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 judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of inorganic analytes in a variety of matrices. These 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 must 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.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: (a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; (b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

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

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

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050, 3051, or 3052.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

Initial calibration verification (ICV) standard: A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must 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. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard. See Method 7000, for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Check Standard: A solution containing a known concentration of analyte derived from externally prepared test materials. The check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion volumes and suggested collection volumes are listed in Table 3-1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that recommended for the individual digestion procedures and to that recommended for sample collection volumes. In all cases for waste testing, representative sampling must be maintained.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and 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 (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

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 must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

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

2. "OSHA Safety and Health Standards, General Industry," 29 CFR 1910.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety.

TABLE 3-1.

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR INORGANIC DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Volume. (mL)[a, c]	Collection Volume (mL)[a,c]	Treatment/ Preservative Holding Time[b]
Inorganic Analytes (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO_3 to pH <2 6 months
Dissolved	100	600	Filter on site; HNO_3 to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2 g	200 g	6 months
Hexavalent Chromium:			
Aqueous	100	400	24 hours Store at 4°± 2°C until analyzed
Solid	2.5 g	100 g	One month to extraction, 4 days after extraction Store at 4°± 2°C until analyzed
Mercury:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2 g	200 g	28 days Store at 4°± 2°C until analyzed

[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows[1]:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 30l0 prepares waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total recoverable metals determinations by furnace 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, EP and mobility-procedure extracts.

Method 3031 prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040 prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. 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 3050 prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, 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 3051 prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052 prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICP-AES, 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.

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[1] Please note that chlorine is an interferant in ICP-MS analyses and its use should be discouraged except when absolutely necessary.

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3.3 METHODS FOR DETERMINATION OF INORGANIC ANALYTES

This section of the manual contains seven analytical techniques for trace inorganic analyte determinations: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrometry (FLAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and back-ground correction to minimize these interferences, analysis for traces of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be traces of inorganic analytes in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA or FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, 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. 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.

Graphite Furnace AAS (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 must occur in a flame or ICP 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.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two 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, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

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