metals and organic compounds resulting from single-point extraction tests which have been designed to simulate the release conditions for the assessment scenario. However, the U.S. EPA Science Advisory Board (U.S. EPA 1991; U.S. EPA 1999b; U.S. EPA 2003), the National Academy of Sciences (NRC 2006) and others (Sanchez et al. 2006; Thorneloe et al. 2009) have criticized these leaching methods for a lack of critical data collection (e.g., final pH is not recorded), overly-broad application for materials and scenarios outside the scope of the test design, and limited mechanistic understanding due to the single release observation provided by the test. In addition, the results of these simulation tests are limited to the pre-determined assessment scenarios and are unlikely to address the range of leaching conditions expected occur in actual disposal or reuse situations.

Recognizing the importance of having a robust, mechanistic environmental assessment methodology, U.S. EPA conducted a review of available methods, sought Science Advisory Board input on the suitability of the available leaching test methods, and ultimately selected the tiered assessment published in the literature (Kosson et al. 2002). The series of recommended leaching tests published with this manuscript have become the basis for development of the methods described in this document.

The recommended testing increases in detail and complexity depending on the overall purpose of the leach testing, the amount of leaching mechanism detail needed, and the scenario to be evaluated. In the proposed tiered testing approach, Tier 1 tests provide the least amount of information used for screening purposes. Single batch extractions and modified versions of the characterization tests shown here may be applicable for screening, much as commonly used leach tests provide screening level data. Tier 2 consists of equilibrium-based testing of the material in order to characterize the LSP over a broad range of plausible management conditions as a function of principle chemical leaching factors of pH and liquid-solid ratio (L/S). The pH- and L/S-dependent leaching tests can also be adapted for compliance testing between batches of like materials or against the previous full detail characterizations, or material specific quality control. Equilibrium tests applicable for Tier 2 analysis include *Methods 1313*, *1314*, and *1316*. The addition of mass transfer rate (monolith or compacted granular materials) testing using *Method 1315* completes the assessment approach for a third tier of testing for (a) detailed characterization, (b) compliance testing, and (c) quality control. The test methods and interpretation protocols recommended in LEAF provide an integrated approach for evaluating leaching behavior of materials using a tiered approach that considers pH, liquid-to-solid ratio (L/S), and waste form properties across a range of plausible field conditions (Kosson et al. 2002; Thorneloe et al. 2010).

3.1 LEACHING TESTS

Various leaching methodologies applicable to a wide variety of waste forms have been reviewed (Garrabrants and Kosson 2005) where it was noted that release from solid materials is most often estimated using the results of one or more extraction tests designed to measure COPC leaching from materials. Although more than 50 leaching tests have been identified for various purposes and materials, only a limited number address a range of test conditions. That is, most leach tests currently being used are designed to simulate constituent release under a single set of assumptions. Many of these tests are only loosely related to the environmental conditions under which leaching of the tested material may actually (or plausibly) occur. In addition, many of the tests that do cover a range of conditions differ in only minor ways, inferring that a limited set of carefully selected tests can provide information on constituent leaching over the expected range of possible exposure conditions (van der Sloot et al. 1997).

In general, leaching test approaches have been designed to simulate release under a specific set of experimental conditions (i.e., attempt to mimic field conditions). Another approach is to challenge the waste material to a broad range of experimental conditions known to affect constituent leaching, with the intent to derive characteristic or fundamental intrinsic parameters that control leaching. The latter approach allows one data set to be used to evaluate a range of management scenarios for a material, representing different environmental conditions (e.g., disposal or beneficial use). This approach is both more transparent and flexible for assessing the characteristic leaching behavior from granular and monolithic materials (Kosson et al. 2002; van der Sloot 2002b; van der Sloot 2002a; van der Sloot and Kosson 2007; van der Sloot et al. 2007).

Leaching test methods may be categorized by whether the intent of the method is to establish equilibrium between the material and the leachant (e.g., "equilibrium-based test") or to measure constituent mass transport as a function of leaching time (e.g., "mass transfer-based tests"). Test procedures additionally may be designed as "batch extraction methods" during which a solid material is challenged to one or more aliquots of a leaching solution over a specified time or as "dynamic leaching methods" where fresh leaching solution is continuously supplied and equilibrium between the test material and the leachant is not intended to be achieved.

The methods supported in this document are designed to provide characterization of leaching from a solid material under a broad range of conditions with equilibrium leaching determined as functions of pH and L/S in addition to mass transport determined as a function of leaching time. Of the four methods described in this document, *Methods 1313* and *1316* are batch leaching procedures, while *Method 1314* is a flow-through dynamic (column) leaching method. The fourth procedure, *Method 1315* is a hybrid of batch and dynamic styles where a series of consecutive batch extraction steps are conducted to measure leaching as a function of time, often referred to either as a "diffusion" or "tank leaching" method.

3.1.1 Influence of pH on Equilibrium

Many of the processes that result in leaching of inorganic constituents (e.g., mineral and precipitate dissolution, adsorption/desorption reactions, and aqueous solubility of inorganic species) are strongly pH-dependent. Since inorganic constituents in solid materials may be (i) incorporated within mineral structures (e.g., strontium or barium substituting for calcium), (ii) adsorbed to surfaces of mineral phases such as iron oxy(hydr)oxides or organic matter, (iii) precipitated as low-solubility solids within pore spaces, or (iv) dissolved within the liquid phase held within the pore structure (Connor 1990), pH is considered a principal variable controlling the equilibrium between the liquid and solid phases for many inorganic contaminants. The recommended leaching test for determining the pH-dependence on LSP is *Method 1313*. In addition to pH-dependent partitioning, this method also provides an acid/base titration curve of the material used to estimate the influence of environmental acidity or alkalinity on changes in resulting eluate pH.

Eluate pH does not directly affect the solubility of most organic contaminants which are primarily concentrated in isolated organic phases (e.g., tars and grease) or adsorbed to particulate organic matter (van der Sloot 2002a; van der Sloot 2002b). However, pH does influence the dissolution of particulate organic matter (POM; i.e., humic substances) which may be more soluble at high pH. The measured concentrations of organic contaminants in eluates may be greater than theoretical aqueous solubility values due to binding with dissolved organic carbon (DOC) or colloidal organic matter. In leachates and eluates, DOC is often measured as total organic carbon (TOC) in solution. *Method 1313* is useful to assess the effect of DOC on the eluate concentration of organic species. For example, when soil with high organic content is solidified with Portland cement, an increase in DOC can result in an increase in the measured leaching concentrations of some contaminants (e.g., metals, polycyclic aromatic hydrocarbons or PAHs). Thus, pH may still be considered a significant leaching parameter for organic species.

3.1.2 Influence of Liquid-to-Solid Ratio on Equilibrium

As water percolates through a column of granular or high permeability material, highly soluble salts (e.g., chloride or nitrate salts of sodium or potassium) are washed out quickly and the more soluble mineral phases are dissolved. Changes in pore water chemistry as more soluble components are released can alter the dissolution of the more stable mineral phases and subsequent pore solutions and leaching of COPCs, as infiltrating water continues to percolate. These effects can be examined using either batch or column tests. Column tests allow for careful control of water contact and analysis of aqueous (local) equilibrium as a function of the amount of fluid passing through the bed mass normalized as an L/S. At low L/S, concentrations provide insight into the composition of the initial pore solution; while concentrations at an L/S greater than or equal to 5 mL/g-dry indicate the effects of long-term exposure on LSP. *Method 1314*, a column percolation procedure, and *Method 1316*, a parallel batch procedure, may be useful in determining how the liquid-solid partitioning is affected by changes in L/S.

3.1.3 Influence of Mass Transfer Rates

Release of constituents from larger particles of granular material or other materials of low permeability may be controlled by mass transport of the constituents through the pore structure to the bulk liquid solid interface. This scenario is the case when a low permeability material is surrounded by higher permeability fill. Infiltrating water or groundwater flows around the low permeability material and release occurs at the interface between the flowing water and the material.

Mass transport is often characterized in terms of the mass flux (i.e., mass released across an exposed surface unit area over a unit time, e.g., mg/m^2yr) or in terms of the cumulated mass released as a function of leaching time. Transport parameters (e.g., diffusivity) and physical characteristics (e.g., effective surface area, tortuosity) may be estimated from leaching test results when certain conditions or assumptions are specified. For example, the observed diffusion coefficient of a COPC represents a simple diffusion case applicable only under the assumption that large gradients (e.g., pH) internal to the matrix do not exist. *Method 1315* includes provisions for integrating the results of the mass transport test with the results of equilibrium-based test *Method 1313* to evaluate leaching test quality control. These provisions also help to approximate the mechanisms that control the release of COPCs from monolithic or compacted granular materials under mass transfer conditions. Of course, these mechanisms are in force only as long as the low permeability material maintains its physical integrity. Equilibrium conditions become more significant as monolithic materials physically degrade or if the material is exposed to very low or intermittent flow conditions.

4 METHOD SUMMARIES AND JUSTIFICATION OF TEST PARAMETERS

In the following sections, each proposed method is briefly summarized followed by the rationale supporting the selection of key test conditions specified as part of each method. Extensive review of international assessment methodologies and leaching test parameters has been presented elsewhere (van der Sloot et al. 2010). Specific test conditions may be justified on the basis of the underlying fundamental phenomena, empirical observation (results of prior testing), numerical simulation, or practicality for implementation. Test specifications for the four methods are provided at the end of Section 4 (see Table 5).

4.1 PRELIMINARY VERSION OF METHOD 1313

Method 1313 - "Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure" is a leaching characterization method consisting of parallel extractions of a particle-size reduced solid material in dilute acid or base.

4.1.1 Method Summary

Method 1313 is a batch extraction procedure with parallel extractions designed to provide information on the partitioning of constituents between solid and liquid phases under specified conditions. A mass of "as tested" solid material equivalent to a specified minimum dry mass is added to nine or ten extraction vessels.[3] Solutions of dilute nitric acid or sodium hydroxide are added to each vessel according to a schedule of acid and base additions formulated from a pre-test titration curve and designed to target specific final pH values (eluate pH values) between 2 and 13. Extract bottles are tumbled in an end-over-end fashion for a specified contact time that depends on the particle size of the sample. The extract liquid is separated from the solid phase via settling or centrifugation, followed by filtration and preservation of analytical solutions.

Recorded data includes equivalents of acid or base added, extract final pH and electrical conductivity (EC) with an option for measuring oxidation/reduction potential (ORP) when it is expected to influence leaching. The concentration of DOC is often measured in eluates and the active fraction for binding of metals and organic contaminants can be determined through fractionation of the various organic carbon phases (ISO, 2009). Extract concentrations for the constituents of concern are measured and plotted as a function of extract pH and compared to quality control and assessment limits. This method provides a titration curve of the solid material and the LSP curve for constituents of concern over a broad pH range that both represents the range of possible environmental leaching conditions, and also illustrates any changes in leaching chemistry that may occur over this range of conditions. LSP data as a function of eluate pH may be used with geochemical speciation models to infer the speciation of solubility-controlling mineral phases and reactive surfaces (e.g., metal oxides, clay and organic matter) for COPCs.

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[3] The method requires conducting extractions under natural conditions (i.e., no acid or base addition) as well as at nine final target pH values. However, if the natural pH of the material falls within the acceptable tolerance of any target pH point, the target pH extraction is not conducted.

4.1.2 Constituents of Potential Concern

This method is applicable for inorganic species (e.g., metals, metalloids and ionic salts), non-volatile organic compounds, and DOC. Given that radionuclides behave chemically as inorganic species, the method is also applicable for radionuclides provided that the appropriate modifications are taken to ensure adequate worker protection. Although the method is capable of providing extracts for evaluation of semi-volatile organic species, the premise that pH controls liquid-solid partitioning is not directly applicable to these constituents; however, a secondary effect based on association of certain organic species (e.g., PAHs) with dissolved organic carbon may be observed.

4.1.3 Target pH Values

The specific target pH values are based on environmental or operationally-defined rationale as shown in Table 1 (also provided as Table 5 in the method text). Within LEAF, the natural pH of the material is defined as the eluate pH of a batch extraction of a <5 mm granular sample in regent water at an L/S of 10 mL/g-dry without addition of acid or base. Full characterization under *Method 1313* requires that a set of eluates be produced with final pH values satisfying the nine specified pH targets shown in Table 1.

If the natural pH of the "as tested" material falls within the range of any target interval (e.g., a natural pH of 6.6 falls within the 7.0±0.5 pH range), there is no need to conduct both the natural pH extraction and the targeted pH extraction. In this case, the natural pH extraction is used to represent that pH range and a total of nine parallel extractions would be conducted (i.e., the natural pH extraction plus eight remaining targeted pH extractions). If that natural pH falls outside all specified target ranges (e.g., a natural pH of 6.4), the natural pH extraction is conducted in addition to the nine specified target conditions shown in Table 1 (i.e., ten parallel extractions in total).

These target pH values were selected to standardize the data across the pH profile and to provide input on the response of the material to environmental stresses over a broad range of pH values. While the extremes of the specified values may not be achieved under anticipated field conditions, these values have been selected in order (i) to estimate the fraction of the total COPC content available for leaching (absent long-term changes in mineral form), (ii) to represent values that may occur as a result of co-management of diverse materials, and/or (iii) to facilitate geochemical modeling of the system.

Table 1. Rationale for *Method 1313* Final pH Targets.

Value	pH Target	Rationale
1	2.0±0.5	Estimates total or available content of cationic and amphoteric COPCs
2	4.0±0.5	Lower pH limit of typical management scenario

3	5.5±0.5	Typical lower range of industrial waste landfills
4	7.0±0.5	Neutral pH region; high release of oxyanions
5	8.0±0.5	Approximately endpoint pH of carbonated alkaline materials
6	9.0±0.5	Minimum of LSP curve for some cationic and amphoteric COPCs[4]
7	10.5±0.5	Minimum of LSP curve for some cationic and amphoteric COPCs[4]
8	12.0±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
9	13.0±0.5	Upper bound (field conditions) for amphoteric COPCs
	variable	Natural pH at L/S 10 mL/g-dry (no acid/base addition)[5]

The concentration of COPCs over this pH range defines the partitioning curve between dissolved species and solid phases as a function of eluate pH and may be used to identify how constituent LSP is influenced in environmental scenarios with different characteristic pH values (e.g., co-management with other materials) or when eluate pH varies over time in response to local environmental conditions (e.g., carbonation of alkali materials, acidification processes through oxidation, depletion by leaching of pH controlling constituents from the material). In reporting results, the final pH of the extract must be reported so that leachate concentrations may be associated with the actual final pH measured in the tests, rather than at the target pH value. Leaching at any non-measured pH value can then be estimated by interpolation of the resultant concentration versus pH curve.

4.1.4 Eluent Composition

Method 1313 requires that the final pH of the extract is controlled by addition of dilute acid or base. The intent is that the pH-controlling agent should be completely dissociated under test conditions. Thus, organic acids are not recommended for lowering pH below the natural pH value. In addition, the acid should not significantly interfere with the chemistry of the system. Nitric acid is specified in the method because, although a mild oxidant, it is less interfering than other inorganic acids which cause precipitation (e.g., sulfuric or phosphoric acids) or form complexes (e.g., chloride from hydrochloric acid). While nitric acid is oxidizing and thereby has the potential to provide a biased estimate of leaching for some constituents expected to be disposed or utilized in a reducing system, the potential exists in many environmental scenarios for reducing systems to become oxidized over time.[6] The

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[4] As a whole, the LSP curves for amphoteric and cationic species tend to approach a minimum value in the pH range between about 9 (e.g., lead) and 11 (e.g., cadmium); therefore, pH targets of 9.0±0.5 and 10.5±0.5 can be useful for estimating the minimum of the LSP curve in most cases.

[5] Natural pH has also been referred to as "own pH" in other publications, e.g., U.S. EPA, Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, EPA-600/R-09/151, December 2009.

[6] In order to address the reverse case where oxidized systems are exposed to reducing conditions, geochemical modeling (e.g., using LeachXS™) may be useful.

base specified in the method is sodium hydroxide; although potassium hydroxide may also be used for cases when sodium is a COPC.

4.1.5 Minimum Dry Mass Equivalent

Minimum amounts of material are specified in order to ensure that a representative subsample is used in the leaching test. Since heterogeneities are somewhat dependent on particle size, the minimum sample amount required to be used varies with the particle size of the "as tested" material. The minimum sample mass for each extracted material aliquot is specified at 20 g-dry for material < 0.3 mm, 40 g-dry for material < 2 mm, and 80 g-dry for material < 5 mm. These specifications are expected to result in a representative sample for most materials provided that adequate initial sample mass is sized reduced, if necessary. The sample amount used in testing may be increased, with corresponding scale up of leachant volumes, if sample heterogeneity is determined to be a problem.

The L/S used in leaching tests are based on the dry mass of a solid; however, oven drying the "as received" material to constant mass prior to testing may be impractical and sometimes deleterious to the mineral structure. In such cases where the "as received" material must be dried before testing, air-drying or drying over a nitrogen blanket (e.g., in the case of oxidation or carbonation sensitive materials) to a moisture content that facilitates material handling (e.g., less than 10% wet basis) is recommended. Since the "as tested" material is likely to contain some level of moisture, the required mass of solid materials is specified on basis of a "dry mass equivalent" (i.e., the mass of an "as tested" sample which, if dried to constant mass, would result in the specified dry mass). The dry mass equivalent for a specified value can be calculated if the solids content or moisture content (wet basis) is known, according to the following equation:

$$M_{test} = \frac{M_{dry}}{SC} = \frac{M_{dry}}{(1 - MC_{wet})} \qquad \text{Equation 1}$$

where: M_{test} is the dry mass equivalent of "as tested" solid material [g]

M_{dry} is the mass of dry material specified in method [g-dry]

SC is the solids content of "as tested" material [g-dry/g], and

MC_{wet} is the moisture content (wet basis) of the "as tested" material [g_{H2O}/g]

The specification for the minimum amount of solid material is based on the homogeneity of the sample and the particle size of the test subsample. The minimum dry mass equivalents specifications shown in the method assume that, after particle size reduction and sieve analysis, the solid material has undergone adequate homogenization. Materials which are visually heterogeneous after sample processing may require more mass to achieve an adequate representative subsample.

4.1.6 Particle Size, Liquid-To-Solid Ratio and Contact Time

In batch testing, the time required to approach equilibrium between the liquid and solid phases depends on a relationship that is a function of particle size, liquid-solid ratio and contact time.[7] Thus, the discussion of one parameter must be conducted in context with the others. Since the goal of equilibrium extractions is to achieve a practical approximation of equilibrium between the solid materials and the liquid extraction fluid, the specified contact time should be long enough to allow for the controlling physical and chemical processes (e.g., dissolution and diffusion into the liquid phase) to occur. To reach a practical approximation of equilibrium, the contact time may be adjusted based on either the maximum particle size of the solid sample or L/S.

4.1.6.1 Particle Size Reduction and Maximum Particle Size

Particle size reduction for solid matrices, especially those matrices which are naturally monolithic in nature, is often a topic of debate. During batch testing, constituent diffusion through larger particles may become the rate-limiting mechanism such that particle size reduction of the material prior to testing is necessary. Decreasing the particle size decreases the time required to approximate equilibrium by reducing the diffusional distance that a solute must traverse to the bulk solution, and increases the surface area for interactions between the solid phase and the bulk solution. However, the desire for a prompt response from a leach test must be offset by practicality in terms of the effort required for particle size reduction.

The method of particle size reduction should not alter the chemical or mineral composition of the material. This means that size reduction operations (e.g., crushing, grind, or milling and associated sieving) should not introduce foreign matter to the sample, cause loss of constituents, or excessively alter the temperature of the sample. For environmental assessment purposes, crushing is less likely to alter the LSP behavior of a material than grinding or milling to a fine powder due, in part, to shearing stress and heat development (van der Sloot et al. 2001). In addition, the process should be conducted in a timely manner in order to minimize the potential for interaction with the atmosphere (e.g., oxidation or carbonation). Alternately, particle size reduction may be conducted under a controlled atmosphere, such as a nitrogen-purged in a glove box, but this is not always practical.

Method 1313 allows selection from three specified maximum particle sizes with associated minimum sample sizes and minimum contact times. Unless it is impractical to do so, all “as received” material to be tested should be size reduced to a maximum of 5 mm diameter. This provides an “as tested” sample at the largest allowable particle size. The portion of “as received” material that is not readily size reduced to less than 5 mm by crushing is discarded

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[7] The contact time to reach equilibrium also is a factor of temperature and the fraction of the total or available constituent content in the solid that is soluble at equilibrium (see Contact Time).

after calculating the mass fraction of the greater than 5 mm and documenting the nature (e.g., rocks, sticks, glass, etc.) and approximate particle size of the discarded fraction. Test results are not corrected to account for the discarded mass.[8] Batch extraction at this level of particle size reduction requires 72 hours of contact time; however, shorter contact times may be used when further particle size reduction to 2 mm or 0.3 mm is employed. During the particle size reduction process, it is likely and unavoidable that a distribution of particle sizes will result rather than a single particle size. Thus, the recommended contact time to be used in *Method 1313* should correspond to the particle size for which 85 wt% of the "as tested" sample passes the specified sieve size (see Contact Time).

4.1.6.2 Liquid-To-Solid Ratio

L/S is defined as the volume of extracting fluid relative to the mass of solid. For batch tests designed to approximate equilibrium, lower values of L/S reduce the amount of constituent mass that is required to saturate the liquid phase and, thus, decreases the time required to reach equilibrium. Although the L/S for fully saturated porous field material (e.g., soils, wastes, cementitious materials) can be significantly less than 1.0 mL/g-dry, it is not practical to routinely work in the laboratory setting with solid slurries which result from batch extraction at very low L/S. At high L/S, differences in eluate concentrations from a similar method at a standard L/S of 10 mL/g-dry and a modified L/S of 100 mL/g-dry were explained based on either availability or solubility controlled release (Dijkstra et al. 2008).[9] In order to provide a standardized L/S value for batch testing, *Method 1313* specifies an L/S of 10 mL/g-dry which provides balance between practicality[10] and time required to approach equilibrium. In addition, an L/S of 10 mL/g-dry is a reasonable value for extended leaching interval in the field, such that observed released masses of COPCs from leaching tests can be used to estimate field behavior.

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[8] By excluding the mass fraction with particle size greater than 5 mm, some bias may be introduced. However, irreducible particles are often not the driver for environmental assessment. In addition, particle size reduction is considered to correlate, to some degree, with durability in use. Therefore, it is unlikely that application conditions would result in significant particle size reduction to < 5 mm for materials an irreducible mass fraction of greater than 20%. For these materials, other leaching tests (e.g., Method 1314 in a large diameter column or Method 1315) may be a more appropriate approach to leaching characterization.

[9] In this context, "availability-controlled" release means that the release is limited to the total amount of a constituent in the solid phase that is available for release under the specified conditions. "Solubility-controlled" release refers to situations where the release of a constituent is consistent with the solubility as a function of pH under the specified conditions. For each constituent, the resultant extract concentration under availability-controlled release is higher than or equal to the solubility-controlled release concentration.

[10] Within the context of L/S ratio, "practicality" refers to reasonable expectations of handling solid-liquid slurries such that a minimum amount of eluate can be expected after filtration.

4.1.6.3 Contact Time

In equilibrium-based leaching tests, the duration of the extraction is set such that the mass transfer rate does not limit release into the liquid phase. The minimum contact time for batch testing of particle size reduced material is based on the minimum mass transport time to reach a fractional equilibrium concentration in a bath of fixed volume surrounding a spherical particle of a particular diameter (Garrabrants 1997). The numerical solution for diffusion of a constituent through a spherical particle of diameter 2a into a finite bath as (Crank 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\,\alpha\,(\alpha+1)\exp\left(-D\,q_n^2\,t/a^2\right)}{9+9\,\alpha+q_n^2\,\alpha^2} \qquad \text{Equation 2}$$

where M_t is the mass release from a sphere at time t [mg]

M_∞ is the mass release at infinite time (i.e., equilibrium condition) [mg]

D is the observed diffusion coefficient [m^2/s]

a is the spherical radius [m]

q_n is the non-zero roots of the relation;

$$\tan(q_n) = \frac{3\,q_n}{3+\alpha\,q_n^2} \qquad \text{Equation 3}$$

where α is the ratio of the volumes of the solution and the sphere [-].

The factional solubility (i.e., the fraction of the available mass that is soluble at equilibrium) can be expressed as a function of the parameter α as:

$$\frac{M_\infty}{M_0} = \frac{1}{1+1/\alpha} \qquad \text{Equation 4}$$

where M_0 is the initial available constituent mass in the sphere [mg].

Figure 2 shows a nomagraph of the contact time required to establish 90% of the equilibrium (vertical axis) in the fixed bath as functions of particle diameter (horizontal axis) and fractional solubility (diagonal axis, not shown). The fractional solubility is defined as the fraction of the available content that is soluble at equilibrium. In the figure, the observed diffusivity of the transporting species is constant at 10^{-13} m^2/s, which is a relatively slow rate of diffusion based on past observations (sodium free diffusion in water is on the order of 10^{-9} m^2/s while diffusion through concrete may be on the order of 10^{-12} m^2/s).

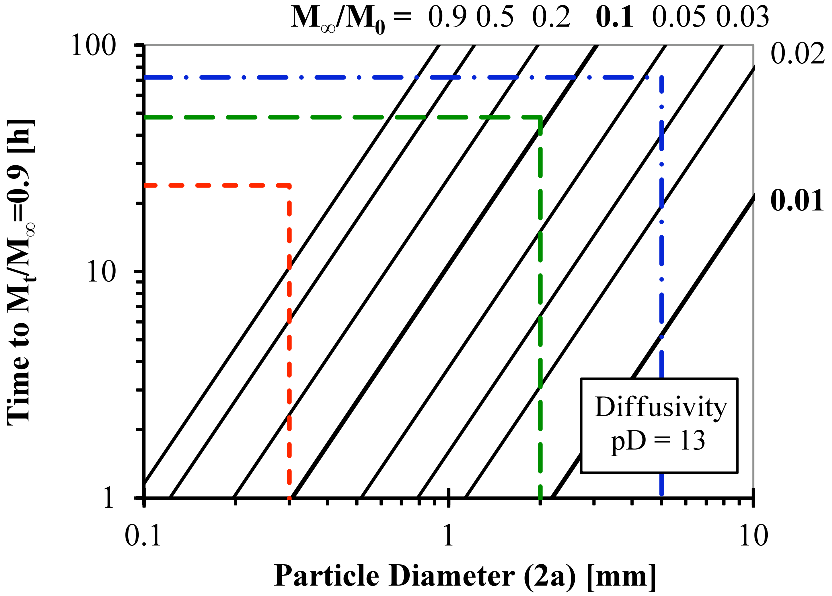

Figure 2. Contact time required for a species with an observed diffusivity of 10^{-13} m^2/s to reach 90% of equilibrium ($M_t/M_\infty = 0.9$) based on mass transport as functions of particle diameter and fractional solubility (M_∞/M_0). Figure modified from Garrabrants, 1997.

The red, short-dashed lines in Figure 2 indicate that spherical particles of 0.3 mm establish 90% of theoretical equilibrium in less than 24 hours regardless of the fractional solubility value. Over a 48-hour period (green, long-dashed lines), 90% of equilibrium can be approached for particles of 2 mm if the fractional solubility is less than 0.1 (i.e., less than 10% of the total or available content is soluble in the fixed bath at infinite time). A 72-hour contact time (blue, dot-dash lines) would allow for particles of 5 mm diameters to approach 90% of equilibrium for fractional solubility values of less than approximately 0.4.

The above caveats with regard to fraction solubility are reasonable for most inorganic species because the more soluble species (e.g., sodium, boron) would likely have higher observed diffusion coefficients and, thus, would not be limited by mass transport through the particle over the test duration.

A similar approach can be used in conjunction with Figure 3 to examine the effect of diffusivity on the horizontal axis, in this case shown as the negative log of the diffusion coefficient (pD), on the time required to reach 90% of equilibrium on the vertical axis as a function of fractional solubility on the diagonal axis (not shown) for a spherical particle of 0.3 mm diameter. The 24-hour test duration specified in *Method 1313* would allow 0.3 mm diameter particles to approach 90% of equilibrium for fractional solubility less than 0.2 for constituents with a mid-range diffusivity of 10^{-14} m2/s (pD=14; green, long dash line) and for fractional solubility less that only 0.01 for constituents with a very low diffusivity of 10^{-16} m^2/s (pD=16; blue, dot-dash line).

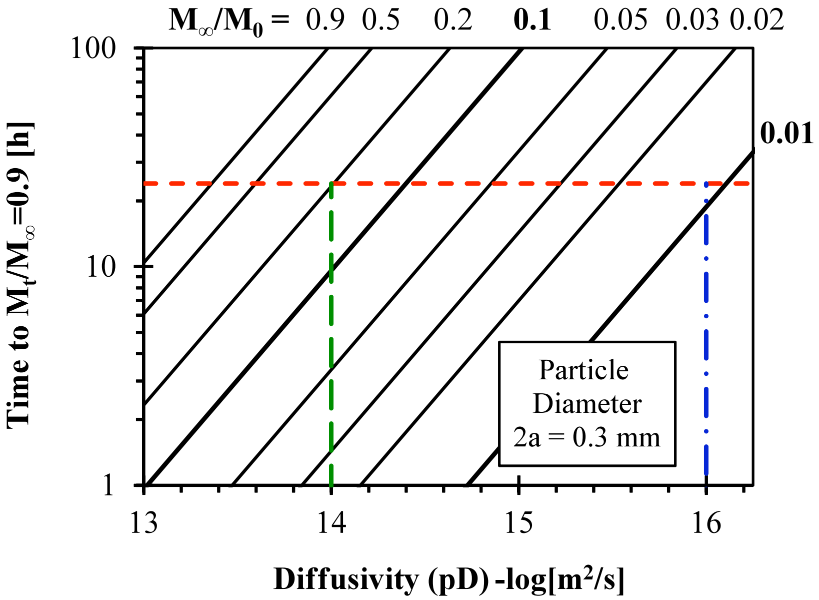

Figure 3. Contact time required for a particle of 0.3 mm diameter to reach 90% of equilibrium ($M_t/M_\infty = 0.9$) as function of diffusivity and fractional solubility (M_∞/M_0). Figure modified from Garrabrants, 1997.

Based, in part, on the analysis of mass transport from a spherical particle into a bath of fixed volume, the specifications for contact time as a function of particle size shown in Table 2 were established.

Table 2. Extraction parameters as function of maximum particle size.

Particle Size (85 wt% less than) [mm]	US Sieve Size	Minimum Dry Mass [g-dry]	Contact Time [hr]	Suggested Vessel Size [mL]
0.3	50	20±0.02	24±2	250
2.0	10	40±0.02	48±2	500
5.0	4	80±0.02	72±2	1000

The above time estimates are based entirely on mass transport considerations assuming that (i) the diffusing species is readily available for mass transport (i.e., dissolution is not rate-limiting) and (ii) the solid phase concentration of the species at the center of the particle is constant (e.g., the species does not deplete). The latter assumption is most likely valid for most solid materials given the relatively low liquid-to-solid ratio. The former assumption that dissolution is not kinetically controlled is not valid for all species (e.g., iron oxide dissolution) and could result in longer required test durations (Dijkstra et al. 2006). The resultant specifications provided in

Table 2 also consider practicality in striking that balance between test duration and increasing effort required for further particle size reduction.

4.1.7 Temperature

All test activities are conducted at 21±2 °C which is assumed to be consistent with room temperature in most laboratories with environmental control. Deviations in temperature of more than approximately 5 °C may result in changes in constituent concentrations such that comparison of test results to tests conducted within specification may be misleading.

4.1.8 Agitation

Method 1313 specifies "end-over-end" tumbling as the method of agitation. This method provides adequate contact between solid and liquid phases as gravity maximizes dispersion of particles. Other methods of agitation (e.g., rolling, linear or orbital shaking) allow for settling and the formation of a consolidated slurry phase with minimum solid-liquid contact area. The rate of agitation is selected to be 30±2 RPM in order to be consistent with commercially available tumbling apparatuses and equipment in place for currently standardized methods (e.g., TCLP).

4.1.9 Filtration

In order to process leaching test solid-liquid mixtures for analysis, the bulk solid and liquid phases must be separated. Coarse separation may be accomplished with settling for 10-15 minutes or centrifugation at an average relative centrifugal force (RCF) of 1,500±100 g for 10±2 minutes. Fine separation for preparation of analytical solutions typically requires filtration. *Method 1313* specifies filtration of solutions for inorganic analysis through 0.45-um polypropylene membranes. The pore size allows for filtration of fine suspended particles consistent with the definition of dissolved metals (Csuros and Csuros 2002). Polypropylene membranes are specified to minimize adsorption of inorganic species onto the filtration membrane. The filtration step can be conducted under vacuum or pressure with an inert gas, although pressure filtration is required if mercury is a COPC.

4.2 PRELIMINARY VERSION OF METHOD 1314

Method 1314 - "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials Using an Up-Flow Percolation Column Procedure" is a leaching characterization test consisting of continuous flow of eluent through a column of moderately packed granular material.

4.2.1 Method Summary

A solid material is packed[11] into a 5 cm diameter by 30 cm long glass column fitted with polytetrafloroethylene (PTFE) end caps. Deionized water or 1 mM calcium chloride as an eluent is introduced in an up-flow pumping mode and a series of nine sequential eluate samples are collected over specific L/S intervals. Up-flow pumping is used to minimize air entrainment and flow channeling. The default eluent for most materials is reagent water; however, a solution of 1 mM calcium chloride in reagent water is specified when testing materials with either a high clay content or high organic matter to prevent deflocculation and colloid formation from clay and POM aggregates from depletion of divalent cations. *Method 1314* is intended to characterize the equilibrium between solid and liquid phases as soluble species are eluted, so the eluate flow rate is maintained between 0.5-1.0 LS/day to increase the likelihood of local equilibrium. An elution rate of 0.75 L/S per day also provides a liquid phase mean residence time for flow through the column that is equivalent to the contact time for batch testing (i.e., *Methods 1313* and *1316*). The pH and conductivity of collected eluate fractions is recorded and analytical samples are filtered, preserved (as appropriate to specific chemical analyses) and chemically analyzed for COPCs.

Eluate data is plotted as a function of L/S. For the purposes of chemical speciation modeling, the entire eluent volume up to 10 mL/g dry sample (g-dry) is analyzed in nine specific fractions. Options are included for applications where less detailed leaching information is required (see Section 4.2.12). These options include compositing collected eluate fractions to form a subset of analytical samples or collected of a limited subset of eluents fractions for analysis.

4.2.2 Particle Size

Accumulated experience from multiple applications for packed bed flow systems has resulted in the generally accepted relationship that the minimum column diameter should be at least 20 times the nominal material particle size to minimize wall effects and channeling. Using this approximation, the calculated maximum particle size for the 4.8-cm inside diameter column described in method is 2.4-mm. In order to provide consistency in sample

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[11] Packing should not inhibit the flow of eluent, but should allow eluent to pass through the packed material.

preparation between the column test and mid-level particle size reduction in the batch testing, the value can be reduced slightly to 2 mm without effecting flow properties.

Since it is unavoidable that a distribution of particle sizes will result from any particle size reduction technique, the criteria for the particle size specification in *Method 1314* is based on at least 85 wt% of the "as tested" material passing a sieve at the specified particle size. Thus, the particle size is specified as 85 wt% less than 2-mm diameter with a maximum particle diameter of 5 mm (1/10 the column diameter).

As described in batch testing, all "as received" material intended for column testing should be particle size reduced to 5 mm unless it is impractical to do so. This process provides an "as tested" sample at the largest allowable particle size. The portion of "as received" material that is not readily size reduced to less than 5 mm by crushing is discarded after calculating the mass fraction of the greater than 5 mm and documenting the nature (e.g., rocks, sticks, glass, etc.) and approximate particle size of the discarded fraction. Test results are not corrected to account for the discarded mass.[12] The mass passing the 5 mm sieve is further particle size reduced until at least 85 wt% is less than 2 mm to provide the final "as tested" material sample.

The specification for particle size reduction in the *Method 1314* column test is a minor modification from the 80% less than 1/20 of column diameter suggested after ruggedness testing of DIN 19528 column test during the *Sickerwasserprognose* (leachate forecast) program conducted in Germany (Grathwohl and Susset 2009; Susset and Grathwohl 2009; Susset et al. 2009), that allows for consistency in material preparation with the batch methods (i.e., *Method 1313* and *Method 1316*).

4.2.3 Constituents of Potential Concern

Method 1314 is applicable for inorganic species (e.g., metals, metalloids and ionic salts), non-volatile organic contaminants and DOC. Given that radionuclides behave chemically as inorganic species, the method is also applicable for radionuclides provided that the appropriate modifications are taken to ensure adequate worker protection. Although the method is capable of providing extracts for evaluation of semi-volatile organic species (e.g., PAHs), the materials of construction for the column, seals and tubing must be modified to minimize adsorption (i.e., stainless steel and glass are preferable construction materials over most plastics, rubber and PTFE).

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[12] By excluding the mass fraction with particle size greater than 5 mm, some bias may be introduced. However, irreducible particles are often not the driver for environmental assessment. In addition, particle size reduction is considered to correlate, to some degree, with durability in use. Therefore, it is unlikely that application conditions would result in significant particle size reduction to < 5 mm for materials an irreducible mass fraction of greater than 20%.

4.2.4 Eluent Composition

In general, regent-grade water is used in all characterization tests due to minimal interference with the chemistry of the extraction or elution. However, in cases where clayey materials or materials with high organic content are tested, a dilute 1 mM solution of calcium chloride is specified. Dilute calcium chloride minimizes disaggregation of clays and dissolution of organic matter that can lead to colloid formation and either obstruction of column flow via plugging in self-filtering materials or washout of very fine particles from the column. The use of 1 mM calcium chloride as a leaching solution also is reasonable in the context that infiltrating water under most field conditions is likely to contain dilute concentrations of divalent cations (Wolt 1994).

4.2.5 Minimum Column Dimensions

The minimum column dimensions are specified as 4.8 cm in diameter and 30-cm long. The volume contained in a column of these dimensions ensures the use of a minimum subsample that is representative of the solid material. In addition, these dimensions and subsample amounts provide adequate analytical sample at the lowest L/S of 0.2 mL/g-dry. This volume of liquid collected in any fraction *i* can be calculated using Equation 5.

$$V_i^{LS} = LS_i * M_{test} * SC \qquad \text{Equation 5}$$

where V_i^{LS} is the volume collected for fraction *i* [mL],

LS_i is the L/S of fraction *i* [mL/g-dry],

M_{test} is the mass of the "as tested" solid material in the column [g], and

SC is the solid content of the "as tested" material [g-dry/g].

4.2.6 Solids Packing

Method 1314 specifies that granular materials should be packed into the columns in approximately 5-cm layers with light tapping or tamping for each layer. This method is intended to minimize subsidence or excessive settling in the column while maintaining flow.

4.2.7 Sand Layers

Method 1314 specifies a 1-cm layer of clean quartz sand (20-30 mesh) placed at top and bottom of the column packing. The top sand layer provides coarse filtration of the eluate and the layer thickness should be maintained as specified. The thickness specification for the bottom sand layer, which serves as bed support and an eluent distribution layer, may be considered a minimum value and the sand layer thickness may be adjusted to modify bed volume of the tested material as necessary. The *Method 1314* sand layer thickness and grain size specifications are approximately consistent with the German *Sickerwasserprognose* program which recommends a 1-cm maximum filtration bed of 1-2 mm grain size quartz sand (Kalbe et al. 2007). The sand layers in both analyses are expected to provide bed support and coarse filtration without significant flow restriction.

4.2.8 Pre-Equilibration

Pre-equilibration of a saturated column is required to ensure that the first eluate fraction is in equilibrium with the solid material. Ruggedness testing of a European column test, CEN/TS 14405, indicates that the pre-equilibration of column material should be a minimum of 18 hours and up to 72 hours (van der Sloot et al. 2010). These specifications were determined by the concentrations of constituent in the first eluate fraction with different pre-equilibration times. Thus, pre-equilibration for overnight and weekend durations are both technically justified and practical.

4.2.9 Flow Rate

In *Method 1314*, a flow rate specification of 0.75±0.25 LS/day is set such that the residence time will be between 0.5 and 1 day in the specified column (i.e., 4.8-cm diameter x 30 cm bed length) with a solid mass of 500-g-dry material packed at a bed porosity of 40%. An estimate of bed porosity for packed columns may be made by weighing the entire column apparatus before and after initial saturation with eluent and calculating the volume of water retained in the bed as a fraction of the total bed volume.

Flow rate may be calculated using the formula:

$$F = \frac{\varepsilon \left[\pi \left(\frac{d}{2} \right)^2 h \right]}{M_{bed} \cdot T_{res}} \qquad \text{Equation 6}$$

Where T_{res} is the residence time in the column [day],

ε is the bed porosity [volume of pores/volume of bed],

d is the bed or column diameter [cm]

h is the bed or column height [cm]

M_{bed} is the dry mass of the bed [g-dry], and

F is the flow rate [LS/day].

Assuming a final L/S of 10 mL/g-dry with eluent flowing at 0.75 L/S per day, the total test time is approximately 14 days. Ruggedness testing for the *Sickerwasserprognose* program required that eluate flow rate be calculated based on bed properties and average contact or residence time. The mean residence time during the testing phases was 16±1 hours (Kalbe et al. 2007; Kalbe et al. 2009; Susset and Grathwohl 2009). The flow rate specification in *Method 1314* should result in a slightly longer residence time than indicated in the German ruggedness testing in order to ensure that local equilibrium has been established. Local equilibrium may be confirmed by comparing the concentration vs. L/S data between two columns prepared in the same manner, but with significantly different flow rates (e.g., 0.5 and 1.0 L/S per day). An option for a faster flow rate is available if local equilibrium conditions during the test can be demonstrated.

4.2.10 Temperature

All test activities are conducted at 21±2 °C which is assumed to be consistent with room temperature in most laboratories with environmental control. Deviations in temperature of more than approximately 5 °C may result in changes in constituent concentrations such that comparison of test results to tests conducted within specification may be misleading.

4.2.11 Filtration and Centrifugation

While eluates in the column test are filtered to some degree through the sand layer at the top of the column, analytical samples with turbidity greater than 100 Formazin Nephelometric Units (FNUs) may result in poor analysis. Typically, solutions with high turbidity may be clarified through a combination of filtration and centrifugation. *Method 1314* specifies filtration of solutions for inorganic analysis through 0.45-um polypropylene membranes for all eluates, consistent with recommendations stemming from ruggedness testing of a proposed German column test DIN 19528 (Susset and Grathwohl 2009). Polypropylene membranes are specified in *Method 1314* in order to minimize adsorption of inorganic species onto the filtration membrane. Eluates prepared for analysis of organic compounds should not undergo supplemental membrane filtration. The *Sickerwasserprognose* program noted significant membrane filtration artifacts and recommended that solutions for organics analysis not be filtered as there are no suitable membrane materials (Susset and Grathwohl 2009). In addition, organic solutions were found to display artifacts of centrifugation such that centrifugation should be limited to only those cases where turbidity is greater than 100 FNUs (Susset and Grathwohl 2009). In *Method 1314*, centrifugation may be required to facilitate filtration of high turbidity eluates; however, the use of calcium chloride as an eluent is intended to reduce turbidity by minimizing colloid formation. The filtration step can be conducted under vacuum or pressure with an inert gas, although pressure filtration is specified if mercury is a COPC.

4.2.12 Eluate Collection and Compositing for Analytical Samples

Eluates are collected over nine fractions at pre-determined cumulative L/S of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10 mL/g-dry. These intervals have been specified in order to allow for three different levels of analysis: complete characterization, limited analysis and index testing. The number of chemical analyses for the limited analysis and index testing levels is reduced through the creation of eluate composites or combinations of eluate fractions (see

Method 1314 Section 12.5 and *Method 1314*, Table 1 for details on compositing). Regardless of the level of analysis, all eluate fractions should be collected to facilitate uniformity in sample collection and column operation for the method. Having all eluate fractions collected also provides a source of analytical solutions should a more detailed analytical scheme be warranted following review of limited analysis or index testing schemes.

4.2.12.1 Complete Characterization

For purposes of developing a comprehensive characterization of the solid material, all eluate samples should be processed for analysis. Results may be shown as a function of L/S for eluate fraction concentrations (see *Method 1314*, Figure 4) or cumulative release, i.e., total mass released up to an L/S (see *Method 1314*, Figure 5). No compositing of eluate fractions is performed for complete characterization, and all eluate fractions are analyzed (see *Method 1314* Table 1, Option A). Eluate concentrations from complete characterization may be used in conjunction with information regarding environmental management scenarios to estimate anticipated leaching concentrations, release rates, and extents of release for individual material constituents in the management scenarios evaluated. In addition, eluate concentrations may be used along with geochemical speciation modeling to infer the mineral phases and partitioning processes that control the LSP in the pore structure of the solid material (van der Sloot and Kosson 2007; van der Sloot et al. 2008).

4.2.12.2 Limited Analysis

Under a limited analysis approach, nine eluate collections and analysis of six analytical samples are required. If evaluation is based on eluate concentrations, six discrete eluate fractions are chemically analyzed (see *Method 1314* Table 1, Option B). If evaluation is based on cumulative release, some eluate fractions may be composited by volume-weighted averaging to create a set of six analytical samples (see *Method 1314* Table 1, Option C). The results of *Method 1314*, Option C cannot be interpreted on the basis of eluate fraction concentrations as the LS fraction structure is not preserved upon solution compositing.

4.2.12.3 Index Testing

For the determination of consistency between the subject material and previously characterized materials, nine eluate collections and analysis of three analytical samples are required. If consistency is to be determined by eluate concentrations, three discrete eluate fractions are chemically analyzed (see *Method 1314* Table 1, Option D). If consistency is to be determined by cumulative release, some eluate fractions are composited by volume-weighted averaging to create a set of three analytical samples (see *Method 1314* Table 1, Option E). The results of *Method 1314*, Option E cannot be interpreted on the basis of eluate fraction concentrations as the L/S fraction structure is not preserved upon solution compositing.

4.3 PRELIMINARY VERSION OF METHOD 1315

Method 1315 - “Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-dynamic Tank Leaching Procedure” is a leaching characterization procedure consisting of continuous emersion of a monolithic or compacted granular material in reagent water at a specified liquid-to-surface area ratio (L/A).

4.3.1 Method Summary

This tank leaching method provides information on the rate of mass transport of constituents through a monolithic or compacted granular sample. Monolithic samples may be cylinders or parallelepipeds, while granular materials are compacted into cylindrical molds at optimum moisture content using Proctor compaction effort. The test sample is moved through a series of nine eluent-filled tanks of fresh reagent water at L/A ratio of 9±1 mL/cm^2 following a schedule of pre-determined test intervals. For each exchange, the sample is freely drained and the mass is recorded to monitor the amount of eluent absorbed into the solid matrix. The eluate pH and specific conductance is measured for each time interval and analytical samples are collected and preserved accordingly based on the subsequent analytical methods.

The outcome of *Method 1315* is nine eluate solutions comprising a set of mass transfer leaching data. Eluate pH, conductivity, and analyte concentrations are plotted as a function of time and compared to internal and external quality control data (see *Method 1315*, Figure 8). Mean interval flux (see *Method 1315*, Figure 10) and cumulative release (see *Method 1315*, Figure 12) are calculated based on eluate concentrations and plotted as a function of time. These data may be used to estimate constituent mass transfer parameters (i.e., observed diffusivity, tortuosity).

4.3.2 Constituents of Potential Concern

This method is applicable for inorganic species (e.g., metals, metalloids and ionic salts), non-volatile organic compounds and DOC. In that radionuclides behave chemically as inorganic species, the method is also applicable for radionuclides given the appropriate modifications to provide adequate worker protection. The method also is adequate for characterization of mass transport for non-volatile organic species (e.g., dissolved organic carbon). However, *Method 1315* is not recommended for characterization of leaching for volatile and semi-volatile species due to low aqueous solubility of organic compounds and the high probability of volatilization losses over the extended leaching intervals. When mercury is a COPC, *Method 1315* is applicable as long as provisions are taken to ensure a sealed leaching vessel with minimal headspace in order to minimize losses due to volatilization.

4.3.3 Sample Preparation and Geometry

Monolithic samples are cut or cored from larger samples or molded to size. Compacted granular samples are compacted at optimum moisture content using either standard or modified Proctor compaction effort depending on the material field density and workability.

The specimen size is subject to a minimum dimension specified to ensure that depletion of COPCs does not occur over the duration of the test. For homogenous monolithic materials (e.g., cement mortars), a minimum specimen dimension of 4 cm is adequate; however, up to 10 or 20 cm might be required in some cases (e.g., concrete containing coarse aggregate) to obtain a representative sample.

Depletion depth may be estimated as a function of observed diffusion coefficient by iteration of the equation for mass transport through a semi-infinite media into an infinite bath (Crank, 1975):

$$\frac{C(x,t)-C_s}{C_o-C_s} = \operatorname{erf}\left(\frac{x}{2\sqrt{D\cdot t}}\right) \qquad \text{Equation 7}$$

where $C(x,t)$ is the time and spatial variant mass concentration in the media [mg/L],

C_s is the constant surface mass concentration [mg/L],

C_o is the initial mass concentration in the media [mg/L],

x is the penetration depth into the sample [cm],

D is the observed diffusion coefficient of a diffusing species [m^2/s], and

t is the leaching time [s].

The assumptions of the semi-infinite diffusion model are that (i) the source term is constant (i.e., depletion does not occur), (ii) the diffusion coefficient is constant, and (iii) the concentration in the leaching fluid is low enough that the driving force for diffusion remains high (i.e., infinite bath). While this model has limitations on a practical basis due to the above assumptions, it can be used to parameterize the depletion depth as a function of diffusion coefficient.[13]

The left hand side of Equation 7 provides the ratio of the remaining concentration in the media to the initial concentration when the surface concentration is zero (C_s=0). This ratio can be set to 80% such that depletion is defined when 20% of the mass has been removed.

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[13] The assumption of an infinite bath results in estimated depth of depletion due to leaching that is conservative (i.e., biased towards greater depth). The test case specified in the method has a relatively large, but finite, bath designed to maintain a dilute, but not zero concentration, boundary condition during test conditions.

Figure 4 shows the mass fraction remaining, $C(x,t)/C_o$ as a function of depth into a semi-infinite media at the end a leaching interval consistent with the 63-day duration of *Method 1315*.

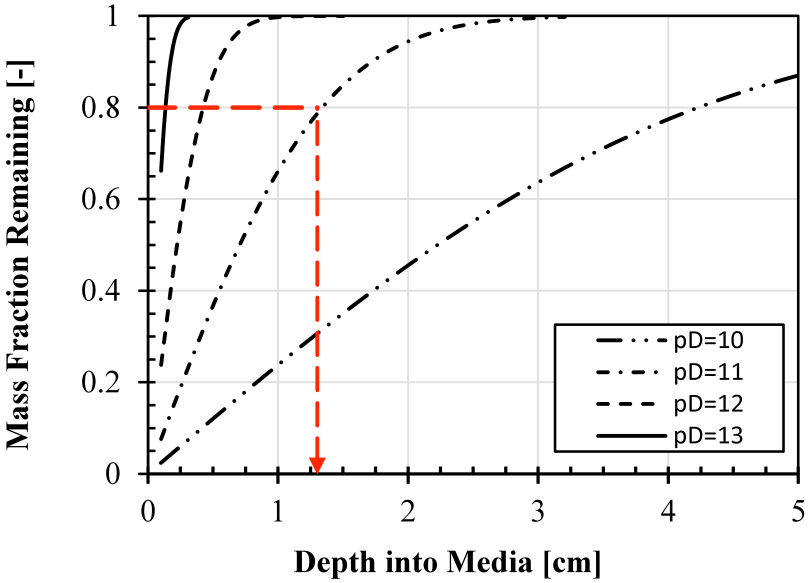

Figure 4. Evaluation of depth of depletion $C(x,t)/C_o$=0.8 as a function of diffusion coefficient (pD is the negative logarithm of the diffusion coefficient).

Four data series are shown spanning the range of diffusivity[14] from very quick (pD=10) to moderately slow (pD=13) diffusion. The range of diffusivity observed in tank leach tests of a broad range of waste materials is $11 < pD < 15$; thus pD=11 represents a reasonable case for a highly mobile constituent. The red dashed line shows that the maximum depletion depth set at $C(x,t)/C_o = 0.8$ is approximately 1.3 cm. Doubling this depletion depth to account for three dimensional leaching, 2.6 cm minimum depletion distance is well within the minimum sample dimension of 4 cm specified in *Method 1315*.

4.3.4 Eluent Composition

In general, regent-grade water is used in all characterization tests due to minimal interference with the chemistry of the extraction or elution. However, in cases where clayey materials or materials with high organic content are tested, a dilute 1 mM solution of calcium chloride is specified. Dilute calcium chloride will minimize disaggregation of clays and dissolution of organic matter that can lead to colloid formation. Use of 1 mM calcium chloride also is

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[14] In this report, diffusivities (D) are indicated in units of [m^2/s], and therefore pD values have units of –log[m^2/s].

reasonable in the context that infiltrating water under most field conditions will contain dilute concentrations of divalent cations.

4.3.5 Liquid-To-Surface Area Ratio

This method specifies a volume of eluent for each step in the tank leaching process based on the exposed surface area of the sample. The exposed surface area for compacted granular materials is equal to the cross sectional area of the mold. For 3-dimensional (3-D) diffusion from monolithic samples, the exposed surface area for cylinders and parallelepipeds may be calculated using following expressions:

$$A_{cyl} = 2\,\pi\,r\,(r + h) \qquad \text{Equation 8}$$

$$A_p = 2\,(h \cdot w) + 2\,(w \cdot l) + 2\,(l \cdot h) \qquad \text{Equation 9}$$

where A_{cyl} and A_p are exposed surface areas of a cylinder and parallelepiped, respectively [cm^2],

r is the radius of the cylinder [cm],

h is the height of the cylinder or parallelepiped [cm],

w is the width of a parallelepiped [cm], and

l is the length of a parallelepiped [cm].

A L/A ratio of 9±1 mL/cm^2, as specified in *Method 1315*, ensures a relatively large, but finite, bath such that the driving force for diffusion is maintained while allowing for eluate concentrations consistent with common analytical methods.

4.3.6 Tank-Sample Geometry

The extraction vessel surrounding the sample (i.e., the "tank" of the tank leaching test) should be sized such that the bulk of the leaching fluid is in contact with the exposed surface area of the sample. There should be at least 2 cm of clearance between the sample surface and the tank wall to ensure enough rapid diffusion from the sample surface into the leaching fluid and minimize the local concentration gradient of leached species external to the sample surface. The geometry of the tank relative to the sample is very important for 1-D mass transport cases (e.g., sealed monoliths or compacted granular samples). For these cases, the inner diameter of the tank should be sized as close as possible to outer diameter of the sample or sample holder such that the bulk of the leaching fluid is in contact with the expose surface area when the sample is submerged.

4.3.7 Temperature

All test activities are conducted at 21±2 °C which is assumed to be consistent with room temperature in most laboratories with environmental control. Deviations in temperature of more than approximately 5 °C may result in changes in constituent concentrations such that comparison of test results to tests conducted within specification may be misleading.

The effect of temperature on diffusion coefficients may be evaluated the Stokes-Einstein equation (Cussler 1997):

$$D = \frac{k_B T}{6 \pi \mu R_o} \qquad \text{Equation 10}$$

where D is the diffusion coefficient [m^2/s],

k_B is the Boltzmann constant [$m^2 kg/s^2 K$],

T is the absolute temperature [K],

μ is the dynamic viscosity of the solvent [Ns/m^2], and

R_o is the radius of the diffusing molecule [m].

For a constant viscosity and radius, the Stokes-Einstein equation indicates that the diffusion coefficient is proportional to temperature, $D \alpha T$. Thus, when measured at two temperatures ($T_1 < T_2$), the diffusion coefficient increases in proportion according to:

$$\frac{D_1}{D_2} \alpha \frac{T_1}{T_2} \text{ or } D_2 \alpha \frac{T_2}{T_1} D_1 \qquad \text{Equation 11}$$

4.3.8 Eluent Exchange Sequence

The pre-determined leaching intervals (see *Method 1315,* Table 1) were selected to balance practicality[15] with eluate concentrations that are consistent with analytical methods. If leaching intervals are short, eluate concentrations could potentially be below analytical detection limits. However, if the duration of leaching intervals is long, the mass accumulated in the eluates until equilibrium is established between the solid and liquid phases and the driving force for mass transport is reduced to zero.

The sequence of leaching intervals specified in *Method 1315* provides several quality control checks to ensure that equilibrium has not been established in eluates during the test duration. Eluate concentrations may be compared to LSP data as a function of eluate pH as obtained

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[15] Practically, in this case, means that eluent exchanges should fall within an 8-hour shift and a 5-day workweek.

from *Method 1313* (see *Method 1315*, Figure 9). Intervals where equilibrium has been established will correspond in concentration to LSP data.

Alternately, a quality control check that equilibrium has not occurred may be conducted by looking at the interval mass flux plotted as a function of arithmetic mean of the time square root. Since mass flux from a semi-infinite media under the assumption of the simple diffusion model is proportional to the square root of time, it is common to compare interval mass flux plotted on log-log axes to a line with a slope of -1/2. However, if chemical saturation with respect to a precipitated solid phase (i.e., the formation of a saturated aqueous phase) has occurred in multiple intervals, the eluate concentrations would be the same since all test fractions use the same volume. Thus, at saturation, the internal mass flux would be dependent on the cumulative leaching time as shown in Figure 5a for several common tank leaching tests.

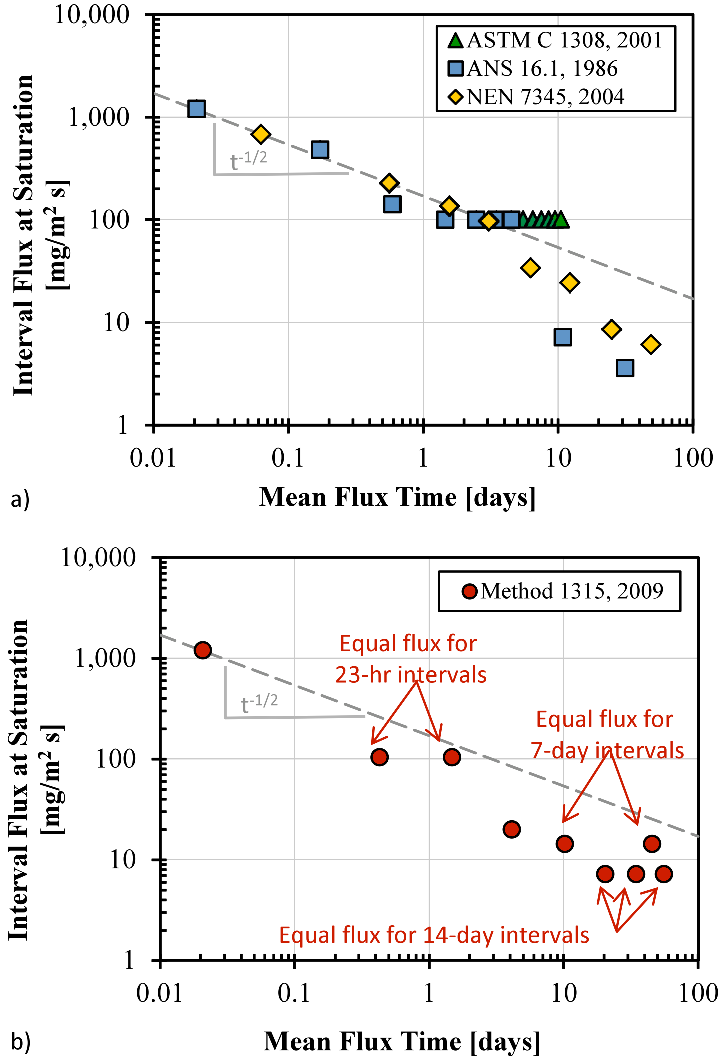

Figure 5. Hypothetical internal mass flux assuming the exchange intervals in the tank leach test were long enough to results in equilibrium between solid and bulk liquid phases: (a) common test methods and (b) *Method 1315*.

The initial flux when the eluates are saturated as shown in Figure 5a closely follow the square root of time (dashed line) due to the selection of leaching intervals in these tests. Therefore, a conclusion that the release is diffusion-controlled based on interpretation of the flux data may be inaccurate. The tank leaching intervals of *Method 1315* have been selected such that intervals of the same duration will display the same internal mass flux if equilibrium has occurred over the leaching interval (Figure 5b). Noting this systematic pattern in flux data could be used to facilitate interpretation by ensuring that saturation of the eluate did not occur during the tank leaching test.

4.3.9 Filtration

Unless the integrity of the sample is compromised during the tank leaching methods, bulk separation of solids and liquids is not necessary in *Method 1315*. However, fine separation for preparation of analytical solutions is required via filtration. *Method 1315* specifies filtration of solutions for inorganic analysis through 0.45-um polypropylene membranes. Polypropylene membranes are specified to minimize adsorption of inorganic species onto the filtration membrane. The filtration step can be conducted under vacuum or pressure with an inert gas, although pressure filtration is specified if mercury is a COPC.

4.4 PRELIMINARY VERSION OF METHOD 1316

Method 1316 - "Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials Using a Parallel Batch Extraction Procedure" is a leaching characterization test consisting of five parallel extractions of a particle-size reduced solid material in reagent water over a range of L/S. This batch test results in LSP data as a function of L/S whereby estimates of initial leachate and pore water composition, as well as cumulative release at L/S=10 mL/g-dry, are comparable to the results of *Method 1314* (Lopez Meza et al. 2008) column test. Whereas the column methods, such as *Method 1314*, allow for collection of eluates at lower L/S than is practical using a batch extraction test, the batch test approach described in *Method 1316* provides a practical implementation advantage over column tests for many materials due to simpler equipment and shorter overall time requirements.

4.4.1 Method Summary

Method 1316 is a batch extraction procedure with five parallel extractions designed to provide information on the liquid-solid partitioning of constituents as a function of L/S. A mass of "as tested" solid material equivalent or greater than to a specified minimum dry mass is added to five extraction vessels. Reagent water is added such that the final L/S in the five extractions is 0.5, 1.0, 2.0, 5.0, and 10.0, respectively. Extracts are tumbled in an end-over-end fashion for a specified contact time that depends on the particle size of the sample. The extract liquid is separated from the solid phase via settling or centrifugation, followed by filtration and preservation of analytical solutions. The pH, conductivity and constituent concentrations for each extract are plotted as functions of L/S and compared to quality control and assessment limits.

4.4.2 Constituents of Potential Concern

This method is applicable for inorganic species (e.g., metals, metalloids and ionic salts), non-volatile organic compounds and DOC. In that radionuclides behave chemically as inorganic species, the method is also applicable for radionuclides given the appropriate modifications to provide adequate worker protection. Although the method is capable of providing extracts for evaluation of semi-volatile organic species (e.g., PAHs), the materials of construction for the extraction vessel must be modified to minimize adsorption.

4.4.3 Eluent Composition

In general, regent-grade water is used in all characterization tests due to minimal interference with the chemistry of the extraction or elution. However, in cases where clayey materials or materials with high organic content are tested, a dilute 1 mM solution of calcium chloride is specified. Dilute calcium chloride will minimize disaggregation of clays and dissolution of organic matter that can lead to colloid formation. Use of 1 mM calcium chloride also is reasonable in the context that infiltrating water under most field conditions will contain dilute concentrations of divalent cations.

4.4.4 Minimum Dry Mass Equivalent

Minimum amounts of material are specified in order to ensure that a representative subsample is used in the leaching test. Since heterogeneities are somewhat dependent on particle size, the minimum sample amount varies with the particle size of the "as tested" material. The minimum sample mass for each extracted material aliquot is specified at 20 g-dry for material < 0.3 mm, 40 g-dry for material < 2 mm, and 80 g-dry for material < 5 mm. These specifications are expected to result in a representative sample for most materials provided that adequate initial sample mass is sized reduced, if necessary. The sample amount used in testing may be increased if sample heterogeneity is determined to be a problem.

The results of leaching tests are often based on the dry mass of a solid; however, oven drying the "as received" material to constant mass prior to testing may be impractical and sometimes deleterious to the mineral structure. In such cases where the "as received" material must be dried before testing, air-drying or drying over a nitrogen blanket (e.g., in the case of oxidation or carbonation sensitive materials) to a moisture content that facilitates material handling (e.g., less than 10% wet basis) is recommended. Since the "as tested" material is likely to contain some level of moisture, the required mass of solid materials is specified on basis of a "dry mass equivalent" (i.e., the mass of an "as tested" sample which, if dried to constant mass, would result in the specified dry mass). The dry mass equivalent for a specified minimum dry mass can be calculated if the solids content or moisture content (wet basis) is known, according to the following equation:

$$M_{test} = \frac{M_{dry}}{SC} = \frac{M_{dry}}{(1 - MC_{wet})} \qquad \text{Equation 1}$$

where: M_{test} is the dry mass equivalent of "as tested" solid material [g]

M_{dry} is the mass of dry material specified in method [g-dry]

SC is the solids content of "as tested" material [g-dry/g], and

MC_{wet} is the moisture content (wet basis) of the "as tested" material [g_{H2O}/g]

The specification for the minimum amount of solid material is based on the homogeneity of the sample and the particle size of the test subsample. The minimum dry mass equivalents specifications shown in the method assume that, after particle size reduction and sieve analysis, the solid material has undergone adequate homogenization. Materials which are visually heterogeneous after sample processing may require more mass to achieve an adequate representative subsample.

Since the purpose of *Method 1316* is to provide adequate eluate for chemical analysis at low L/S, the amount of solid material used in each of the five parallel extractions may exceed, and should exceed in practice, the minimum sample specification. The amount of solid material may be increased in order to provide adequate solution volume after filtration. For example, if 200 mL of eluate is required to complete all analytical methods, the amount of solid materials for the five extractions should follow the scheme shown in Table 3.

Table 3. Suggested Solid Amounts for *Method 1316*.

Test Position	L/S [mL/g-dry]	Desired Eluate [mL]	Solid Material [g-dry]
T01	10	200	20
T02	5	200	40
T03	2	200	100
T04	1	200	200
T05	0.5	200	400

4.4.5 Specified Liquid-To-Solid Ratios

In order to provide a standardized set of L/S values for batch testing, *Method 1316* specifies L/S of 10, 5, 2, 1 and 0.5 mL/g-dry. This range covers the range of L/S consistent with *Method1313* and *Method 1314*, balanced with the practicality of recovering eluate from extracts of granular materials at low L/S. In addition, an L/S of 10 mL/g-dry is a reasonable value for extended leaching interval in the field, such that observed released masses of COPCs from leaching tests can be used to estimate field behavior.

4.4.6 Particle Size, Liquid-To-Solid Ratio, and Contact Time

In batch testing, the time required to approach equilibrium between the liquid and solid phases depends on a relationship that is a function of particle size, liquid-solid ratio and contact time.[16] Thus, the discussion of one parameter must be conducted in context to the others. Since the goal of equilibrium extractions is to achieve a practical approximation of equilibrium between the solid materials and the liquid extraction fluid, the specified contact time should be long enough to allow for the controlling physical and chemical processes (e.g., dissolution and diffusion into the liquid phase) to occur. To reach a practical approximation of equilibrium, the contact time may be adjusted, to some degree, based on either the maximum particle size of the solid sample or L/S.

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[16] The contact time to reach equilibrium also is a factor of temperature and the fraction of the total or available constituent content in the solid that is soluble at equilibrium (see Contact Time).

4.4.6.1 Particle Size Reduction and Maximum Particle Size

Particle size reduction for solid matrices, especially those matrices which are naturally monolithic in nature, is often a topic of debate. During batch testing, diffusion through larger particles may become the rate-limiting mechanism such that particle size reduction of the material prior to testing is necessary. Decreasing the particle size decreases the time required to approximate equilibrium by reducing the diffusional distance that a solute must traverse to the bulk solution and increasing the surface area for interactions between the solid phase and the bulk solution. However, the desire for a prompt response from a leach test must be offset by practicality in terms of the effort required for particle size reduction.

The approach for particle size reduction should not alter the chemical or mineral composition of the material. This means that size reduction operations (e.g., crushing, grind, or milling and associated sieving) should not introduce foreign matter to the sample, cause loss of constituents, or alter the temperature the sample excessively. In addition, the process should be conducted as quickly as is reasonably possible in order to minimize the potential for interaction with the atmosphere (e.g., oxidation or carbonation). Alternately, particle size reduction may be conducted under a controlled atmosphere, such as a nitrogen-purged in a glove box, but this is not always practical.

Method 1316 allows selection from three specified maximum particle sizes with associated minimum sample sizes and minimum contact times. Unless it is impractical to do so, all "as received" material to be tested should be size reduced to a maximum of 5 mm diameter. This provides an "as tested" sample at the largest allowable particle size. The portion of "as received" material that is not readily size reduced to less than 5 mm by crushing is discarded after calculating the mass fraction of the greater than 5 mm and documenting the nature (e.g., rocks, sticks, glass, etc.) and approximate particle size of the discarded fraction. Test results are not corrected to account for the discarded mass.[17] Batch extraction at this level of particle size reduction requires 72 hours of contact time; however, shorter contact times may be used when further particle size reduction to 2 mm or 0.3 mm is employed. During the particle size reduction process, it is likely and unavoidable that a distribution of particle sizes will result rather than a single particle size. Thus, the recommended contact time to be used in *Method 1316* should correspond to the particle size for which 85 wt% of the "as tested" sample passes the specified sieve size (see Contact Time).

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[17] By excluding the mass fraction with particle size greater than 5 mm, some bias may be introduced. However, irreducible particles are often not the driver for environmental assessment. In addition, particle size reduction is considered to correlate, to some degree, with durability in use. Therefore, it is unlikely that application conditions would result in significant particle size reduction to < 5 mm for materials an irreducible mass fraction of greater than 20%. For these materials, other leaching tests (e.g., Method 1314 in a large diameter column or Method 1315) may be a more appropriate approach to leaching characterization.

4.4.6.2 Liquid-To-Solid Ratio

The volume of extracting fluid relative to the mass of solid is the liquid-to-solid (LS) ratio. For batch tests designed to approximate equilibrium, lower L/S reduce the amount of constituent mass that is required to saturate the liquid phase and, thus, decreases the time required to reach equilibrium. Although the L/S of fully saturated porous field material (e.g., soils, wastes, cementitious materials) can be significantly less than 1.0 mL/g-dry, it is not practical to routinely work in the laboratory setting will solid slurries which result from batch extraction at very low L/S. At high L/S, differences in eluate concentrations from a similar method at a standard L/S of 10 mL/g-dry and a modified L/S of 100 mL/g-dry were explained based on availability or solubility controlled release (Dijkstra et al. 2008). [18]

4.4.6.3 Contact Time

In equilibrium-based leaching tests, the duration of the extraction is set such that the mass transfer rate does not limit release into the liquid phase. The minimum contact time for batch testing of particle size reduced material is based on the minimum mass transport time to reach a fractional equilibrium concentration in a bath of fixed volume surrounding a spherical particle of a particular diameter (Garrabrants 1997). The numerical solution for diffusion of a constituent through a spherical particle of diameter 2a into a finite bath as (Crank 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\,\alpha\,(\alpha+1)\exp\left(-D\,q_n^2\,t/a^2\right)}{9+9\,\alpha+q_n^2\,\alpha^2} \qquad \text{Equation 2}$$

where M_t is the mass release from a sphere at time t [mg]

M_∞ is the mass release at infinite time (i.e., equilibrium condition) [mg]

D is the observed diffusion coefficient [m^2/s]

a is the spherical radius [m]

q_n is the non-zero roots of the relation;

$$\tan\left(q_n\right) = \frac{3\,q_n}{3+\alpha\,q_n^2} \qquad \text{Equation 3}$$

where α is the ratio of the volumes of the solution and the sphere [-].

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[18] In this context, “availability-controlled” release means that the release is limited to the total amount of a constituent in the solid phase that is available for release under the specified conditions. “Solubility-controlled” release refers to situations where the release of a constituent is consistent with the solubility as a function of pH under the specified conditions. For each constituent, the resultant extract concentration under availability-controlled release is higher than or equal to the solubility-controlled release concentration.

The factional solubility (i.e., the fraction of the available mass that is soluble at equilibrium) can be expressed as a function of the parameter α as:

$$\frac{M_\infty}{M_0} = \frac{1}{1 + 1/\alpha} \qquad \text{Equation 4}$$

where M_0 is the initial available constituent mass in the sphere [mg].

Figure 2 shows the contact time required to establish 90% of the equilibrium (vertical axis) in the fixed bath as functions of particle diameter (horizontal axis) and fractional solubility (diagonal axis, not shown). The fractional solubility is defined as the fraction of the available content that is soluble at equilibrium. In the figure, the observed diffusivity of the transporting species is constant at 10^{-13} m^2/s, which is a relatively slow rate of diffusion based on past observations (sodium free diffusion in water is on the order of 10^{-9} m^2/s while diffusion through concrete may be on the order of 10^{-12} m^2/s).

The red, short dashed lines in Figure 6 indicate that spherical particles of 0.3 mm established 90% of theoretical equilibrium in less than 24 hours regardless of the fractional solubility value. Over a 48-hour period (green, long dash lines), 90% of equilibrium can be approached for particles of 2 mm if the fractional solubility is less than 0.1 (i.e., less than 10% of the total or available content is soluble in the fixed bath at infinite time). A 72-hour contact time (blue, dot-dash lines) would allow for particles of 5 mm diameters to approach 90% of equilibrium for fractional solubility values of less than approximately 0.4. These caveats with regard to fraction solubility are reasonable for most inorganic species because the more highly soluble species (e.g., sodium, boron) would likely have higher observed diffusion coefficients and, thus, would not be limited by mass transport through the particle over the test duration.

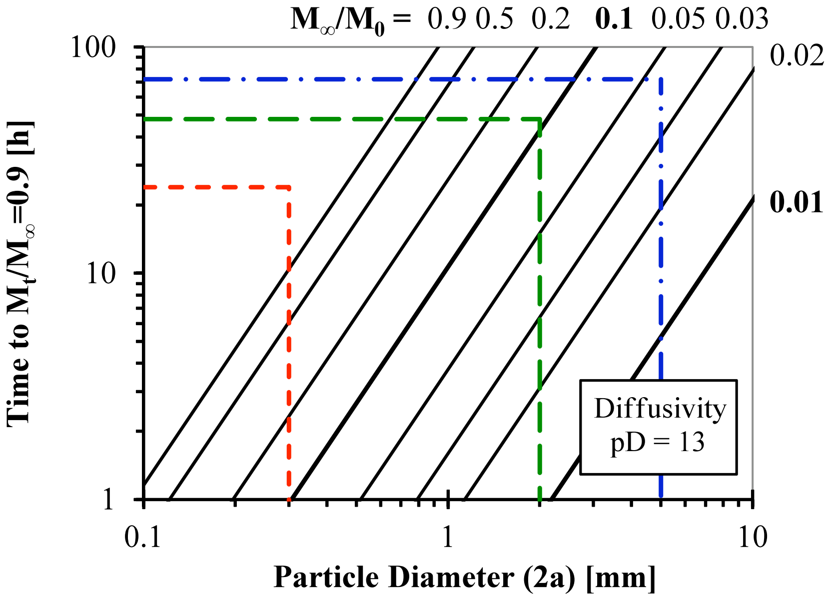

Figure 6. Contact time required for a species with an observed diffusivity of 10^{-13} m^2/s to reach 90% of equilibrium ($M_t/M_\infty = 0.9$) based on mass transport as functions of particle diameter and fractional solubility (M_∞/M_0). Figure modified from Garrabrants, 1997.

A similar approach can be used in conjunction with Figure 7 to examine the effect of diffusivity (horizontal axis), in this case shown as pD or the negative log of the diffusion coefficient, on the time required to reach 90% of equilibrium (vertical axis) as a function of fractional solubility (diagonal axis not shown) for a spherical particle of 0.3 mm diameter. The 24-hour test duration specified in *Method 1316* would allow 0.3 mm diameter particles to approach 90% of equilibrium for fractional solubility less than 0.2 for constituents with a mid-range diffusivity of 10^{-14} m2/s (pD=14; green, long dash line) and for fractional solubility less that only 0.01 for constituents with a very low diffusivity of 10^{-16} m^2/s (pD=16; blue, dot-dash line).

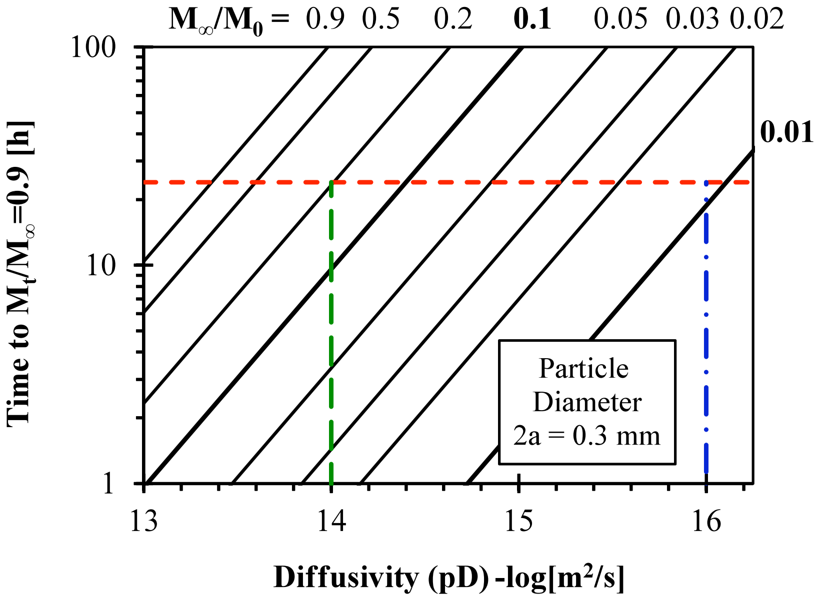

Figure 7. Contact time required for a particle of 0.3 mm diameter to reach 90% of equilibrium ($M_t/M_\infty = 0.9$) as function of diffusivity and fractional solubility (M_∞/M_0). Figure modified from Garrabrants, 1997.

Based, in part, on the analysis of mass transport from a spherical particle into a bath of fixed volume, the specifications for contact time as a function of particle size shown in

Table 2 were established. The above time estimates are based entirely on mass transport considerations assuming that (i) the diffusing species is readily available for mass transport (i.e., dissolution is not rate-limiting) and (ii) the solid phase concentration of the species at the center of the particle is constant (e.g., the species does not deplete). The latter assumption is most likely valid for most solid materials given the relatively low liquid-to-solid ratio. The former assumption that dissolution is not kinetically controlled is not valid for all species (e.g., iron oxide dissolution) and could result in longer required test durations (Dijkstra et al. 2006). The resultant specifications provided in Table 4 also consider practicality in striking that balance between test duration and increasing effort required for further particle size reduction.

Table 4. Extraction Parameters as Function of Maximum Particle Size.

Particle Size (85 wt% less than) [mm]	U.S. Sieve Size	Minimum Dry Mass [g-dry]	Contact Time [hr]	Suggested Vessel Size [mL]
0.3	50	20±0.02	24±2	250
2.0	10	40±0.02	48±2	500
5.0	4	80±0.02	72±2	1000

4.4.7 Temperature

All test activities are conducted at 21±2 °C which is assumed to be consistent with room temperature in most laboratories with environmental control. Deviations in temperature of more than approximately 5 °C may result in changes in constituent concentrations such that comparison of test results to tests conducted within specification may be misleading.

4.4.8 Agitation

Method 1316 specifies “end-over-end” tumbling as the method of agitation. This method provides adequate contact between solid and liquid phases as gravity maximizes dispersion of particles. Other methods of agitation (e.g., rolling, linear or orbital shaking) allow for settling and the formation of a consolidated slurry phase with minimum solid-liquid contact area. The rate of agitation is selected to be 30±2 RPM in order to be consistent with commercially available tumbling apparatuses and equipment in place for currently standardized methods (e.g., TCLP).

4.4.9 Filtration

In order to process leaching test solid-liquid mixtures for analysis, the bulk solid and liquid phases must be separated. Coarse separation may be accomplished with settling for 10-15 minutes or centrifugation at an average relative centrifugal force (RCF) of 1,500±100 g for 10±2 minutes. Fine separation for preparation of analytical solutions typically requires filtration. *Method 1316* specifies filtration of solutions for inorganic analysis through 0.45-um polypropylene membranes. Polypropylene membranes are specified to minimize adsorption of inorganic species onto the filtration membrane. The filtration step can be conducted under vacuum or pressure with an inert gas, although pressure filtration is specified if mercury is a COPC.

Table 5. Comparison of Test Specifications for Preliminary Versions of *Methods 1313*, *1314*, *1315*, and *1316*.

Test Name	***Method 1313***	***Method 1314***	***Method 1315***	***Method 1316***
Test Type	Equilibrium; pH-dependence	Equilibrium; L/S	Mass transfer; mass transport rates	Equilibrium; L/S
Test Description	Parallel batch extractions as function of pH	Column test performed in up-flow mode	Tank test with periodic eluent renewal	Parallel batch extractions as function of L/S
Sample Type **Dimension**	Granular Particle size of 85% (mass/mass) less than 0.3 mm, 2.0 mm, or 5.0 mm	Granular Particle size of 85% (mass/mass) less than 2 mm and 100% (m/m) less than 5 mm	Monolithic - cylinder or cube with 40-mm minimum dimension Granular - compacted cylinder with 40-mm minimum height	Granular Particle size of 85% (mass/mass) less than 0.3 mm, 2.0 mm, or 5.0 mm
Target Constituents	Inorganic, non-volatile, and semi-volatile organic species	Inorganic, non-volatile, and semi-volatile organic species	Inorganic and non-volatile organic species	Inorganic, non-volatile, and semi-volatile organic species
Eluent Composition	Reagent water with additions of HNO_3 or NaOH	Reagent water or 1 mM $CaCl_2$	Reagent water or 1 mM $CaCl_2$	Reagent water or 1 mM $CaCl_2$
pH Range	<2 to >12 at specified targets	pH dictated by solid buffering	pH dictated by solid buffering	pH dictated by solid buffering
Minimum Amount of Solid	20 g-dry each extract	300 g	500 g	20 g-dry each extract
Eluent Volume	L/S of 10 mL/g-dry	L/S varies with percolation time	Liquid-surface area ratio (L/A) of 10 mL/cm^2	L/S of 10, 5.0, 2.0, 1.0 and 0.5 mL/g-dry
Number of Test Fractions	9 (10 if natural pH is not within a target range)	9	9	5

Test Name	*Method 1313*	*Method 1314*	*Method 1315*	*Method 1316*
Contact Time per Test Fraction	Based on particle size: 24 hr (0.3 mm) 48 hr (2 mm) 72 hr (5 mm)	Based on flow rate (Total test duration ~10 days)	Eluent renewal at specified intervals of 2, 23 and 23 hr; 5, 7, 14, 7, and 14 days	Based on particle size: 24 hr (0.3 mm) 48 hr (2 mm) 72 hr (5 mm)
Temperature	21±2 ºC	21±2 ºC	21±2 ºC	21±2 ºC
Agitation	End-over-end rotation at 30±2 rpm	None	None	End-over-end rotation at 30±2 rpm
Assays	pH, electrical conductivity, redox (optional), IC/DOC, COPC concentrations	pH, electrical conductivity, redox (optional), IC/DOC, COPC concentrations	pH, electrical conductivity, redox (optional), IC/DOC, COPC concentrations	pH, electrical conductivity, redox (optional), IC/DOC, COPC concentrations
Filtration	Settling/ centrifugation; filtration at 0.45- m	Settling/ centrifugation; filtration at 0.45- m	Settling/ centrifugation; filtration at 0.45- m	Settling/ centrifugation; filtration at 0.45- m
Comments	Extensive QA/QC including method blanks (maximum acid addition, maximum base addition, reagent water) and analytical quantification/ detection limits	Extensive QA/QC including method blanks (reagent water), comparison to *Method 1313*, and analytical quantification / detection limits	Extensive QA/QC including method blanks (reagent water), comparison to *Method 1313*, and analytical quantification / detection limits	Extensive QA/QC including method blanks (reagent water), comparison to *Method 1313*, and analytical quantification / detection limits

5 ESTIMATES OF LABORATORY PROCESSING TIME, MATERIAL REQUIREMENTS AND SUPPLY/EQUIPMENT COSTS

This document provides estimates of time, material and costs for each of the four test methods as a means of illustrating the required resources to complete these tests.

5.1 LABOR/PROCESSING TIME

Table 6 shows approximate labor time (in hours) and process time (in days) to complete a test run and two subsequent test replicates. Process time considers the duration of time from when the subject material is received to the completion of the test replicate and includes all preparatory steps as specified in the test method. Labor time considers only that time when a technician is actively working on a test method which is often a fraction of the total processing time (e.g., the technician is free to work elsewhere when batch tests are tumbling or column test are not being monitored).

Table 6. Summary of Estimates for Labor Time and Total Processing Time

	Test (singlet)		**+1 Replicate (duplicate)**		**+2 Replicates (triplicate)**	
	Labor [hr]	Process [d]	Labor [hr]	Process [d]	Labor [hr]	Process [d]
Method 1313	10[a]-15	7[a]-12	15[a]-20	7[a]-14	20[a]-25	7[a]-14
Method 1314	12	21	20	21	28	21
Method 1315	15	64[b]-69	25	69	35	69
Method 1316	6	7	8	7	10	7

[a] Labor and processing time are reduced if prior knowledge of material behavior is available (e.g., titration curve).

[b] Processing time is longer for granular materials due to added steps (e.g., optimum density analysis, packing samples).

A step-by-step breakdown of labor time estimates is presented in Table E-1 through Table E-4 found in Appendix E. Labor time estimates consider that the laboratory technician is familiar with the test method, but not significantly experienced. Thus, the labor time required to conduct the initial tests when a technician is still learning the test method sequence may be longer than provided in the table, whereas significant time reduction may be seen for well-experienced laboratory technicians. All labor time estimates account for reduced time based on “economy of scale” (e.g., moisture content, drying, particle-size reduction may be conducted for all replicates at one time).

A useful presentation of process time is a Gantt style chart as shown in Figure 8 through Figure 11. These figures show the method task duration and the critical path relationship between tasks. For example, the “as received” moisture content of a subject material is independent of other task; whereas, particle size analysis or reduction of “as received” material to produce an “as tested” sample is essential for all subsequent tasks for *Method 1313*, *Method 1314*, and *Method 1315*. Some processing time may be saved if air drying of granular “as received” material is not necessary. All task durations estimates are based on previous experience and are considered to be conservative (i.e., over-estimate task duration). Schedules for batch extraction procedures (*Method 1313* and *Method 1316*) are based on working days, whereas schedules for flow-dependent and time-dependent procedures (*Method 1314* and *Method 1315*, respectively) are include weekends.

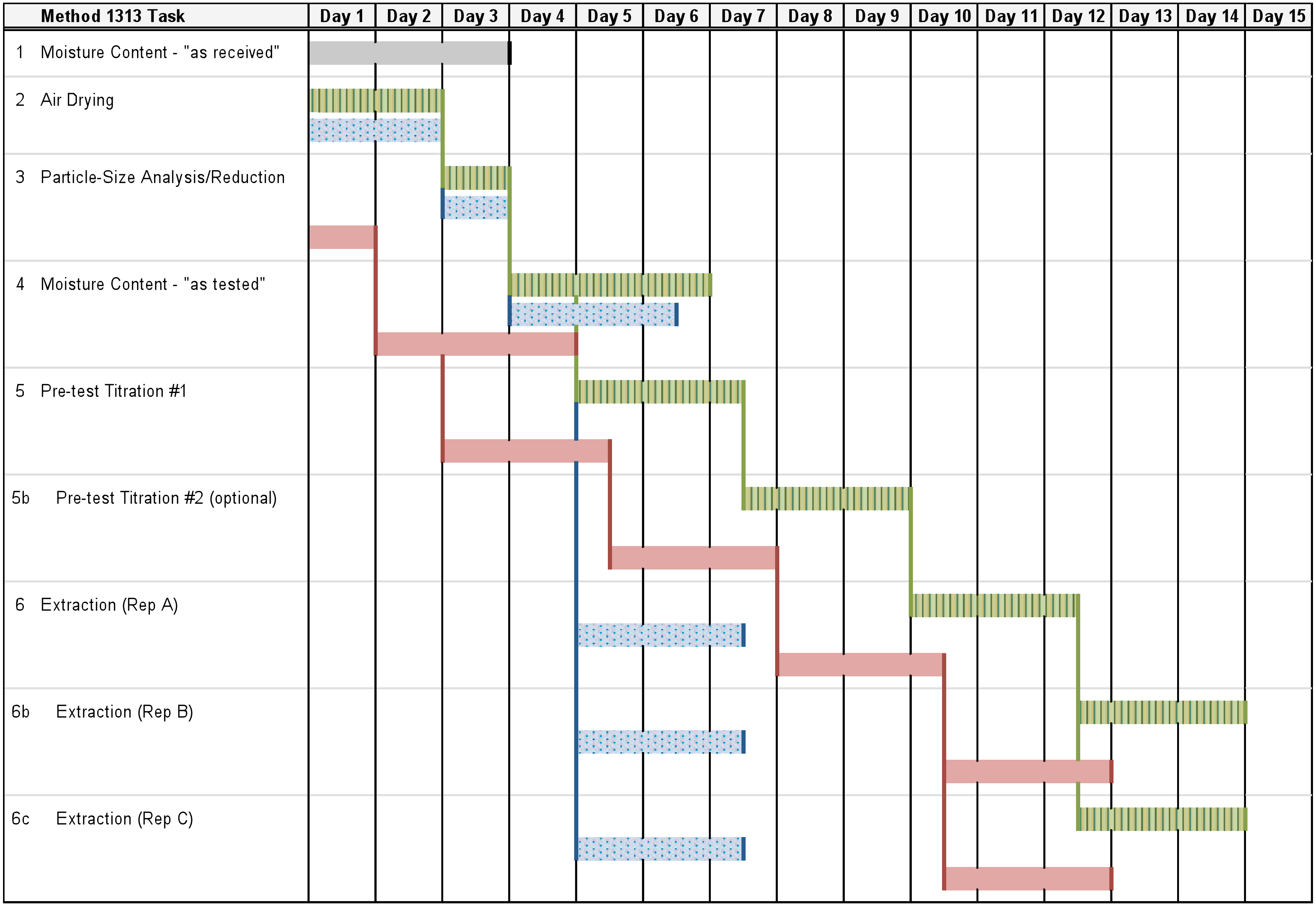

Figure 8. Gantt Style Chart of A Typical *Method 1313* Processing Schedule.

Notes on Figure 8.

1) Schedule is based on workdays (i.e., weekends will add time to total).
2) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar/pestle.
3) Green case (hatched) – baseline case with air drying and two rounds of pre-test titration (10 pre-test titration points in all).
4) Red case (solid) – shortened case when air drying is not required for particle-size analysis/reduction.
5) Blue case (dotted) – shortened case when prior titration knowledge is adequate to complete extractions.

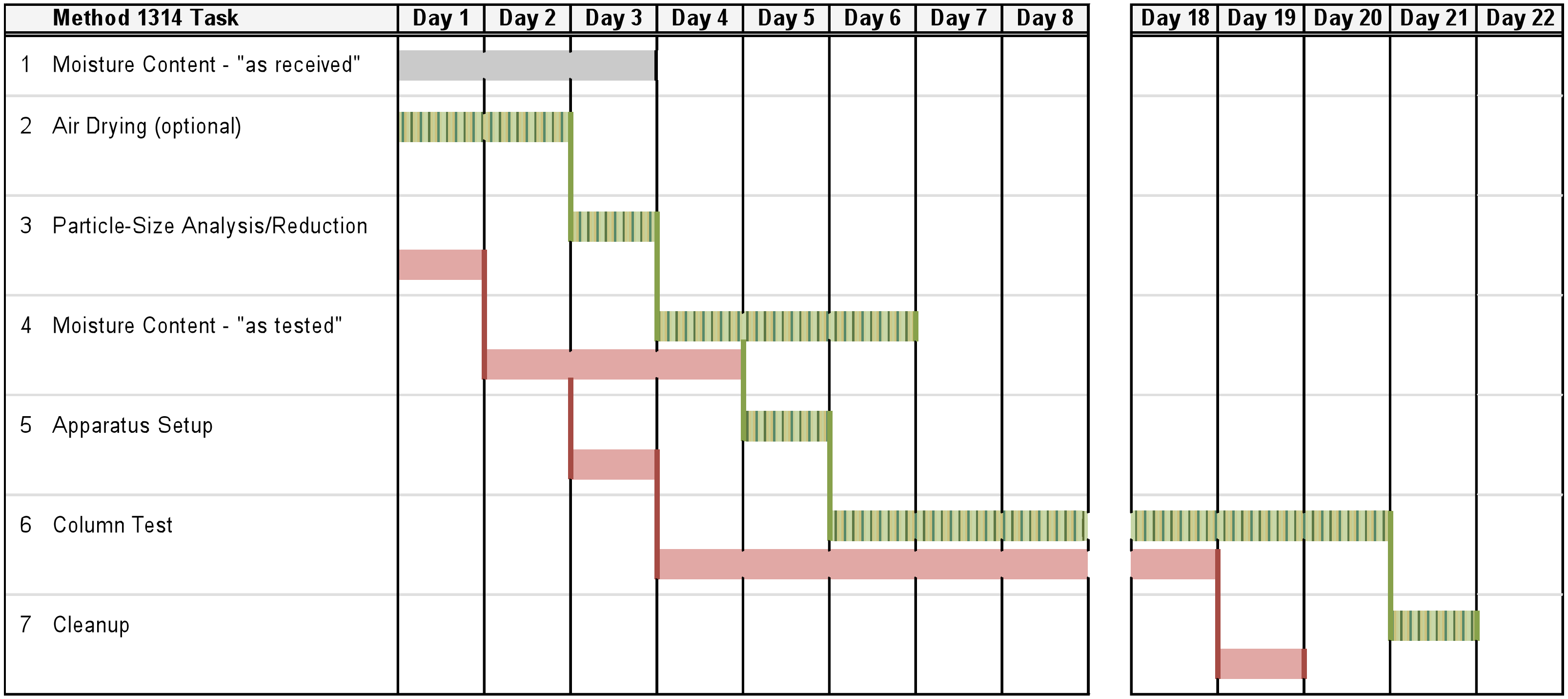

Figure 9. Gantt Style Chart of a Typical *Method 1314* Processing Schedule.

Notes on Figure 9.

1) Schedule is based on calendar days (i.e., column/fraction collection continues over weekends).
2) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar/pestle.
3) Apparatus set includes sample wetting and equilibration overnight.
4) Green case (hatched) – baseline case.
5) Red case (solid) – shortened case when air drying is not required for particle-size analysis/reduction.

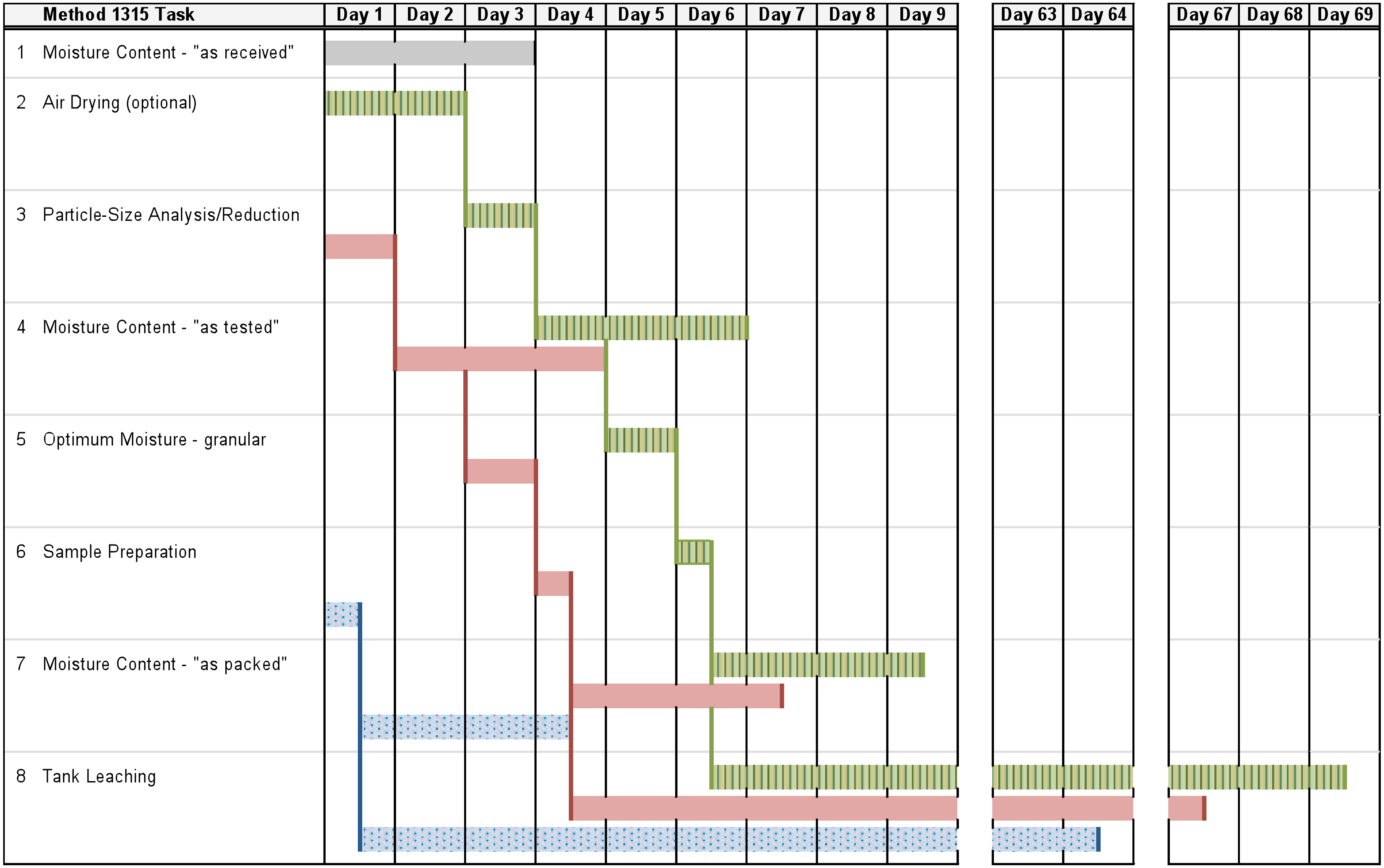

Figure 10. Gantt Style Chart of a Typical *Method 1315* Processing Schedule.

Notes on Figure 10.

1) Schedule is based on calendar days (i.e., tank leaching and refreshes continue over weekends).
2) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar/pestle.
3) Green case (hatched) – baseline case for granular materials with air drying.
4) Red case (solid) – shortened case for granular materials when air drying is not required for particle-size analysis/reduction.
5) Blue case (dotted) – baseline case for monolithic materials.

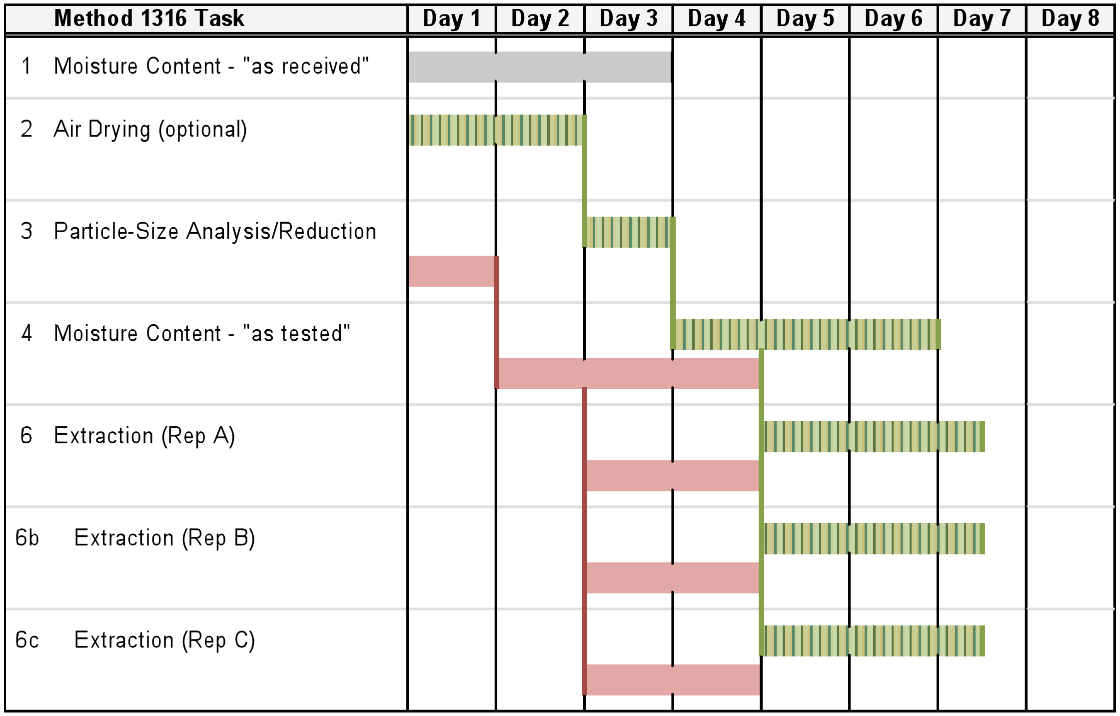

Figure 11. Gantt Style Chart of a Typical *Method 1316* Processing Schedule.

Notes on Figure 11.

1) Schedule is based on workdays (i.e., weekends will add time to total).
2) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar/pestle.
3) Green case (hatched) – baseline case with air drying.
4) Red case (solid) – shortened case when air drying is not necessary for particle-size analysis/reduction.

5.2 MATERIAL REQUIREMENTS

An estimate of the amount of solid material required to conduct all steps in each test method is shown in Table 7 for a single test and two subsequent test replicates. These estimates are based on minimum required dry mass for each test with allowance for a 50% safety factor and an assumed "as received" moisture content of 20% on a wet basis (i.e., solids content of 80%). Thus, the estimates shown in Table 7 may be considered to be conservative for most cases and should provide sufficient material to allow for minor mistakes in laboratory procedures.

Table 7. Summary of Solid Materials Required for Test Methods

	Test (singlet)	**+1 Replicate (duplicate)**	**+2 Replicates (triplicate)**
Method 1313	800 g-dry	1,200 g-dry	1,600 g-dry
Method 1314	700 g-dry	1,400 g-dry	2,100 g-dry
Method 1315 (granular)	5,000 g-dry	6,500 g-dry	8,000 g-dry
Method 1316	1,000 g-dry	2,000 g-dry	3,000 g-dry
Subtotal [kg-dry]	**7.5**	**10.0**	**15.0**
w/ 50% safety [kg-dry]	**11.0**	**15.0**	**22.0**
Mass at 80% Solids Content [kg]	**15.0**	**20.0**	**30.0**

The material estimate for *Method 1315* is based on testing of a compacted granular sample. In this case, material in addition to that required for the test samples must be provided in order to determine the optimum moisture/density relationship and determine a target moisture content for packing of test samples. Thus, the compact granular case typically requires more sample mass than the monolithic material case. When testing monolithic materials, the amount of sample for *Method 1315* will depend on sample geometry and dimensions as well as material density. For example, a 10-cm diameter by 10-cm long cylinder of a monolithic material with a density of 2.0 g/cm^3 would require a sample of approximately 1,600 g.

5.3 SUPPLIES AND EQUIPMENT

Total estimated costs of supplies and equipment for the first test run and two subsequent replicate tests are shown in Table 8 for each of the four test methods. Supplies costs include consumable items which are not reused after the tests (e.g., filter paper, bottles, etc.) whereas equipment cost include both capital purchases (e.g., tumblers, pumps, compaction rammers, etc.) and supplies which may be cleaned and reused between test replicates (e.g., filter holders).

Table 8. Summary of Estimated Supply and Equipment Costs (as of July 2010)

	Test (singlet)		**+1 Replicate (duplicate)**		**+2 Replicates (triplicate)**	
	Supply	Equip.	Supply	Equip.	Supply	Equip.
Method 1313	$200	$8,200	$310	$9,100	$430	$10,000
Method 1314	$110	$4,400	$210	$5,800	$310	$7,100
Method 1315[a]	$170	$2,000	$260	$3,000	$350	$4,000
Method 1316	$85	$7,500	$160	$8,000	$230	$8,600

[a] Method 1315 cost shown for more expensive material type (granular).

These cost estimates in Table 8 are based on items and costs for supplies and equipment found primarily in the Fisher Scientific online catalog as detailed in Appendix G. The items presented in the appendix have been selected as examples of items which may be used to complete these test methods, but selection does not denote endorsement of vendor, manufacturer or product by the authors or U.S. EPA.

The cost estimates for test replicates account for “economy of scale” within each method (e.g., blanks as assumed to be conducted once for all test replicates). However, some savings may occur by limiting equipment purchases when a laboratory is preparing the conduct multiple test methods (e.g., the same tumbler may be used to conduct both *Method 1313* and *Method 1314*, all test may use the same set of filter holders).

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APPENDIX A

METHOD 1313 (R2) –

LIQUID-SOLID PARTITIONING AS A FUNCTION OF EXTRACT pH IN SOLID MATERIALS USING A PARALLEL BATCH PROCEDURE

PRELIMINARY VERSION[1] OF METHOD 1313

LIQUID-SOLID PARTITIONING AS A FUNCTION OF EXTRACT pH IN SOLID MATERIALS USING A PARALLEL BATCH PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute quality control (QC) acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide aqueous extracts representing the liquid-solid partitioning (LSP) curve as a function of pH for inorganic constituents (e.g., metals and radionuclides), semi-volatile organic constituents (e.g., polycyclic aromatic hydrocarbons or PAHs) and non-volatile organic constituents (e.g., dissolved organic carbon) in solid materials. The LSP curve is evaluated as a function of final extract pH at a liquid-to-solid ratio (L/S) of 10 mL extractant/g dry sample (g-dry) and conditions that approach liquid-solid chemical equilibrium. This method also yields the acid/base titration and buffering capacity of the tested material at an L/S of 10 mL extractant/g-dry sample. The analysis of extracts for dissolved organic carbon and the solid phase for total organic carbon allow for the evaluation of the impact of organic carbon release and the influence of dissolved organic carbon on the LSP of inorganic constituents.

1.2 This method is intended to be used as part of an environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness and site remediation options.

1.3 This method is suitable for a wide range of solid materials. Examples of solid materials include: industrial wastes, soils, sludges, combustion residues, sediments, stabilized materials, construction materials, and mining wastes.

1.4 This method is a leaching characterization method that is used to provide values for intrinsic material parameters that control leaching of inorganic and some organic

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[1] Preliminary Version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846. This method has been derived from published procedures (Kosson et al, 2002) using reviewed and accepted methodologies (U.S. EPA2006, 2008, 2009). The method has been submitted to the U.S. EPAOffice of Resource Conservation and Recovery and is currently under review for development of interlaboratory validation studies to develop precision and bias information.

species under equilibrium conditions. This test method is intended as a means for obtaining a series of extracts of a solid material (i.e., the eluates), which may be used to estimate the LSP (e.g., solubility and release) of constituents as a function of pH under the laboratory conditions described in the method. Eluate constituent concentrations may be used in conjunction with information regarding environmental management scenarios to estimate the anticipated leaching concentrations, release rate and extent for individual material constituents under the management to be evaluated. Eluate constituent concentrations generated by this method may also be used along with geochemical speciation modeling to infer the mineral phases that control the LSP in the pore structure of the solid material.

1.5 This method is not applicable for characterizing the release of volatile organic analytes (e.g., benzene, toluene, xylenes).

1.6 The relationships between eluate concentrations observed from this method and field leachate must be considered in the context of the material being tested and the field scenario being evaluated. This method provides solutions considered indicative of eluate under field conditions, only where the field leaching pH is the same as the final laboratory extract pH and the LSP is controlled by aqueous phase saturation of the constituent of interest.

1.7 The maximum mass of constituent released over the range of method pH conditions ($2 \leq pH \leq 13$) may be considered an estimate of the maximum mass of the constituent leachable under field leaching conditions for intermediate time frames and the domain of the laboratory test pHs.

1.8 The solvents used in this method include dilute solutions of nitric acid (HNO_3) and potassium hydroxide (KOH) in reagent water.

1.9 Analysts are advised to take reasonable measures to ensure that the sample is homogenized to the extent practical, prior to employment of this method. Particle-size reduction may provide additional assurance of sample homogenization and also facilitate achievement of equilibrium during the test procedure. Table 1 of this standard designates a recommended minimum dry mass of sample to be added to each extraction vessel and the associated extraction contact time as a function of particle diameter. If the heterogeneity of the sample is suspected as the cause of unacceptable precision in replicate test results or is considered significant based on professional judgment, the sample mass used in the test procedure may be increased to a greater minimum dry mass than that shown in Table 1 with the amount of extractant increased proportionately to maintain the designated L/S.

1.10 In the preparation of solid materials for use in this method, particle-size reduction of samples with a large grain size is performed in order to enhance the approach towards equilibrium under the designated contact time interval of the extraction process. The extract contact time for samples reduced to a finer maximum particle size will consequently be shorter (see Table 1).

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045, and 9050, and the determinative methods for the target analytes), QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the concentration levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application. Guidance on defining data quality objectives can be obtained at http://www.epa.gov/QUALITY/qs-docs/g4-final.pdf

1.12 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method consists of parallel extractions of a particle size-reduced solid material in dilute acid or base and reagent water. A flowchart for performing this method is shown in Figure 1. Particle-size reduction of the material to be tested is performed according to Table 1. A schedule of acid and base additions is formulated from a pre-test titration curve or prior knowledge indicating the required amount of acid or base (equivalents/g) to be added to a series of extraction vessels so as to yield a series of eluates with final pH at nine specified target pH values in the range of 2-13. Extraction at natural conditions (e.g., extraction with regeant water only at a liquid-solid ratio of 10 mL/g-dry) may be used to substitute for a specified target pH if the natural pH falls within the acceptable tolerance for any of the nine specified target pH values. If the natural pH does not fall with any acceptable tolerance, an additional extraction vessel is required to conduct an extraction at natural pH conditions. In addition to the test position extractions, three method blanks without solid sample are carried through the procedure in order to verify that analyte interferences are not introduced as a consequence of reagent impurities or equipment contamination. The extraction bottles (i.e., eight or nine test positions, natural pH, and three method blanks) are tumbled in an end-over-end fashion for a specified contact time, which depends on the particle size of the sample (see Table 1). At the end of the specified contact interval, the liquid and solid phases are roughly separated via settling or centrifugation. Eluate pH and specific conductivity measurements are then made on an aliquot of the liquid phase and the remaining bulk of the eluate is clarified by either pressure or vacuum filtration. In cases where rough separation is not practical or results in grossly incomplete clarification, eluate measurements may be taken immediately following filtration. Analytical samples of the filtered eluate are collected and preserved as appropriate for the desired chemical analyses. The eluate concentrations of constituents of potential concern (COPCs) are determined and reported. In addition, COPC concentrations may be plotted as a function of eluate pH and compared to quality control and assessment limits for the interpretation of method results.

3.0 DEFINITIONS

3.1 COPC — A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.2 Release — The dissolution or partitioning of a COPC from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.3 LSP — The distribution of COPCs between the solid and liquid phases at the conclusion of the extraction.

3.4 L/S — The fraction of the total liquid volume (including the moisture contained in the "as used" solid sample) to the dry mass equivalent of the solid material. L/S is typically expressed in volume units of liquid per dry mass of solid material (mL/g-dry).

3.5 "As-tested" sample — The solid sample at the conditions (e.g., moisture content and particle-size distribution) present at the time of the start of the test procedure. The "as-tested" conditions will differ from the "as-received" sample conditions if particle-size reduction and drying were necessarily performed.

3.6 Dry-mass equivalent — The mass of "as-tested" (i.e., "wet") sample that equates to the mass of dry solids plus associated moisture, based on the moisture content of the "as-tested" material. The dry-mass equivalent is typically expressed in mass units of the "as-tested" sample (g).

3.7 Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapters Three and Four for general guidance on the cleaning of laboratory apparatus prior to use.

4.2 If potassium is a COPC, the use of KOH as a base reagent will interfere with the determination of actual potassium release. In this case, sodium hydroxide (NaOH) of the same grade and normality may be used as a substitute.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 During preparation of extracts and processing of extracts, some waste materials may generate heat or evolve potentially harmful gases when contacted with acids and bases. Adequate prior knowledge of the material being tested should be used to establish appropriate personal protection and workspace ventilation.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and setting used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented. This section does not list common laboratory glassware (e.g., beakers and flasks) which nonetheless may be required to perform the method.

6.1 Extraction vessels

6.1.1 Twelve wide-mouth bottles (i.e., nine for test positions plus three for method blanks) constructed of inert material, resistant to high and low pH values and interaction with COPCs as described in the following sections.

NOTE: Depending on the value of the natural pH (determined from prior knowledge or the results of the pre-test titration), thirteen extraction bottles may be necessary per test replicate.

6.1.1.1 For the evaluation of inorganic COPC mobility, bottles made of high density polyethylene (HDPE) (e.g., Nalgene #3140-0250 or equivalent), polypropylene (PP), or polyvinyl chloride (PVC) are recommended.

6.1.1.2 For the evaluation of non-volatile organic and mixed organic/inorganic COPC mobility, bottles made of glass or Type 316 stainless steel are recommended. Polytetrafluoroethylene (PTFE) is not recommended for non-volatile organics due to the sorption of species with high hydrophobicity (e.g., PAHs). Borosilicate glass is recommended over other types of glass, especially when inorganic analytes are of concern.

6.1.2 The extraction vessels must be of sufficient volume to accommodate both the solid sample and an extractant volume, based on an L/S of 10 ± 0.5 mL extractant/g-dry. The head space in the bottle should be minimized to the extent possible when semi-volatile organics are COPCs. For example, Table 1 indicates that 250-mL volume bottles are recommended when the minimum 20 g-dry mass equivalent is contacted with 200 mL of extractant.

6.1.3 The vessel must have a leak-proof seals that can sustain end-over-end tumbling for the duration of the designated contact time.

6.1.4 If centrifugation is anticipated to be beneficial for initial phase separation, the extraction vessels should be capable of withstanding centrifugation at 4000 ± 100 rpm for a minimum of 10 ± 2 min. Alternately, samples may be extracted in bottles that do not meet this centrifugation specification (e.g., Nalgene I-Chem #311-

0250 or equivalent) and the solid-liquid slurries transferred into appropriate centrifugation vessels for phase separation as needed.

6.2 Balance — Capable of 0.01-g resolution for masses less than 500 g.

6.3 Rotary tumbler — Capable of rotating the extraction vessels in an end-over-end fashion at a constant speed of 28 ± 2 rpm (e.g., Analytical Testing, Werrington, PA or equivalent).

6.4 Filtration apparatus — Pressure or vacuum filtration apparatus composed of appropriate materials so as to maximize the collection of extracts and minimize loss of the COPCs (e.g., Nalgene #300-4000 or equivalent) (see Sec. 6.1).

6.5 Filtration membranes — Composed of polypropylene or equivalent material with an effective pore size of 0.45-µm (e.g., Gelman Sciences GH Polypro #66548 from Fisher Scientific or equivalent).

6.6 pH Meter — Laboratory model with the capability for temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) and a minimum resolution of 0.1 pH units.

6.7 pH combination electrode — Composed of chemically-resistant materials.

6.8 Conductivity meter — Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value.

6.9 Conductivity electrodes — Composed of chemically-resistant materials.

6.10 Adjustable-volume pipettor — Oxford Benchmate series or equivalent. The necessary delivery range will depend on the buffering capacity of the solid material and acid/base strength used in the test.

6.11 Disposable pipettor tips.

6.12 Centrifuge (recommended) — Capable of centrifuging the extraction vessels at a rate of 4000 ± 100 rpm for 10 ± 2 min.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specification are available. Other grades may be used, provided it is first ascertained that the reagents are of sufficiently high purity to permit use without lessening the accuracy of the determination. Inorganic reagents and extracts should be stored in plastic to prevent interaction of constituents from glass containers.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Nitric acid (2.0 N), HNO_3 – Trace-metal grade or better, purchased at strength or prepared by diluting concentrated nitric acid with reagent water. Solutions with alternate normality may be used as necessary. In such cases, the amounts of HNO_3 solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions (see Sec. 11.4).

7.4 Potassium hydroxide (1.0 N), KOH – ACS grade, purchased at strength or prepared by diluting concentrated potassium hydroxide solution with reagent water, or otherwise by dissolving 56.11 g of solid potassium hydroxide in 1 L of reagent water. Solutions with alternate normality may be used as necessary. In such cases, the amounts of KOH solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions (see Sec. 11.4).

7.5 Consult Methods 9040, 9045 and 9050 for additional information regarding the preparation of reagents required for pH and specific conductance measurements.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three “Inorganic Analytes” and Chapter Four “Organic Analytes.”

8.2 All samples should be collected using an appropriate sampling plan.

8.3 All analytical sample containers should be composed of materials that minimize interaction with solution COPCs. For further information, see Chapters Three and Four.

8.4 Preservatives should not be added to samples before extraction.

8.5 Samples can be refrigerated, unless refrigeration results in an irreversible physical change to the sample.

8.6 Analytical samples should be preserved according to the guidance given in the individual determinative methods for the COPCs.

8.7 Extract holding times should be consistent with the aqueous sample holding times specified in the determinative methods for the COPCs.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 In order to demonstrate the purity of reagents and sample contact surfaces, method blanks should be tested at the extremes of the acid and base additions, as well as when only reagent water (no acid or base addition) is used for extraction.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific quality control procedures.

9.4 Solid materials should be tested within one month of receipt unless the project requires that the "as-received" samples are tested sooner (e.g., the material is part of a time-dependent study or the material may change during storage due to oxidation or carbonation).

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified at a minimum annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PREPARATORY PROCEDURES

A flowchart for the method procedure is presented in Figure 1.

11.1 Particle-size reduction (if required)

11.1.1 In this method, particle-size reduction is used for sample homogenization and to prepare large-grained samples for extraction so that the approach toward liquid-solid equilibrium is enhanced and mass transport through large particles is minimized. A longer extract contact time is required for larger maximum particle-size designations. This method designates three maximum particle sizes and associated contact times (see Table 1). The selection of an appropriate maximum particle size from this table should be based on professional judgment regarding the practical effort required to size-reduce the solid material.

11.1.2 Particle-size reduction of “as received” samples may be achieved through crushing, milling or grinding with equipment made from chemically-inert materials. During the reduction process, care should be taken to minimize the loss of sample and potentially volatile constituents in the sample.

11.1.3 If the moisture content of the “as received” material is greater than 15% (wet basis), air drying or desiccation may be necessary. Oven drying is not recommended for the preparation of test samples due to the potential for mineral alteration and volatility loss. In all cases, the moisture content of the "as received" material should be recorded.

NOTE: If the solid material is susceptible to interaction with the atmosphere (e.g., carbonation, oxidation), drying should be conducted in an inert environment.

11.1.4 When the material appears to be of a relatively uniform particle size, calculate the percentage less than the sieve size as follows:

$$\%\ \text{Passing} = \frac{M_{\text{sieved}}}{M_{\text{total}}} \times \mathbf{100}\,\%$$

Where: M_{sieved} = mass of sample passing the sieve (g)
M_{total} = mass of total sample (g) (e.g., M_{sieved} + mass not passing sieve)

11.1.5 The fraction retained by the sieve should be recycled for further particle-size reduction until at least 85% of the initial mass has been reduced below the designated maximum particle size. Calculate and record the final percentage passing the sieve and the designated maximum particle size. For the uncrushable fraction of the "as received" material, record the fraction mass and nature (e.g., rock, metal or glass shards, etc).

11.1.6 Store the size-reduced material in an airtight container in order to prevent contamination via gas exchange with the atmosphere. Store the container in a cool, dark and dry place prior to use.

11.2 Determination of solids and moisture content

11.2.1 In order to provide the dry mass equivalent of the "as-tested" material, the solids content of the subject material should be determined. Often, the moisture content of the solid sample is recorded. In this method, the moisture content is determined and recorded on the basis of the "wet" or "as-tested" sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable or explosive materials.

11.2.2 Place a 5–10-g sample of solid material into a pre-tared dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Periodically check the sample mass after allowing the sample to cool to room temperature (20 ± 2 °C) in a desiccator.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.2.3 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content (g-dry/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.2.4 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: $MC_{(wet)}$ = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.3 Pre-test titration (if required)

In order to conduct the parallel batch test in Sec. 12.0, a schedule of acid and base additions should be formulated from either a pre-test titration or based on prior knowledge of the acid/base titration curve of the sample. This section describes the procedure for obtaining a titration curve of the test material, when sufficient prior knowledge is unavailable.

If the schedule of acid and base additions will be generated from prior knowledge, proceed to Sec. 11.4. If the schedule of acid and base additions is already known, proceed to Sec. 12.0.

Figures 2-4 show example titration curves for a wide variety of solid materials. Table 2 indicates how these materials may be classified as (a) low alkalinity; (b) moderate alkalinity; or (c) high alkalinity in terms of the equivalents of acid required for obtaining final extraction pH values in the range of 2-13.

11.3.1 Predict the classification of the neutralization behavior of the solid material based on professional judgment, preliminary data, or the material examples shown in Table 2 and Figures 2-4.

11.3.2 Conduct a five-point parallel extraction test using 10-g-dry samples of the solid following the pre-test schedule shown in Table 3 for the chosen classification. One position in the five-point pre-test must be an extraction under natural test conditions (e.g., extraction with reagent water only at liquid-solid ratio of 10 mL/g-dry). Perform the extraction following the procedure in Sec. 12.0, omitting the filtration, method blanks, and analytical sample collection.

11.3.3 Plot the pre-test titration curve (e.g., the extract pH as a function of the equivalents of acid added) considering base equivalents as the negative sign of acid equivalents.

11.3.4 If a higher resolution in the titration curve is desired in order to determine intermediate acid/base additions for all target pH values, reiterate the pre-test extraction until the 2-13 pH range can be resolved.

NOTE: Additional pre-test point(s) interpolating or extrapolating from the pre-test schedule may be necessary to provide adequate resolution in the titration curve.

11.3.5 Pre-test titration using provided Microsoft® Excel template

The "Pre-Test" worksheet in the provided Excel template may be used to calculate pre-test extraction formulations and plot the pre-test titration curve. Mandatory input data for the template includes:

a) particle size of the "as tested" material (see Sec. 11.1);
b) solids content of the "as tested" material (see Sec. 11.2); and
c) five acid/base additions based on the predicted response classification of the solid material (see Sec. 11.3).

Enter the eluate pH and plot the pre-test titration curve. Compare the resulting titration curve to the target pH values as designated in Table 4.

11.4 Formulation of acid and base additions schedule

A schedule of acid and base additions is used in the main extraction procedure (Sec. 12.0) to set up nine extractions of the test material plus three method blanks. Based on either prior knowledge of the acid/base titration curve of the sample or the results of the pre-test titration procedure in Sec. 11.3, formulate a schedule of test extractions using the example in Table 4 and the following steps.

11.4.1 Using the extraction parameters in Table 1, identify the recommended minimum dry-mass equivalent associated with the particle size of the "as-tested" sample. Calculate and record the amount of "as tested" material equivalent to the dry-material mass from Table 1 as follows:

$$M_{test} = \frac{M_{dry}}{SC}$$

Where: M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)
M_{dry} = mass of dry material specified in the method (g-dry)
SC = solids content of "as-tested" material (g-dry/g)

11.4.2 Label Column A of the schedule table with consecutive numbers for the nine test positions (shown in Table 4 as "TXX" labels) and three method blanks (shown in Table 4 as "BXX" labels).

11.4.3 Copy the nine target pH points as shown in Table 5 and enter this data into <u>Column B</u> of the schedule table. The natural pH value (e.g., pH resulting from extraction with reagent water only at L/S 10) may be used as a substitute for a test position pH value if it falls within the tolerance of the specified target pH. For example, if the natural pH is 11.8 and would satisfy the target pH of 12.0 ± 0.5, the extraction at natural conditions would be conducted and the specified target point of 12.5 ± 0.5 would be removed from Table 5.

11.4.4 For each test position, determine the equivalents of acid or base required to meet the target pH from the pre-test titration curve (see Sec. 11.3). Enter this data into <u>Column C</u> of the schedule table. Interpolate intermediate acid additions on the pre-test titration curve using linear interpolation or other regression techniques.

<u>NOTE</u>: Linear interpolation will have some inherent error, which may result in an extract pH that falls outside of the target pH tolerance. Additional pre-test points interpolating or extrapolating from the pre-test schedule in Table 3 may be necessary to provide adequate resolution of the titration curve.

11.4.5 Enter the acid volumes in <u>Column D</u> and base volumes in <u>Column E</u> of the schedule after converting the equivalents of acid and base to volume as follows:

$$V_{a/b} = \frac{Eq_{a/b}}{N_{a/b}}$$

Where: $V_a/_b$ = volume of acid or base to be entered in the schedule table (mL)
$Eq_{a/b}$ = equivalents of acid or base selected for the target pH as determined from the pre-test titration curve (meq/g)
$N_{a/b}$ = normality of the acid or base solution (meq/mL)

11.4.6 In <u>Column F</u> of the schedule table, calculate the volume of moisture contained in the “as tested” sample as follows:

$$V_{W,sample} = \frac{M_{test} \times (1 - SC)}{\rho_w}$$

Where: $V_{W,sample}$ = volume of water in the “as tested” sample (mL)
M_{test} = mass of the “as tested” sample (g)
SC = solids content of the “as tested” sample (g-dry/g)
ρ_w = density of water (1.0 g/mL at room temperature)

11.4.7 In <u>Column G</u> of the schedule table, calculate the volume of reagent water required to bring each extraction to an L/S of 10 mL/g-dry solid as follows:

$$V_{RW} = M_{dry} \times LS - V_{W,sample} - V_{a/b}$$

Where: V_{RW} = volume of reagent water required to complete L/S (mL)
M_{dry} = dry mass equivalent of solid sample (g)
L/S= liquid-to-dry-solid ratio (10 mL/g)
$V_{W,sample}$ = volume of water in “as used” sample (mL)
$V_{a/b}$ = volume of acid or base for the extraction recipe (mL)

11.4.8 Method Blanks

In the schedule table, include three additional extractions for processing method blanks. Method blanks extractions are performed using the same equipment, reagents, and extraction process as the test positions, but without solid sample. The three method blanks should include:

a) reagent water (B01 in Table 4);
b) reagent water + maximum volume of acid in the schedule (B02 in Table 4); and
c) reagent water + maximum volume of base in the schedule (B03 in Table 4).

NOTE: If multiple materials or replicate tests are carried out in parallel, only one set of method blanks is necessary.

11.4.9 Schedule formulation using Excel template

The “Test Data” worksheet in the provided Excel template may be used to automatically calculate a schedule of acid and base additions, as well as to plot the response eluate pH and conductivity as a function of acid addition. Mandatory input data for the template includes:

a) particle size of the “as tested” material (see Sec. 11.1);
b) solid content of the “as tested” material (see Sec. 11.2); and
c) nine acid/base additions determined from the pre-test titration curve with respect to target pH values designated in Table 5.

Subsequent to the extraction procedure, eluate pH, conductivity, and oxidation/reduction potential (optional) for up to three replicates may be entered and plotted as a function of acid added.

12.0 EXTRACTION PROCEDURE

Use the schedule of acid and base additions (Sec. 11.4) as a guide to set up nine test extractions and three method blanks as follows:

12.1 Label bottles with test position and method blank numbers according to the schedule of acid and base additions (see Column A in Table 4).

12.2 Use the extraction parameters in Table 1 to identify the recommended dry-mass equivalent associated with the particle size of the "as tested" sample. Calculate and record the amount of "as tested" material equivalent to the identified dry mass from Table 1 as follows:

$$M_{test} = \frac{M_{dry}}{SC}$$

Where: M_{test} = mass of "as tested" solid equivalent to g of dry material (g)
M_{dry} = mass of dry material specified in method (g)
SC = solids content of "as tested" material (g/g)

12.3 Place the dry equivalent mass (± 0.1 g) of the "as tested" sample, calculated above, into each of the test position extraction vessels.

NOTE: Do NOT put solid material in the method blank extraction vessels.

12.4 Add the appropriate volume of reagent water (± 5% of target value) to both the test position and method blank extraction vessels, as specified in the schedule for the L/S makeup (see Column G in Table 4).

12.5 Add the appropriate volume of acid or base (± 1% of target value) to each vessel, using a continuously adjustable pipettor, as designated in the schedule for acid/base addition (see Column D and Column E in Table 4).

12.6 Tighten the leak-proof lid on each bottle and tumble all extractions (i.e., test positions and method blanks) in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature (20 ± 2 °C). The contact time for this method will vary depending on the sample particle size as shown in Table 1.

NOTE: The length of the contact time is designed to enhance the approach toward liquid-solid equilibrium. Longer contact times are required for larger particles to compensate for the effects of intra-particle diffusion. See Table 1 for recommended contact times based on particle size.

12.7 Remove the extraction vessels from the rotary tumbler and clarify the extractants by allowing the bottles to stand for 15 ± 5 min. Alternately, centrifuge the extraction vessels at 4000 ± 100 rpm for 10 ± 2 min.

NOTE: If clarification is significantly incomplete after settling or centrifugation, eluate measurements for pH, conductivity, and oxidization-reduction potential (ORP) may be taken on filtered samples. In this case, perform the filtration in 12.9 prior to eluate measurement in 12.8 and note the deviation from the written procedure.

CAUTION: Following separation from the solid phase, eluate samples lack the buffering provided by the solid phase and therefore may be susceptible to pH change resulting from interaction with air.

12.8 For each extract vessel, decant a minimum volume (~ 5 mL) of clear, unpreserved supernatant into a clean container. Measure and record the pH, specific conductivity, and oxidation-reduction potential (optional, but strongly recommended) of the extracts (see Methods 9040, 9045, and 9050).

NOTE: Eluate measurements for pH, conductivity, and ORP should be taken as soon as possible after the settling and preferably within 1 hour after completion of tumbling (12.6).

12.9 Separate the solid from the remaining liquid in each extraction vessel by pressure or vacuum filtration through a clean 0.45-µm pore size membrane (Sec. 6.5). The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

NOTE: If it is suspected that COPCs (e.g., mercury) might be lost under vacuum, the samples may be pressure-filtered using an inert gas (e.g., nitrogen or argon).

12.10 Immediately, preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

13.0 DATA ANALYSIS AND CALCULATIONS (EXCEL TEMPLATE PROVIDED)

13.1 Data reporting

13.1.1 Figure 5 shows an example of a data sheet that may be used to report the concentration results of this method. This example is included in the Excel template. At a minimum, the basic test report should include:

a) Name of the laboratory
b) Laboratory technical contact information
c) Date at the start of the test
d) Name or code of the solid material
e) Particle size (85 wt% less than)
f) Type of acid and/or base used in test
g) Extraction contact time (h)
h) Ambient temperature during extraction (°C)
i) Eluate specific information (see Sec. 13.1.2 below)

13.1.2 The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Mass of "as tested" solid material used (g)
c) Moisture content of material used (g_{H_2O}/g)
d) Volume (mL) and normality (N) of acid and/or base used
e) Volume of water added (mL)
f) Target pH
g) Measured final eluate pH
h) Measured eluate conductivity (mS/cm)
I) Measured ORP (mV) (optional)
j) Concentrations of all COPCs
k) Analytical QC qualifiers as appropriate

13.2 Data interpretation (optional)

13.2.1 Acid/base neutralization curve

Plot the pH of each extract as a function of the equivalents of acid or base added per dry gram of material to generate an acid/base neutralization curve.

NOTE: For materials in which both acid and base were used, equivalents of base can be presented as the opposite sign of acid equivalents (i.e., 5 meq/g-dry of base would correspond to -5 meq/g-dry of acid).

The titration curve can be interpreted as showing the amount of acid or base that is needed to shift the pH of the subject material. This is helpful when evaluating field scenarios where the pH of leachates is not buffered by the acidity or alkalinity of the solid material.

13.2.2 LSP curve

An LSP curve can be generated for each COPC following chemical analyses of all extracts by plotting the target analyte concentration in the liquid phase as a function of the measured extract pH for each extract. As an example, Figure 6 illustrates the LSP curves for arsenic and selenium from a coal combustion fly ash and indicates the limits of quantitation (shown as ML and MDL) and the natural concentration response.

13.2.2.1 The lower limit of quantitation (LLOQ) of the determinative method for each COPC may be shown as a horizontal line. COPC concentrations below this line indicate negligible or non-quantitative concentrations.

NOTE: The lower limit of quantitation is highly matrix dependent and should be determined as part of a QA/QC plan.

13.2.2.2 Natural response is defined as the eluate pH and COPC concentration measured when the solid material is extracted with reagent water at an L/S of 10 mL/g-dry. The natural response values can be shown on the LSP curve as a vertical line from the *x*-axis (at the replicate average natural pH) intersected with a horizontal line (at the replicate average COPC concentration). Alternatively, the natural response can be indicated in results using a different symbol from other results.

13.2.2.3 The values on the curve indicate the eluate concentration of the constituent of interest at an L/S of 10 mL/g-dry over a pH range. The shape of the LSP curve is indicative of the speciation of the COPC in the solid phase with four characteristic LSP curve shapes (i.e., relative locations of maxima and minima) presented schematically in Figure 7.

Cationic Species (e.g., Cd) — The LSP curve of cationic species typically has a maximum concentration in the acidic pH range that decreases to lower values at alkaline pH.

Amphoteric Species (e.g., Pb, Cr(III), Cu.) — The LSP curves tend to be similar in shape to cationic LSP curves with greater concentrations in the acidic pH range. However, the concentrations pass through a minimum in the near neutral to slightly acid pH range only to increase again for alkaline pH values. Typically, the increase at high pH is due to the solubility of hydroxide complexes (e.g., $[Pb(OH_3)]^-$).

Oxyanionic Species (e.g. $[AsO_4]^-$, $[SeO_4]^-$, $[MnO_4]^-$) — The LSP curves often show maxima in the neutral to slightly alkaline range.

Highly Soluble Species (e.g., Na^+, K^+, Cl^-) — The LSP curve is only a weak function of pH.

The idealized LSP curves in Figure 7 can be compared with the general shape of the test data to infer the speciation of the COPC in the solid matrix. Concentration results from this method may be simulated with geochemical speciation models to infer the mineral phases, adsorption reactions, and soluble complexes that control the release of the COPC (see Ref. 1).

14.0 METHOD PERFORMANCE

14.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.2 Refs. 2 and 3 may provide additional guidance and insight on the use, performance and application of this method.

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the U.S. EPA recommends recycling as the next best option as long as the management option if protective of human health and the environment.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

16.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in Sec. 14.2.

17.0 REFERENCES

1. H. A. van der Sloot, P.F.A.B. Seignette, J.C.L. Meeussen, O. Hjelmar and D.S. Kosson, (2008), “A Database, Speciation Modeling and Decision Support Tool for Soil, Sludge, Sediments, Wastes and Construction Products: LeachXS™-ORCHESTRA,” in Venice 2008: Second International Symposium on Energy from Biomass and Waste, Venice, Italy, 17-20 November 2008 (also see www.leaching.com).

2. D.S. Kosson, H.A. van der Sloot, F. Sanchez and A.C. Garrabrants, (2002), “An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials,” Environmental Engineering Science, 19(3) 159-204.

3. D.S. Kosson, A.C. Garrabrants, H.A. van der Sloot (2009) “Background Information for the Development of Leaching Test Draft Methods 1313 through Method 1316”, (in preparation).

4. U.S. EPA(2006) Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, February 2006.

5. U.S. EPA(2008) Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control, EPA-600/R-08/077, July 2008.

6. U.S. EPA(2009) Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, EPA-600/R-09/151, December 2009.

18.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXTRACTION PARAMETERS AS FUNCTION OF MAXIMUM PARTICLE SIZE

Particle Size (85 wt% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Suggested Vessel Size (mL)
0.3	50	20 ± 0.02	24 ± 2	250
2.0	10	40 ± 0.02	48 ± 2	500
5.0	4	80 ± 0.02	72 ± 2	1000

TABLE 2

MATERIAL NEUTRALIZATION CLASSIFICATIONS

Neutralization Classification	Material Types
Low Alkalinity	soils; sediments; CCR fly ash; CCR bottom ash; coal milling rejects; MSWI fly ash, MSWI bottom ash; sewage sludge amended soil
Moderate Alkalinity	soils; wood preserving waste; MSWI bottom ash; steel slag; electric arc furnace dust; MSW compost; nickel sludge; Portland cement mortar
High Alkalinity	Portland cement clinker; steel blast furnace slag, solidified waste (fly ash, blast furnace slag, Portland cement)

NOTE: CCR = Coal combustion residue
MSWI = Municipal solid waste incinerator

TABLE 3

PRE-TEST TITRATION: ACID EQUIVALENT SCHEDULE

Neutralization Classification	Equivalents of Acid (meq/g-dry)				
	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5
Low Alkalinity	-2.0	-1.0	0	1.0	2.0
Moderate Alkalinity	-2.0	0	2.0	5.0	10.0
High Alkalinity	0	5.0	10.0	15.0	25.0

NOTE: 1) Base additions shown as opposite sign of acid equivalents.
2) Additional pre-test point(s) interpolating or extrapolating from the pre-test schedule may be necessary to provide adequate resolution in the titration curve.

TABLE 4

EXAMPLE SCHEDULE OF ACID AND BASE ADDITIONS

A	B	C	D	E	F	G
Test position	Target extract pH	Equivalents of Acid (meq/g-dry)	Volume of 2N HNO_3 (mL)	Volume of 1N KOH (mL)	Volume of moisture in sample (mL)	Volume of reagent water (mL)
T01	13.0	-1.10	-	22.0	2.22	176
T02	12.0	-0.75	-	15.0	2.22	183
T03	10.5	-0.38	-	7.60	2.22	190
T04	9.0	-0.15	-	3.0	2.22	195
T05	8.0	-0.05	-	1.0	2.22	197
T06	Natural	0	-	-	2.22	198
T07	5.5	0.12	1.20	-	2.22	197
T08	4.0	0.90	9.00	-	2.22	189
T09	2.0	3.10	31.0	-	2.22	167
B01	QA/QC	0	-	-	-	200
B02	QA/QC	3.10	31.0	-	-	169
B03	QA/QC	-1.10	-	22.0	-	178

NOTE: 1) This schedule is based on “as tested” sample mass of 22.2±0.1 g (i.e., equivalent “as tested” mass for a 20.0 g-dry sample at a solids content of 0.90 g-dry/g).
2) In this example, the natural pH is assumed to be 7.0±0.5.
3) Test positions marked B01, B02, and B03 are method blanks of reagent water, reagent water + maximum acid addition, and reagent water + maximum base addition, respectively.

Data modified from Ref. 2.

TABLE 5

FINAL EXTRACT PH TARGETS

pH Target	Rationale
2.0±0.5	Provides estimates of total or available COPC content
4.0±0.5	Lower pH limit of typical management scenario
5.5±0.5	Typical lower range of industrial waste landfills
7.0±0.5	Neutral pH region; high release of oxyanions
8.0±0.5	Endpoint pH of carbonated alkaline materials
9.0±0.5	Minimum of LSP curve for some cationic and amphoteric COPCs
10.5±0.5	Minimum of LSP curve for some cationic and amphoteric COPCs
12.0±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
13.0±0.5	Upper bound (field conditions) for amphoteric COPCs
variable	Natural pH at L/S 10 ml/g-dry (no acid/base addition)

FIGURE 1

METHOD FLOWCHART

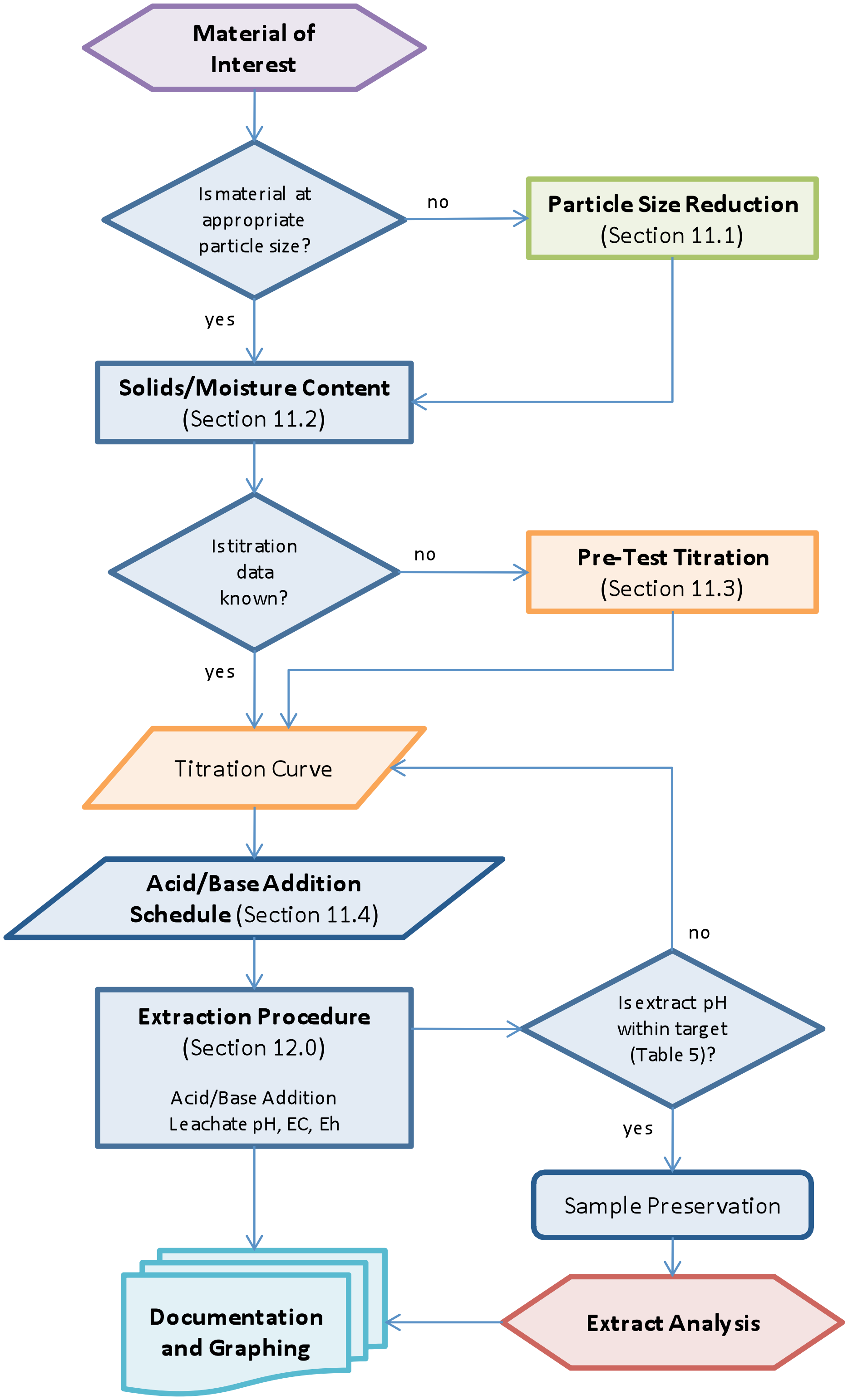
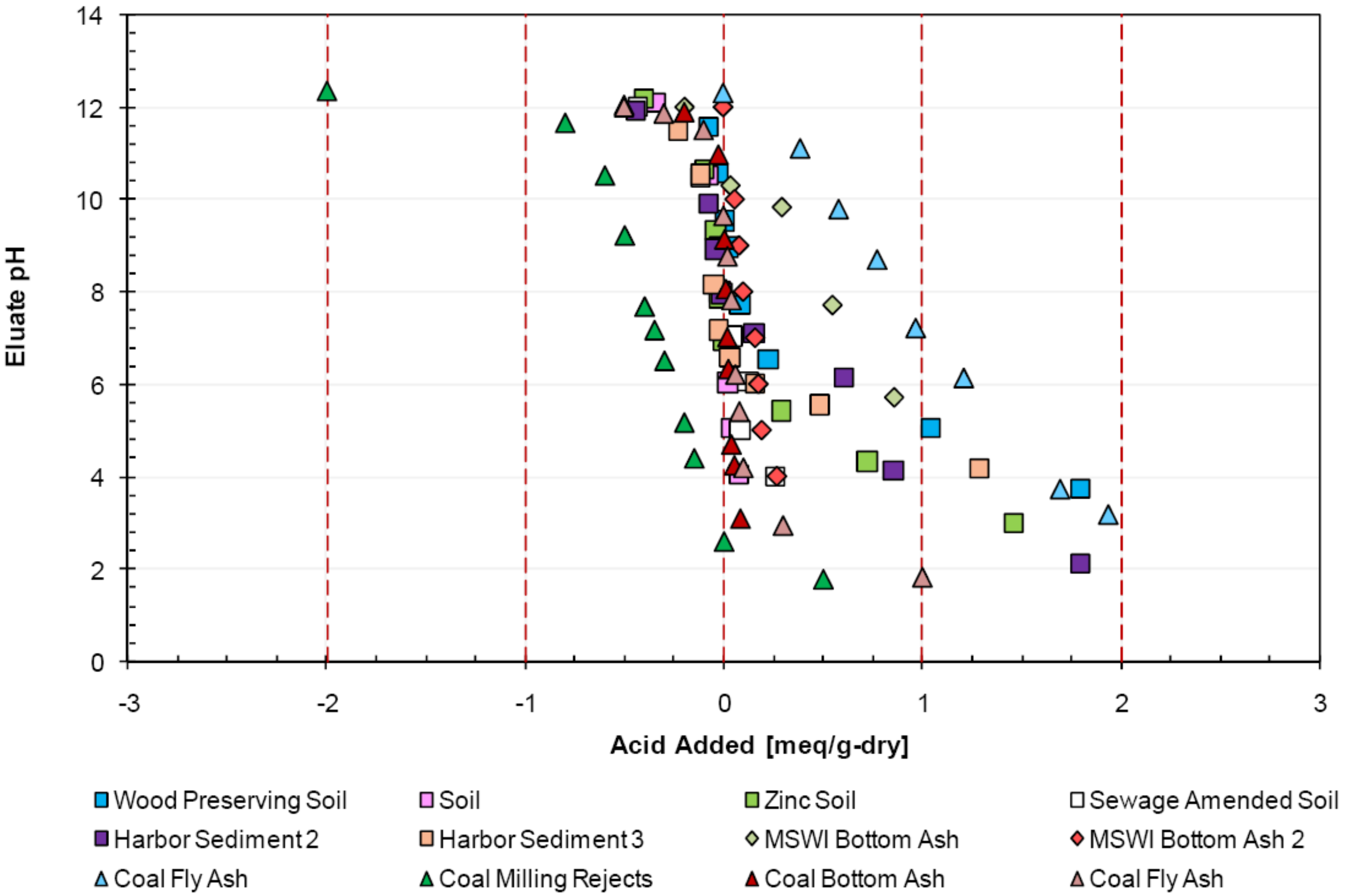


FIGURE 2

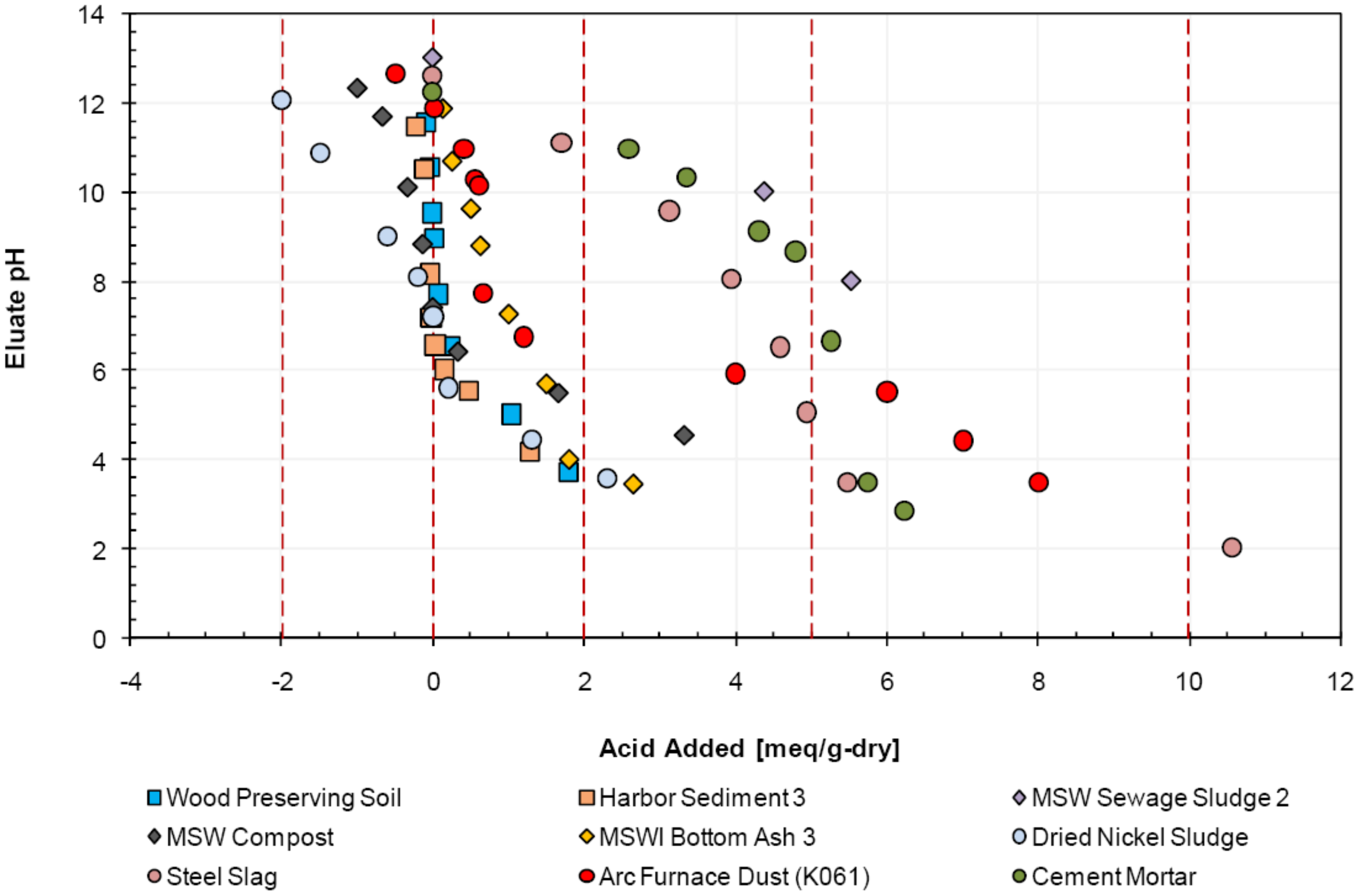
EXAMPLE TITRATION CURVES FOR SELECTED “LOW ALKALINITY” WASTES



Some data taken LeachXS database (Ref. 1).

FIGURE 3

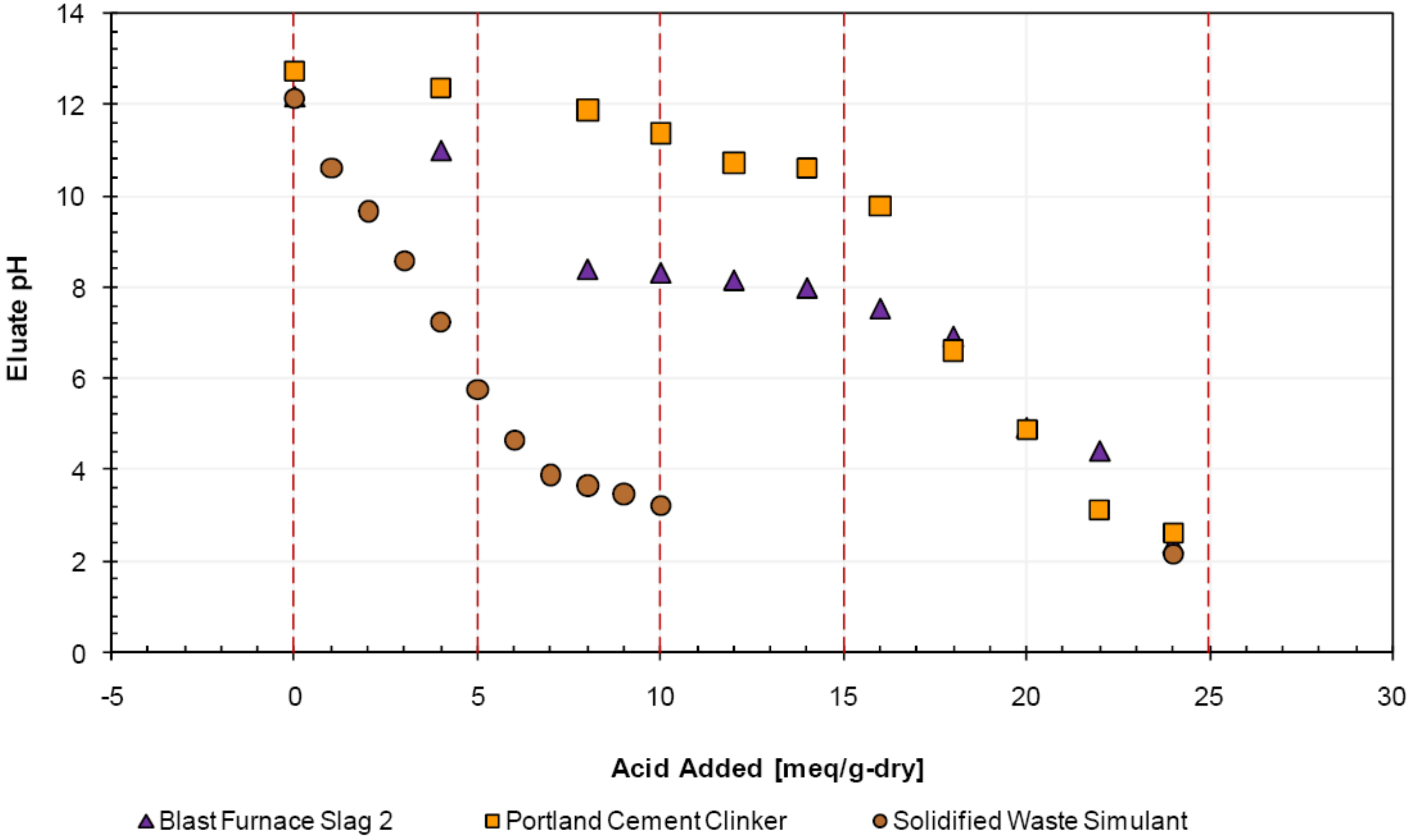
EXAMPLE TITRATION CURVES FOR SELECTED “MODERATE ALKALINITY” WASTES



Some data taken from LeachXS database (Ref. 1).

FIGURE 4

EXAMPLE TITRATION CURVES FOR SELECTED "HIGH ALKALINITY" WASTES



Some data taken from LeachXS database (Ref. 1).

FIGURE 5

EXAMPLE DATA REPORT FORMAT

EPA METHOD 1313
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code: **XYZ**
Material Type: Coal Combustion Fly Ash
Date Received: 10/1/20xx
Test Date: 11/1/20xx
Report Date: 12/1/20xx

Particle Size: 88% passing 2-mm sieve
Contact Time: 48 hours
Lab Temperature: 21 ± 2 °C
Acid Used: Nitric acid
Base Used: Sodium hydroxide

Test Position	**Replicate**	**Value**	**Units**	**Method**	**Note**
T01	**A**				
	Eluate Sample ID	**XYZ-1313-T01-A**			
	Solid Material	40.0	g		
	Moisture Content	0.01	g		
	Water Added	386.0	g_{H_2O}/g		
	Acid Added	14.0	mL		
	Acid Strength	2.0	mL		
	Base Added	-	N		
	Base Strength	1.0	mL		
	Target pH	2.0 ± 0.5	-		
	Eluate pH	1.89	-	EPA 9040	
	Eluate Conductivity	12.6	mS/c	EPA 9050	
	Eluate ORP	203	mv		

Chemical Analysis	**Value**	**Units**	**QC Flag**	**Method**	**Date**	**Dilution Factor**
Al	216.0	mg/L		EPA 6020	11/7/20xx	1000
As	0.64	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/9/20xx	1

Test Position	**Replicate**	**Value**	**Units**	**Method**	**Note**
T02	**A**				
	Eluate Sample ID	**XYZ-1313-T02-A**			
	Solid Material	40.0	g		
	Moisture Content	0.01	g		
	Water Added	400.0	g_{H_2O}/g		
	Acid Added	14.0	mL		
	Acid Strength	2.0	mL		
	Base Added	-	N		
	Base Strength	1.0	mL		
	Target pH	4.0 ± 0.5	-		
	Eluate pH	3.86	-	EPA 9040	Natural pH
	Eluate Conductivity	0.99	mS/c	EPA 9050	
	Eluate ORP	180	mv		

Chemical Analysis	**Value**	**Units**	**QC Flag**	**Method**	**Date**	**Dilution Factor**
Al	449.0	mg/L		EPA 6020	11/7/20xx	1000
As	0.979	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (< "LLOQ")

FIGURE 6

EXAMPLE LSP CURVES FROM A COAL COMBUSTION FLY ASH SHOWING ASSESSMENT ZONES FOR A LANDFILL SCENARIO

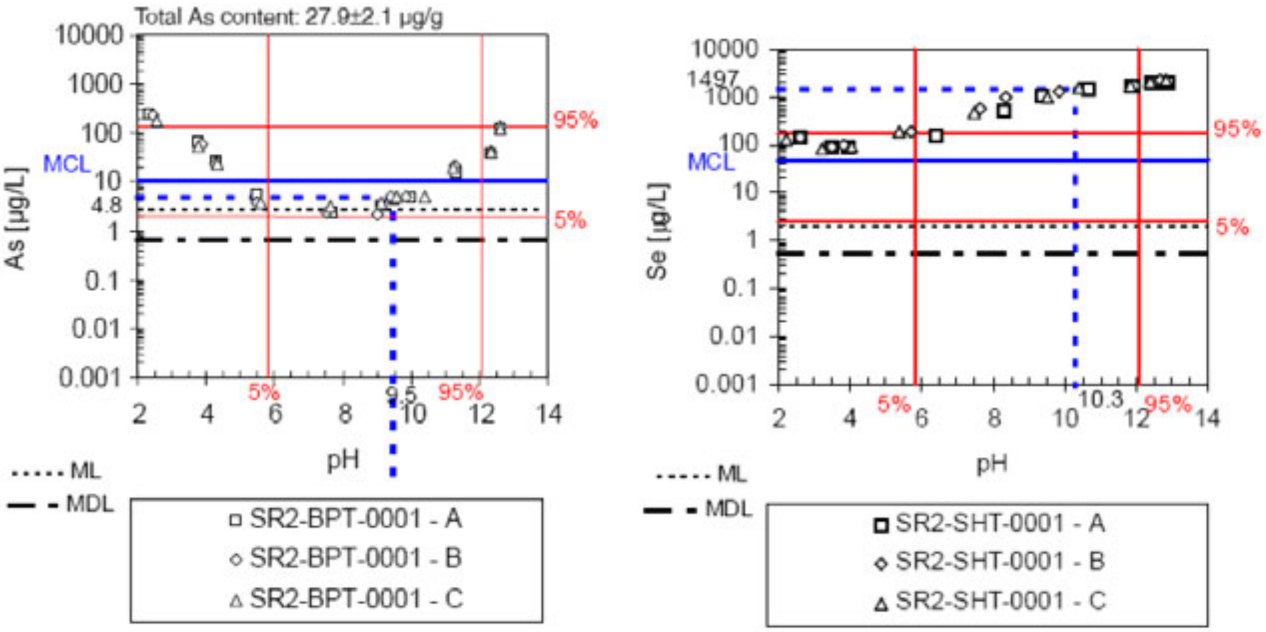


Figure taken from Ref. 4.

FIGURE 7

SCHEMATIC LSP CURVES OF CATIONIC, AMPHOTERIC, AND OXYANIONIC SPECIES

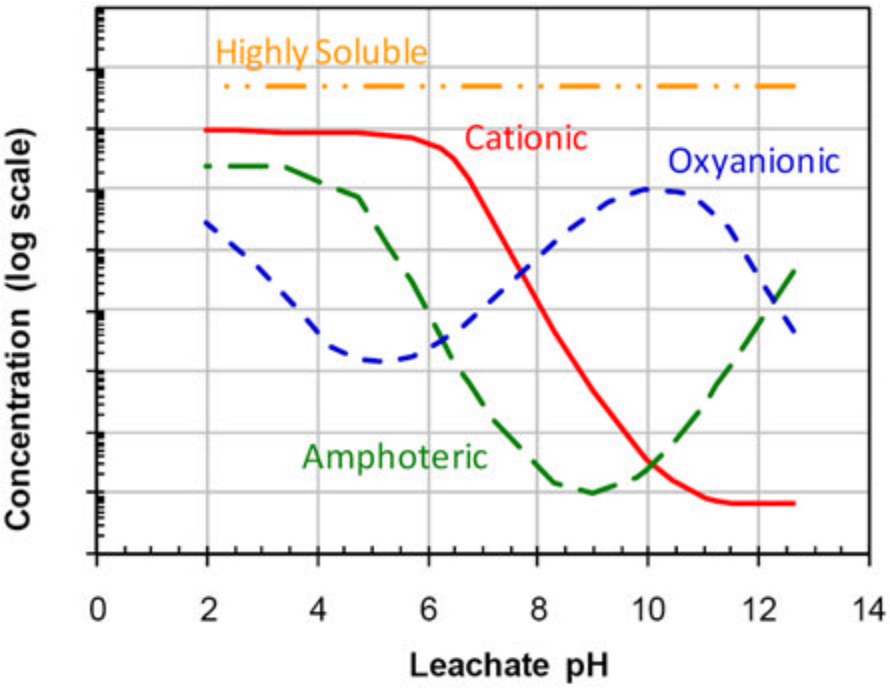


Figure taken from Ref. 2.

APPENDIX B

METHOD 1314 –

ULIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-SOLID RATIO FOR CONSTITUENTS IN SOLID MATERIALS USING AN UP-FLOW PERCOLATION COLUMN PROCEDURE

PRELIMINARY VERSION[1] OF METHOD 1314

LIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-SOLID RATIO FOR CONSTITUENTS IN SOLID MATERIALS USING AN UP-FLOW PERCOLATION COLUMN PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide the liquid-solid partitioning (LSP) of inorganic constituents (e.g., metals, radionuclides) and non-volatile organic constituents (e.g., polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon) in a granular solid material as a function of liquid-to-solid (LS) ratio under percolation conditions. The first eluates of the column test provide insight into pore solution composition either in a granular bed (e.g., soil column) or in the pore space of low-permeability material (e.g., solidified monolithic or compacted granular fill). Analyses of eluates for dissolved organic carbon and of the solid phase for total organic carbon afford evaluation of the impact of organic carbon release and the influence of dissolved organic carbon on the LSP of inorganic constituents.

1.2 This method is intended to be used as part of environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness and site remediation.

1.3 This method is suitable to a wide range of granular solid materials. Example materials include industrial wastes, soils, sludges, combustion residues, sediments, construction materials, and mining wastes. This method is not suitable to monolithic materials (e.g., cement-based and stabilized materials) without particle-size reduction prior to testing.

1.4 This test method is intended as a means for obtaining a series of extracts (i.e., the eluates) of a granular solid material which may be used to show eluate concentrations

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[1] Preliminary Version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846. This method has been derived from published procedures (Kosson et al, 2002). The method has been submitted to the U.S. EPAOffice of Resource Conservation and Recovery and is currently under review for development of interlaboratory validation studies to develop precision and bias information.

and/or cumulative release as a function of LS ratio which can be related to a time scale when data on mean infiltration rate, density and height of application are available.

1.5 This method provides options for the preparation of analytical samples that provide flexibility based on the level of detail required. For example, when the purpose of characterization is for comparison to previous testing, compositing of eluates may be possible to create a reduced set of analytical samples. Table 1 outlines the eluate fractions and collection options, based on whether concentration or cumulative release is to be reported. The collection schemes are described below.

1.5.1 Complete characterization

For complete characterization of eluate concentration and cumulative release as a function of LS ratio, nine discrete eluate collections and analyses are required (see Table 1, Option A). No compositing of eluate fractions is performed for complete characterization, and all eluate fractions are analyzed.

Eluate concentrations from complete characterization may be used in conjunction with information regarding environmental management scenarios to estimate anticipated leaching concentrations, release rates, and extents of release for individual material constituents in the management scenarios evaluated. Eluate concentrations may also be used along with geochemical speciation modeling to infer the mineral phases that control the LSP in the pore structure of the solid material.

1.5.2 Limited analysis

Under a limited analysis approach, nine eluate collections and analysis of six analytical samples are required. If evaluation is based on eluate concentrations, six discrete eluate fractions are chemically analyzed (see Table 1, Option B). If evaluation is based on cumulative release, some eluate fractions are composited by volume-weighted averaging to create a set of six analytical samples (see Table 1, Option C). The concentrations of composite analytical samples cannot be interpreted along with eluate fractions on the basis of concentration.

1.5.3 Index testing

For the determination of consistency between the subject material and previously characterized materials, nine eluate collections and analysis of three analytical samples are required. If consistency is to be determined by eluate concentrations, three discrete eluate fractions are chemically analyzed (see Table 1, Option D). If consistency is to be determined by cumulative release, some eluate fractions are composited by volume-weighted averaging to create a set of three analytical samples (see Table 1, Option E). The concentrations of composited analytical samples cannot be interpreted along with eluate fractions on the basis of concentration.

1.6 This method is not applicable to characterize the release of volatile organic analytes.

1.7 This method provides eluate solutions considered indicative of leachate under field conditions only where the field leaching pH is controlled by the alkalinity or acidity of the solid material and the field leachate is not subject to dilution or other attenuation mechanisms. The cumulative mass of constituent released over a LS ratio range may be considered an estimate of the maximum mass of that constituent to be leached under field leaching over intermediate time frames (e.g., up to 100 years) and the domain of laboratory test pH.

1.8 Prior to employing this method, analysts are advised to take reasonable measures to ensure that the granular sample is homogenized to the extent practical. Particle-size reduction may provide additional assurance of sample homogenization.

1.9 In preparation of solid materials for use in this method, particle-size reduction or exclusion of samples with large grain size is used to enhance the approach towards liquid-solid equilibrium over the residence time of eluant in the column.

1.10 The structure and use of this method is similar to that of NEN 7343 (see Ref. 1) and CEN TS 14405 (see Ref. 2).

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045, and 9050, and the determinative methods for the target analytes), quality control (QC) acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the concentration levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application. Guidance on defining data quality objectives can be obtained at http://www.epa.gov/QUALITY/qs-docs/g4-final.pdf

1.12 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

Eluant is introduced into a column of moderately-packed granular material in an up-flow pumping mode, with eluate collection performed as a function of the cumulative LS ratio. Up-flow pumping is used to minimize air entrainment and flow channeling. The default eluant for most materials is reagent water. However, a solution of 1.0 mM calcium chloride in reagent water is used when testing materials with either a high clay content (i.e., to prevent deflocculation of clay layers) or high organic matter (i.e., to moderate mobilization of dissolved organic carbon). The flow rate is maintained between 0.5-1.0 LS/day to increase the likelihood of local equilibrium between the solid and liquid phases, due to residence times longer than 1 day. Eluate volumes are chemically analyzed for a combination of inorganic and non-volatile organic analytes depending on the constituents of potential concern (COPC). For the purposes of chemical speciation modeling, the entire eluant volume up to 10 mL/g dry sample (g-dry) is collected in nine specific aliquots of varying volume. A limited subset of eluants volumes within the same LS ratio range may be collected and analyzed for regulatory and compliance purposes. A flowchart for performing this method is shown in Figure 1.

3.0 DEFINITIONS

3.1 COPC — A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.2 Release — The dissolution or partitioning of a COPC from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.3 LSP — The distribution of COPCs between the solid and liquid phases at the conclusion of the extraction.

3.4 LS ratio — the fraction of the total liquid volume (including the moisture contained in the “as used” solid sample) to the dry mass equivalent of the solid material. LS ratio is typically expressed in volume units of liquid per dry mass of solid material (mL/g-dry).

3.5 “As-tested” sample — The solid sample at the conditions (e.g., moisture content and particle-size distribution) present at the time of the start of the test procedure. The “as-tested” conditions will differ from the "as-received" sample conditions if particle-size reduction and drying were necessarily performed.

3.6 Dry-mass equivalent — The mass of “as-tested” (i.e., “wet”) sample that equates to the mass of dry solids plus associated moisture, based on the moisture content of the “as-tested” material. The dry-mass equivalent is typically expressed in mass units of the “as-tested” sample (g).

3.7 Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapters Three and Four for general guidance on the cleaning of laboratory apparatus prior to use.

4.2 When the test method is applied to solid materials with a clay content greater than 10% or an organic matter content greater than 1%, a solution of 1.0 mM calcium chloride in reagent water is recommended to minimize deflocculation of clay minerals. However, the use of calcium chloride solution will interfere with the determination of actual calcium and chloride release.

NOTE: The critical values of clay and organic matter content are verified during ruggedness testing.

4.3 When this method is applied to fine-grained, granular materials, tamping during column preparation may result in flow problems due to a low-permeability sample bed. This problem can be resolved by incorporating 20-50% inert material (e.g., 20–30-mesh normal sand or 2-mm borosilicate glass beads) into the solid sample. Alternatively, mass release from low-permeability materials may be measured using Method 1315.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and setting other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Column apparatus

This method recommends the use of a specific column apparatus (see Figure 2). Equipment with equivalent specifications may be substituted. The apparatus should have valves and quick connectors (e.g., Luer lock fittings) such that the column with end caps can be removed for packing with test material and mass measurements.

6.1.2 A 30-cm, straight cylindrical column with an inner diameter (ID) of 5-cm and constructed of inert material, resistant to high- and low-pH conditions and interaction with constituents of interest.

6.1.2.1 For the evaluation of inorganic COPC mobility, equipment composed of borosilicate glass (e.g., Kimble-Kontes CHROMAFLEX #420830-3020 or equivalent), polytetra-fluoroethylene (PTFE), high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) is recommended.

6.1.2.2 For the evaluation of non-volatile organic and mixed organic/inorganic COPCs, equipment composed of glass or Type 316 stainless steel is recommended. PTFE is not recommended for non-volatile organics, due sorption of species with high hydrophobicity (e.g., PAHs). Borosilicate glass is recommended over other types of glass, especially when inorganic analytes are of concern.

6.1.3 The column must be of sufficient volume to accommodate a minimum of a 300–g-dry material plus a 1-cm layer of silica sand (20-30 mesh) used at the bottom of the column to distribute eluant flow and at the top of the column to form a coarse filter for eluate particulates.

6.1.4 The column must have end cap materials that form a leak-proof seal and that can withstand pressures, such as encountered when pumping eluant through the column.

6.2 Eluant feed stock container — Resealable bottle or other container, constructed of inert material, capable of withstanding extreme pH conditions and interaction with any constituents of interest (see guidance in Sec. 6.1.2.).

6.3 Eluant feed tubing — 2-mm or similarly small ID tubing composed of chemically-inert material such as polyvinyl chloride or equivalent.

NOTE: Larger ID tubing may be required if a single eluent stock container is used to feed multiple column set-ups.

6.4 Eluate collection bottles — capable of assembly with column apparatus using simple water locks in order to prevent the intrusion of air (see Figure 2).

6.5 20–30-mesh normal washed quartz sand

6.6 Balance — Capable of 0.01-g resolution for masses less than 500 g.

6.7 Filtration apparatus — Pressure or vacuum filtration apparatus composed of appropriate materials so as to maximize the collection of extracts and minimize loss of the COPCs (e.g., Nalgene #300-4000 or equivalent) (see Sec. 6.1).

6.8 Filtration membranes — Composed of PP or equivalent material with an effective pore size of 0.45-µm (e.g., Gelman Sciences GH Polypro #66548 from Fisher Scientific or equivalent).

6.9 pH Meter — Laboratory model with the capability for temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) and a minimum resolution of 0.1 pH units.

6.10 pH combination electrode — Composed of chemically-resistant materials.

6.11 Conductivity meter — Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value.

6.12 Conductivity electrodes — Composed of chemically-resistant materials.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemical must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specification are available. Other grade may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Inorganic reagents and extracts should be stored in plastic to prevent interaction of constituents from glass containers.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Calcium chloride (1.0 mM), $CaCl_2$ — Prepared by dissolving 0.11 g of ACS grade or better solid calcium chloride in 1 L of reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three “Inorganic Analytes” and Chapter Four “Organic Analytes.”

8.2 All samples should be collected using an appropriate sampling plan.

8.3 All analytical sample containers should be composed of materials that minimize interaction with solution COPCs. For further information, see Chapters Three and Four.

8.4 Preservatives should not be added to samples before extraction.

8.5 Samples can be refrigerated, unless refrigeration results in an irreversible physical change to the sample.

8.6 Extracts should be preserved according to the guidance given in the individual determinative methods for the COPCs.

8.7 Extract holding times should be consistent with the aqueous sample holding times specified in the determinative methods for the COPCs.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 In order to demonstrate the purity of reagents, at least one eluant blank should be tested. If multiple batches of eluant are employed, one eluant blank from each batch should be analyzed.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific quality control procedures.

9.4 Unless the "as-received" samples are part of a time-dependent (e.g., aging) study, solid materials should be processed and tested within one month of their receipt.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified at a minimum annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PREPARATORY PROCEDURES

11.1 Particle-size reduction (if required)

11.1.1 In this method, particle-size reduction is used to prepare large-grained samples for the column test so that the approach toward liquid-solid equilibrium is enhanced and fluid channeling along column walls is minimized. The maximum particle size of the solid should ≤ 1/20 of the column diameter. For the column recommended in this method, a maximum particle size of 2.5 mm is acceptable. Therefore, 85% of the test material should pass through a 2.38-mm (U.S. No. 8) sieve. If less than 15% of the solid material is larger than the maximum acceptable particle size, this fraction of the solid may be excluded from the material tested, rather than particle size-reduced. The mass and nature of the discarded fraction should be documented.

11.1.2 Particle-size reduction of “as received” sample may be achieved through crushing, milling or grinding with equipment made from chemically-inert materials. During the reduction process, care should be taken to minimize the loss of sample and potentially volatile constituents in the sample.

11.1.3 If the moisture content of the “as received” material is greater than 15% (wet basis), air drying or desiccation may be necessary. Oven drying is not recommended for the preparation of test samples due to the potential for mineral alteration and volatility loss. In all cases, the moisture content of the “as received” material should be recorded.

NOTE: If the solid material is susceptible to interaction with the atmosphere (e.g., carbonation, oxidation), drying should be conducted in an inert environment.

11.1.4 When the material seems to be of a somewhat uniform particle size, calculate the percentage less than the sieve size as follows:

$$\% \text{ Passing} = \frac{M_{sieved}}{M_{total}} \times \mathbf{100}\,\%$$

Where: M_{sieved} = mass of sample passing the sieve (g)
M_{total} = mass of total sample (g) (e.g., M_{sieved} + mass not passing sieve)

11.1.5 The fraction retained by the sieve should be recycled for further particle-size reduction until at least 85% of the initial mass has been reduced below the designated maximum particle size. Calculate and record the final percentage passing the sieve and the designated maximum particle size. For the uncrushable fraction of the "as received" material, record the fraction mass and nature (e.g., rock, metal or glass shards, etc).

11.1.6 Store the size-reduced material in an airtight container in order to prevent contamination via gas exchange with the atmosphere. Store the container in a cool, dark and dry place prior to use.

11.2 Determination of solids and moisture content

11.2.1 In order to calculate eluate collection as a function of the dry-mass equivalent of "as tested" sample material, the solids content of the solid sample material should be determined and recorded. In this method, the moisture content is determined and recorded on the basis of the "wet" or "as-tested" sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable or explosive materials.

11.2.2 Place a 5–10-g sample of solid material into a clean, pre-tared dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Periodically check the sample mass after allowing the sample to cool to room temperature (20 ± 2 °C) in a desiccator.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.2.3 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content (g-dry/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of “as-tested” sample (g)

11.2.4 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: $MC_{(wet)}$ = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of “as-tested” sample (g)

11.3 Column preparation

11.3.1 Prepare the column test apparatus as depicted in Figure 2. Eluant feed should be directed through the lower end cap and upwards into the column, in order to minimize air retention in the packed bed and fluid channeling along the column walls.

NOTE: When solid samples may be affected by dissolved oxygen in the feed stock, an inert gas (e.g., nitrogen or argon) may be bubbled through the feed solution to displace oxygen or used to purge the headspace above the feed solution.

NOTE: When alkaline or other air-sensitive eluates are expected, the vapor space of empty collections bottles may be purged with an inert gas (e.g., nitrogen or argon) prior to eluate collection.

11.3.2 Record the mass of the empty column with end caps and any tubing leads that are needed to separate the column from the entire apparatus.

11.3.3 Place an approximately 1-cm thick layer of quartz sand (Sec. 6.5) on the bottom of the column using a small scoop or spoon. Record the mass of the column and sand layer. Level the sand layer by tapping the sides of the column.

11.3.4 Pack the main body of the column with a minimum 300-g dry-mass equivalent of “as tested” sample in approximately five layers with light tamping with a glass rod to level the material between layers. The top of the packed sample should be approximately 1 cm from the level of the column interface with the top end cap. Record the mass of the column, lower sand layer, and “as tested” sample.

11.3.5 Place a layer of sand to fill the approximate 1-cm gap between the top of the sample packing and the interface between the column and top-end cap. Record the total mass of the completely-packed column.

11.3.6 Determine the “as tested” mass of the sample packing by subtracting the mass of the column and lower sand layer (Sec. 11.3.3) from the mass of the column, sand layer and packing (Sec. 11.3.4).

11.3.7 Calculate the dry-mass equivalent packed of “as tested” sample into the column using the solids content as follows:

$$M_{dry} = SC - M_{test}$$

Where: M_{dry} = dry-mass equivalent of sample in column (g-dry)
SC = solids content (g-dry/g)
M_{test} = mass of “as tested” sample in column (g)

11.4 Pump setup

11.4.1 Prior to the start of the test, set the flow rate of the pump to a value that will provide an eluate production rate of 0.75 ± 0.25 LS/day. For example, given a dry-mass equivalent of 350 g-dry, an LS ratio of 0.5 would translate to 175 mL/g-dry, in which case the pump should be set to a flow rate of 175 mL/day.

11.4.2 Prime the tubing with eluant

11.4.2.1 Detach the inlet tubing from the bottom of the column and place the open end into a waste container.

11.4.2.2 Turn on the pump and allow the inlet tubing to fill with eluent. Remove any air bubbles trapped in the inlet tubing.

11.4.2.3 When the inlet tubing is full with eluant, stop the pump and reconnect the tubing to the bottom of the column.

11.5 Eluant collection schedule

11.5.1 Table 2 provides a schedule of fraction end-point LS ratios, interval LS ratios, and eluate fraction volumes for collection, assuming a dry-mass equivalent of 300 g-dry. The minimum volume of each collection bottle should be sized so as to capture the entire eluate fraction.

11.5.2 Using the assumed pump rate and the dry-mass equivalent of the sample, calculate the durations of column testing required to reach the target eluate collection LS ratios shown in Table 2 as follows:

$$T_i = \frac{M_{dry} - \sum LS_i}{R_i}$$

Where: T_i = target time from start for collection of eluant fraction i (day)
M_{dry} = dry-mass equivalent of sample in column (g-dry)
$\sum LS_i$ = target cumulative LS ratio for interval i from Table 1 (mL/g-dry)
R_i = pump rate assumed for interval i (mL/day)

Alternatively, use the provided Microsoft® Excel spreadsheet template to develop the schedule of target collection times.

NOTE: The schedule of predicted collection times is for reference purposes only. Typically, the eluate collection rate is slower that predicted initially, due in part to pump inefficiencies, back pressure and dead-volume lag times. The decision to switch collection bottles should be made based on the volume of eluate collected with time. The schedule may be revised with each eluate fraction collected, so that the prediction of future collections may be more accurate. Pump flow-rate adjustment may be necessary.

12.0 COLUMN TEST PROCEDURE

12.1 Column/eluant equilibration

12.1.1 Turn on the pump and allow the column to fill with eluant, thus wetting the column packing.

12.1.2 When the column packing is completely wetted and the eluant level is even with the top of the column (or just beginning to be seen through the effluent tubing at the top of the column apparatus), stop the pump and allow the column to equilibrate for 24 hours.

12.2 Column test

12.2.1 Following equilibration, begin the column test by starting the pump and recording the date and time.

NOTE: The eluate production rate should be monitored frequently during the column test and the pump rate adjusted, such that the eluate production rate is maintained at approximately 0.75 ± 0.25 LS/day.

12.2.2 When the eluate fraction has reached the target volume according to the predicted collection schedule, release the Luer lock connecting the active collection bottle and attach the eluant tubing to a new collection bottle.

12.3. Eluate processing

12.3.1 Decant a minimum volume (~ 5 mL) of the eluate fraction from the collection vessel in order to measure the solution characteristics.

12.3.2 Measure and record the pH, specific conductivity, and oxidation-reduction potential (ORP) (optional, but strongly recommended) of the eluate (see Methods 9040, 9045, and 9050).

12.3.3 Separate any suspended particulates from the remaining liquid in the collection bottle by pressure or vacuum filtration through a 0.45-μm filtration membrane (Sec.6.8).

NOTE: If either low-volatility organic species or mercury is a COPC, pressure filtration is recommended over vacuum filtration in order to minimize volatility losses.

12.3.4 Immediately, preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

12.4 Reiterate Secs. 12.2.2-12.3.4 until nine eluate fractions are collected up to an LS ratio of 10 ± 0.2 mL/g-dry.

NOTE: In order to complete this method, all nine eluate fractions must be collected from the column. However, for purposes of limited analysis or index testing with interpretation based on cumulative release, fractions may be composited by volume-weighted averaging to create a single analytical sample from multiple eluate fractions.

12.5. Analytical sample preparation options

This method allows for options in the preparation of analytical samples based on the detail of characterization required (e.g., complete, limited or index) and the basis for data reporting (e.g., concentration or cumulative release). However, the complete set of nine eluate fractions must be collected in all cases.

12.5.1 Table 1 shows the analytical preparation scheme for Options A-E described in the following sections. Each composite sample may be created either by combining the total eluate volumes and preserving the total sample for analysis; or combining aliquots of two eluate fractions using volume-weighted averages. However, it is recommended that composite analytical samples be prepared using aliquots of eluate fractions whenever possible, rather than whole eluate fractions as this approach allows for potential analysis of discrete eluate fractions if desired at a later date.

12.5.1.1 Option A — This sample preparation option is used for complete characterization and includes analysis of all eluate fractions. Since the entire cumulative release curve is captured in nine discrete fractions, reported data may be based on either eluate concentrations or cumulative release.

12.5.1.2 Option B — This sample preparation option is used only for limited analyses based on eluate concentration. Six discrete eluate fractions are analyzed. Data obtained using this option cannot be used for cumulative release since there are sections of the cumulative release curve not analyzed.

12.5.1.3 Option C — This sample preparation option is used only for limited analysis based on cumulative release. Six analytical samples are created from three discrete eluate fractions and three composite samples. In the scheme shown in Table 1, the following fractions are composited:

- T04 and T05
- T06 and T07
- T08 and T09

12.5.1.4 Option D — This sample preparation option is used only for index testing based on eluate concentration. Three discrete eluate fractions are analyzed. Data obtained using this option cannot be used for cumulative release since there are sections of the cumulative release curve not analyzed.

12.5.1.5 Option E — This sample preparation option is used only for index testing based on cumulative release. Three analytical samples are created from one discrete eluate fraction and two composite samples. In the scheme shown in Table 1, the following fractions are composited:

- T02, T03, T04, and T05
- T06, T07, T08, and T09

12.5.2 Volume-weighted composites

12.5.2.1 The volume of aliquots of eluate fractions for composite analytical samples may be calculated using the Excel template provided or the following formula:

$$V_i = \frac{F_i}{\sum_i^n F_i} \times V_{sample}$$

Where: V_i = the volume of an aliquot from eluate fraction i (mL)
F_i = the collected volume of eluate fraction i (mL)
V_{sample} = the total volume of the analytical sample (mL)
n = total number of eluate fractions to be composited

As an illustration of volume-weighted averaging, eluate fraction aliquots are calculated as required to create an analytical sample by compositing eluate fractions T06 through T09 for index testing based on cumulative release. The calculation follows the example volumes shown in Table 2 and assumes that an analytical sample volume of 100 mL is required.

$$\sum_i^n F_i = F_{T\mathbf{06}} + F_{T\mathbf{07}} + F_{T\mathbf{08}} + F_{T\mathbf{09}} = \mathbf{450}\ \text{mL} + \mathbf{150}\ \text{mL} + \mathbf{1350}\ \text{mL} + \mathbf{150}\ \text{mL} = \mathbf{2100}\ \text{mL}$$

$$V_{T\mathbf{06}} = \frac{F_{T\mathbf{06}}}{\sum_{i}^{n} F_i} \times V_{sample} = \frac{\mathbf{450}\ \mathrm{mL}}{\mathbf{2100}\ \mathrm{mL}} \times \mathbf{100}\ \mathrm{mL} = \mathbf{21}.\mathbf{5}\ \mathrm{mL}$$

$$V_{T\mathbf{07}} = \frac{F_{T\mathbf{07}}}{\sum_{i}^{n} F_i} \times V_{sample} = \frac{\mathbf{150}\ \mathrm{mL}}{\mathbf{2100}\ \mathrm{mL}} \times \mathbf{100}\ \mathrm{mL} = \mathbf{7}.\mathbf{1}\ \mathrm{mL}$$

$$V_{T\mathbf{08}} = \frac{F_{T\mathbf{08}}}{\sum_{i}^{n} F_i} \times V_{sample} = \frac{\mathbf{1350}\ \mathrm{mL}}{\mathbf{2100}\ \mathrm{mL}} \times \mathbf{100}\ \mathrm{mL} = \mathbf{64}.\mathbf{3}\ \mathrm{mL}$$

$$V_{T\mathbf{09}} = \frac{F_{T\mathbf{09}}}{\sum_{i}^{n} F_i} \times V_{sample} = \frac{\mathbf{150}\ \mathrm{mL}}{\mathbf{2100}\ \mathrm{mL}} \times \mathbf{100}\ \mathrm{mL} = \mathbf{7}.\mathbf{1}\ \mathrm{mL}$$

$$V_{sample} = V_{T\mathbf{06}} + V_{T\mathbf{07}} + V_{T\mathbf{08}} + V_{T\mathbf{09}} = \mathbf{21}.\mathbf{5}\ \mathrm{mL} + \mathbf{7}.\mathbf{1}\ \mathrm{mL} + \mathbf{64}.\mathbf{3}\ \mathrm{mL} + \mathbf{7}.\mathbf{1}\ \mathrm{mL} = \mathbf{100}.\mathbf{0}\ \mathrm{mL}$$

NOTE: The above illustration uses example eluate fraction volumes based on interval LS ratios and an assumed test material mass. When calculating the aliquots of collected eluates fractions for composite samples, the actual collected fraction volumes should be used.

13.0 DATA ANALYSIS AND CALCULATIONS (EXCEL TEMPLATE PROVIDED)

13.1 Data reporting

Figure 3 presents an example of a data sheet that may be used to report the concentration results of this method. This example is included in the Excel template. At a minimum, the basic test report should include the following:

a) Name of the laboratory
b) Laboratory contact information
c) Date and time at the start of eluate flow (start of test)
d) Name or code of the solid material tested
e) Particle size (85 wt% less than)
f) Packed bed dimensions (column ID and bed depth (cm))
g) Mass of solid material in column packing
h) Moisture content of solid material packed in column (g_{H_2O}/g)
i) Eluate specific information (see below)

The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Eluate collection date and time
c) Amount of eluate collected (mass or volume)
d) Measured eluate pH

e) Measured eluate conductivity (mS/cm)
f) Measured ORP (mV) (optional)
g) Concentration of all COPCs
h) Analytical QC qualifiers as appropriate

13.2 Data Interpretation (optional)

13.2.1 Concentration as a function of LS ratio

13.2.1.1 A curve of the eluate concentration as a function of LS ratio can be generated for each COPC after chemical analysis of all extracts by plotting the constituent concentration in the liquid phase as a function of the cumulative collected LS ratio. The curve indicates the nominal equilibrium concentration of the constituent of interest as a function of LS ratio from 0 to 10 mL/g-dry at natural pH. An example such curve is provided in Figure 4.

13.2.1.2 The lower limit of quantitation (LLOQ) of the determinative method for each COPC may be shown as a horizontal line. COPC concentrations below this line indicate negligible or non-quantitative concentrations.

NOTE: The lower limit of quantitation is highly matrix dependent and should be determined as part of a QA/QC plan.

13.3 Cumulative release as a function of LS ratio

13.4.1 The cumulative mass release of a COPC per unit solid material may be calculated as follows:

$$\Sigma M_i = \sum_i [C_i(\Sigma LS_i - \Sigma LS_{i-1})]$$

Where: ΣM_i = the cumulative mass release through interval i (mg/kg-dry])
C_i = the concentration of the COPC in the eluant collected during interval i (mg/L)
ΣLS_i = the cumulative LS ratio of eluate collected through interval i (L/kg-dry)
ΣLS_{i-1} = the cumulative LS ratio of eluate collected through interval i-1 (L/kg-dry)

13.4.2 Prepare a curve of the cumulative mass release generated for each COPC by plotting the cumulative mass release calculated in Sec. 13.4.1 as a function of the cumulative collected LS ratio. This curve provides an interpretation of the cumulative mass expected to be leached from a column of material as a function of LS ratio percolating through the column.

13.4.3 A comparison of the slope of the mass release curve to a unity slope, which is indicative of solubility-controlled release, may be made by plotting the cumulative mass release calculated in Sec. 13.4.1 versus the logarithm of the cumulative collected LS ratio. An example is provided in Figure 5.

14.0 METHOD PERFORMANCE

14.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.2 Refs. 3 and 4 may provide additional guidance and insight on the use, performance and application of this method.

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

16.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous 1314 - 18 Rev 0 January 2009 Pre-release DRAFT for comment waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in Sec. 15.2.

17.0 REFERENCES

1. NEN 7343, (1995), “Leaching Characteristics of Solid Earth and Stony Materials – Leaching Tests – Determination of the leaching of Inorganic Constituents from Powdery and Granular Materials with the Percolation Test,” Dutch Standardization Institute, Delft, The Netherlands.

2. CEN TS/14405, (2004), “Characterization of Waste – Leaching Behaviour Tests – Up-flow Percolation Test (Under Specified Conditions),” European Committee for Standardization (CEN), Brussels, Belgium.

3. D.S. Kosson, H.A. van der Sloot, F. Sanchez and A.C. Garrabrants, (2002), “An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials,” Environmental Engineering Science, 19(3) 159-204.

4. D.S. Kosson, A.C. Garrabrants, H.A. van der Sloot, (2009), “Background Information for the Development of Leaching Test Draft Methods 1313 through Method 1316,” (in preparation).

18.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

SCHEDULE OF FRACTION COLLECTIONS AND ANALYTICAL SAMPLES

Option		A		B	C	D	E
Fraction Label	ΣLS Ratio (mL/g-dry)	Characterization		Limited Analysis		Index Testing	
		Conc.	ΣRel	Conc.	ΣRel	Conc.	ΣRel
T01	0.2 ± 0.1	✓	✓	✓	✓	✓	✓
T02	0.5 ± 0.1	✓	✓	✓	✓		↓
T03	1.0 ± 0.1	✓	✓	✓	✓		↓
T04	1.5 ± 0.2	✓	✓		↓		↓
T05	2.0 ± 0.2	✓	✓	✓	✓T05c	✓	✓T05c
T06	4.5 ± 0.2	✓	✓		↓		↓
T07	5.0 ± 0.2	✓	✓	✓	✓T07c		↓
T08	9.5 ± 0.2	✓	✓		↓		↓
T09	10.0 ± 0.2	✓	✓	✓	✓T09c	✓	✓T09c

NOTE: ΣRel = Cumulative release.
✓ = Collect eluate fraction (or pool of fractions) as analytical sample.
↓ = composite eluate fraction with next fraction to create analytical sample.

TABLE 2

SCHEDULE OF ELUATE FRACTIONS FOR COLLECTION WITH EXAMPLE VOLUMES

Interval Label	End Point ΣLS Ratio (mL/g-dry)	Fraction ΣLS Ratio (mL/g-dry)	Example Fraction Volume (mL)
T01	0.2 ± 0.1	0.2	60
T02	0.5 ± 0.1	0.3	90
T03	1.0 ± 0.1	0.5	150
T04	1.5 ± 0.2	0.5	150
T05	2.0 ± 0.2	0.5	150
T06	4.5 ± 0.2	1.5	450
T07	5.0 ± 0.2	0.5	150
T08	9.5 ± 0.2	4.5	1350
T09	10.0 ± 0.2	0.5	150
B01	Eluant		100

NOTE: Example fraction volumes based on assumed packing mass of 300 g-dry.

FIGURE 1

EXAMPLE DATA REPORT FORMAT

EPA METHOD 1314
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code: **XYZ**
Material Type: Coal Combustion Fly Ash
Date Received: 10/1/20xx
Test Date: 11/1/20xx
Report Date: 12/1/20xx

Particle Size: 88% passing 2-mm sieve
Mass used in Column: 360 g
Moisture Content: 0.002 g_{H_2O}/g
Column ID: 4.8 cm
Packing Bed Depth: 28 cm
Eluant: ASTM Type II Water
Lab Temperature: 21 ± 2 °C

Test Position	Replicate	Value	Units	Method	Note
T01	**A**				
	Eluate Sample ID	**XYZ-1314-T01-A**			
	Collection Date	11/1/20xx			
	Collection Time	12:35	PM		
	Eluate Mass	70.4	g		
	Eluate pH	8.82	-	EPA 9040	
	Eluate Conductivity	5.4	mS/c	EPA 9050	
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	4.72	mg/L		EPA 6020	11/7/20xx	1000
As	0.12	mg/L		EPA 6020	11/7/20xx	10
Cl	5.42	mg/L		EPA 9056	11/9/20xx	1

Test Position	Replicate	Value	Units	Method	Note
T02	**A**				
	Eluate Sample ID	**XYZ-1314-T02-A**			
	Collection Date	11/1/20xx			
	Collection Time	9:15	AM		
	Eluate Mass	105.1	g		
	Eluate pH	9.15	-		
	Eluate Conductivity	2.3	mS/c		
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	2.99	mg/L		EPA 6020	11/7/20xx	1000
As	0.21	mg/L		EPA 6020	11/7/20xx	10
Cl	4.20	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (< "LLOQ")

FIGURE 2

METHOD 1314 FLOWCHART

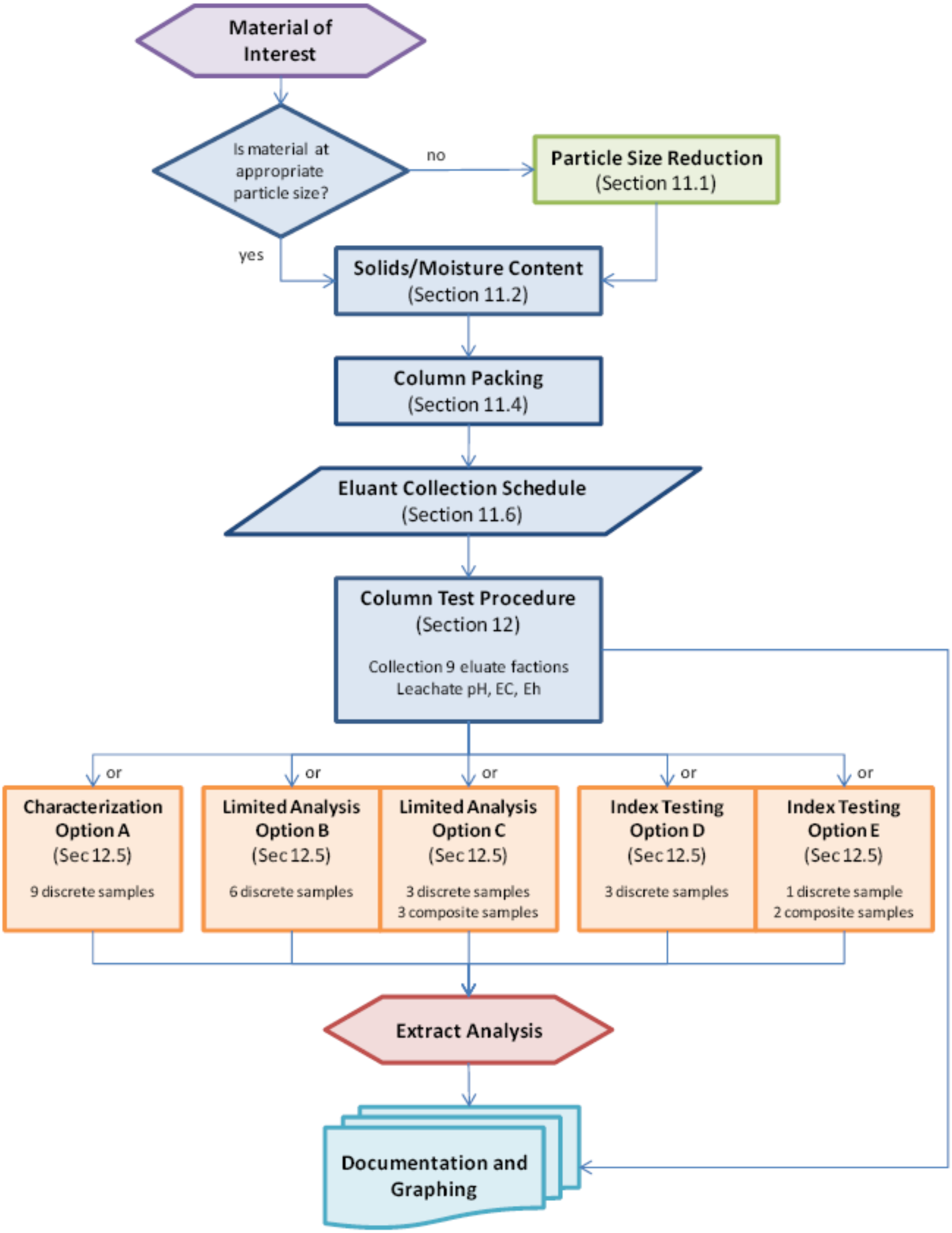
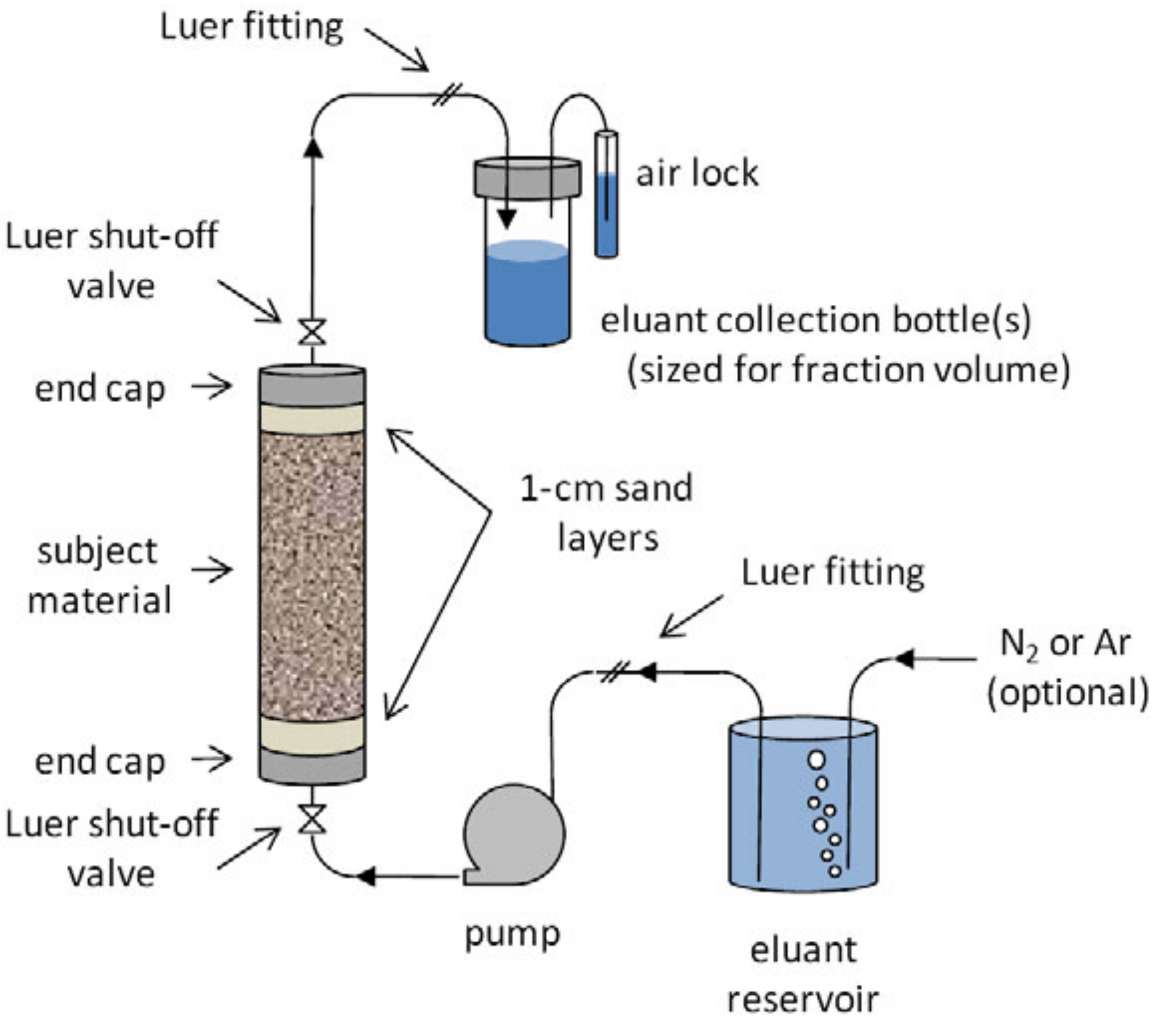


FIGURE 3

SCHEMATIC OF COLUMN TEST APPARATUS



NOTE: Figure not drawn to scale

FIGURE 4

EXAMPLE ELUATE CONCENTRATION CURVES FOR COMPLETE CHARACTERIZATION OF A COAL COMBUSTION FLY ASH

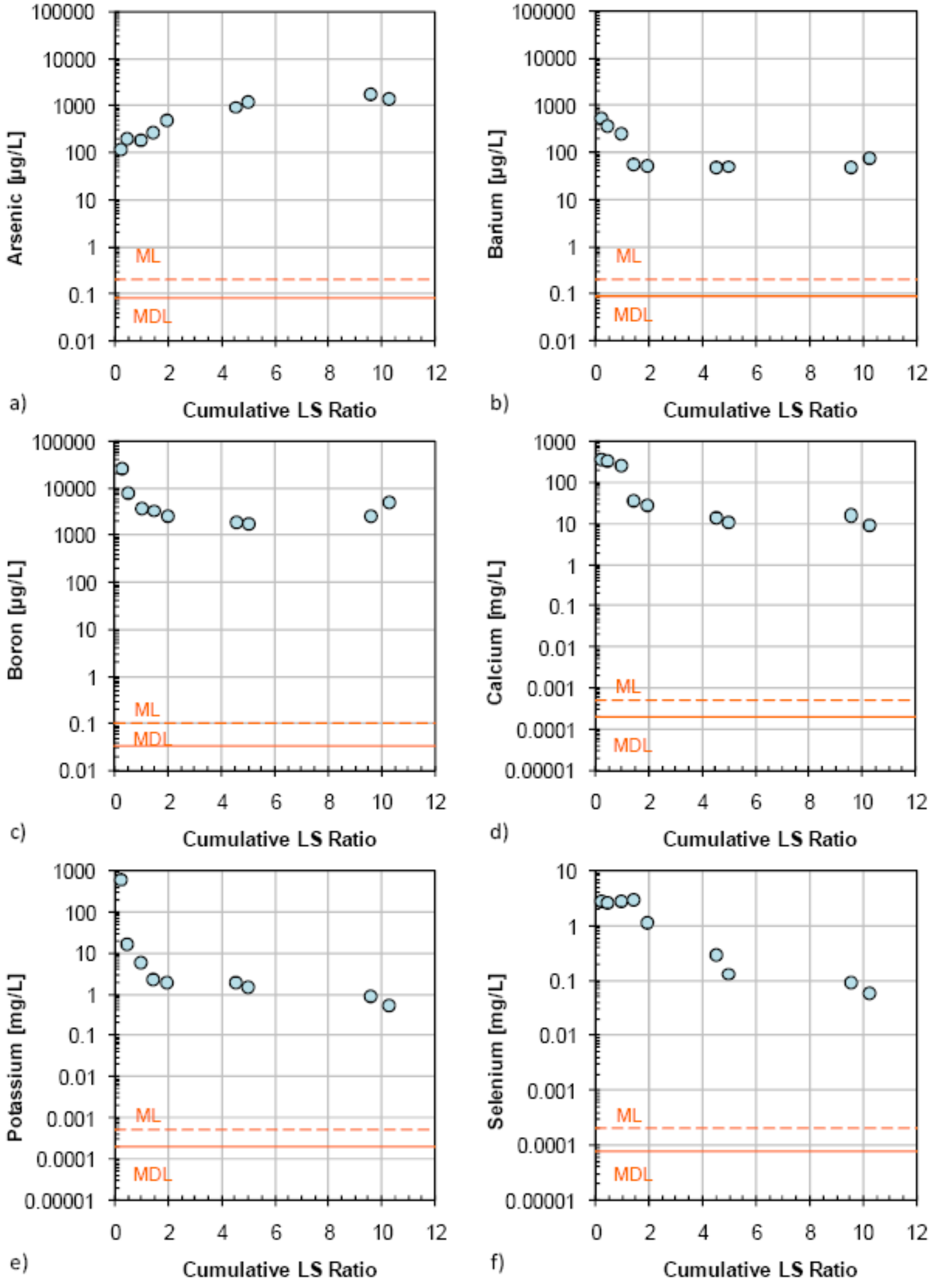
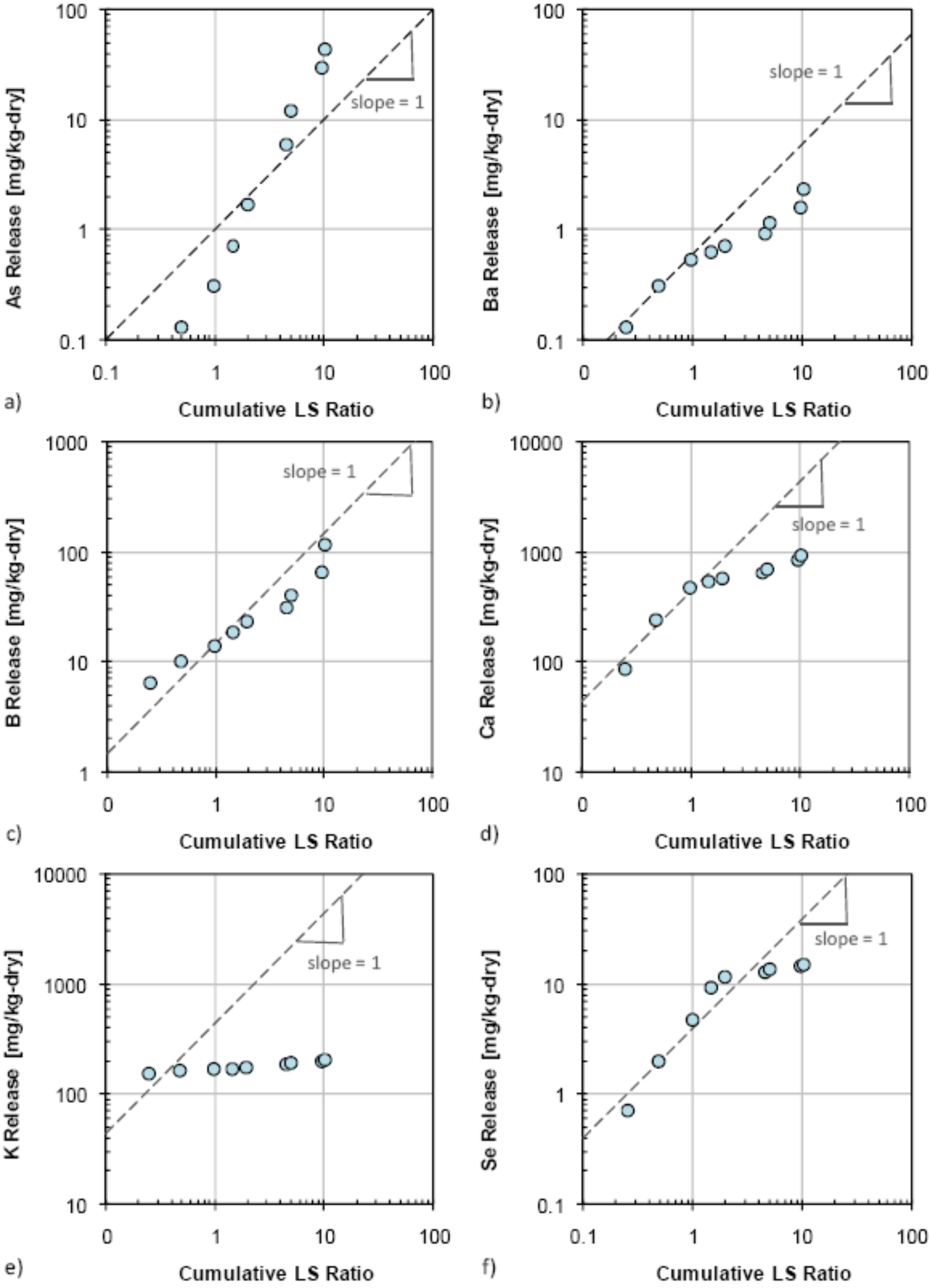


FIGURE 5

EXAMPLE CUMULATIVE RELEASE CURVES FOR COMPLETE CHARACTERIZATION OF A COAL COMBUSTION FLY ASH



<u>NOTE</u>: Dashed line represents solubility control (slope = 1).

APPENDIX C

METHOD 1315 –

U MASS TRANSFER RATES OF CONSTITIUENTS IN MONOLITHIC OR COMPACTED GRANULAR MATERIALS USING A SEMI-DYNAMIC TANK LEACHING PROCEDURE

PRELIMINARY VERSION[1] OF METHOD 1315

MASS TRANSFER RATES OF CONSTITIUENTS IN MONOLITHIC OR COMPACTED GRANULAR MATERIALS USING A SEMI-DYNAMIC TANK LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic or compacted granular material, under diffusion-controlled release conditions, as a function of leaching time. Observed diffusivity and tortuosity may be estimated through analysis of the resulting leaching test data.

1.2 This method is suitable to a wide range of solid materials which may be in monolithic form (e.g., cements, solidified wastes) or may be compacted granular materials (e.g., soils, sediments, stacked granular wastes) which behave as a monolith in that the predominant water flow is around the material and release is controlled by diffusion to the boundary.

1.3 This leaching characterization method provides intrinsic material parameters for release of inorganic species under mass transfer-controlled leaching conditions. This test method is intended as a means for obtaining a series of eluants which may be used to estimate the diffusivity of constituents and physical retention parameter of the solid material under specified laboratory conditions.

1.4 This method is not applicable to characterize the release of volatile or semi-volatile organic analytes.

1.5 This method is a characterization method and does not provide a solution considered to be representative of eluate under field conditions. This method is similar in structure and use to predecessor methods such as MT001.1 (see Ref. 1), NEN 7345 (see Ref.

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[1] Preliminary Version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846. This method has been derived from published procedures (Kosson et al, 2002). The method has been submitted to the U.S. EPAU.S. EPA Office of Resource Conservation and Recovery and is currently under review for development of interlaboratory validation studies to develop precision and bias information.

2), ANSI/ANS 16.1 (see Ref. 3), and ASTM C1308 (see Ref. 4). However, this method differs from previous methods in that: (a) leaching intervals are modified to improve quality control, (b) sample preparation accounts for mass transfer from compacted granular samples, and (c) mass transfer may be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling

1.7 The geometry of monolithic samples may be rectangular (e.g., bricks, tiles), cubes, wafers, cylinders. Samples may also have a variety of faces exposed to eluant forming anything from 1-dimensional (1-D) through 3-dimensional (3-D) mass transfer cases. In all cases, a minimum sample size of 5 cm in the direction of mass transfer must be employed and the liquid-surface-area (LSa) ratio must be maintained at
9 ± 1 mL/cm^2.

Monolithic samples should be suspended or held in the leaching fluid such that at least 98% of the entire sample surface area is exposed to eluant and the bulk of the eluant (e.g., a minimum of 2 cm between any exposed surface and the vessel wall) is in contact with the exposed sample surface. Figure 1 provides examples of appropriate sample holders and leaching configurations for 3-D and 1-D cases.

1.8 Compacted granular materials are granular solids, screened to pass a 2-mm sieve, compacted following a modified Proctor compaction effort (see Ref. 5). The sample geometry must be open-faced cylinders due to limitations of mechanical packing. However, the diameter and height of the sample holder may be altered to correspond appropriately with the diameter and volume of the leaching vessel. In all cases, the sample size of at least 5 cm in the direction of mass transfer must be employed and the LSa ratio must be maintained at 9 ± 1 mL/cm^2.

The sample should be positioned at the bottom of the leaching vessel with a minimum of 5 cm of distance between the solid-liquid interface and the top of the vessel. The distance between the non-leaching faces (i.e., outside of the mold surfaces) and the leaching vessel wall should be minimized to < 0.5 cm, such that the majority of the eluant volume is on top of the sample. Figure 2 shows an example of a holder and leaching configuration for a compacted granular sample.

1.9 The solvent system used in this characterization method is reagent water. Other systems (e.g., groundwater, seawater, and simulated liquids) may be used to infer material performance under specific environmental conditions. However, interaction between the eluant and the solid matrix may result in precipitation and pore blocking, which may interfere with characterization or complicate data interpretation.

1.10 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045) for additional information on QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.11 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method comprises leaching of continuously water-saturated monolithic or compacted granular material in an eluant-filled tank with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen such that the sample is fully immersed in the leaching solution. Monolithic samples may be cylinders or parallelepipeds, while granular materials are compacted into cylindrical molds at optimum moisture content using modified Proctor compaction methods (see Ref. 5). In either case, the exposure of a regular geometric area to the eluant is recommended. Samples are contacted with reagent water at a specified LSa ratio. The leaching solution is exchanged with fresh reagent water at nine pre-determined intervals (see NOTE below). The sample is freely drained and the mass is recorded to monitor the amount of eluant absorbed into the solid matrix at the end of each leaching interval. The eluate pH and specific conductance is measured for each time interval and analytical samples are collected and preserved accordingly based on the determinative methods to be performed. Eluate concentrations are plotted as a function of time, as a mean interval flux and as cumulative release as a function of time. These data are used to estimate mass transfer parameters (i.e., observed diffusivity) for each constituent of potential concern (COPC). A flowchart for performing this method is shown in Figure 3.

NOTE: The leaching schedule may be extended for additional exchanges with individual intervals of 14 days to provide more information about longer-term release.

3.0 DEFINITIONS

3.1 COPC — A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.2 Release — The dissolution or partitioning of a COPC from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.3 LSa ratio — The ratio representing the total liquid volume used in the leaching interval to the external geometric surface area of the solid material. LSa ratio is typically expressed in units of mL of eluent/cm^2 of exposed surface area.

3.4 Observed mass diffusivity —the apparent, macroscopic rate of release due to mass transfer from a solid into a liquid as measured using a leaching test under conditions where mass transfer controls release. The observed diffusivity accounts for all physical and chemical retention factors influencing mass transfer and is typically expressed in units of cm^2/s.

3.5 Effective mass diffusivity — The intrinsic rate of mass transfer in a porous medium accounting for physical retention. The effective mass diffusivity is typically expressed in units of cm^2/s.

3.6 Physical retention factor — A mass transfer rate term that describes the retardation of diffusion due to intrinsic physical properties of a porous medium (e.g., effective porosity, tortuosity).

3.7 Chemical retention factor — A mass transfer rate term that describes the chemical processes (e.g., dissolution/precipitation, adsorption/desorption, complexation) occurring at the pore water interface with the solid mineral phases within the porous structure of the solid material.

3.8 Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on QC procedures and to Chapters Three and Four for general guidance on the cleaning of laboratory apparatus prior to use.

4.2 The reaction of atmospheric gases can influence the measured concentrations of constituents in eluates. For example, reaction of carbon dioxide with eluants from highly alkaline or strongly-reducing materials will result in neutralization of eluate pH and precipitation of carbonates. Leaching vessels, especially those used when testing highly alkaline materials, should be designed to be air-tight in order to minimize the reaction of samples with atmospheric gases.

4.3 Use of certain solvent systems may lead to precipitation at the material surface boundary which may reduce mass transport rates. For example, exposure of cement-based materials to seawater leads to sealing of the porous block (see Ref. 6).

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and setting used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and setting other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Sample holder

6.1.1 Monolithic samples

6.1.1.1 A mesh or structured holder constructed of an inert material such as high-density polyethylene (HDPE) or other material resistant to high and low pHs is recommended.

6.1.1.2 The holder should be designed such that at least 98% of the sample external surface area may be exposed to eluant.

6.1.1.3 The holder should be designed to match the geometry of the mass transfer such that the bulk of the eluant may be in contact with the sample and the exposed surfaces of the sample centered within the leaching fluid.

NOTE: In the case of 1-D mass transfer from the axial face of a cylindrical sample, the outer diameter (OD) of the holder should be matched as closely as possible to the inner diameter (ID) of the leaching vessel so that the majority of the eluant is above the sample (e.g., in contact with the exposed material surface), while allowing for easy placement and removal of the holder in the leaching vessel (see Figure 1).

6.1.2 Compacted granular samples

6.1.2.1 A cylindrical mold constructed of an inert material such as HDPE or other material resistant to high and low pH is recommended.

6.1.2.2 The holder should be capable of withstanding the compaction force required to prepare the sample (see Sec 11.3.5) without breaking or distorting.

NOTE: The outer diameter of the holder for a compacted granular sample should be matched as closely as possible to the inner diameter of the leaching vessel so that the majority of the eluant is above the sample (e.g., in contact with the exposed material surface) while allowing for easy placement and removal of the holder in the leaching vessel.

6.2 Leaching vessel

6.2.1 A straight-sided container constructed of a material resistant to high and low pH is recommended. Jars or buckets composed of HDPE, polycarbonate (PC), polypropylene (PP), or polyvinyl chloride (PVC) are recommended when evaluating the mobility of inorganic species.

6.2.2 The leaching vessel should have an air-tight seal that can sustain long periods of standing without gas exchange with the atmosphere.

6.2.3 The container must be of sufficient volume to accommodate both the solid sample and an eluant volume based on an LSa ratio of 9 ± 1 mL eluant/cm^2 sample surface area. Ideally, the vessel should be sized such that the headspace is minimized within the tolerance of the LSa ratio.

6.3 Leaching setup

Example photos of three possible leaching equipment arrangements for monolithic and compacted granular samples are shown in Figures 1 and 2, respectively. The equipment used in the each of these cases is described below.

6.3.1 Figure 1a shows a monolithic sample 3-D configuration with the following accessories:

Sample holder — PP sink washers, 43-mm OD, 37-mm ID, 6-mm high, with four holes drilled at the quadrants to accept
2-mm OD nylon string knotted at top.

Sample stand — PVC pipe, 47-mm OD, 51-mm high, cut to have four legs approximately 8-mm wide and 30-mm high.

Leaching Vessel — PP bucket, 140-mm ID at top, 120-mm ID at bottom, 200-mm high (Berry Plastics #T51386CP3, VWR Scientific, or equivalent).

6.3.2 Figure 1b shows a monolithic sample 1-D configuration with the following accessories:

Sample holder — Polyethylene (PE) mold, 54-mm OD, 100-mm high (MA Industries, Peach Tree City, GA, or equivalent), with the test sample cured in mold and cut to 51-mm high.

Leaching vessel — 250-mL PC jar, (60-mm ID, 100-mm high, (Nalgene #2116-0250, Fisher Scientific, or equivalent).

6.3.3 Figure 2 shows a compacted granular sample 1-D Configuration with the following accessories:

Sample holder — PE mold, 100-mm OD, 200-mm high, (MA Industries, Peach Tree City, GA, or equivalent) cut to 63-mm high with three tabs drilled for 0.7-mm fishing line knotted at the top.

Leaching vessel — 1000-mL PC jar, 110-mm ID at top, 130-mm high (Nalgene #2116-1000, Fisher Scientific, or equivalent).

Glass beads, borosilicate — 2-mm diameter

6.4 Filtration apparatus — Pressure- or vacuum-filtering apparatus made of appropriate materials to maximize the collection of extracts and minimize the loss of COPCs (Nalgene #300-4000 or equivalent).

6.5 Filtration membranes — Composed of hydrophilic PP or similar material with an effective pore size of 0.45-µm (e.g., Andwin Scientific GH Polypro 28143-288 or equivalent).

6.6 pH Meter — Laboratory model with the capability for temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) and a minimum resolution of 0.1 pH units.

6.7 pH combination electrode — Composed of chemically-resistant materials.

6.8 Conductivity meter — Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value.

6.9 Conductivity electrodes — Composed of chemically-resistant materials.

6.10 Proctor compactor (for compacted granular samples only) — Equipped with a slide hammer capable of dropping a 4.5-kg weight over a 0.46-m interval (see Ref. 5 for further details).

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specification are available. Other grade may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Other reagents may be used in place of reagent water on a case-specific basis.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three "Inorganic Analytes."

8.2 Both plastic and glass containers are suitable for the collection of samples. All sample containers must be prewashed with a metal-free detergent and triple rinsed with nitric acid and reagent water, depending on the history of the container. For further information, see Chapter Three.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Method blanks – In order to demonstrate the purity of reagents and container surfaces, a method blank should be tested for each leaching interval. Refer to Chapter One for specific QC procedures.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific quality control procedures.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified at a minimum annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PREPARATORY PROCEDURES

A flowchart of this method, including preparatory and leaching procedures, is shown in Figure 3.

11.1 Determination of solids and moisture content

The moisture and solids content of the sample material are used to relate leaching results to dry-material masses. When preparing compacted granular samples for testing, the moisture content or solid content is used to determine the optimum moisture content following the modified Proctor test. This method calculates moisture content on the basis of the "wet" or "as tested" sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable or explosive materials.

11.1.1 Place a 5–10-g sample of solid material into a clean, pre-weighed dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Periodically check the sample mass after allowing the sample to cool to room temperature (20 ± 2 °C) in a desiccator.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.1.2 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content (g-dry/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.1.3 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: $MC_{(wet)}$ = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.2 Preparation of monolithic samples

11.2.1 If the material to be tested is granular, disregard this section and proceed to Sec. 11.3.

11.2.2 A representative sample of monolithic material should be obtained by molding material components in place (e.g., cementitious media) or by coring or cutting a sample from a larger existing specimen.

11.2.3 The geometry of monolithic samples may be rectangular (e.g., bricks, tiles), cubes, wafers, cylinders. Samples may also have a variety of faces exposed to eluant forming 1-, 2-, or 3-D mass-transfer cases. Example monolithic sample leaching setups are shown in Figure 1.

11.2.4 A minimum sample size of 5 cm in the direction of mass transfer must be employed and the LSa ratio must be maintained at 9 ± 1 mL/cm^2.

NOTE: Since, the sample holder and leaching vessel must correspond to the specifications in Sec 6.1, it is often easier to modify the sample size and geometry rather than the holder and vessel dimensions.

11.2.5 Proceed to Sec. 12.0.

11.3 Preparation of compacted granular samples

Compacted granular materials, for most cases, must be open-faced cylinders due to the limitations of mechanical packing. However, the diameter and height of the sample holder may be altered to work appropriately with the diameter and volume of the leaching vessel. In all cases, a minimum sample size of 5 cm in the direction of mass transfer must be employed and the LSa ratio must be maintained at 9 ± 1 mL/cm^2.

Granular samples are compacted into the sample holder using a variation on the modified Proctor compaction (see Ref. 5) to include the use of 6-cm high test molds compacted in three layers (rather than the five layers specified in Ref. 5) to maintain the total compaction effort. The granular sample should be compacted at optimum moisture content in order to obtain packing densities that approximate field conditions. Optimum moisture content refers to the amount of moisture or fractional mass of water (g_{H_2O}/g material) in the granular sample that is present at the optimum packing density (g-dry material/cm^3). Optimum packing density is defined in Ref. 5. The optimum moisture content of the test material is determined from a pretest measuring the packing density of granular materials compacted at different levels of moisture content.

11.3.1 Pre-test to determine optimum moisture content

The pre-test is conducted as a series of five batch-wise packing trials with consecutive increases in moisture content until the maximum packing density has been surpassed. The optimum moisture content is determined as the maximum of a third-order polynomial fit through the graph of dry-packing density as a function of moisture content (wet basis).

11.3.1.1 Place 1500 g of "as received" material into a pail or bowl and mix well by hand to homogenize. As an alternate to hand mixing, a mechanical paddle mixer may used.

NOTE: The pretest may be conducted from a bulk supply of solid material (e.g., 10 kg total for five batches) as long as the starting mass for each trial is recorded and incremental water additions are used.

1.3.1.2 Mix a known amount of tap water with the bulk material in the pail or bowl until homogenized based on visual inspection. For the first point in the pre-test, no water needs to be added.

NOTE: The amount of water added should be enough increase the moisture content in approximately 3-5% increments. Smaller additions may be needed in order to provide finer resolution of the packing density as a function of moisture content curve.

11.3.1.3 Calculate the new moisture content for the trial as follows:

$$MC^{i}_{(wet)} = \frac{M_{test} \times MC_{wet} + W_{added}}{M_{test} + W_{added}}$$

Where: $MC^{i}_{(wet)}$ = moisture content (wet basis) of the pre-test trial (g_{H_2O}/g)
M_{test} = mass of "as-tested" material used in the trial (g)
$MC_{(wet)}$ = moisture content (wet basis) of the "as-tested" material (g_{H_2O}/g)
W_{added} = mass of water added to the "as-tested" material (g_{H_2O}/g)

11.3.1.4 Compact approximately 1000 g of material into a pre-tared 10-cm diameter mold into three consecutive layers of material. The compacted mass should have a level flat surface as a top face.

11.3.1.5 Measure and record the height, diameter, and mass of the resulting compacted material.

11.3.1.6 Calculate and record the packing density (dry basis) as follows:

$$\rho_{pack} = \frac{m \times SC}{\pi \times h} \left(\frac{2}{d}\right)^{2}$$

Where: ρ_{pack} = packing density (dry basis) (g-dry/cm^3)
m = mass of the compacted sample (g)
SC = solids content of the "as -received" granular material (g-dry/g)
d = measured diameter of the compacted sample (cm)
h = measured height of the compacted sample (cm)

11.3.1.7 Repeat Secs. 11.3.1.1-11.3.1.6 for four subsequent trials until the value of the calculated packing density decreases.

11.3.1.8 Plot the packing density as a function of moisture content. Figure 4 shows an example of a packing density curve.

11.3.1.9 Determine the optimum moisture content at the maximum of the packing density curve. This value may be read directly from the graph or determined by the maximum of a third-order polynomial fit through the five pre-test data points (see the provided Microsoft® Excel Template).

11.3.2 Compacted granular test sample preparation

11.3.2.1 Using the optimum moisture content determined in Sec. 11.3.1.9, calculate the amount of "as-received" material that is required to pack the sample holder to within 3 mm of the rim of the holder.

$$M_{test} = \frac{\rho_{opt} \times \pi \times (h - 0.3)}{SC} \left(\frac{d}{2}\right)^2$$

Where: M_{test} = mass of "as tested" sample (g)
ρ_{opt} = optimal packing density (dry basis) (g-dry/cm^3) determined in Sec. 11.3.1.9.
SC = solids content of the "as received" granular material (g-dry/g)
d = measured diameter of the sample mold (cm)
h = measured height of the sample mold (cm)

11.3.2.2 Adjust the moisture content of the "as-received" material to the optimum moisture content using reagent water and mix until homogenized.

11.3.2.3 Pack the sample material into the sample holder using the modified Proctor compaction as described in Ref. 5.

11.3.2.4 Place a mono-layer of borosilicate glass beads (Sec. 6.3.3) on the exposed sample surface to minimize scouring and mass loss during testing.

11.3.2.5 Begin the leach test procedure promptly or cover the sample with plastic wrap to minimize moisture loss to the atmosphere.

12.0 LEACHING PROCEDURE

This protocol is a semi-dynamic, tank-leaching procedure (see schematic in Figure 5) where the sample is exposed to eluate for a series of leaching intervals interspersed with eluant exchanges. The chemical composition of each eluate is determined and mass transfer from the bulk solid is determined as a function of cumulative leaching time. The schedule of leaching intervals for this method is shown in Table 1.

12.1 Pre-test measurements

12.1.1 For the surface area calculation, measure and record the dimensions of the test specimen (i.e., diameter and height for a cylinder; length, width and depth for a parallelepiped; or diameter of exposed surface for a compacted granular sample).

12.1.2 Measure and record the mass of the specimen. This value should be monitored for each eluant exchange.

12.1.3 If a holder is used, place the specimen in the monolith holder.

12.1.4 Measure and record the mass of the specimen and holder, if applicable.

12.1.5 The recommended temperature for conducting this method is room temperature (20 ± 2 °C). When conducted at temperatures readings or variations other than those recommended, record the ambient temperature at each eluant renewal.

12.2 Eluant exchange

12.2.1 Fill a clean leaching vessel with the required volume of reagent water based on an LSa ratio of 9 ± 1 mL/cm^2. Record the amount of eluant used.

12.2.2 Carefully place the specimen or the specimen and holder in the leaching vessel (Figure 6a) so that the sample is centered in the eluant (see Figure 6b). Submersion should be gentle enough so that the physical integrity of the monolith is maintained and scouring of the solid is minimized.

12.2.3 Cover the leaching vessel with the air-tight lid and place in a safe location until the end of the leaching interval. Table 1 shows the schedule of leaching intervals and cumulative release times for this method.

12.2.4 Prior to the end of the leaching interval, repeat Sec. 12.2.1 in order to prepare a vessel for the next leaching interval.

12.2.5 At the end of the leaching interval (see Table 1), carefully remove the specimen or the specimen and holder from the vessel (Figure 6c). Drain the liquid from the surface of the specimen into the eluate for approximately 20 sec.

12.2.6 Measure and record the mass of the specimen or the mass of the specimen and holder (Figure 6d).

NOTE: The change in sample mass between intervals is an indication of the potential absorption of eluant by the matrix (mass gain) or erosion of the matrix (mass loss). In the case where a holder is used, moisture may condense on the holder during the leaching intervals and sample absorption may not be evident.

CAUTION: Mass gain may also be indicative of carbonate precipitation if the vessel is not tightly sealed and carbon dioxide is absorbed from the atmosphere.

12.2.7 Place the specimen or the specimen and holder into the clean leaching vessel filled with new eluant as prepared in Sec. 12.2.4.

12.2.8 Cover the new leaching vessel with the air-tight lid and place in a safe location until the end of the leaching interval.

12.3 Eluate processing

12.3.1 Measure and record the pH, specific conductivity, and oxidation-reduction potential (ORP) (optional, but strongly recommended) of the eluate of the decanted eluate from the previous leaching interval (see Methods 9040, 9045, and 9050).

12.3.2 Filter the remaining eluate through a 0.45-μm membrane (Sec. 6.5).

12.3.3 Immediately, preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

12.3.4 Collect all subsequent eluate by repeating the eluant exchange and eluate processing procedures in Secs. 12.2 and 12.3.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 Data reporting

Figure 7 shows an example of a data sheet which may be used to report the concentrations results of this method. This example is included in the Excel template. At a minimum, the basic test report should include the following:

a) Name of the laboratory
b) Laboratory contact information
c) Date and time at the start of the test
d) Name or code of the solid material
e) Material Description (including monolithic or compacted granular)
f) Moisture content of material used (g_{H_2O}/g)
g) Dimensions (cm) and geometry of sample used
h) Mass of solid material used (g)
i) Mass of sample and holder at start of test (g)
j) Eluate type (e.g., reagent water)
k) Eluate specific information (see below)

The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Target eluant exchange date and time
c) Actual eluant exchange date and time
d) Volume of eluant used (mL)
e) Mass of sample and holder (g)
f) Measured eluate pH

g) Measured eluate conductivity (mS/cm)
h) Measured ORP (mV) (optional)
i) Concentration of all COPCs
j) Analytical QC qualifiers as appropriate

13.2 Data presentation

13.2.1 Interval concentrations

13.2.1.1 At the conclusion of the schedule of leaching intervals (see Table 1), the concentration of COPCs in each eluate may be plotted as a function of cumulative leaching time. An example of this is shown in Figure 8 for mass transport from a monolithic field sample of fixated scrubber sludge and lime.

13.2.1.2 If data is available from Method 1313, interval concentrations and Method 1313 data may be plotted on the same graph as a function of eluate pH. This QC step is conducted in order to determine if the concentration of COPCs approached equilibrium in any leaching interval (i.e., the driving force for mass transport from the matrix may not be constant which is a common assumption of dynamic-tank leach testing). Figure 9 shows this type of graph for the release from a field sample of fixated scrubber sludge and lime.

13.2.2 Interval mass release

At the conclusion of the schedule of leaching intervals (see Table 1), the interval mass released can be calculated for each leaching interval as follows:

$$M_{t_i} = \frac{C_i \times V_i}{A}$$

Where: M_{t_i} = Mass released during the current leaching interval i (mg/m^2)
C_i = constituent concentration in the eluate for interval i (mg/L)
V_i = eluate volume in interval i (L)
A = specimen external geometric surface area exposed to the eluant (m^2)

13.2.3 Mean interval flux

The flux of a COPC in an interval may be plotted as a function of the generalized mean of the square root of cumulative leaching time ($\sqrt{t}$). An example of a flux graph is show in Figure 10 for the release from a field sample of fixated scrubber sludge with lime. This graph may be used to interpret the mechanism of release (see Ref. 7. for further details).

13.2.3.1 The flux across the exposed surface of the sample can be calculated by dividing the interval mass release by the interval duration as follows:

$$F_i = \frac{M_i}{t_i - t_{i-1}}$$

Where F_i = flux for interval, i ($mg/m^2 \cdot s$)

Mi= mass released during the current leaching interval i (mg/m2)

t_i = cumulative time at the end of the current leaching interval i (s)

t_{i-1} = cumulative time at the end of the previous leaching interval i-1 (s)

13.2.3.2 The time used to plot each interval mass is the generalized mean of the square root of the cumulative leaching time using the cumulative time at the end of the ith interval, t_i, and the cumulative time at the end of the previous interval, t_{i-1}.

$$\overline{t_i} = \left(\frac{\sqrt{t_i} + \sqrt{t_{i-1}}}{2}\right)^2$$

Where $\overline{t_i}$: = generalized mean leaching time for the current interval, i (s)

t_i = cumulative time at the end of the current leaching interval, i (s)

t_{i-1} = cumulative time at the end of the previous leaching interval, i-1 (s)

NOTE: If the concentrations of a COPC in the eluates approach that shown in Method 1313 for liquid-solid equilibrium, the flux curve will show the pattern in Figure 10 with intervals of the same duration having the same flux value. When the eluate concentration approaches saturation, the driving force for mass transfer approaches zero, interval flux is limited, and intervals with like durations will display similar flux limitations.

13.2.4 Cumulative release

13.2.4.1 The interval release calculated in 13.2.2 can be summed to provide the cumulative mass release as a function of leaching time. Figure 11 shows the cumulative release curves for a field sample of fixated scrubber sludge with lime.

13.2.4.2 Interpretation of the cumulative release of constituents is illustrated using the analytical solution for simple radial diffusion from a cylinder into an infinite bath presented by Crank (see Ref. 6).

$$M_t = 2\rho C_o \left(\frac{D^{obs}\ t}{\pi}\right)^{1/2}$$

Where: M_t = cumulative mass released during leaching interval, i (mg/m^2)
ρ = density of the "as-tested" sample (kg/m^3)
C_o = concentration of available COPC in the solid matrix (mg/kg)
D^{obs} = observed diffusivity (m^2/s)
t = leaching time (s)

When transformed to a log-log scale, the analytical solution presented by Crank becomes becomes linear with the square root of time.

$$\log\left[M_t\right] = \log\left[2\rho C_o \left(\frac{D^{obs}}{\pi}\right)^{1/2}\right] + \frac{1}{2}t$$

Thus, under the assumptions of the analytical solution presented by Crank, the mass release should be proportional to the square root of time. A line showing the square root of time is plotted in Figure 11 along with the data. Since flux is the derivative of release, a similar treatment of flux as a function of leaching time using the simple diffusion model would be proportional to the negative square root of time as shown in Figure 10.

Other models than the simple diffusion model presented by Crank may also be used to interpret mass release. For example, the Shrinking Unreacted Core Model (see Ref. 8) and the Coupled Dissolution-Diffusion Model (see Ref. 9) incorporate chemical release parameters (e.g., as derived from Method 1313 data) into the model to better estimate release mechanisms and predictions (see Ref. 7 for further details).

13.2.5 Observed diffusivity

An observed diffusivity for each COPC can be determined using the logarithm of the cumulative release plotted versus the logarithm of time. In the case of a diffusion-controlled mechanism, this plot is expected to be a straight line with a slope of 0.5. An observed diffusivity can then be determined for each leaching interval where the slope is 0.5 ± 0.15 (see Refs. 10 and 11) by the following:

$$D_i^{obs} = \pi \left[\frac{M_{t_i}}{2\rho C_o\left(\sqrt{t_i} - \sqrt{t_{i-1}}\right)}\right]^2$$

Where: D_i^{obs} = observed diffusivity of a COPC for leaching interval, i (m^2/s)
M_{t_i} = mass released during leaching interval, i (mg/m^2)
t_i = cumulative contact time after leaching interval, i (s)
t_{i-1} = cumulative contact time after leaching interval, i - 1 (s)
C_o = initial leachable content (i.e., available release potential) (mg/kg)
ρ = sample density ($kg\text{-}dry/m^3$)

The mean observed diffusivity for each COPC is then determined by taking the average of the interval observed diffusivities. It should be reported with the computed uncertainty (i.e., standard deviation).

NOTE: Since the analysis presented above assumes a diffusion process, only those interval mass transfer coefficients corresponding to leaching intervals with slopes of 0.50 ± 0.15 are included in the overall average mass-transfer coefficient.

13.3 Data representation by constituent

A concise representation of all relevant data for a single constituent may be presented as shown in Figure 12 for arsenic from a field core of FSSL material. The data shows eluate pH generation as a function of leaching time (Figure 12a), comparison between eluate concentrations and Method 1313 data as a function of eluate pH (Figure 12b), constituent flux as a function of generalized mean cumulative leaching time (Figure 12c), and constituent release as a function of cumulative leaching time (Figure 12d).

14.0 METHOD PERFORMANCE

14.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.2 Refs. 1 and 7 may provide additional guidance and insight on the use, performance and application of this method.

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

16.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in Sec. 15.2.

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18.0
TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method

TABLE 1

SCHEDULE OF ELUATE RENEWALS

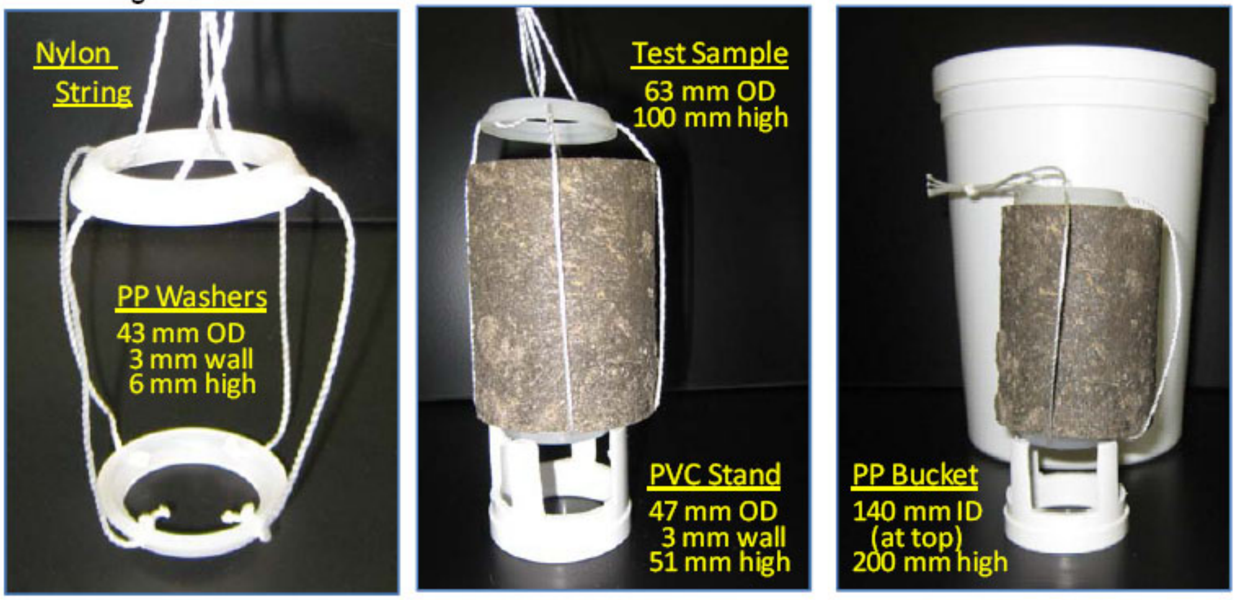
Interval Label	Interval Duration (h)	Interval Duration (d)	Cumulative Leaching Time (d)
T01	2.0 ± 0.25	–	0.08
T02	23.0 ± 0.5	–	1.0
T03	23.0 ± 0.5	–	2.0
T04	–	5.0 ± 0.1	7.0
T05	–	7.0 ± 0.1	14.0
T06	–	14.0 ± 0.1	28.0
T07	–	14.0 ± 0.1	42.0
T08	–	7.0 ± 0.1	49.0
T09	–	14.0 ± 0.1	63.0

NOTE: This schedule may be extended for additional 14-day contact intervals to provide more information regarding longer-term release.

FIGURE 1

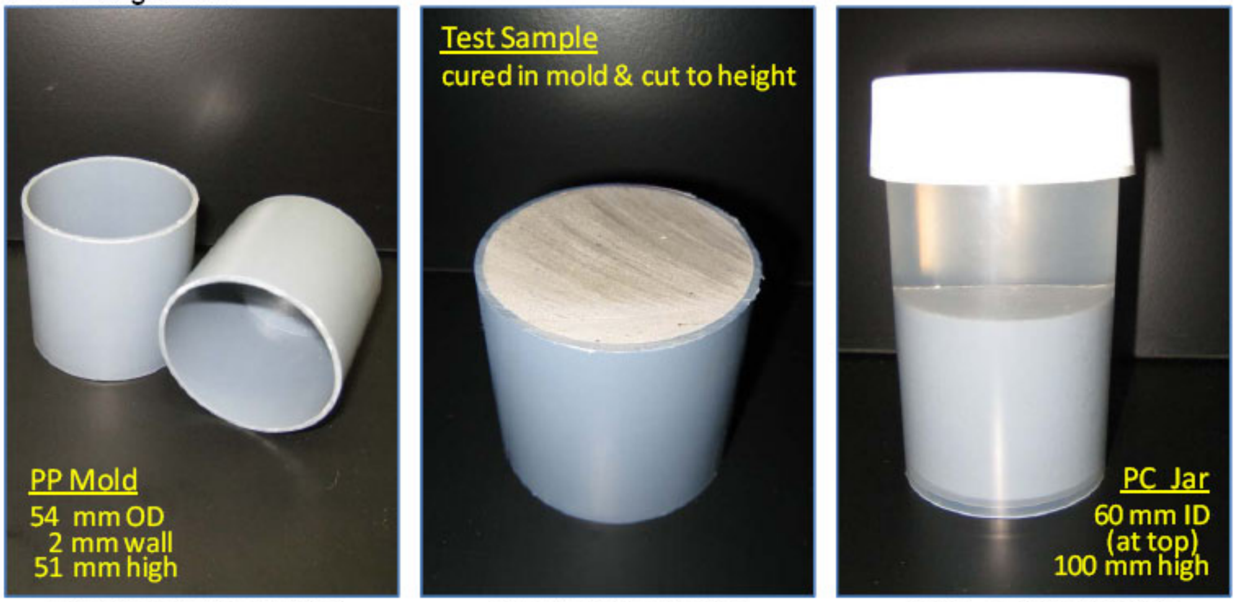
EXAMPLES OF MONOLITHIC SAMPLE HOLDERS

a) 3-D Configuration



Sample Holder — Sample, Holder and Stand — 3-D Leaching Setup

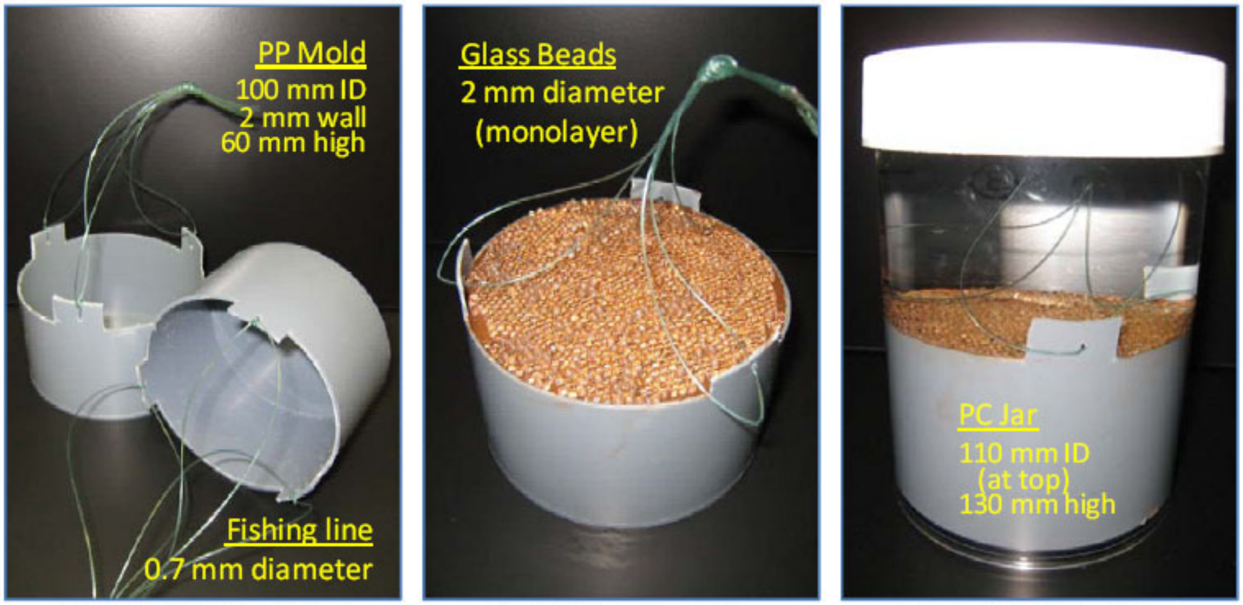
b) 1-D Configuration



Empty Sample Holder — Full Sample Holder — 1-D Leaching Setup

FIGURE 2

EXAMPLE COMPACTED GRANULAR SAMPLE HOLDER AND SETUP



Empty Sample Holder Compacted Sample 1-D Leaching Setup

FIGURE 3

METHOD 1315 FLOWCHART

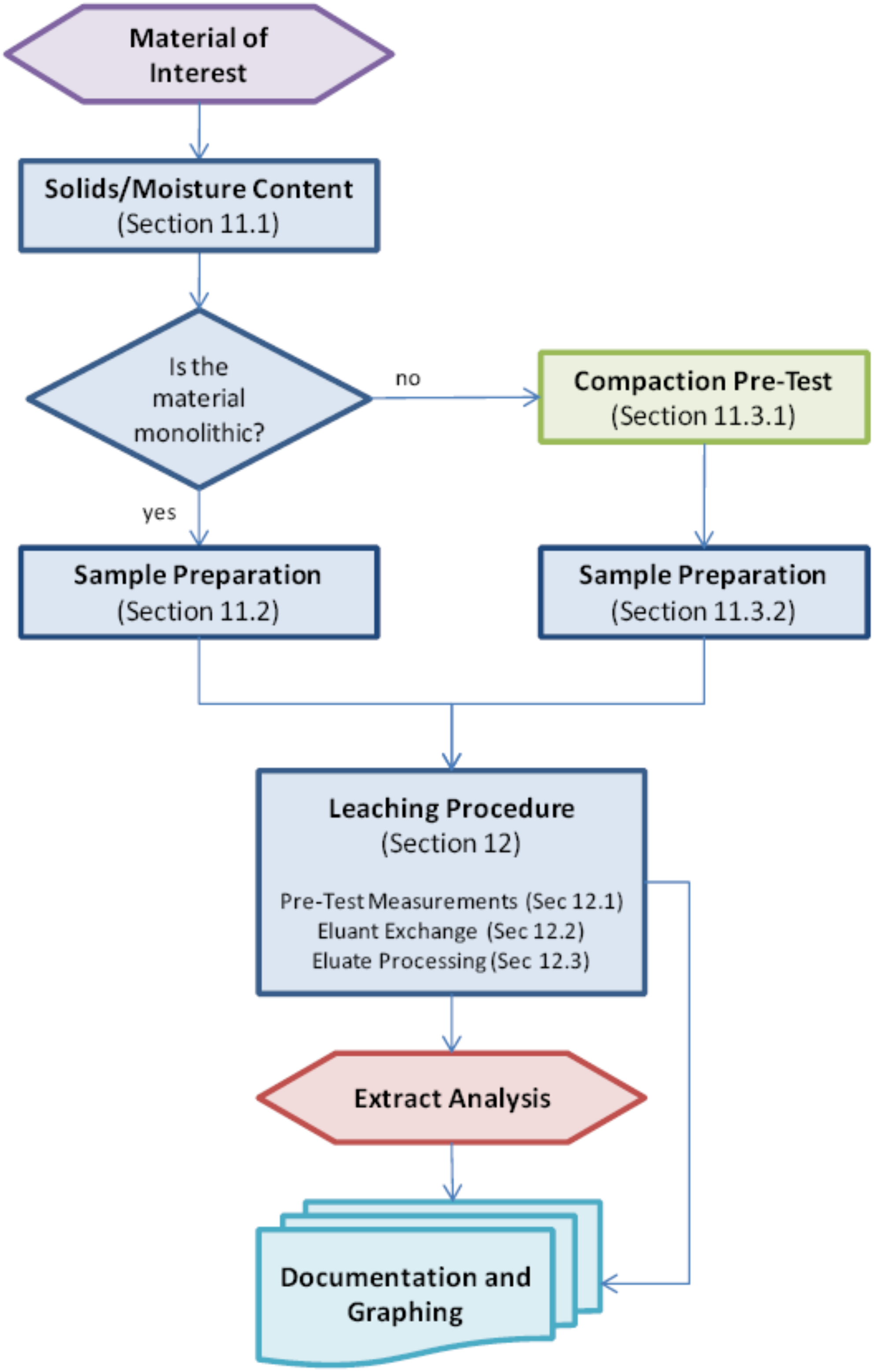


FIGURE 4

EXAMPLE CURVE OF PACKING DENSITY AS A FUNCTION OF MOISTURE CONTENT

$$y = 55.975x^3 – 65.036x^2 + 1.8352$$

$$r^2 = 0.983$$

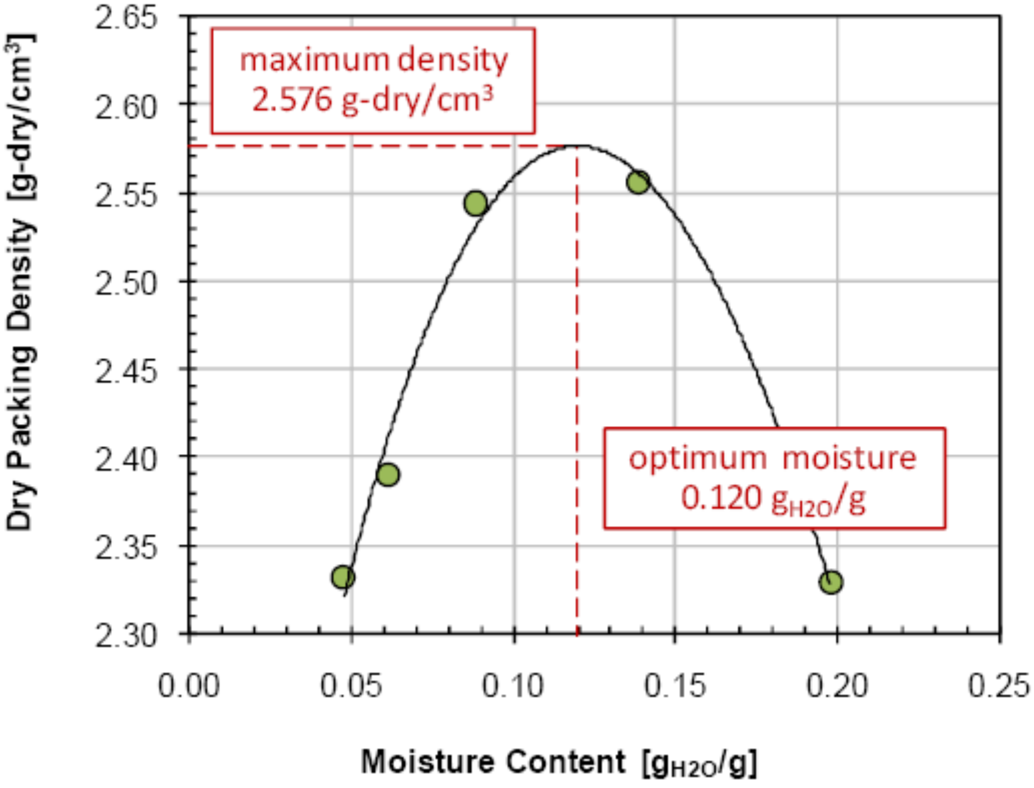


FIGURE 5

SCHEMATIC OF SEMI-DYNAMIC MASS TRANSFER TEST PROCESS

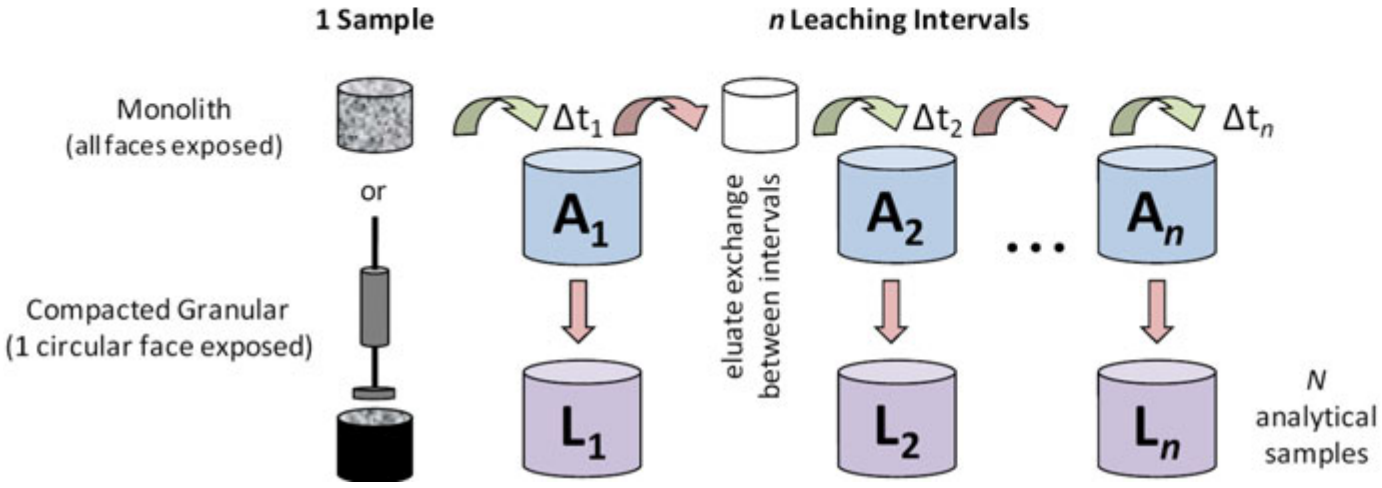
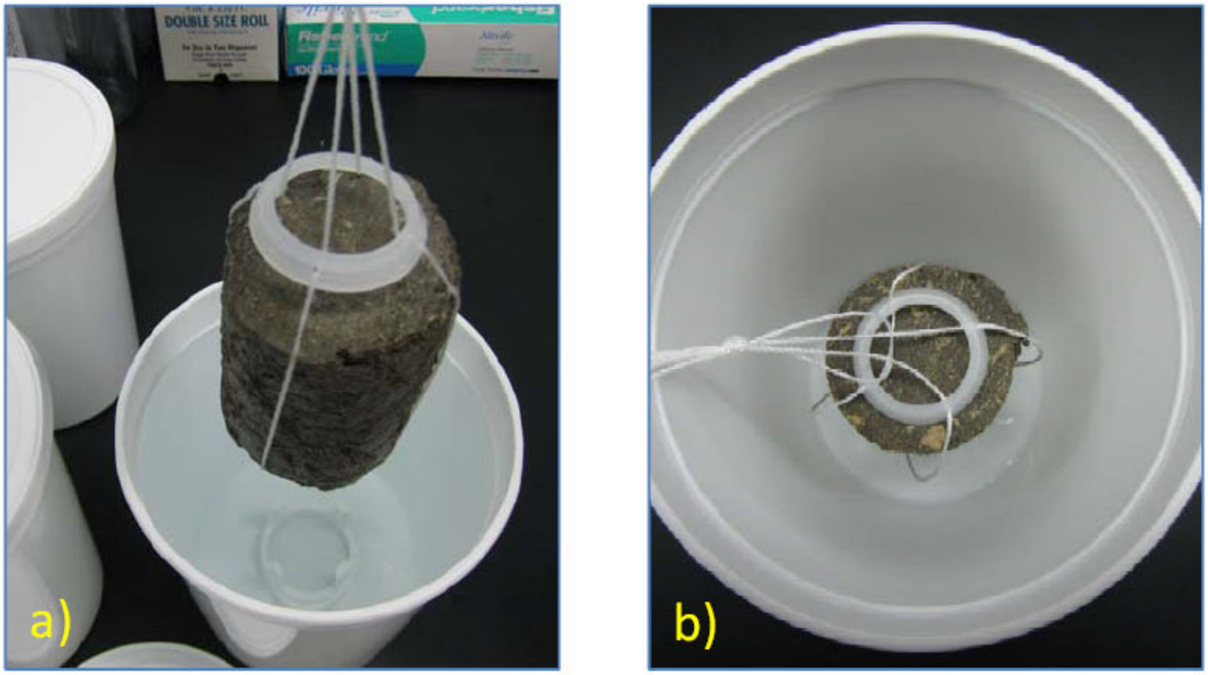


Figure obtained and modified from Ref. 11.

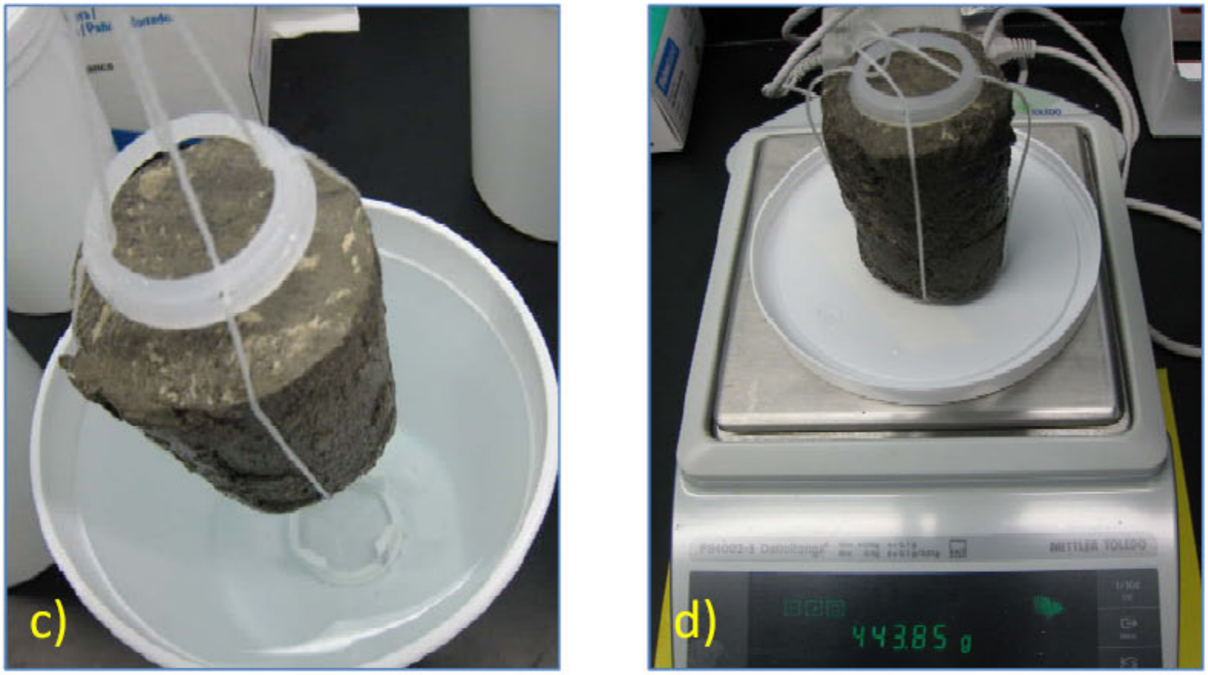
FIGURE 6

EXAMPLE LEACHING PROCEDURE STEPS



Start of Leaching Interval

Sample Centered in Eluant (top view)



Removing Sample for Exchange

Mass of Sample and Holder

FIGURE 7

EXAMPLE DATA REPORTING SHEET

EPA METHOD 1315
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code:	**XYZ**	Particle Size:	88% passing 2-mm sieve
Material Type:	Coal Combustion Fly Ash	Mass used in Column:	860 g
Date Received:	10/1/20xx	Moisture Content:	0.002 g_{H_2O}/g
Test Start Date:	11/1/20xx	Sample Geometry:	Cylinder
Report Date:	12/1/20xx	Sample Diameter	10.0 cm
		Sample Depth:	60.3 cm
Test Type:	Compacted Granular	Mass of Sample & Holder	1020 g
Eluant:	ASTM Type II Water	Lab Temperature:	21 ± 2 °C

Test Position	Replicate	Value	Units	Method	Note
T01	**A**				
	Eluate Sample ID	**XYZ-1315-T01-A**			
	Exchange Date	11/1/20xx			
	Target Exchange Time	12:00	PM		
	Actual Exchange Time	12:15	PM		
	Mass of Sample & Holder	1026	g		
	Eluate Mass	730.4	g		
	Eluate pH	8.82	-	EPA 9040	
	Eluate Conductivity	5.4	mS/c	EPA 9050	
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	4.72	mg/L		EPA 6020	11/7/20xx	1000
As	0.12	mg/L		EPA 6020	11/7/20xx	10
Cl	5.42	mg/L		EPA 9056	11/9/20xx	1

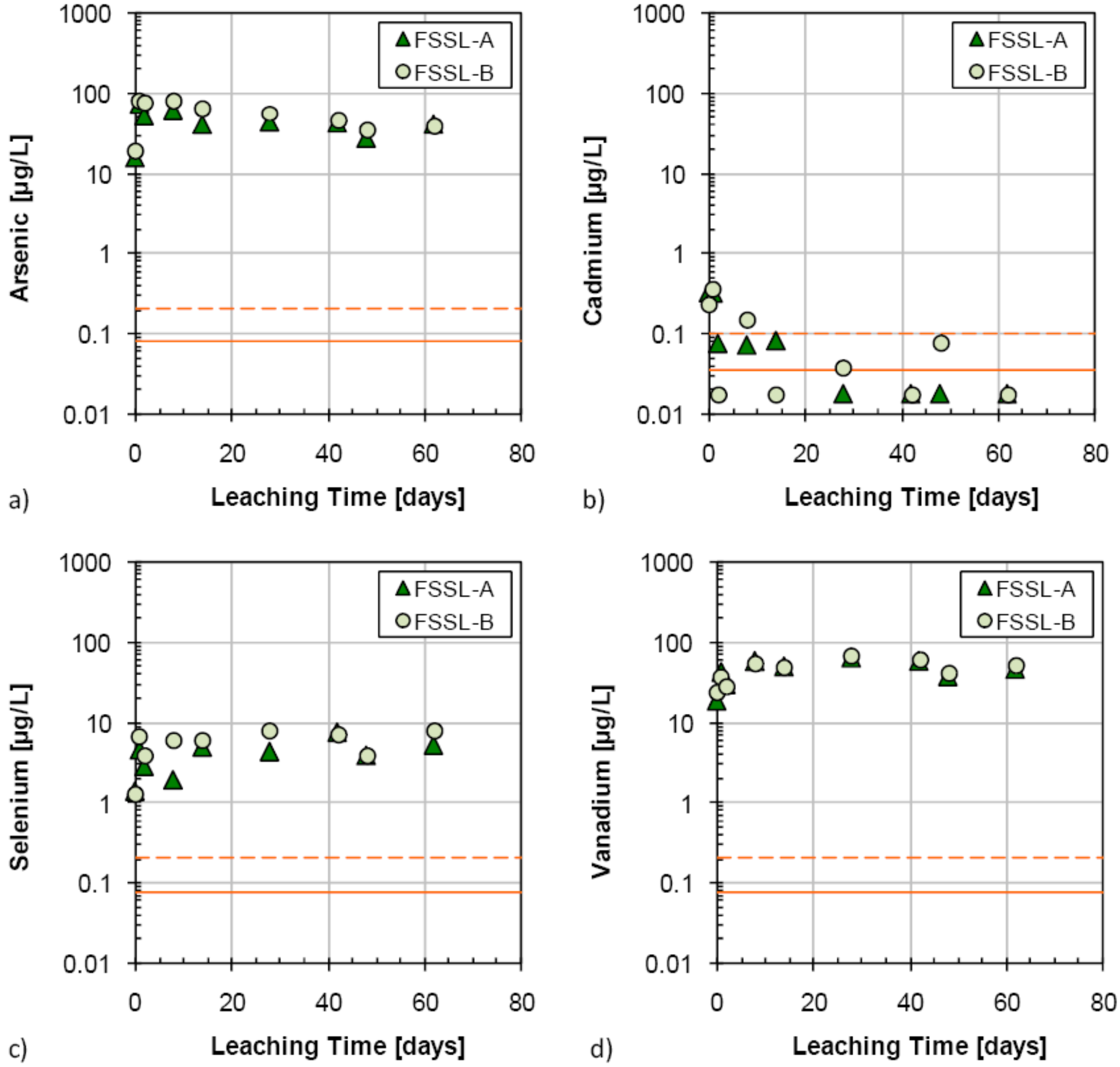
Test Position	Replicate	Value	Units	Method	Note
T02	**A**				
	Eluate Sample ID	**XYZ-1315-T02-A**			
	Exchange Date	11/1/20xx			
	Target Exchange Time	12:00	PM		
	Actual Exchange Time	12:18	PM		
	Mass of Sample & Holder	1027	g		
	Eluate Mass	725.0	g		
	Eluate pH	9.15	-	EPA 9040	
	Eluate Conductivity	2.8	mS/c	EPA 9050	
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	2.99	mg/L		EPA 6020	11/7/20xx	1000
As	0.21	mg/L		EPA 6020	11/7/20xx	10
Cl	4.20	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (< "LLOQ")

FIGURE 8

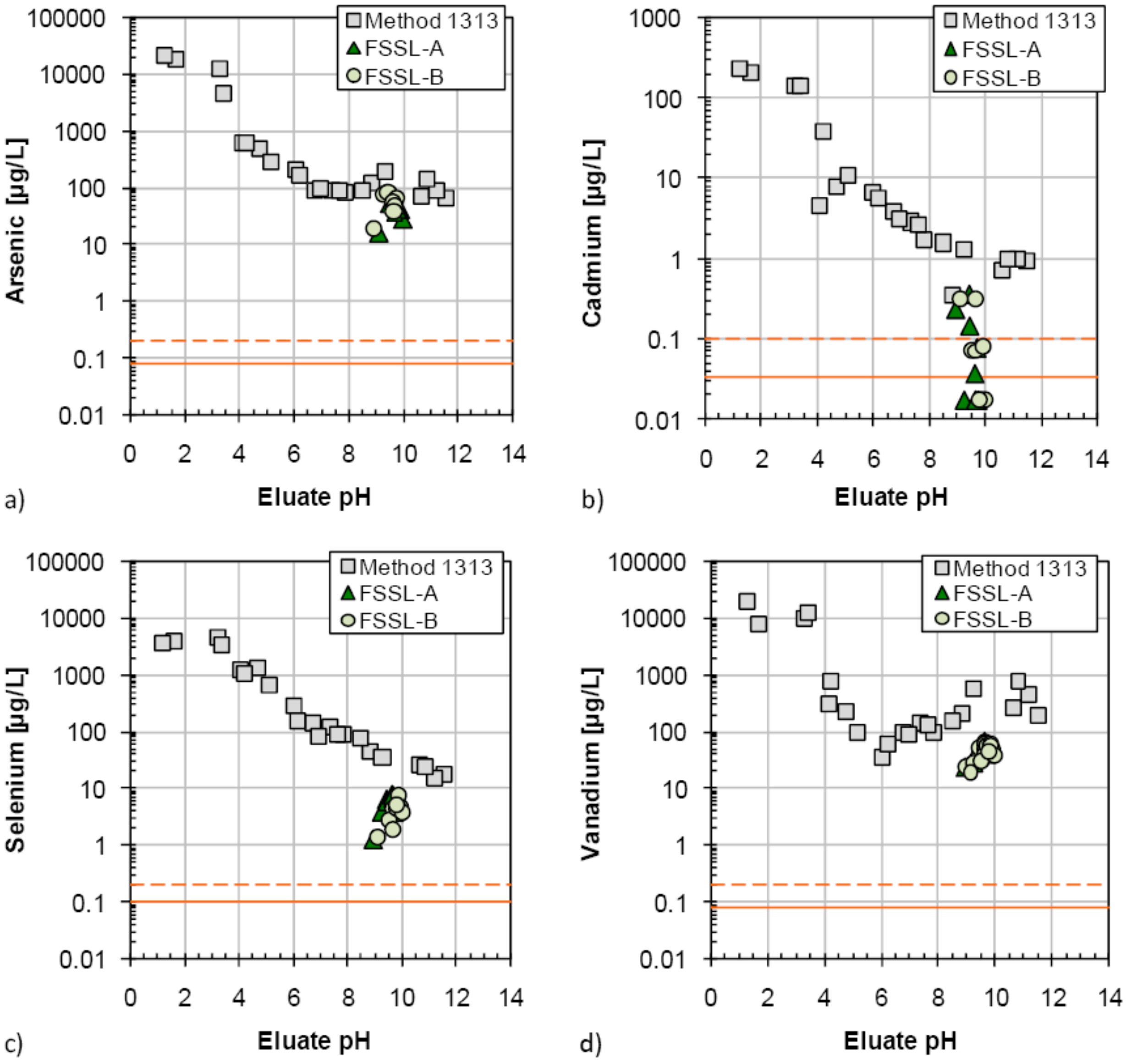
EXAMPLE INTERVAL CONCENTRATION GRAPHS



NOTE: Orange lines represent cumulative release if all eluate extracts were at the quantitation limit (dashed) and detection limit (solid). Chemical analyses below the detection limit are shown at ½ the detection limit value.

FIGURE 9

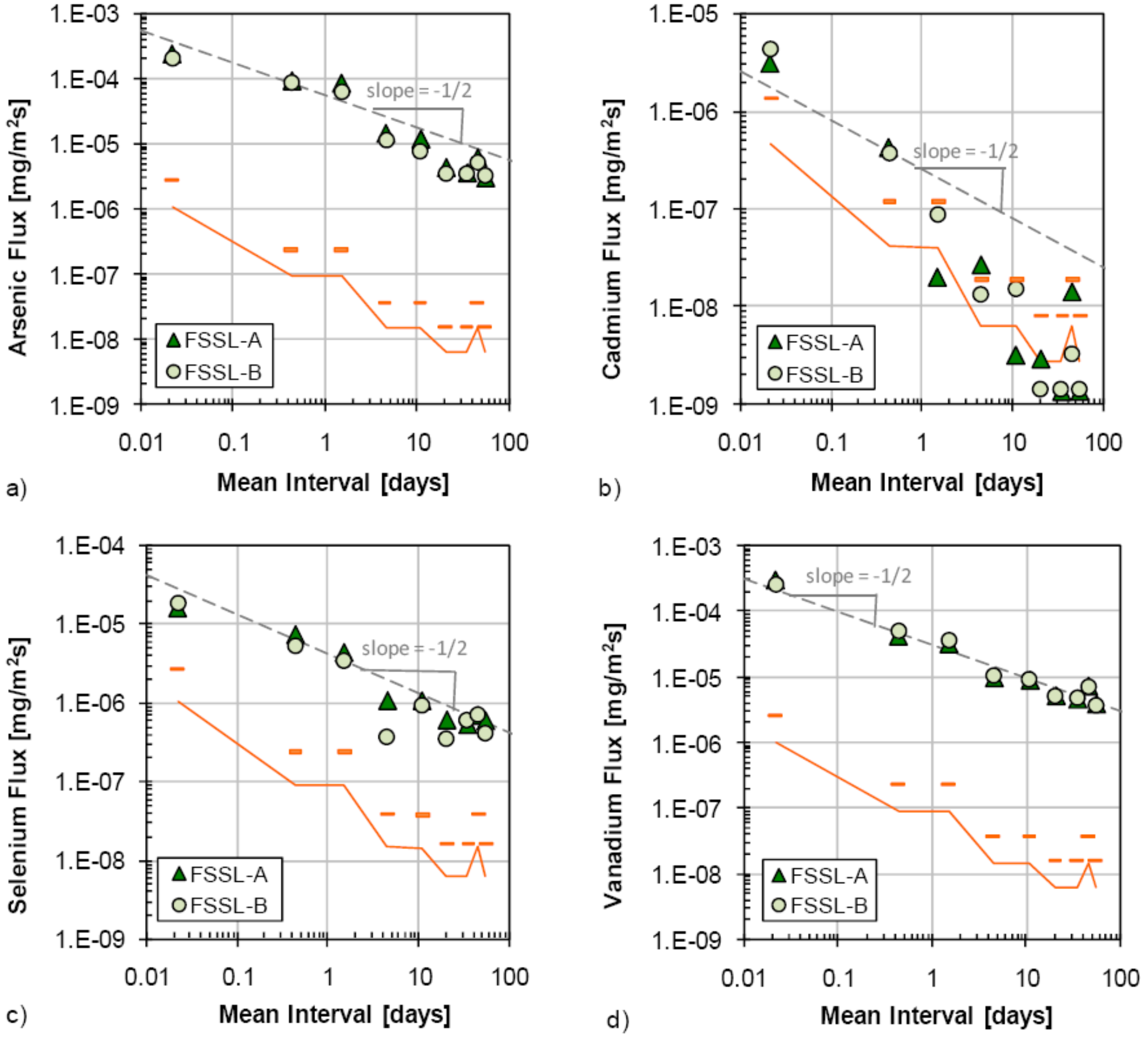
EXAMPLE OF SATURATION CHECK BETWEEN INTERVAL CONCENTRATIONS AND METHOD 1313 DATA



<u>NOTE</u>: Orange lines represent cumulative release if all eluate extracts were at the quantitation limit (dashed) and detection limit (solid). Chemical analyses below the detection limit are shown at ½ the detection limit value.

FIGURE 10

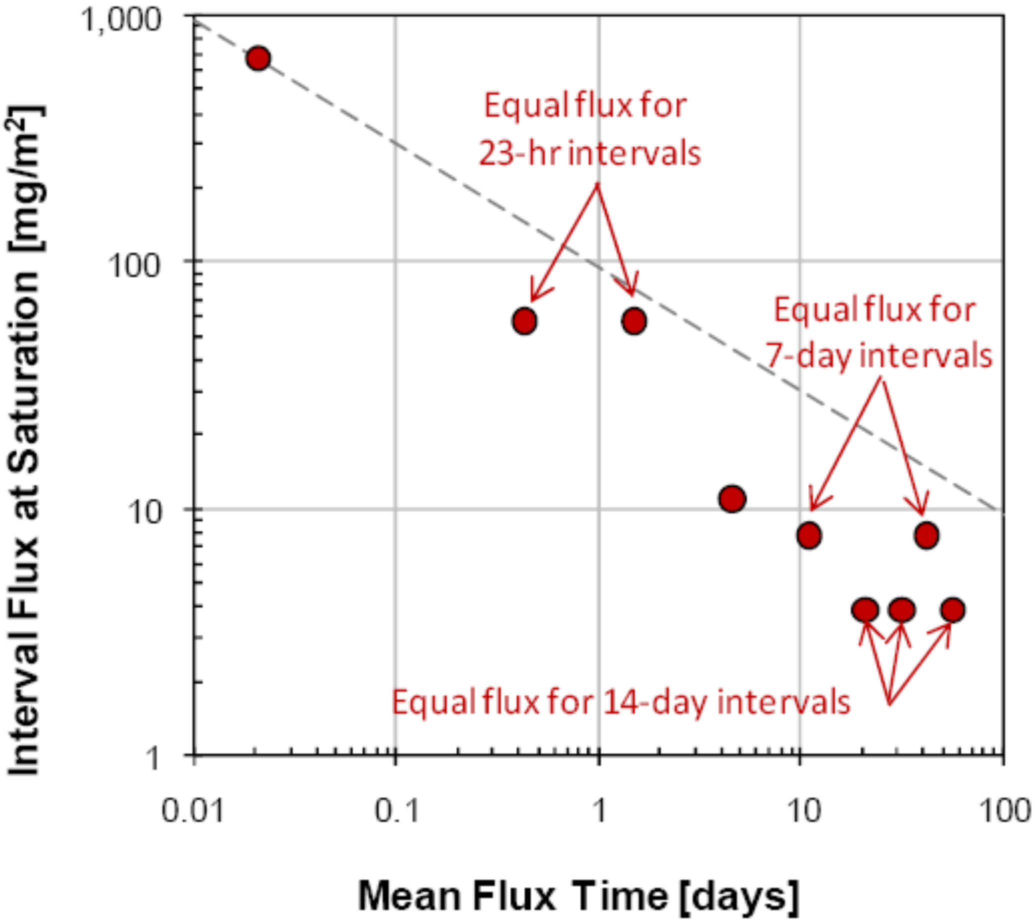
EXAMPLE INTERVAL FLUX GRAPHS



NOTE: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

FIGURE 11

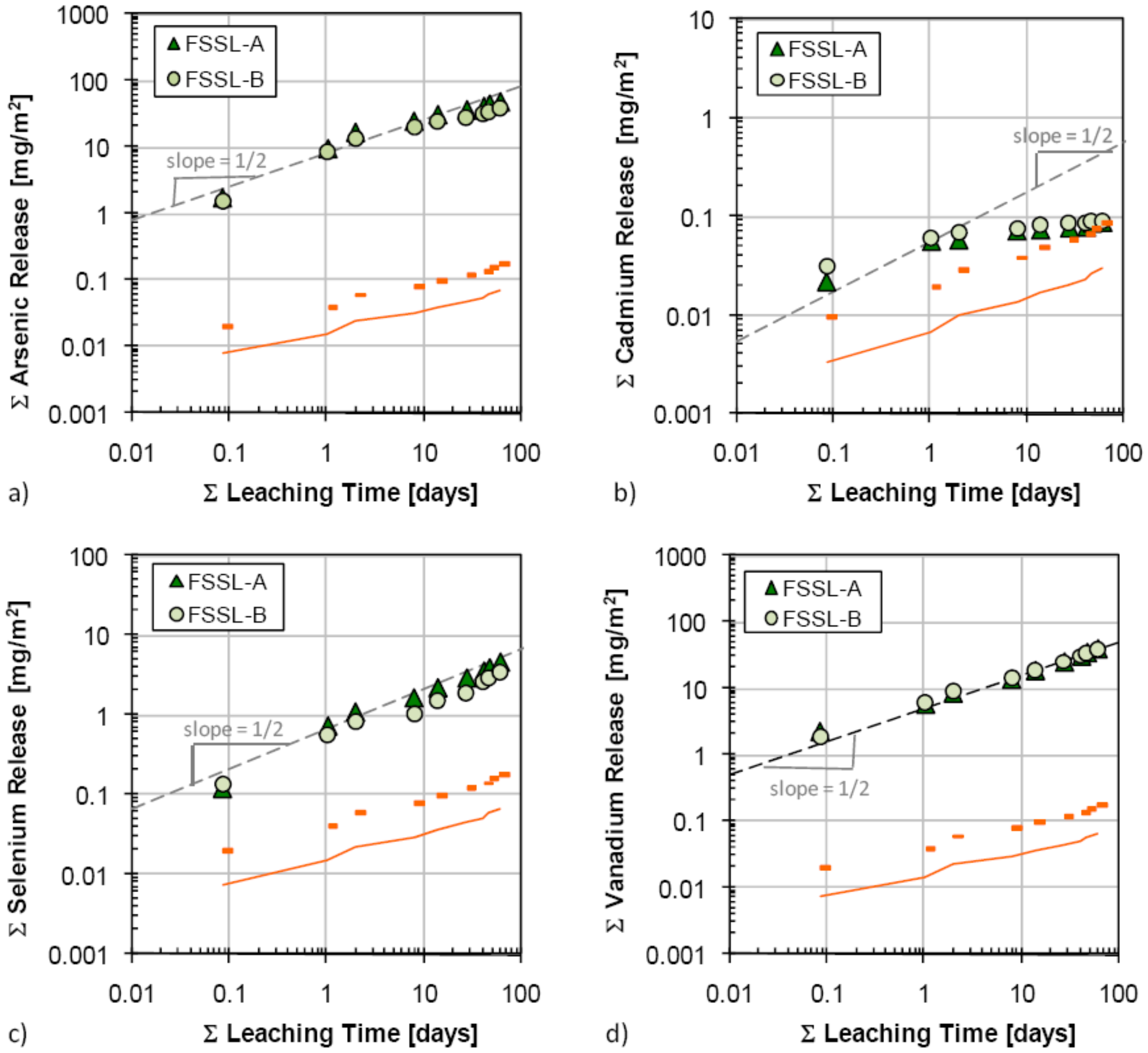
INTERVAL FLUX AT ELUATE SATURATION



<u>NOTE</u>: This figure assumes that the concentration in the eluate approaches saturation during the leaching interval (i.e., the driving force for diffusion approaches zero). When the leaching solution is saturated, the resulting mass release and interval flux is constant for intervals of the same duration.

FIGURE 12

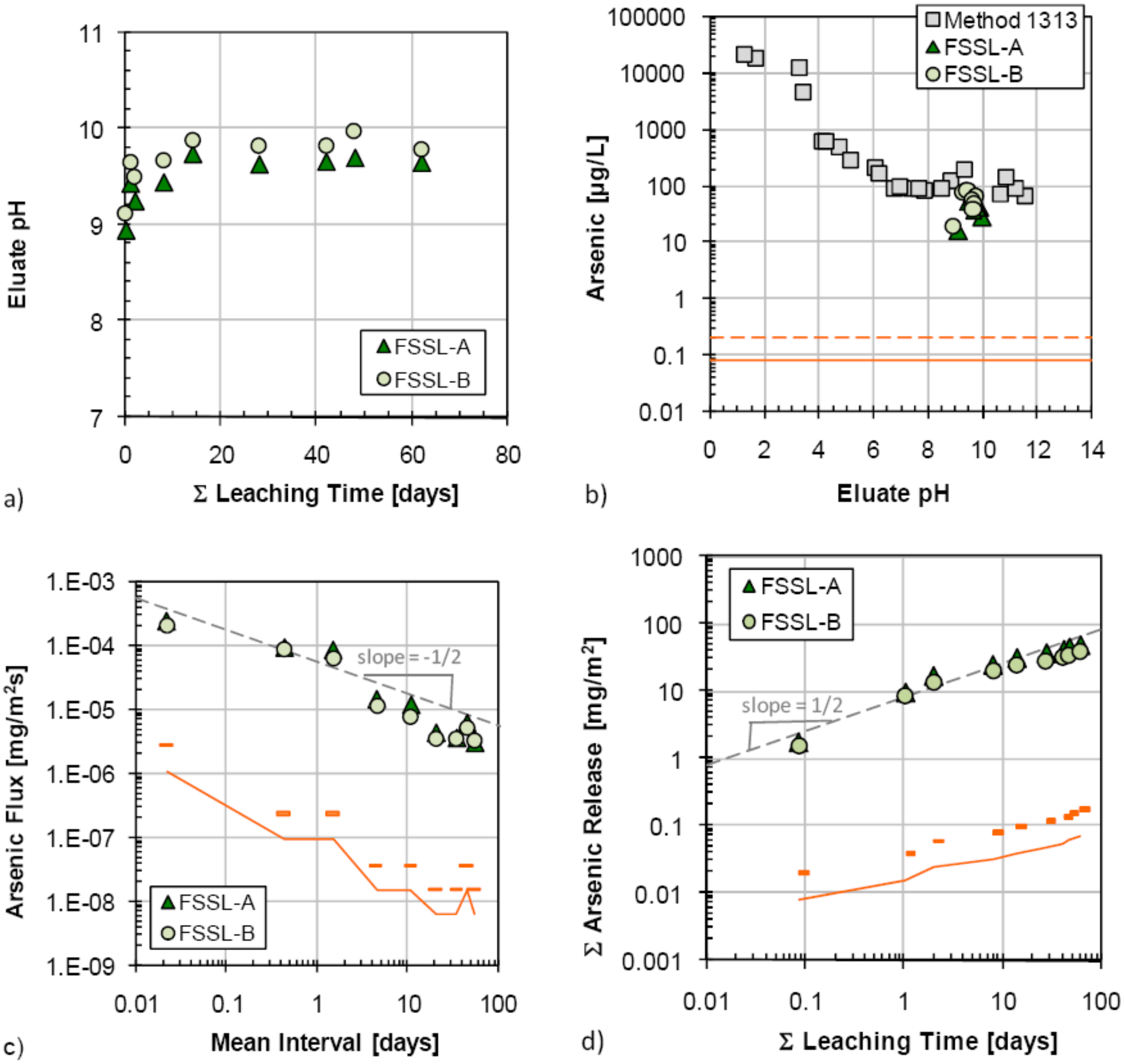
EXAMPLE CUMULATIVE RELEASE GRAPHS



<u>NOTE</u>: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

FIGURE 13

DATA REPRESENTATION BY CONSTITUENT (QUAD FORMAT)



<u>NOTE</u>: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

APPENDIX D

METHOD 1316 –

LIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-TO-SOLID RATIO IN SOLID MATERIALS USING A PARALLEL BATCH PROCEDURE

PRELIMINARY VERSION[1] OF METHOD 1316

LIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-TO-SOLID RATIO IN SOLID MATERIALS USING A PARALLEL BATCH PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide the liquid-solid partitioning (LSP) of inorganic constituents (e.g., metals, radionuclides) and non-volatile organic constituents (e.g., polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon) at the natural pH of the solid material as a function of liquid-to-solid ratio (L/S) under conditions that approach liquid-solid chemical equilibrium. Table 1 shows the range of target L/S values tested under this method.

1.2 The eluate concentrations at a low L/S provide insight into pore solution composition either in a granular bed (e.g., soil column) or in the pore space of low-permeability material (e.g., solidified monolithic or compacted granular fill). In addition, analysis of eluates for dissolved organic carbon and of the solid phase for total organic carbon allow for evaluation of the impact of organic carbon release and the influence of dissolved organic carbon on the LSP of inorganic constituents.

1.3 This method is intended to be used as part of environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness and site remediation.

1.4 This method is suitable to a wide range of solid materials. Example solid materials include industrial wastes, soils, sludges, combustion residues, sediments, stabilized materials, construction materials, and mining wastes.

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[1] Preliminary Version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846. This method has been derived from published procedures (Kosson et al, 2002) using reviewed and accepted methodologies (USEPA 2006, 2008, 2009). The method has been submitted to the USEPA Office of Resource Conservation and Recovery and is currently under review for development of interlaboratory validation studies to develop precision and bias information.

1.5 This method is a leaching characterization method used to provide intrinsic material parameters that control leaching of inorganic species under equilibrium conditions. This test method is intended as a means for obtaining an extract (i.e., the eluate) of a solid material which may be used to estimate the solubility and release of inorganic constituents under the laboratory conditions described in this method. Extract concentrations may be used in conjunction with information regarding environmental management scenarios to estimate anticipated leaching concentrations, release rate and extent for individual material constituents in the management scenarios evaluated. Extract concentrations may also be used along with geochemical speciation modeling to infer the mineral phases that control the LSP in the pore structure of the solid material.

1.6 This method is not applicable to characterize the release of volatile organic analytes.

1.7 This method provides solutions that are considered to be indicative of eluate under field conditions only where the field leaching pH and L/S is the same as the laboratory extract final conditions and the LSP is controlled by aqueous-phase saturation of the constituent of interest.

1.8 The solvent used in this method is reagent water

1.9 Analysts are advised to take reasonable measures to ensure that the sample is homogenized to the extent practical prior to employment of this method. Particle-size reduction may provide additional assurance of sample homogenization. Table 2 designates a minimum dry equivalent mass of sample to be added to each extraction vessel and the associated extraction contact time as a function maximum particle diameter. If the heterogeneity of the sample is suspected as the cause of unacceptable levels of precision in replicate test results or is considered significant based on professional judgment, the sample mass used in the test procedure may be increased to a greater minimum dry equivalent mass than shown in Table 1 with the amount of extractant increased proportionately to maintain the designated L/S.

1.10 In the preparation of solid materials for use in this method, particle-size reduction of samples with large grain size is used to enhance the approach towards liquid-solid equilibrium under the designated contact time interval of the extract process. The extract contact time for samples reduced to a finer maximum particle size will be shorter.

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045), quality control (QC) acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.12 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method consists of five parallel extractions of a particle-size reduced solid material in reagent water over a range of L/S values from 0.5 to 10 mL eluant/g dry material (see Table 1). In addition to the five test extractions, a method blank without solid sample is carried through the procedure in order to verify that analyte interferences are not introduced as a consequence of reagent impurities or equipment contamination (If multiple materials or replicate tests are carried out in parallel, only one set of method blanks is necessary). In total, six bottles (i.e., five test positions and one method blank) are tumbled in an end-over-end fashion for a specified contact time based on the maximum particle size of the solid (see Table 2). At the end of the contact interval, the liquid and solid phases are roughly separated via settling or centrifugation. Extract pH and specific conductance measurements are then taken on an aliquot of the liquid phase. The bulk of the eluate is clarified by pressure or vacuum filtration in preparation for constituent analysis. Analytical aliquots of the extracts are collected and preserved accordingly based on the determinative methods to be performed. The eluate constituent concentrations are plotted as a function of L/S and compared to QC and assessment limits.

3.0 DEFINITIONS

3.1 Release — The dissolution or partitioning of a constituent of potential concern (COPC) from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.2 COPC — A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.3 LSP — The distribution of COPCs between the solid and liquid phases at the conclusion of the extraction.

3.4 L/S — the fraction of the total liquid volume (including the moisture contained in the “as used” solid sample) to the dry mass equivalent of the solid material. L/S is typically expressed in volume units of liquid per dry mass of solid material (mL/g-dry).

3.5 “As-tested” sample — The solid sample at the conditions (e.g., moisture content and particle-size distribution) present at the time of the start of the test procedure. The “as-tested” conditions will differ from the "as-received" sample conditions if particle-size reduction and drying were necessarily performed.

3.6 Dry-mass equivalent — The mass of “as-tested” (i.e., “wet”) sample that equates to the mass of dry solids plus associated moisture, based on the moisture content of the “as-tested” material. The dry-mass equivalent is typically expressed in mass units of the “as-tested” sample (g).

3.7 Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapters Three and Four for general guidance on the cleaning of laboratory apparatus prior to use.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and setting used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and setting other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Extraction vessels

6.1.1 Six wide-mouth bottles (i.e., five for test positions plus one for a method blank) constructed of an inert material resistant to high and low pH conditions or interaction with the constituents of interest.

6.1.1.1 For the evaluation of inorganic COPC mobility, bottles composed of high density polyethylene (HDPE) (e.g., Nalgene #3140-0250 or equivalent), polypropylene (PP), or polyvinyl chloride (PVC) are recommended.

6.1.1.2 For the evaluation of non-volatile organic and mixed organic/inorganic COPCs, equipment composed of glass or Type 316 stainless steel is recommended. PTFE is not recommended for non-volatile organics, due sorption of species with high hydrophobicity (e.g., PAHs). Borosilicate glass is recommended over other types of glass, especially when inorganic analytes are of concern.

6.1.2. The extraction vessels must be of sufficient volume to accommodate both the solid sample and an extractant volume based on the schedule of L/S values shown in Table 1. For example, a 500-mL bottle is recommended when 100 g dry equivalent mass is contacted with 200 mL of eluant (see T03 in Table 1).

6.1.3 The vessels must have a leak-proof seals that can sustain end-over-end tumbling for the duration of the designated contact time.

6.1.4 If centrifugation is anticipated to be beneficial for initial phase separation, the extraction vessels should be capable of withstanding centrifugation at 4000 ± 100 rpm for a minimum of 10 ± 2 min. Alternately, samples may be extracted in bottles that do not meet this centrifugation specification (e.g., Nalgene I-Chem #311-0250 or equivalent) and the solid-liquid slurries transferred into appropriate centrifugation vessels for phase separation as needed.

6.2 Balance — Capable of 0.01-g resolution for masses less than 500 g.

6.3 Rotary tumbler — Capable of rotating the extraction vessels in an end-over-end fashion at a constant speed of 28 ± 2 rpm (e.g., Analytical Testing, Werrington, PA or equivalent).

6.4 Filtration apparatus — Pressure or vacuum filtration apparatus composed of appropriate materials so as to maximize the collection of extracts and minimize loss of the COPCs (e.g., Nalgene #300-4000 or equivalent) (see Sec. 6.1).

6.5 Filtration membranes — Composed of polypropylene or equivalent material with an effective pore size of 0.45-µm (e.g., Gelman Sciences GH Polypro #66548 from Fisher Scientific or equivalent).

6.6 pH Meter — Laboratory model with the capability for temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) and a minimum resolution of 0.1 pH units.

6.7 pH combination electrode — Composed of chemically-resistant materials.

6.8 Conductivity meter — Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value.

6.9 Conductivity electrodes — Composed of chemically-resistant materials.

6.10 Adjustable-volume pipettor — Oxford Benchmate series or equivalent The necessary delivery range will depend on the buffering capacity of the solid material and acid/base strength used in the test.

6.11 Disposable pipettor tips.

6.12 Centrifuge (recommended) — Capable of centrifuging the extraction vessels at a rate of 4000 ± 100 rpm for 10 ± 2 min.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specification are available. Other grades may be used, provided it is first ascertained that the reagents are of sufficiently high purity to permit use without lessening the accuracy of the determination. Inorganic reagents and extracts should be stored in plastic to prevent interaction of constituents from glass containers.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Consult Methods 9040 and 9050 for additional information regarding the preparation of reagents required for pH and specific conductance measurements.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three “Inorganic Analytes” and Chapter Four “Organic Analytes.”

8.2 All samples should be collected using an appropriate sampling plan.

8.3 All analytical sample containers should be composed of materials that minimize interaction with solution COPCs. For further information, see Chapters Three and Four.

8.4 Preservatives should not be added to samples before extraction.

8.5 Samples can be refrigerated, unless refrigeration results in an irreversible physical change to the sample.

8.6 Analytical samples should be preserved according to the guidance given in the individual determinative methods for the COPCs.

8.7 Extract holding times should be consistent with the aqueous sample holding times specified in the determinative methods for the COPCs.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 In order to demonstrate the purity of reagents and sample contact surfaces, a method blank (e.g., a bottle without solid material but with eluant carried through the extraction, filtration and analytical sample preparation process) should be tested.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific quality control procedures.

9.4 Solid materials should be tested within one month of receipt unless the project requires that the "as-received" samples are tested sooner (e.g., the material is part of a time-dependent study or the material may change during storage due to oxidation or carbonation).

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified at a minimum annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PREPARATORY PROCEDURES

A flowchart of the method is presented in Figure 1.

11.1 Particle-size reduction (if required)

11.1.1 In this method, particle-size reduction is used to prepare large-grained samples for extraction so that the approach toward liquid-solid equilibrium is enhanced and mass transport through large particles is minimized. A longer extract contact time is required for larger maximum particle-size designations. This method designates three maximum particle sizes and associated contact times (see Table 2). The selection of an appropriate maximum particle size from this table should be based on professional judgment regarding the practical effort required to size reduce the solid material.

11.1.2 Particle-size reduction of “as received” sample may be achieved through crushing, milling or grinding with equipment made from chemically inert materials. During the reduction process, care should be taken to minimize loss of sample and potentially volatile constituents in the sample.

11.1.3 If the moisture content of the “as-received” material is greater than 15% (wet basis), air drying or desiccation may be necessary. Oven drying is not recommended for preparation of test samples due to the potential for mineral alteration. In all cases, the moisture content of the “as received” material should be recorded.

NOTE: If the solid material is susceptible to interaction with the atmosphere (e.g., carbonation, oxidation), drying should be conducted in an inert environment.

11.1.4 When the material seems to be of a relatively uniform particle size, calculate the percentage less than the sieve size as follows:

$$\%\ Pas\sin g = \frac{M_{sieved}}{M_{total}} \times 100\%$$

Where: M_{sieved} = mass of sample passing the sieve (g)
M_{total} = mass of total sample (g) (e.g., M_{sieved} + mass not passing sieve)

11.1.5 The fraction retained by the sieve should be recycled for further particle-size reduction until at least 85% of the initial mass has been reduced below the designated maximum particle size. Calculate and record the final percentage passing the sieve and the designated maximum particle size. For the uncrushable fraction of the “as received” material, record the fraction mass and nature (e.g., rock, metal or glass shards, etc).

11.1.6 Store the size-reduced material in an airtight container in order to prevent contamination via gas exchange with the atmosphere. Store the container in a cool, dark and dry place prior to use.

11.2 Determination of solids and moisture content

11.2.1 In order to provide the dry mass equivalent of the “as-tested” material, the solids content of the subject material should be determined. Often, the moisture content of the solid sample is recorded. In this method, the moisture content is determined and recorded on the basis of the “wet” or “as-tested” sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable or explosive materials.

11.2.2 Place a 5–10-g sample of solid material into a pre-tared dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Periodically check the sample mass after allowing the sample to cool to room temperature (20 ± 2 °C) in a desiccator.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.2.3 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content (g-dry/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.2.4 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: $MC_{(wet)}$ = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of oven-dried sample (g-dry)
M_{test} = mass of "as-tested" sample (g)

11.3 Extraction setup schedule (Microsoft® Excel template provided)

This method provides an Excel template which may be used to set up the extraction schedule. If using the provided template, disregard Sec. 11.3 and proceed to the extraction procedure Sec. 11.4.

11.3.1 Using the schedule shown in Table 1 as a guide, set up five test extractions and one method blank. The mass of solids in an extraction may be scaled to minimize headspace in each extraction vessel. However, the volume of eluant should always be based on the target L/S in Column B of Table 1.

11.3.2 Calculate and record the amount of "as-tested" material equivalent to the dry mass in Column D of Table 1 as follows:

$$M_{test} = \frac{M_{dry}}{SC}$$

Where: M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)
M_{dry} = mass of dry material specified in the method (g-dry)
SC = solids content of "as-tested" material (g-dry/g)

11.3.3 Calculate and record the volume of moisture contained in the "as-tested" sample in Column E of Table 1 as follows:

$$V_{W,sample} = \frac{M_{test} \times (1 - SC)}{\rho_w}$$

Where: $V_{W,sample}$ = volume of water in the "as tested" sample (mL)
M_{test} = mass of the "as tested" sample (g)
SC = solids content of the "as tested" sample (g-dry/g)
ρ_w = density of water (1.0 g/mL at room temperature)

11.3.4 Calculate and record the volume of reagent water required to bring each extraction to the target L/S in Column F of Table 1 as follows:

$$V_{RW} = M_{dry} \times LS - V_{W,sample}$$

Where: V_{RW} = volume of reagent water required to complete L/S (mL)
M_{dry} = dry mass equivalent of solid sample (g)
LS = liquid-to-dry-solid ratio (10 mL/g)
$V_{W,sample}$ = volume of water in "as used" sample (mL)

The size of the extraction bottle should be sufficient to contain the combined volume of solid material and eluant, ideally with a minimum amount of headspace.

12.0 EXTRACTION PROCEDURE

12.1 Label five bottles with test position numbers and an additional bottle as a method blank according to Column A in Table 1.

12.2 Place the dry-mass equivalent (± 0.1 g) of "as-tested" sample as shown in Column D in Table 1 into each of the five test position extraction vessels.

NOTE: Do not put solid material in the method blank extraction vessel

12.3 Add the appropriate volume (± 0.5 mL) of reagent water to both the test position and method blank extraction vessels as specified in Column F of Table 1.

12.4 Tighten the leak-proof lid on each bottle and tumble all extractions (i.e., test positions and method blanks) in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature (20 ± 2 °C). The contact time for this method will vary depending on the maximum particle size as shown in Table 2.

NOTE: The length of the contact time is designed to enhance the approach toward liquid-solid equilibrium. Longer contact times are required for larger particles to compensate for the effects of intra-particle diffusion. See Table 2 for required contact times based on the maximum particle size.

12.5 Remove the extraction vessels from the rotary tumbler and clarify the extractants by allowing the bottles to stand for 15 ± 5 min. Alternately, centrifuge the extraction vessels at 4000 ± 100 rpm for 10 ± 2 min.

NOTE: If clarification is significantly incomplete after settling or centrifugation, eluate measurements for pH, conductivity, and oxidization-reduction potential (ORP) may be taken on filtered samples. In this case, perform the filtration in 12.7 prior to eluate measurement in 12.6 and note the deviation from the written procedure.

CAUTION: Following separation from the solid phase, eluate samples lack the buffering provided by the solid phase and therefore may be susceptible to pH change resulting from interaction with air.

12.6 For each extraction vessel, decant a minimum volume (~ 5 mL) of clear, unpreserved supernatant into a clean container. Measure and record the pH, specific conductivity, and oxidation-reduction potential (ORP) (optional, but strongly recommended) of the extracts (see Methods 9040, 9045, and 9050).

12.7 Separate the solid from the remaining liquid in each extraction vessel by pressure or vacuum filtration through a clean 0.45-µm pore size membrane (Sec. 6.5). The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

NOTE: Eluate measurements for pH, conductivity, and ORP should be taken as soon as possible after the settling and preferably within 1 hour after completion of tumbling (12.6).

12.8 Immediately, preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

13.0 DATA ANALYSIS AND CALCULATIONS (EXCEL TEMPLATE PROVIDED)

13.1 Data reporting

13.1.1 Figure 2 shows an example of a data sheet that may be used to report the concentration results of this method. This example is included in the Excel template. At a minimum, the basic test report should include:

a) Name of the laboratory
b) Laboratory contact information
c) Date at the start of the test
d) Name or code of the solid material
e) Particle size (85 wt% less than)
f) Ambient temperature during extraction (°C)
g) Extraction contact time (h)
h) Eluate specific information (see Sec. 13.1.2 below)

13.1.2 The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Target L/S (mL/g-dry)
c) Mass of “as tested” solid material used (g)
d) Moisture content of material used (g_{H_2O}/g)
e) Volume of eluant used (mL)
f) Measured final eluate pH
g) Measured eluate conductivity (mS/cm)
h) Measured ORP (mV) (optional)
i) Concentrations of all COPCs
j) Analytical QC qualifiers as appropriate

13.2 Data interpretation and presentation (optional)

13.2.1 LSP curve

13.2.1.1 A constituent LSP curve can be generated for each COPC after chemical analysis of all extracts by plotting the constituent concentration in the liquid phase as a function of L/S used for each extraction. The curve indicates the equilibrium concentration of the COPC as a function of L/S at the natural pH.

13.2.1.2 The lower limit of quantitation (LLOQ) for the analytical technique for each COPC may be shown as a horizontal line. COPC concentrations below this line indicate negligible or non-quantitative concentrations.

<u>NOTE</u>: The LLOQ is highly matrix dependent and should be determined as part of a QA/QC plan.

13.2.1.3 Figure 3 provides example LSP curves as a function of L/S for a coal combustion fly ash and a coal combustion flue gas desulfurization filter cake.

14.0 METHOD PERFORMANCE

14.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation</u>.

14.2 Refs. 1 and 2 may provide additional guidance and insight on the use, performance and application of this method.

15.0
POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

16.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in Sec. 15.2.

17.0 REFERENCES

1. D.S. Kosson, H.A. van der Sloot, F. Sanchez and A.C. Garrabrants (2002) “An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials,” Environmental Engineering Science, 19(3) 159-204.

2. D.S. Kosson, A.C. Garrabrants, H.A. van der Sloot (2009) “Background Information for the Development of Leaching Test Draft Methods 1313 through Method 1316,” (in preparation).

3. USEPA (2006) Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, February 2006.

4. USEPA (2008) Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control, EPA-600/R-08/077, July 2008.

5. USEPA (2009) Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, EPA-600/R-09/151, December 2009.

18.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method

TABLE 1

EXAMPLE SCHEDULE FOR EXTRACTION SETUP

A	B	C	D	E	F	G
Test Position	Target LS	Minimum Dry Mass (g-dry)	Mass of "As-Tested" Sample (g)	Moisture in "As-Tested" Sample (mL)	Volume of Reagent Water (mL)	Recommended Bottle Size (mL)
T01	10.0	20	22.2	2.2	198	250
T02	5.0	40	44.4	4.4	196	250
T03	2.0	100	111.1	11.1	189	500
T04	1.0	200	222.2	22.2	178	500
T05	0.5	400	444.4	44.4	156	1000
B03	QC	–			200	250
Total		–	844.4		1120	

<u>NOTE</u>: 1) This schedule assumes a target liquid volume of 200 mL.
2) This schedule is based on “as tested” solids content of 0.90 g-dry/g.
3) Test position marked B01 is a method blank of reagent water.

Table data modified from Ref. 1.

TABLE 2

EXTRACTION PARAMETERS AS FUNCTION OF MAXIMUM PARTICLE SIZE

Particle Size (85% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Recommended Vessel size (mL)
0.3	50	20 ± 0.05	24 ± 2	250
2.0	10	40 ± 0.1	48 ± 2	500
5.0	4	80 ± 0.1	72 ± 2	1000

FIGURE 1

METHOD FLOWCHART

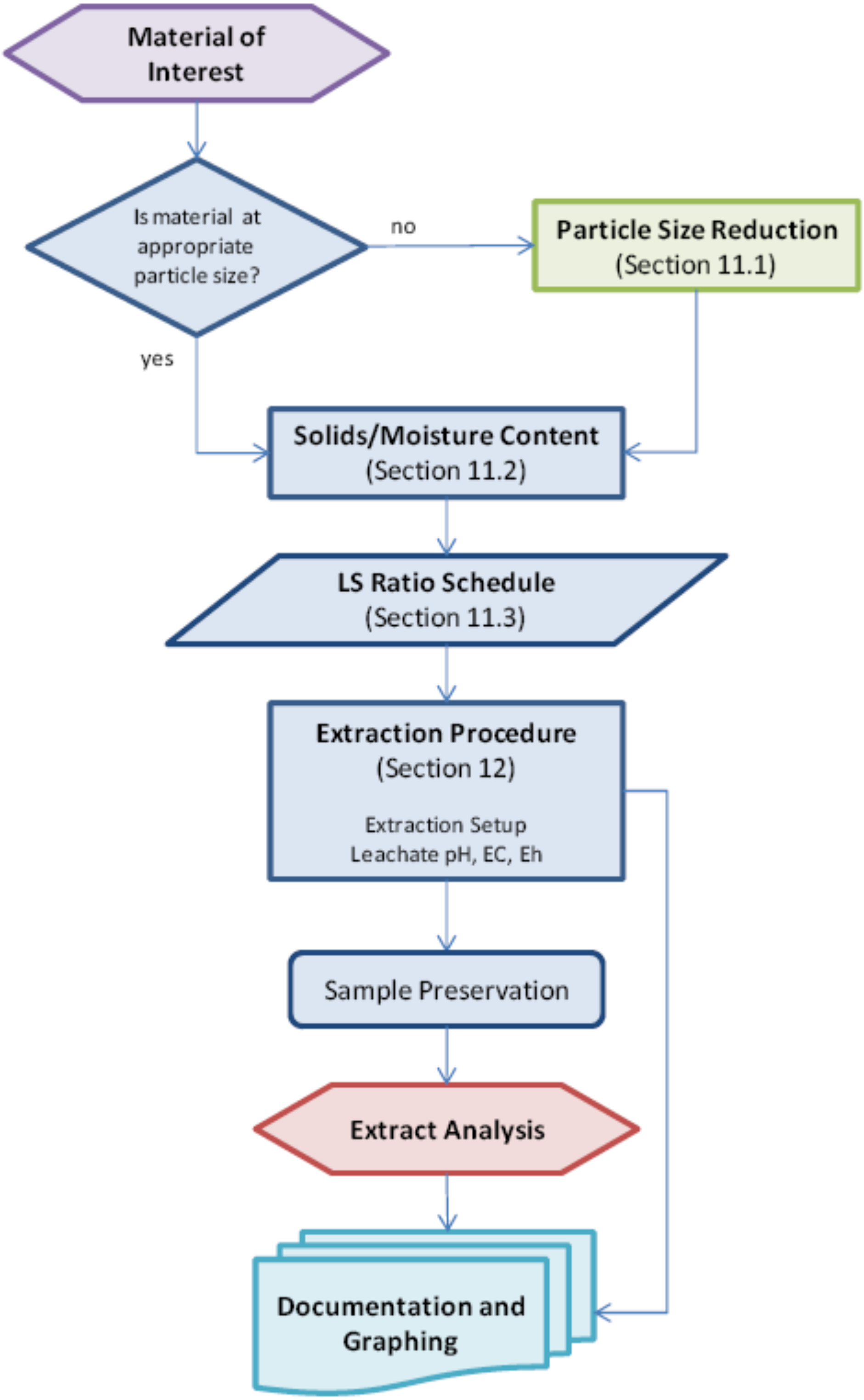


FIGURE 2

EXAMPLE DATA REPORTING SHEET

EPA METHOD 1316
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code: **FAX**
Material Type: Coal Combustion Fly Ash
Date Received: 10/1/20xx
Test Start Date: 11/1/20xx
Report Date: 12/1/20xx

Particle Size: 88% passing 2-mm sieve
Contact Time: 860 g
Lab Temperature: 21 ± 2 °C
Eluant Used: ASTM Type II Water

Test Position	Replicate	Value	Units	Method	Note
T01	**A**				
	Eluate Sample ID	**XYZ-1316-T01-A**			
	Solid Material	40.0	g		
	Moisture Content	0.01	g_{H_2O}/g		
	Water Added	386.0	mL		
	Target L/S	10.0	mL/g-dry		
	Eluate pH	1.89	–	EPA 9040	
	Eluate Conductivity	12.6	mS/cm	EPA 9050	
	Eluate ORP	203	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	216.0	mg/L		EPA 6020	11/7/20xx	1000
As	7.64	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/9/20xx	1

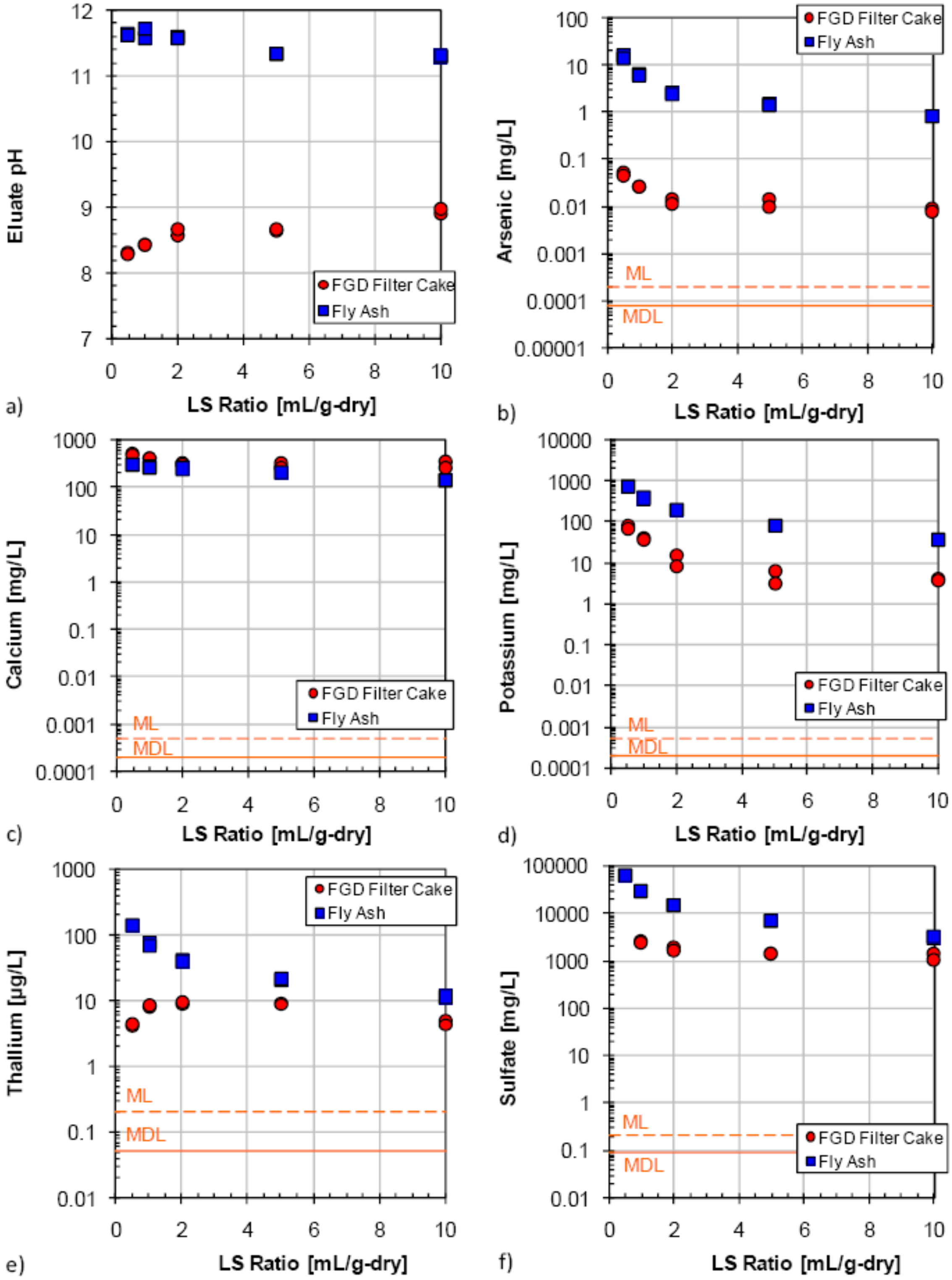
Test Position	Replicate	Value	Units	Method	Note
T02	**A**				
	Eluate Sample ID	**XYZ-1316-T02-A**			
	Solid Material	20.0	g		
	Moisture Content	0.01	g_{H_2O}/g		
	Water Added	400.0	mL		
	Target L/S	5.0	mL/g-		
	Eluate pH	3.86	–	EPA 9040	
	Eluate Conductivity	0.99	mS/cm	EPA 9050	
	Eluate ORP	180	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	449.0	mg/L		EPA 6020	11/7/20xx	1000
As	97.9	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (< "LLOQ")

FIGURE 3

EXAMPLE CONCENTRATON RESULTS FROM A COAL COMBUSTION FLY ASH AND FLUE-GAS DESULFURIZATION FILTER CAKE



APPENDIX E. DETAILS OF TIME, MATERIALS, AND COST ESTIMATES BY METHOD

Table E-1. Detailed Labor Time Estimates for Method 1313.

Task **Subtask**	**Units per Test**	**Subtask Time [min]**	**Task Time [h]**
Moisture Content ("as received")	2		0.5
Air Drying (1-2 days assumed)	1		0.5
Particle-size Analysis/Reduction	1		1.5
Sieving	1	30	
Grinding	1	60	
Moisture Content ("as tested")	2		0.5
Pre-Test Titration (2 x 5 extracts)	10		2.5
Labeling bottles	10	10	
Solids-filling, weighing & recording	10	20	
Liquid-filling, weighing & recording	10	20	
Acid/base addition	10	20	
pH measurement & recording	10	50	
Data template management	2	30	
Extraction Procedure (9 extracts + 3 QC)	12		6.2
Labeling bottles	12	12	
Solids-filling, weighing & recording	9	18	
Liquid-filling, weighing & recording	12	24	
Acid/base addition	11	22	
pH/EC/Eh measurement & recording	12	60	
Eluate filtration	12	60	
Sample preservation	24	24	
Data template management	3	60	
Clean Up (12 filter holders)	3	90	
		Total Labor Time	**11.7**

Notes:

1) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar and pestle.

2) Pre-test titration step assumes two rounds of five extractions are required to adequately define the titration curve (10 pre-test extractions in all).

Table E-2. Detailed Labor Time Estimates for Method 1314.

Task **Subtask**	**Units per Test**	**Subtask Time [min]**	**Task Time [h]**
Moisture Content ("as received")	2		0.5
Air Drying (1-2 days assumed)	1		0.5
Particle-size Analysis/Reduction	1		1.5
Sieving	1	30	
Grinding	1	60	
Moisture Content ("as tested")	2		0.5
Column Setup	1		1.8
Column packing, weighing & recording	1	30	
Eluant preparation	1	15	
Pump adjustment	1	60	
Column Test Procedure (9 eluates + 1 QC)	10		6.9
Checking system & flowrate (daily)	15	75	
Bottle exchange (9 eluates – 8 changes)	8	40	
pH/EC/Eh measurement & recording	9	30	
Eluate filtration	10	30	
Sample preservation	20	60	
Data template management (daily)	15	75	
Clean up (1 filter holders per exchange)	8	100	
Clean up (column)	1		1.0
		Total Labor Time	**12.7**

Notes:

1) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar and pestle.
2) Column operation assumes light to moderate daily systems maintenance (e.g., pump adjustment, flow rate measurement & recording).

Table E-3. Detailed Labor Time Estimates for Method 1315 (Granular Material).

Task **Subtask**	**Units per Test**	**Subtask Time [min]**	**Task Time [h]**
Moisture Content ("as received")	2		0.5
Air Drying (1-2 days assumed)	1		0.5
Particle-size Analysis/Reduction	1		1.5
Sieving	1	30	
Grinding	1	60	
Moisture Content ("as tested")	2		0.5
Optimum Moisture/Density (5 trials)	5		3.5
Moisture adjustment	5	50	
Sample packing	5	80	
Dimension measurement & recording	5	25	
Mass measurement & recording	5	25	
Data template management	1	30	
Compacted Granular Sample Preparation	1		1.0
Moisture Content ("as packed")	2		0.5
Test Procedure (9 fractions + 9 QC)	18		7.8
Eluant-filling, weighing & recording	9	18	
Sample exchange, weighing & recording	9	18	
pH/EC/Eh measurement & recording	18	54	
Eluate filtration	18	36	
Sample preservation	10	50	
Data template management	36	108	
Clean Up (2 vessels + 2 filter holders)	9	180	
		Total Labor Time	**15.8**

Notes:

1) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar and pestle.
2) Monolithic samples are assumed to be provided at an appropriate size such that no cutting or coring is necessary.
3) In most cases, testing of a monolithic sample would require only "as received" moisture content and the test procedure steps, totaling approximately 8.5 labor hours.

Table E-4. Detailed Labor Time Estimates for Method 1316.

Task **Subtask**	**Units per Test**	**Subtask Time [min]**	**Task Time [h]**
Moisture Content ("as received")	2		0.5
Air Drying (1-2 days assumed)	1		0.5
Particle-size Analysis/Reduction	1		1.5
Sieving	1	30	
Grinding	1	60	
Moisture Content ("as tested")	2		0.5
Extraction Procedure (5 extracts + 1 QC)	6		3.6
Labeling bottles	6	6	
Solids-filling, weighing & recording	5	12	
Liquid-filling, weighing & recording	6	12	
pH/EC/Eh measurement & recording	6	30	
Eluate filtration	6	30	
Sample preservation	12	36	
Data template management	1	30	
Clean Up (12 filter holders)	1	60	
		Total Labor Time	**6.6**

Notes:

1) Particle-size reduction assumes a relatively easy material to reduce (e.g., coal combustion residues, soils) via mechanical grinder or light hand grinding with mortar and pestle.

Table E-5. Minimum Solid Material Required for Method 1313.

Method 1313	**Number of Solid Samples**	**Sample Mass [g-dry]**	**Mass Required [g-dry]**
Moisture Content (MC)	2 analyses x 2 replicates	10	40
Pre-Test Titration	2 trials x 5 extracts	40	400
Batch Test Extracts	9 extracts	40	360
		Mass Required for Method 1313	**800**

Table E-6. Minimum Solid Material Required for Method 1314.

Method 1314	Number of Solid Samples	Sample Mass [g-dry]	Mass Required [g-dry]
MC	2 analyses x 2 replicates	10	40
Column Test	1 column		660
Mass Required for Method 1314			**700**

[a] Mass estimate assumes cylindrical column (5-cm dia. x 30 cm) and packing density of 1.2 g-dry/cm^3.

Table E-7. Minimum Solid Material Required for Method 1315.

Method 1313	Number of Solid Samples	Sample Mass [g-dry]	Mass Required [g-dry]
MC – monolith	3 analyses x 2 replicates	10	60
MC – granular	2 analysis x 2 replicates	10	20
Optimum Density[a]	5 samples	700	3500
Tank Test[b]	1 sample	1400	1400
Mass Required for Method 1315 (granular)[c]			**4960**
Mass Required for Method 1315 (monolithic)			**1420**

[a] Estimate assumes packing ½ volume of test sample per optimum density trial.
[b] Mass estimate assumes cylindrical sample (10-cm dia. x 10 cm) and packed density of 1.7 g-dry/cm^3.
[c] Optimum density assessment is conducted only for 1st test.

Table E-8. Minimum Solid Material Required for Method 1316.

Method 1313	Number of Solid Samples	Sample Mass [g-dry]	Mass Required [g-dry]
MC	2 analyses x 2 replicates	10	40
Batch Test Extracts	5 extracts @ different LS		950
	LS=10 mL/g-dry	25	
	LS=5 mL/g-dry	50	
	LS=2 mL/g-dry	125	
	LS=1 mL/g-dry	250	
	LS=0.5 mL/g-dry	500	
Mass Required for Method 1316			**990**

Table E-9. Estimate of Supply Costs for Batch Method 1313.(1)

Item Description	Fisher Scientific Catalog #	Required for 3 Test Reps	Unit Price(2)	Cost for 3 Test Reps
Moisture Content				
Aluminum weighing dish, 2.3 fl. oz., Fisherbrand	08-732-103	12	$0.57	$6.84
Granular Material Storage				
I-Chem HDPE wide-mouth bottle, 1000 mL	05-719-357	3	$5.23	$15.69
Pre-Test Titration				
I-Chem HDPE wide-mouth bottle, 250 mL	05-719-353	10	$2.95	$29.50
Nitric Acid, tracemetal grade, Fisher Chemical	A509-212	50 mL	$0.05	$2.50
Sodium Hydroxide solution, 2N, Fisher Chemical	SS264-1	50 mL	$0.06	$3.00
BD Falcon 15 mL conical centrifuge tube	14-959-49B	10	$0.42	$4.20
Extraction Setup				
I-Chem HDPE wide-mouth bottle, 250 mL	05-719-353	30	$2.95	$88.50
Nitric Acid, tracemetal grade, Fisher Chemical	A509-212	~150 mL	$0.05	$7.50
Sodium Hydroxide solution, 2N, Fisher Chemical	SS264-1	~150 mL	$0.06	$9.00
Eluate Processing				
BD Falcon 15 mL conical centrifuge tube	14-959-49B	30	$0.42	$12.60
GH Polypro filter, 0.45-µm pore, Andwin Scientific	NC9035907	30	$2.47	$74.10
I-Chem HDPE wide-mouth bottle, 125 mL	05-719-351	60(3)	$2.39	$143.40
Nitric acid, optima grade, Fisher Chemical	A467-500	30 mL	$0.75	$22.50
			Total Supplies Cost per Test	**$419.33**
Equipment and Durable Items				
12-port tumbler, LE-1002, Environmental Express	09-732-79	1	$6,880.00	$6,880.00
Polycarbonate filter holder, 250 mL, Nalgene	09-740-23A	12(4)	$104.52	$1,254.24
			Total Equipment Cost per Test	**$8,134.24**

Notes:

(1) Supply and equipment costs are shown as example costs associated with conducting the method and do not denote any endorsement by the authors or USEPA of a specific vendor, manufacturer or product.

(2) Prices based on Fisher Scientific online catalog (www.fishersci.com) as of 3/25/10 unless otherwise noted.

(3) Assumes two analytical samples per test position with one preserved using optima nitric acid.

(4) Filtration holders may be soap-water washed, rinsed with 10% nitric acid, and triple reagent water rinsed between uses. Thirty (30) filter holders are recommended if washing between replicates is not anticipated.

Table E-10. Estimate of Supply and Equipment Costs for Column Method 1314.(1)

Item Description	Fisher Scientific Catalog #	Required for 3 Test Reps	Unit Price(2)	Cost for 3 Test Reps
Moisture Content				
Aluminum weighing dish, 2.3 fl. oz., Fisherbrand	08-732-103	12	$0.57	$6.84
Granular Material Storage				
I-Chem HDPE wide-mouth bottle, 1000 mL	05-719-357	3	$5.23	$15.69
Column Setup				
PTFE column bed support, 4.8-cm, Kimble-Kontes	K420809-2040	6	$6.51	$39.06
Tygon R-3603 tubing, 1/16” ID, St. Gobain	14-169-1B	30 ft	$0.28	$8.40
Calcium chloride dihydrate, ACS, Fisher Chemical	C79-500	1.5 g/10L	$0.05	$0.50
Eluate Processing				
BD Falcon 15 mL conical centrifuge tube	14-959-49B	28	$0.42	$11.76
GH Polypro filter, 0.45-µm, Andwin Scientific	NC9035907	28	$2.47	$69.16
I-Chem HDPE wide-mouth bottle, 125 mL	05-719-351	56(3)	$2.39	$133.84
Nitric acid, optima grade, Fisher Chemical	A467-500	~30 mL	$0.75	$22.50
			Total Supplies Cost per Test	**$307.75**
Equipment and Durable Items				
Chromaflex column, 4.8-cm ID, Kimble-Kontes	K420830-3020	3	$318.95	$956.85
Nalgene filter holder, 250 mL, Thermo Scientific	09-740-23A	28(4)	$104.52	$2,926.56
Manostat “Carter” pump, 12/6, Thermo Scientific	13-875-249	1	$2,818.82	$2,818.82
Pump link, pharmed, 0.89 mm, Thermo Scientific	13-875-296	3	$7.52	$22.56
LDPE Carboy, 20 L, Nalgene	02-961-60E	1	$124.83	$124.83
Polycarbonate straight-side jar, 250 mL, Nalgene	11-815-10D	18	$3.77	$67.86
Polypropylene mason jar, 2000 mL, Nalgene	11-825C	3	$16.79	$50.37
Polypropylene mason jar, 3000 mL, Nalgene	11-825D	3	$21.58	$64.74
			Total Equipment Cost per Test	**$7,032.59**

Notes:

(1) Supply and equipment costs are shown as example costs associated with conducting the method and do not denote any endorsement by the authors or USEPA of a specific vendor.

(2) Estimates based on Fisher Scientific online catalog (www.fishersci.com) as of 3/25/10 unless otherwise noted.

(3) Assumes two analytical samples per test position with one preserved using optima nitric acid.

(4) Filtration holders may be soap-water washed, rinsed with 10% nitric acid, and triple reagent water rinsed between uses such that less than 28 holders are required.

Table E-11. Estimate of Supply and Equipment Costs for Mass Transport Method 1315.(1)

Item Description	Fisher Scientific Catalog #	Required for 3 Test Reps	Catalog Price(2)	Cost for 3 Test Reps
Moisture Content				
Aluminum weighing dish, 2.3 fl. oz., Fisherbrand	08-732-103	12	$0.57	$6.84
Granular Material Storage (Granular Only)				
I-Chem HDPE wide-mouth bottle, 1000 mL	05-719-357	3	$5.23	$15.69
Optimum Density Analysis (Granular Only)				
Concrete cylinder molds, 4” ID x 8” (cut to 3”)	NA(a)	5	$0.98	$4.90
Sample Preparation (Granular Only)				
Concrete cylinder molds, 4” ID x 8” (cut to 3”)	NA(a)	3	$0.98	$2.94
Eluate Processing				
BD Falcon 15 mL conical centrifuge tube	14-959-49B	36	$0.42	$15.12
GH Polypro filter disc, 0.45-µm, Andwin Scientific	NC9035907	36	$2.47	$88.92
I-Chem HDPE wide-mouth bottle, 125 mL	05-719-351	72	$2.39	$172.08
Nitric acid, Optima grade, Fisher Chemical	A467-500	36 mL	$0.75	$27.00
Total Supplies Cost per Test (Granular Material)				**$333.49**
Total Supplies Cost per Test (Monolithic Material)				**$309.96**
Equipment and Durable Items				
Compaction rammer (granular)	NA(b)	1	$100.00	$100.00
Polycarbonate straight-side jar, 1000 mL (granular)	11-815-10F	8	$8.07	$64.56
LDPE 170 oz container (monolithic), Nalge Nunc	12-566-113	8	$4.00	$32.00
Polycarbonate filter holder, 250 mL, Nalgene	09-740-23A	36(3)	$104.52	$3,762.72
Total Equipment Cost per Test (Granular Material)				**$2,013.64**
Total Equipment Cost per Test (Monolithic Material)				**$1,897.36**

Notes:

(1) Supply and equipment costs are shown as example costs associated with conducting the method and do not denote any endorsement by the authors or USEPA of a specific vendor.

(2) Estimates based on Fisher Scientific online catalog (www.fishersci.com) as of 3/25/10 unless otherwise noted.

[a] available as item #004-873 through MA Industries, Peachtree City, GA at www.maind.com.

[b] available as item #EL24-0963 through ELE International at www.ele.com/usa (cost approximated).

(3) Filtration holders may be soap-water washed, rinsed with 10% nitric acid, and triple reagent water rinsed between uses such that less than 36 holders are required.

Table E-12. Estimate of Supply Costs for Batch Method 1316.(1)

Item Description	**Fisher Catalog #**	**Required for 3 Test Reps**	**Catalog Price(2)**	**Cost for 3 Test Reps**
Moisture Content				
Fisherbrand aluminum weighing dish, 2.3 fl. oz.	08-732-103	12	$0.57	$6.84
Granular Material Storage				
I-Chem HDPE wide-mouth bottle, 1000 mL	05-719-357	3	$5.23	$15.69
Extraction Setup				
I-Chem HDPE wide-mouth bottle, 500 mL	05-719-349	16	$4.24	$67.84
Eluate Processing				
BD Falcon 15 mL conical centrifuge tube	14-959-49B	16	$0.42	$6.72
Andwin Scientific GH Polypro filter, 0.45-µm	NC9035907	16	$2.47	$39.52
I-Chem HDPE wide-mouth bottle, 125 mL	05-719-351	32	$2.39	$76.48
Fisher Chemical Nitric acid (optima grade)	A467-500	~16 mL	$0.75	$12.00
Total Supply Cost per Test				**$225.09**
Durable Supplies				
Environmental Express LE-1002 tumbler, 12 port	09-732-79	1	6,880.00	$6,880.00
Nalgene polycarb filter holder, 250 mL	09-740-23A	16(3)	$104.52	$1,672.32
Total Durables Cost per Test				**$8,552.32**

Notes:

(1) Supply and equipment costs are shown as example costs associated with conducting the method and do not denote any endorsement by the authors or USEPA of a specific vendor.

2) Estimates based on Fisher Scientific online catalog (www.fishersci.com) as of 2/01/10 unless otherwise noted.

3) Filtration holders may be soap-water washed, rinsed with 10% nitric acid, and triple reagent water rinsed between uses such that less that 30 holders are required.