CHAPTER THREE
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CHAPTER THREE

INORGANIC ANALYTES

        Prior to employing the methods in this chapter, analysts are advised to consult the
disclaimer statement at the front of this manual and the information in Chapter Two for guidance
on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless
specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal
testing requirements. The information contained in each procedure is provided by EPA as
guidance to be used by the analyst and the regulated community in making judgments
necessary to meet the data quality objectives or needs for the intended use of the data.

        For a summary of changes in Chapter Three, please see Appendix A at the end of this
document.

3.0   INTRODUCTION

        This chapter provides guidance for the analysis of inorganic analytes in a variety of
matrices. The analytical methods are written as specific steps in the overall analysis scheme --
sample handling and preservation, sample digestion or preparation, and sample analysis for
specific inorganic components. From these methods, the analyst should assemble a total
analytical protocol which is appropriate for the sample to be analyzed and for the information
required. This introduction discusses the options available in general terms, provides
background information on the analytical techniques, and highlights some of the considerations
to be made when selecting a total analysis protocol.

3.1   DEFINITIONS

                The following terms are relevant for the determination of inorganic analytes:

                Calibration blank: The calibration blank is a sample of analyte-free media
                prepared with the same amounts of acids or other reagents as were the standards
                and samples that can be used along with prepared standards to calibrate the
                instrument. A calibration blank may also be used to verify absence of instrument
                contamination (e.g., initial calibration blank and continuing calibration blank).

                Calibration curve: The functional relationship between instrument response and
                target analyte concentration determined for a series of calibration standards. The
                calibration curve is obtained by plotting the instrument response versus
                concentration and performing a regression analysis of the data.

                Calibration standards: A series of solutions containing the target analyte at known
                and various concentrations used to calibrate the instrument response with respect
                to analyte concentration (i.e., preparation of the calibration curve).

                Continuing calibration verification (CCV): A solution containing a known
                concentration of analyte typically derived from the same source as the calibration
                standards. The CCV is used to assure calibration accuracy during each analysis
                run. It should be run for each analyte as described in the particular analytical
                method. At a minimum, it should be analyzed at the beginning of the run and after

the last analytical sample. The CCV concentration should be at or near the mid-range levels of the calibration curve.

Dissolved metals: The concentration of metals determined in an aqueous sample after the sample is filtered through a 0.45-µm filter (see Method 3005).

Initial calibration verification (ICV) standard: A certified or independently-prepared solution from a source other than used for the calibration standards and used to verify the accuracy of the initial calibration.

Instrument detection limit (IDL): Typically used in metals analysis to evaluate the instrument noise level and response changes over time for analytes of interest. IDLs in µg/L can be estimated as the mean of the blank results plus three times the standard deviation of 10 replicate analyses of the reagent blank solution. (Use zero for the mean if the mean is negative). Each measurement should be performed as though it were a separate calibration standard (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least once using new equipment, after major instrument maintenance such as changing the detector, and/or at a frequency designated by the project. An instrument log book should be kept with the dates and information pertaining to each IDL performed.

Laboratory control sample (LCS): A volume of reagent water spiked with known concentrations of analytes and carried through the sample preparation and determinative procedure. It is used to monitor laboratory performance on analyte loss/recovery in a clean matrix. The LCS should be prepared from the same source as the calibration standards to remove potential error contribution from standards of different sources. An independently prepared LCS may also be obtained as or prepared from a certified reference solution or prepared from a certified reagent solid or from an alternate lot reagent solid relative to the calibration standards source if, for each analytical batch, at least one LCS is prepared from the same source as the calibration standards. In this way, if the recoveries of both the LCS and the matrix spike are outside the acceptance limits, the analyst will be able to determine whether the problem is due to calibration error or matrix interference.

Linear range: In both inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) analysis, the concentration range over which instrument response is linear. The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover within 10% of the true value, and if successful, establishes the linear range. The linear range standards must be analyzed in the same instrument run as the calibration they are associated with (i.e., on a daily basis) but may be analyzed anywhere within that run. If a linear range standard is not analyzed for any specific element, the highest standard in the calibration becomes the linear range.

NOTE: Other standards exist that have alternative methods for determining the linear range (e.g., ISO 17025). Therefore, the method used to define and verify the linear range should meet the requirements of the project.

Lower limit of quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve, which is ideally less than or equal to the desired regulatory action levels based on the stated project requirements. Laboratory-specific recovery limits should be established when the laboratory has determined sufficient data points exist. <u>Individual methods specify recovery limits for use until the laboratory has sufficient data to determine acceptance limits statistically.</u>

Method blank: A volume of reagent water equal to that used for aqueous samples, or, otherwise, a clean, empty container, equivalent to that used for actual solid samples, processed through each sample preparation and determinative procedure. Analysis of a method blank is used to assess contamination from the laboratory environment, sample processing equipment, and/or reagents.

Method of standard addition (MSA): An alternative calibration procedure employed when the instrument response of the analyte of interest is different in a particular matrix than when it is in reagent water. The procedure is generally reserved for analyzing complex matrices. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical responses versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept. See Method 7000, for more information.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed. Different times may be specified for holding field samples prior to extraction, digestion, or other such preparation procedures versus holding prepared samples (e.g., an extract or a digestate) prior to analysis.

Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration (Reference 1). For metals analysis, the following methods are commonly employed to determine sensitivity.

> (a) Atomic absorption (AA): The concentration of metal, in mg/L, that produces a transmission of 1%.

> (b) Graphite furnace AA (GFAA): The mass of analyte required to give a response of 0.044 absorbance-seconds.

> (c) Inductively coupled plasma (ICP-OES or ICP-MS): Sensitivity is measured in terms of the instrument detection limits as defined elsewhere in the definitions.

Spectral Interference Check solution (SIC): A solution containing both interfering and analyte elements of known concentration that can be used in ICP-OES and ICP-MS analysis to verify background and inter-element correction factors.

Suspended metals: The concentration of metals determined in the portion of an aqueous sample that is retained by a 0.45-µm filter (Method 3005).

Total acid soluble/recoverable metals: The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid by Methods 3005, 3010, 3015, 3020, 3050, or 3051.

NOTE: Methods 3010 and 3020 state they are used to determine "total metals". However, because these methods do not use hydrofluoric acid, they are unable to break down silicates and have been defined here for the "total acid soluble/recoverable metals" fraction.

Total metals: The concentration of metals determined in a sample following digestion by Method 3052.

3.2   SAFETY

The methods in this chapter do not address all safety issues associated with their 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 specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The following additional references to laboratory safety are available:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "Handbook of Chemical Health and Safety," American Chemical Society, Oxford University Press, New York, 2001.

3. "NIOSH Pocket Guide to Chemical Hazards," Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, Publication No. 2005-149, September 2005.

4. "Occupational Safety and Health Standards," 29 CFR Part 1910, Occupational Safety and Health Administration, Department of Labor.

5. "Safety in Academic Chemistry Laboratories," 7th Edition, Volumes 1 and 2, American Chemical Society, Committee on Chemical Safety, Washington, D.C., 2003.

3.3   SAMPLING CONSIDERATIONS

3.3.1   Sample Collection

The fundamental goal of all field sampling activities is to collect samples that are representative of the water, soil or waste from which they were collected. Thus, representative sampling may be considered to be the sampling analog to analytical accuracy. Of equal importance is sampling precision for ensuring consistency both within a single sampling event and between sampling events conducted over time. Sampling

imprecision can be a significant source of measurement error. High quality field practices are, therefore, necessary for generating representative samples on a consistent basis. Sampling quality assurance includes the development of a quality assurance plan, data quality objectives and the generation of field quality control samples including equipment rinsates, trip blanks and field duplicates. Regardless of the specific program needs, the documentation of all relevant field and sample information is the final essential component of a sampling event for providing evidence that proper procedures and quality assurance were performed during sample collection. Use of inadequate field procedures and documentation can jeopardize an entire sampling program despite adequate planning, analytical facilities, and personnel.

While advances in analytical sensitivity are continuing to be made that allow for quantification of environmental contaminants at ultra-trace levels (i.e., < 0.1 ppb), clean sampling techniques are consequently being devised and practiced in order to minimize or eliminate sources of contamination during the collection of samples intended for ultra-trace contaminant testing. Such clean sampling and analysis techniques are not generally needed or required under the RCRA program and are beyond the scope of this chapter. However, as an introduction to this topic, Sec. 3.4 provides a more detailed discussion on the special category and requirements of clean analysis for determining constituents at ultra-trace levels.

3.3.2   Sample Containers

Sample container materials can introduce either positive or negative errors in measurement, particularly at low or ultra-trace levels, by contributing contaminants through leaching or surface desorption, or by depleting concentrations through adsorption. Additionally, the sample containers should be compatible with the reagents used for sample preservation. Thus, the collection and containment of the sample prior to analysis requires particular attention. Sample contamination introduced through field collection activities including sample containment and shipment can be assessed from the analysis of equipment rinsates. Guidelines on the selection of appropriate sample container materials for the collection of inorganic analytical samples are provided in Table 3-1.

3.3.3   Cleaning of Sample Containers

Sample containers should be scrupulously clean so as not to introduce contaminants that could interfere with quantification of the target analyte(s). This is of particular importance when determining trace or ultra-trace analyte concentration levels. The following cleaning sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or PTFE:

- Phosphate-free detergent
- Tap water
- 1:1 HNO_3
- Tap water
- 1:1 HCl
- Tap water
- Reagent water

NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products may be used in place of chromic acid, if adequate cleaning is documented by an analytical quality control program. Chromic acid should not be used with plastic bottles.

3.3.4 Sample Handling and Preservation

Recommended materials to use for sample collection are listed in Table 3-1. Sample holding times, recommended collection volumes or masses and recommended digestion volumes, and preservatives are listed in Table 3-2. The sample collection and digestion amounts depend on the combination of digestion or extraction and determinative procedures that will be employed for a given sample as well as the sensitivity and tolerable sampling errors that are required for a specific project (see References 20 through 22). Likewise, the use of alternative preservatives to those indicated in Table 3-2 may be necessary depending on the objectives of the project. In all cases, the sample quantity that is collected should be representative of the bulk material whenever feasible.

3.3.5 Sample Preparation

For all non-speciated digestion methods, great reduction in analytical variability can be achieved through the use of appropriate sample preparation procedures. Generally, a reduction in subsampling variance can be accomplished by increasing the subsample aliquot size, reducing the sample particle size, and/or thoroughly mixing the resulting fines (see References 20 through 23 for additional information on sampling and sub-sampling). Under most circumstances, it is recommended that the sample be analyzed without drying. If it is necessary to report the analytical data on a dry-weight basis, then a separate aliquot may be analyzed for moisture content and the wet-weight data corrected accordingly.

If the sample cannot be well-mixed and homogenized in the form in which it was received by the laboratory, then air- or oven-drying at 30 °C or less, crushing, sieving, grinding, and mixing should be performed as needed or feasible to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, it should be noted that in certain unusual circumstances there could be loss of volatile metals (e.g., mercury, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state) caused by inappropriate sample preparation procedures.

Variability due to sample heterogeneity is assessed by analyzing individually prepared sample replicates such as field duplicates (FD), laboratory matrix duplicates (MD), and matrix spike (MS)/matrix spike duplicate (MSD). Variability inherent in the analytical determinative procedure can be assessed by matrix spiking of individually digested samples (i.e., post-digestion matrix spike) or by analyzing laboratory splits of the digestate.

3.4 SPECIAL CONSIDERATIONS FOR DETERMINING INORGANIC ANALYTES AT ULTRA-TRACE CONCENTRATION LEVELS

3.4.1 Clean Sampling Techniques

For the determination of ultra-trace analyte concentrations in environmental samples, it is essential that samples be collected and subsequently managed using techniques specifically designed to minimize sample contamination from field collection activities and to ensure target analyte stability. Such techniques represent a special category of sampling procedures designed specifically for ultra-trace analyses and are commonly referred to as clean or ultra-clean sampling procedures. Clean sampling methods are generally not intended for the determination of discharges from industrial

facilities. Rather, they are primarily applicable for the determination of ambient element concentrations at levels of 0.1 ppb or less. At these concentrations, the opportunity for sample contamination during sample collection or analysis in the laboratory is significant and should be managed accordingly. Figure 3-1 provides a demonstration of the impact of clean sampling and analysis techniques on data obtained for estuarine waters. Clean sampling typically involves the following key steps:

- Special container pre-cleaning and pre-packaging requirements
- Specific sampling equipment and container materials selection
- Specific cleaning protocols for sampling equipment
- Equipment and container blank determinations prior to field use
- "Clean hands/dirty hands" sample collection techniques based on a 2-person sampling crew
    - Dirty hands sampler manages sampling equipment only
    - Clean hands sampler manages the sample container
- Special sample packaging prior to shipment
- Use of a laboratory trained and properly equipped to perform clean analysis of the analytes of interest

Given the laboratory resources required to perform clean analysis techniques, it is paramount that samples be collected using ultra-clean techniques and conditions in the field. Otherwise, subsequent analytical efforts become futile. The information provided in this section is intended only as an introduction to the topic of clean sampling. Specific guidelines for clean sampling may be found in Reference 2 and other sources.

3.4.2   Clean Analysis and the Analytical Blank

The significant role of the analytical blank in chemical analysis of trace metals cannot be overemphasized. Sensitive instrumentation such as ICP-MS, ICP-OES, and GFAA requires that sample preparation be at least as sophisticated as the instruments used for analysis. The analytical blank is normally a primary source of error in ultra-trace element analysis. Ultra-trace analysis is as dependent on control of the analytical blank as it is on the bias and precision of the instrument making the measurement. Inability to control contamination is frequently the limiting factor in trace (parts per million (ppm) to parts per billion (ppb)) and ultra-trace (ppb to parts per trillion (ppt)) analysis. Analytical blank contributions occur from the following four major sources (References 3 through 7):

- The atmosphere in which the sample preparation and analysis are conducted
- The purity and the quantities of the reagents used in sample preparation, including all reagents added directly to the sample
- The materials and equipment used in digestion or extraction vessels that come in contact with the sample during the sample preparation and analysis (i.e., the cleanliness and maintenance as well as their material properties).
- The analyst's technique and skill in preparing the samples and performing the analyses

The four primary areas that affect the analytical blank can be demonstrated using standard reference materials in analysis. Table 3-3 illustrates and isolates the main influencing parameters on the blank: environment, reagents, materials, and analyst skills. The skill of the analyst was kept constant as the same analyst changed the environment, reagents, and combinations of these parameters in the analysis (see Reference 6). The trace elements in glass (TEG) standard reference material from the National Institute of Standards and Technology (NIST) was used to keep sample homogeneity constant and to permit removal of the sampling error by using sample sizes in which appropriate

homogeneity had previously been demonstrated. It is important to note that the relationship of the precision and measurement remained relatively constant. The significance of the first two major sources of contamination, environment and reagents, is evaluated. The contamination in the laboratory air and in the acid used for the reagent blank altered the accuracy of the example above by over two orders of magnitude for both lead and silver. The larger influence of the two sources in this example is the laboratory environment in which the samples were prepared.

3.4.2.1 Sample Preparation and Analysis Atmosphere

The atmosphere in which the sample is prepared is a major source of contamination for most target analytes when analyzing at ultra-trace levels. With the exception of some rare constituents, contamination from airborne sources represents the most significant of the four main contamination sources. For example, the mercury in a dental amalgam filling may cause blank contamination. To illustrate this point, Table 3-4 presents concentrations of lead found in samples of ambient air.

This contamination can also be seen in the comparison of 58,000 particles per liter of air measured in a normal laboratory in Pittsburgh, PA, and inside a clean chamber in an adjacent laboratory five meters away. Figure 3-2 demonstrates the dramatic difference between the two environments. Cost-effective methods of creating clean chambers for sample preparation are documented along with this data in Reference 4.

Any laboratory air that comes into contact with the sample may deposit airborne contamination into the sample. The sample is especially vulnerable when it is being digested with acid. When samples are being digested with acid(s), contamination of the sample by particulates in the laboratory air can cause results that are biased high.

To prevent air from contaminating a sample for ultra-trace analysis, the sample should be processed in a clean environment. This is much easier to accomplish than it may appear at first. These precautions are becoming state-of-the-art in many analytical and environmental laboratories. The prevention of airborne contamination is most frequently dealt with by employing a laminar flow clean bench or a clean laboratory facility. Instructions are referenced for the construction of both from component parts; both are relatively inexpensive and uncomplicated, once the concepts are understood (Reference 4).

There are many sources of airborne contamination. Several of the sources have been described and their particle size ranges are provided in Figure 3-3. These sources primarily provide particulates in discrete size ranges. Depending on whether the laboratory is located in an industrial, urban, or rural area, or near the sea, the distribution of these source particles will be different, as will their composition. The vertical dashed line in Figure 3 indicates the particle size cutoff, usually 0.5 µm, for the high efficiency particulate air (HEPA) filter used to prevent particulate contamination. Particles above this size cannot pass through a HEPA filter that is in good working order. These filters are in common use today (References 4 and 8).

The definition of clean air is derived from International Standard ISO 14644-1, which defines cleanliness levels. Table 3-5 lists these conditions.

"Laminar flow" is directed coherent air movement that does not contain any turbulence.

A dramatic reduction in airborne contaminants can be achieved by using HEPA-filtered air in laminar-flow clean hoods or entire clean laboratories. Table 3-6 demonstrates the dramatic differences in airborne contaminant concentrations in an ordinary laboratory, a clean laboratory, and a clean hood inside a clean laboratory.

3.4.2.2 Reagent Purity for Ultra-trace Analysis

The purity of the reagents used for acid digestion, leaching, and extraction is extremely important to the overall level of the blank. Reagents have very different purities, depending on their processing grade and purpose. Frequently, the analyst should purchase special reagents, or purify lesser-grade reagents prior to use, in order to minimize the analytical blank.

In addition to the purity of the reagents, the quantity of reagent that is added to the sample may have a significant impact. When reagents are added, they bring with them elemental and molecular components that exist as contaminants. Increasing the reagent used in excess of the stoichiometric reaction, leads to greater potential for blank contamination. Reagents of high purity should either be purchased or produced in the laboratory.

In the preparation of high purity reagents, there is only one significant and practical choice for the method of purification, i.e., sub-boiling distillation (References 9 through 11). Different from normal distillation, sub-boiling distillation uses an infrared radiation source to heat the reagent to a temperature just below the boiling point. This use prevents the formation of bubbles that rise and burst at the surface of the liquid. Thus, the aerosolized solution particles are left in solution and prevented from physically transporting contaminants throughout the distillation apparatus. Sub-boiling distillation is a slower but very reliable method of purifying all of the common mineral acids and many organic reagents used in analytical methods. It relies exclusively on the vapor pressure of the reagent, and contaminant, and can therefore be specifically optimized for purification of the mineral acids if the object is to remove metal ions. Of all acids, nitric acid, for a variety of reasons, can be purified to excellent quality. Sources for sub-boiling apparatus equipment and methods for constructing one are provided in the references. Purchasing sub-boiling acids from commercial sources is also an option. Construction or purchase of sub-boiling reagent purification equipment may be cost effective for some laboratories depending on the quantity of reagents required for sample throughput.

3.4.2.3 Materials for Sample Preparation, Storage, and Analysis

For ultra-trace analyses, only certain materials are preferred for use in the construction of sample vessels and instrument components that come into contact with the sample. Over the past two decades, materials identified as being non-contaminating have become the top choices for bottles, beakers, reaction vessels, storage containers, nebulizers, and instrument components for trace and ultra-trace analysis. The materials are the same as those currently being used in many digestion vessels, bomb liners, and microwave vessels. The materials are characterized by being thermally durable, chemically resistant or inert, non-contaminating, and possessing appropriate compression and tensile

strength. Table 3-7 lists, in order of preference, several types of, non-contaminating materials that are chemically inert to most acid reactions. These materials have been evaluated and tested extensively for their potential to contaminate (References 4, 6, 7, 12, and 13).

With the exception of polyethylene, the materials listed in Table 3-7 are those most commonly used for sample preparation vessels, both atmospheric pressure vessels and closed vessel liners that come into contact with the sample. These materials are the most stable to acid reactions (with the exception of quartz and glass if hydrofluoric acid is used). Fluoropolymers are the most common and were adapted from other chemical uses for application in pressure systems. The fluoropolymers have the highest range of use temperatures for most plastics, ranging from 270-300 °C. They are also chemically inert to the majority of mineral acids and combinations thereof. Sulfuric acid has a boiling point of approximately 330 °C and can damage all fluoropolymers by melting them. Quartz and glass can safely contain sulfuric acid at these high temperatures, but borosilicate glass is not appropriate for ultra-trace elemental analysis (References 7 and 13). Glass actually forms a gel layer that hydrates and leaches, transferring contaminants from the glass to the sample solution. While these quantities may be considered minute, they would be detected in blanks and samples undergoing ultra-trace analyses.

Polyethylene is suitable for storage of diluted samples after digestion, but it does not have a thermal-use temperature appropriate for digestion. It is also not sufficiently inert to be useful as a digestion vessel or vessel liner, similar to polycarbonate and polypropylene. The low cost of polyethylene and its relative inertness to cool, weakly acidic solutions make it an excellent storage container for trace element solutions (Reference 4).

3.4.2.4 Analytical Technique and Synergistic Equipment

The fourth significant source of analytical blank contamination is the skill of the analyst and the appropriateness of the technique being performed. Analytical blank control has been explained as the combination of atmosphere, reagent, material, and protocol being performed. Also, the skill and awareness of the analyst as well as the way in which the combinations of the aforementioned clean chemistry techniques are applied will have a significant effect on the final contamination error and analytical blank control. Sample preparation instrumentation may also assist in these protocols. For example, microwave sample preparation assists each of these parameters in synergistic ways, thus lowering the analytical blank, improving blank precision, and enhancing overall quality control and transferability of methods. Some instrumentation and fundamental processes involved in specific sample preparation procedures assists the analyst by incorporating useful clean chemistry concepts into instrumentation and method structure. Such instrumentation is pertinent since microwave methods now exist that provide sample preparation for leaching or total analysis of many target analytes simultaneously. As an example, the skill of the analyst with regard to clean chemistry is assisted by the method structure and microwave equipment as indicated below:

- If a closed or controlled atmospheric microwave vessel is prepared in a clean hood and sealed before leaving the clean environment, the sample will not be affected by atmospheric contamination during the reaction, since it has not been removed from a clean environment.

- The vessel materials described previously might not normally be used by many laboratories, and therefore the advantages of the fluoropolymers would not be realized if they were not required in most microwave reaction vessels as they commonly are.

- The time that the sample spends in digestion, leaching, or extraction may be reduced from hours to minutes, thus reducing the potential leaching of contaminants from the container walls.

- Because most microwave systems are sealed systems, evaporation of the reagent before it reacts productively is prevented and smaller quantities of reagents are used, thus preventing excess and unnecessary accumulation of contaminants in the blank.

By reducing the exposure variables, the blank variability is consequently reduced in size and is more consistent. An example of these components working together has been provided in the literature, where analysis under different conditions has verified these conclusions (References 4, 14 and 15). The example illustrates the isolation of the blank optimization areas: environment, reagents, materials, and analyst skills. The skill of the analyst is kept more constant as the instrument dictates cleaner, chemically-appropriate procedures.

3.5   REAGENT PURITY

The purity of the reagents used for sample preservation, acid digestion, leaching, extraction and analysis is extremely important for preventing or minimizing sample contamination. Reagents have very different purities, depending on their processing grade and purpose. Reagent grade, ACS grade or better are recommended for use with most SW-846 methods. Sample contamination introduced through sample preservation, handling, preparation and analysis is assessed from the analysis of method blanks.

3.6   SAMPLE DIGESTION METHODS

Many of the methods listed below employ HCl in the digestion process. Chlorine is an interferant in ICP-MS analysis and its use in sample digestion is discouraged except when absolutely necessary or when the instrument manufacturer has indicated that the use of HCl will not adversely affect the equipment and accurate quantitation of the desired target analytes. However, please note that recoveries of certain metals may be biased low when using nitric acid only. Interference from chlorine may be minimized by use of collision or reaction cell instrumentation.

The methods in SW-846 for sample digestion or dissolution include:

Method 3005A: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy

This method may be used for the preparation of ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-OES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy

This method may be used for the preparation of waste samples for total recoverable metal determinations by FLAA, ICP-OES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

This method may be used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-OES, or ICP-MS. Nitric acid and hydrochloric acid are added to the sample in a PTFE digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy

This method may be used for the preparation of waste samples for total recoverable metals determinations by GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3031: Acid Digestion of Oils for Metals Analysis by Atomic Absorption or ICP Spectrometry

This method may be used for the preparation of waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-OES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040A: Dissolution Procedure for Oils, Greases, or Waxes

This method may be used for the preparation of oily waste samples for determination of soluble metals by FLAA and ICP-OES. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050B: Acid Digestion of Sediments, Sludges, and Soils

This method may be used for the preparation of waste samples for total recoverable metals determinations by FLAA and ICP-OES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

This method may be used for the preparation of sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-OES or ICP-MS. Nitric acid and hydrochloric acid are added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices

This method may be used for the preparation of siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total metals analysis by FLAA, CVAA, GFAA, ICP-OES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis.

Method 3060A: Alkaline Digestion for Hexavalent Chromium

This method may be used for the preparation of soils, sludges, sediments and similar waste materials for hexavalent chromium determination. The samples are digested and heated to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

Method 3200: Mercury Species Fractionation and Quantification by Microwave Assisted Extraction, Selective Solvent Extraction and/or Solid Phase Extraction

This method uses sequential extraction and separation procedures to differentiate mercury species that are present in soils and sediments into four distinct fractions: extractable organic mercury, extractable inorganic mercury, semi-mobile mercury and non-mobile mercury. Extraction is accomplished with the aid of either microwave irradiation or ultrasound. Quantification of mercury in the different fractions may be performed using any appropriate determinative method, (e.g., Method 7473, 1631, or Methods 7470 and 7471). The test method also contains provisions for separating and quantifying individual extractable mercury species using HPLC.

3.7   METHODS FOR DETERMINATION OF INORGANIC ANALYTES

This section of the manual contains analytical techniques for trace inorganic analyte determinations. Instrumental techniques include:

- Inductively coupled argon plasma optical emission spectrometry (ICP-OES),
- Inductively coupled plasma mass spectrometry (ICP-MS),
- Direct-aspiration or flame atomic absorption spectrophotometry (FLAA),
- Graphite furnace atomic absorption spectrophotometry (GFAA),
- Hydride-generation atomic absorption spectrometry (HGAA),
- Cold-vapor atomic absorption spectrometry (CVAA),
- Cold-vapor atomic fluorescence spectrometry (CVAF),
- Anodic stripping voltammetry (ASV),
- X-ray fluorescence (XRF),
- Ion chromatography (IC)
- Capillary electrophoresis (CE)
- Speciated isotope dilution mass spectrometry (SIDMS) and
- Several procedures for hexavalent chromium analysis.

Each of these (except the individual hexavalent chromium analyses) is discussed briefly below. Some advantages, disadvantages, and cautions for the analysis of wastes are provided.

ICP-OES allows simultaneous or rapid sequential determination of many elements in a short time. Aerosol samples are introduced into an extremely hot plasma source which vaporizes, atomizes, and ionizes the sample components. Upon exiting the plasma, the

electronically excited analytes emit characteristic photons that are detected via emission spectrometry. A primary disadvantage of ICP-OES is the occurrence of background radiation from other elements and the plasma gases. Although all ICP-OES instruments utilize high-resolution optics and background correction to minimize these interferences, analysis of trace levels of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be trace levels of inorganic analytes in an alloy or trace metals in a limed (high calcium) waste. ICP-OES and FLAA have comparable detection limits (within a factor of 4) except that ICP-OES exhibits greater sensitivity for refractories (Al, Ba, etc.). Further, the wide dynamic ranges and multi-element capabilities make ICP-OES instruments more productive. GFAA, in general, will exhibit lower detection limits than either ICP-OES or FLAA.

ICP-MS allows sensitive, simultaneous determination of many elements in a short time frame using MS detection in place of OES. In general ICP-MS exhibits greater sensitivity than GFAA, FLAA or ICP-OES for most elements. The main disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements or molecular species forming ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences, but the most effective means of removal of molecular isobaric interferences is the collision or reaction cell.

FLAA direct-aspiration determinations, as opposed to ICP-OES or ICP-MS, are normally completed as single-element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state, making analyte atoms available for absorption of light and spectrophotometric detection. In the analysis of some elements, the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

GFAA replaces the flame with an electrically-heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of dissolution, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms, which should occur in a flame or plasma in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

HGAA utilizes a chemical reduction to reduce and separate arsenic, selenium, or antimony selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: (1) easily reduced metals (Cu, Ag, and Hg); (2) high concentrations of transition metals (>200 mg/L); (3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

CVAA uses chemical reduction to reduce mercury to its volatile elemental form. The procedure is sensitive, though not as sensitive as CVAF, but is subject to interferences from some volatile organics, chlorine, and sulfur compounds. CVAA may be more appropriate than CVAF for samples with higher mercury concentrations.

CVAF uses chemical reduction to reduce mercury to its volatile elemental form. The procedure is extremely sensitive, approximately one to two orders of magnitude more sensitive than CVAA. CVAF may be more appropriate than CVAA for samples with low mercury

concentrations. Because of the extreme sensitivity of CVAF, contamination during sampling and analysis is a major concern.

ASV is an electrochemical method that can be used for determining free dissolved metals such as arsenic and mercury. The analyte of interest is reduced at the electrode surface during a deposition step and oxidized from the electrode during a stripping step; the current measured during the stripping step is proportional to the analyte concentration. ASV detects dissolved divalent mercury species and cannot directly distinguish between organic and inorganic mercury compounds. The sensitivity of this method for mercury is similar to CVAA. ASV detects dissolved inorganic arsenic species and can distinguish between As(III) and As(V) by adjusting the potential applied during the deposition step. The sensitivity of this method for arsenic is about an order of magnitude more sensitive than ICP-MS, GFAA, or HGAA. This method is subject to interferences from suspended solids, organics, and other metals. Samples can be modified (e.g., digested, addition of chelating agent, etc.) to determine the concentration of various species of the analyte of interest (e.g., total fraction, methylmercury, etc.)

XRF uses sealed radioisotope sources or other suitable X-ray source to irradiate samples with X-rays. When a sample is irradiated with X-rays, the source X-rays may undergo either scattering or absorption by sample atoms. This later process is known as the photoelectric effect. When an atom absorbs the source X-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of X-rays characteristic of the given atom. The emission of X-rays, in this manner, is termed X-ray fluorescence.

IC generally refers to the separation of ions through ion exchange chromatography. In this technique, an aqueous sample is injected into a mobile solution that is carried into a chromatography column. As the sample travels through the column, the sample analytes are temporarily retained on the column, the stationary phase, via electrostatic forces. The separated analytes are identified as they are released from the column based on their retention time. Detection and quantification in IC are most commonly performed using conductivity detection. IC is typically used for the determination of anionic analytes in waste samples.

CE refers to the electrophoretic separation of ions dissolved or suspended in an electrolyte. Samples are introduced into a capillary tube containing an electrolytic buffer. Under the application of an electric field the cations in the sample migrate toward the negatively charged electrode (cathode) and the anions migrate toward the positively charged electrode (anode). This technique may be coupled with a variety of determinative techniques for quantitative analysis. Inorganic anions can be determined in environmental samples using CE and indirect UV detection, in which analytes are detected and quantified based on proportional decreases in the absorbance of the buffer solution. CE is a complementary technique to IC and typically offers shorter analysis times than IC.

SIDMS is a quantitative method for determining elemental species based on the measurement of isotope ratio(s) in each species of a nuclide using mass spectrometry after speciated isotope dilution. Samples are mixed with one or more isotopic spikes which have different isotopic abundances and are artificially converted to chemical forms corresponding to the species to be analyzed. The spiked samples are then subjected to the separation of the species and the measurement of the altered isotope ratios in each species. Both species concentrations and species conversions can be mathematically derived.

The following methods are included in this section:

Method 6010D: Inductively Coupled Plasma-Optical Emission Spectrometry
Method 6020B: Inductively Coupled Plasma-Mass Spectrometry
Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
Method 6500: Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis
Method 6800: Elemental and Speciated Isotope Dilution Mass Spectrometry
Method 7000B: Flame Atomic Absorption Spectrophotometry
Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry
Method 7061A: Arsenic (Atomic Absorption, Gaseous Hydride)
Method 7062: Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)
Method 7063: Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
Method 7195: Chromium, Hexavalent (Coprecipitation)
Method 7196A: Chromium, Hexavalent (Colorimetric)
Method 7197: Chromium, Hexavalent (Chelation/Extraction)
Method 7198: Chromium, Hexavalent (Differential Pulse Polarography)
Method 7199: Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography
Method 7470A: Mercury in Liquid Waste (Manual Cold-Vapor Technique)
Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
Method 7472: Mercury in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
Method 7474: Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
Method 7580: White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography
Method 7741A: Selenium (Atomic Absorption, Gaseous Hydride)
Method 7742: Selenium (Atomic Absorption, Borohydride Reduction)

3.8   REFERENCES FOR PREVIOUS SECTIONS AND THE TABLES AND FIGURES

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TABLE 3-1

MATERIALS FOR USE IN SAMPLE COLLECTION FOR
INORGANIC ANALYTE DETERMINATIONS

Analyte	Recommended Container Material
Metals	PTFE, plastic, glass
Chloride	PTFE, plastic, glass
Cyanide	PTFE, plastic
Fluoride	PTFE, plastic
Nitrate	PTFE, plastic, glass
pH	PTFE, plastic, glass
Specific Conductance	PTFE, plastic, glass
Sulfate	PTFE, plastic, glass
Sulfide	PTFE, plastic, glass

[a]These recommendations are intended as guidance only and not inclusive of all possible analytes and materials. The selection of sample container should be made based on the nature of the sample, the intended end use of the data and the project data quality objectives.

TABLE 3-2

RECOMMENDED SAMPLE HOLDING TIMES, PRESERVATION, COLLECTION QUANTITIES, AND DIGESTION VOLUMES/MASS FOR SELECTED INORGANIC ANALYTE DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES[a,b]

Analyte	Matrix	Fraction	Minimum Collection Volume/Mass	Preservation[1]	Digestion Volume	Holding Time[2]
Metals (except Hg and Cr^{6+})	Aqueous	Total/total recoverable	600 mL	HNO_3 to pH<2	100 mL	6 months
		Dissolved	600 mL	Filter on site; HNO_3 to pH<2	100 mL	6 months
		Suspended	600 mL	Filter on site;	100 mL	6 months
	Solid	Total	200 g	None	2 g	6 months
Hexavalent chromium	Aqueous		400 mL	≤6 °C	100 mL	24 hours
	Solid		100 g	≤6 °C		30 days to extraction
				≤6 °C	2.5 g	7 days from extraction to analysis
Mercury	Aqueous	Total	400 mL	HNO_3 to pH<2	100 mL	28 days
		Dissolved	400 mL	Filter; HNO_3 to pH<2	100 mL	28 days
	Solid	Total	200 g	≤6 °C	0.2 g	28 days
	Solid	Species	200 g	≤6 °C	0.2 g	5 days
Chloride	Aqueous		50 mL	≤6 °C	—	28 days
Cyanide	Aqueous		500 mL	≤6 °C; NaOH to pH>12	—	14 days
	Solid		100 g	≤6 °C	—	14 days
Fluoride	Aqueous		300 mL	≤6 °C	—	28 days
Nitrate	Aqueous		1000 mL	≤6 °C	—	28 days
Hexane Extractable Material (HEM; Oil & Grease)	Aqueous		1000 mL	≤6 °C HCl or H_2SO_4 to pH <2	—	28 days
	Solid		100 g	≤6 °C		28 days
				HCl or H_2SO_4 to pH <2		when practical

TABLE 3-2

RECOMMENDED SAMPLE HOLDING TIMES, PRESERVATION, COLLECTION QUANTITIES, AND DIGESTION VOLUMES/MASS FOR SELECTED INORGANIC ANALYTE DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES[a,b]

Analyte	Matrix	Fraction	Minimum Collection Volume/Mass	Preservation[1]	Digestion Volume	Holding Time[2]
pH	Aqueous		25 mL	NA	—	Analyze immediately
	Solid		20 g	NA	—	Analyze immediately
Specific Conductance	Aqueous		100 mL	NA	—	Analyze immediately
Sulfate	Aqueous		50 mL	≤6 °C	—	28 days
Sulfide	Aqueous		100 mL	4 drops 2N zinc acetate/100 mL sample; NaOH to pH>9; Minimize aeration; Store headspace free at ≤6 °C	—	7 days
	Solid		100 g	Fill sample surface with 2N zinc acetate until moistened; Store headspace free at ≤6 °C	—	7 days
Organic Carbon, Total (TOC)	Aqueous		200 mL	≤6 °C store in dark HCl or H_2SO_4 to pH <2;	—	28 days
	Solid		100 g	≤6 °C	—	28 days

[a] These recommendations are intended as guidance only. The selection of sample and digestion volumes/mass and preservation and holding times should be made based on the nature of the sample, the intended end use of the data and the data quality objectives.

[b] Additional sample quantities may need to be collected in order to allow for the preparation and analysis of QC samples, such as matrix spikes and duplicates.

[1] The exact sample extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for standards. Alternative temperatures may be appropriate based on demonstrated analyte stability within a matrix, provided the data quality objectives for a specific project are still attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected by preservation, storage and analyses performed outside the recommended holding times.

TABLE 3-3

EXAMPLES OF THE ANALYTICAL BLANK INFLUENCE ON
ULTRA-TRACE ANALYSIS OF ELEMENTS IN GLASS

Conditions	Pb (ng)	Ag (ng)
Initial analysis of TEG* standard	330 ± 250	970 ± 500
Analysis using sub-boiled distilled acids	260 ± 200	-
Analysis in a Class 100 hood	20 ± 8	207 ± 200
Analysis using sub-boiled acids in a Class 100 hood	2 ± 1	3 ± 2

* TEG = Trace element in glass

Data are taken from Reference 6.

TABLE 3-4

EXAMPLES OF LEAD CONCENTRATIONS IN AIR

Site	Lead Concentration ($\mu g/m^3$)	Source
Downtown St. Louis, MO	18.84	Reference 16
Rural park, Southeastern MO	0.77	Reference 17
NIST Laboratory, MD	0.4	Reference 6

TABLE 3-5

CLEANLINESS LEVELS IN INTERNATIONAL STANDARD ISO 14644-1

ISO classification number	Maximum concentration limits (particles/m^{-3} of air) for particles equal to and larger than the considered sizes shown below					
	0.1 µm	0.2 µm	0.3 µm	0.5 µm	1 µm	5 µm
ISO Class 1	10	2				
ISO Class 2	100	24	10	4		
ISO Class 3	1,000	237	102	35	8	
ISO Class 4	10,000	2,370	1,020	352	83	
ISO Class 5	100,000	23,700	10,200	3,520	832	29
ISO Class 6	1,000,000	237,000	102,000	35,200	8,320	293
ISO Class 7				352,000	83,200	2,930
ISO Class 8				3,520,000	832,000	29,300
ISO Class 9				35,200,000	8,320,000	293,000

NOTE: Uncertainties related to the measurement process require that concentration data with no more than three significant figures be used in determining the classification level

TABLE 3-6

PARTICULATE CONCENTRATIONS IN LABORATORY AIR

	Concentration (µg/m³)			
Location	Iron	Copper	Lead	Cadmium
Ordinary laboratory	0.2	0.02	0.4	0.002
Clean room	0.001	0.002	0.0002	ND
Clean hood	0.0009	0.007	0.0003	0.0002

ND = Not Detected

Data are taken from Reference 17.

TABLE 3-7

NON-CONTAMINATING MATERIALS AND FOR USE AS DIGESTION VESSELS
AND SAMPLE CONTAINERS IN ULTRA-TRACE ANALYSES

Listed from highest to lowest preference for use in sample containment

Fluoropolymers: PFA*, TFM, TFE*, FEP*, Tefzel*

Quartz - Synthetic

Polyethylene (suitable for storage only, not for acid digestion)

Quartz - Natural

Borosilicate Glass

* Various forms of PTFE

Data are taken from Reference 8.

FIGURE 3-1

COMPARISON OF CLEAN VERSUS CONVENTIONAL SAMPLING AND ANALYSIS
TECHNIQUES USED IN THE ANALYSIS OF SOUTH TEXAS ESTUARY WATERS
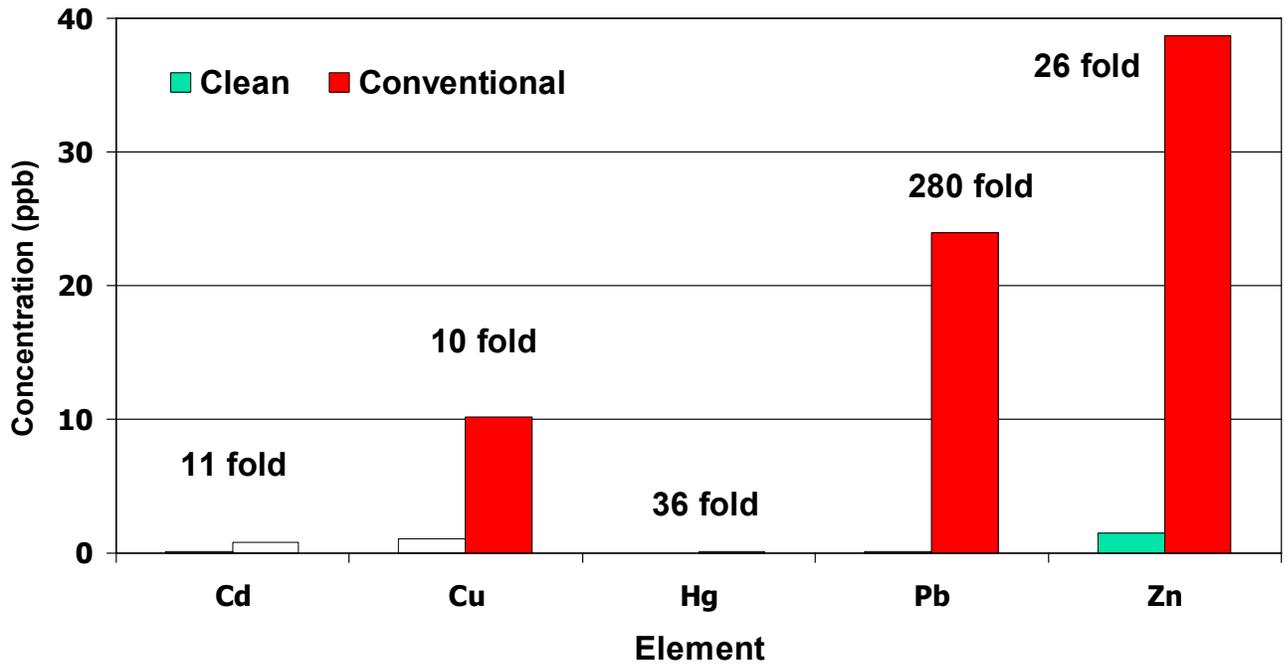
Taken from Reference 18.

FIGURE 3-2

COMPARISON OF PARTICLE COUNT ANALYSIS OF A CLEAN ROOM AND
A STANDARD LABORATORY AT DUQUESNE UNIVERSITY IN PITTSBURGH, PA
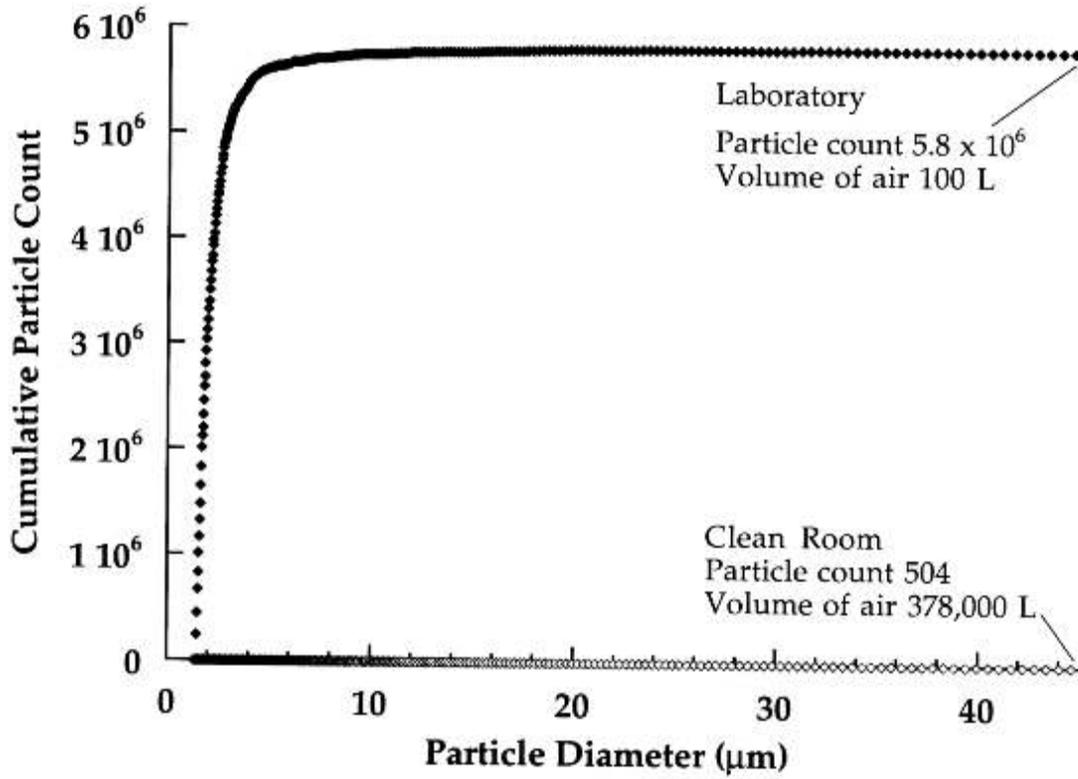
Taken from Reference 4.

FIGURE 3-3

PARTICLE SIZE COMPARISON CHART FOR COMMON PARTICULATES
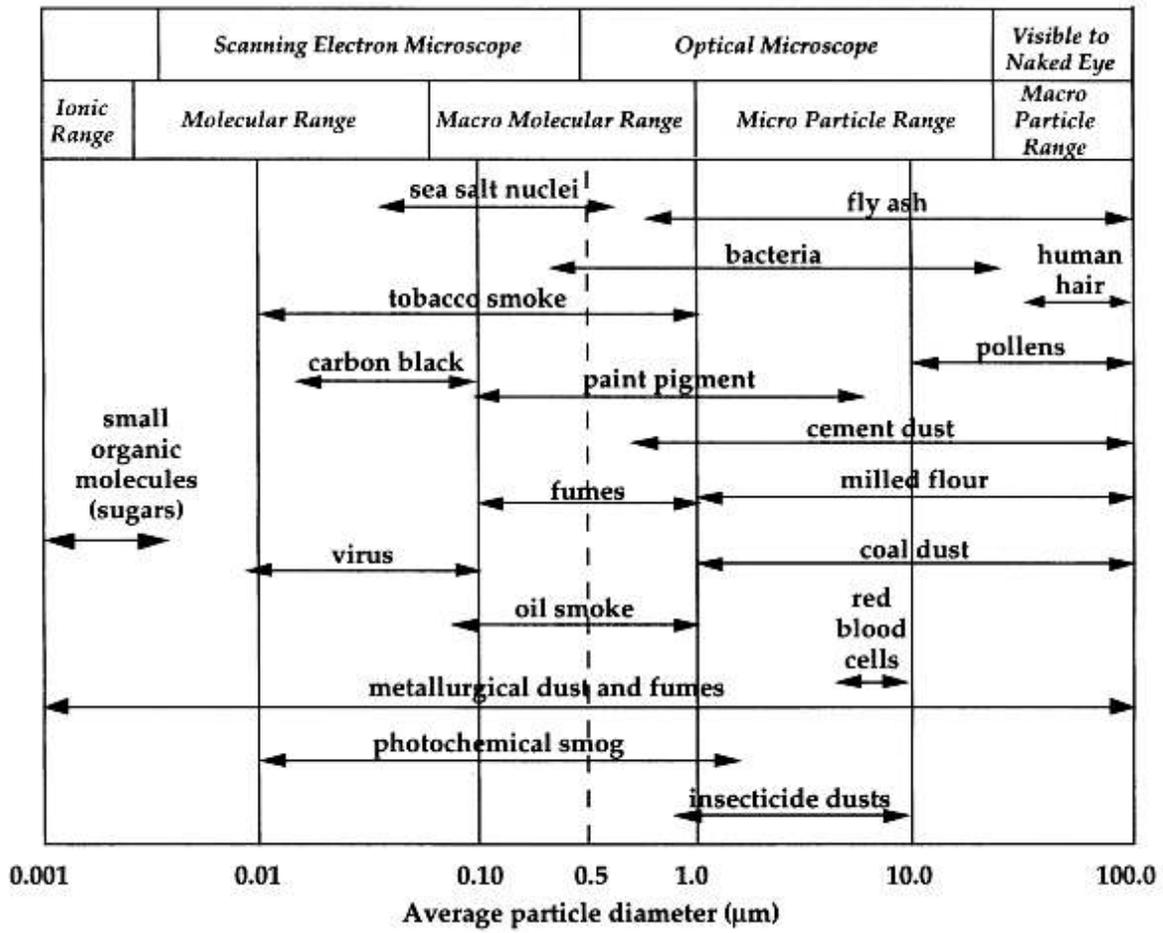
Taken from Reference 4, 19.

APPENDIX A
SUMMARY OF UPDATES/CHANGES IN CHAPTER THREE

1. The entire document was formatted in Microsoft Word .docx format from the original .wpd and .pdf files.
2. The revision number was changed to five and the date published to July 2014.
3. Minor editorial and grammatical changes were made throughout the Chapter.
4. Method 3200 was added to Section 3.6.
5. Method numbers were revised to reflect the assigned number for Update V.
6. Definition for instrument detection limit (IDL) was revised to be consistent with methods 6010D and 6020B.
7. The term "accuracy" was replaced by "bias" where appropriate.
8. Definition for linear range was revised to be consistent with methods 6010D and 6020B.
9. All references to atomic emission spectrometry were changed to optical emission spectrometry throughout the chapter.
10. Replaced the definition of interference check sample (ICS) with the spectral interference check (SIC) solution to be consistent with methods 6010D and 6020B.
11. Added a note to clarify the methods that can be used for total acid soluble/recoverable metals.
12. References 20-22 were added as guidance for minimizing sampling bias.
13. The term "decomposition" was replaced by "digestion" where appropriate.
14. Descriptions of cold vapor atomic fluorescence and anodic stripping voltammetry were added to Section 3.7.
15. Collision/reaction cell technology was added to Sections 3.6 and 3.7 as an effective method for removing isobaric interferences when analyzing by ICP-MS.
16. The terms "analytical" and "analysis" were changed to "instrument" or "determinative", where appropriate.
17. The term "signal" was changed to "instrument response".
18. The method for assessing sensitivity for ICP-OES and ICP-MS in Section 3.1 was modified.
19. The term "optimum concentration range" was removed from Section 3.1.
20. Antimony was added to the HGAA method described in Section 3.7.
21. The definition for "laboratory control sample" was revised to recommend the use of a spiking solution from the same source as the calibration standards.
22. A minimum collection mass of 100 g was added to Table 3-2 for solid samples collected for sulfide analysis.