

III. Inorganic (Metals) Analyses

A. General Information

SAMPLING: Aqueous samples should be collected in plastic containers, with volumes dependent upon the number of analytical techniques required. Refrigeration is not required for aqueous samples.

Soils should be collected in glass containers, and refrigerated at 4°C from sampling until analysis.

PRESERVATIVES: Aqueous samples are preserved with nitric acid to a pH < 2 (usually 2 mL of 1:1 nitric acid per 500 mL).

Soils, samples requiring TCLP, and waste matrices do not require chemical preservation. All non-aqueous samples should be maintained at 4°C unless being submitted for TCLP analysis, and such refrigeration results in irreversible sample changes.

HOLDING TIMES: 6 months for all elements except mercury; 28 days for mercury.

COMMENTS: Samples may be preserved with nitric upon arrival at the lab. Keep in mind when submitting samples that the TCLP extraction is an eighteen hour procedure prior to any preparation or analysis. The addition of acid increases the solubility of metals.

If high amounts of solids are present, quite often the addition of acid leaches the metals out of the solid and into solution. In most cases, filtration of such samples can reduce the total metals concentration. However, the EPA considers a filtered sample as dissolved metals and this procedure requires field filtration prior to preservation.

Note: The EPA-recommended filter for dissolved metals is 0.45 µm. The Florida Department of Environmental Protection required filter for dissolved metals is 1.0 µm. Other programs may vary.

PREFERRED SAMPLING CONTAINER:

Aqueous Samples: 250 mL - 1 L HDPE, depending upon the number of techniques required.

Soils: 2-4 oz, preferably borosilicate glass unless boron or silica are analytes of interest.

B. Analysis Types

There are essentially five types of metal analyses: total, dissolved, acid extractable, recoverable, and Toxicity Characteristic Leaching Procedure (TCLP). It is important to distinguish between which type of analysis you would require prior to submitting a sample for metals analysis.

A *total metal analysis* represents the total amount of a particular metal present in a sample. Metals present in any sediment or silt in the samples will be reflected in the final concentration. Samples are typically preserved immediately following sampling to a pH <2. Once received in the laboratory, samples are subjected to a rigorous acid digestion procedure to ensure that all metals present in the sample, including those adsorbed to particulates are brought into the final acid solution, or digestate. This analysis should not be confused with the sample preparation procedures required. NPDES and 200 series methods specify Total Recoverable Metals prep, where as TCLP requirements specify Total Metals prep.

In a *dissolved metal analysis*, the sample is filtered through either a 0.45 or 1.0 micron membrane, depending upon state or regulatory program. Only the portion that is in solution will pass through the membrane. Filtration must be performed in the field at the time of sampling. Samples are preserved after filtration, as the addition of acid to the sample prior to filtration could leach some of the metals present in the sediments or particulates into solution, biasing the filtered results high. At the laboratory, the filtrate is then acid digested using the same or similar digestion procedure as total metals.

Acid extractable metals analyses have become more popular over the last few years as an alternative to either of the total or dissolved analyses. In theory, the acid extractable procedure removes many of the biases that can be introduced into the metals quantification process through improper or varying well construction and installation, well development prior to sampling, and sample preparation. The acid extractable procedure requires that *total* samples be collected, in that no filtration is permitted in the field. Samples are preserved with nitric acid to a pH <2 at the time of collection. Within 72 hours of sampling, the samples must be prepared for analysis, typically by Std Method 3030C. This preparation is a less vigorous digestion procedure, and metals contained in or adsorbed to particulate materials present in the sample are less likely to be brought into solution for analysis.

TCLP metal analysis is a theoretical simulation of ground water contamination resulting from disposing of a sample in a landfill. The procedure was designed to mimic mildly acidic rain water leaching metals from the sample and eventually migrating into the ground water. The procedure is most commonly used to profile waste materials destined for land disposal. (The TCLP procedure actually refers to the sample preparation (extraction) prior to metals preparation and analysis.) The TCLP extraction isolates the portion of sample that will not pass through a 0.7 micron membrane. An extraction fluid is added to the non-filterable phase, agitated (rotated) for eighteen hours, and filtered. The original filtrate and extracted filtrate are combined resulting in the TCLP extract. This extract is then acid digested and analyzed by the appropriate analytical technique. (For those who don't care: we mix the soil with a slightly acidic buffer, filter and analyze the liquid.)

Note: The SPLP, or *Synthetic Precipitate Leaching Procedure* is identical to the TCLP in application, and differs only by the type of extraction fluid utilized. The type of the extraction fluid used is based on the region of the country where the samples originate.

C. Analysis Methods

Once the determination has been made as to what type of metal procedure is to be performed, the sample is typically digested with acid. Following digestion, if any solid particulate is present, the digestate is filtered. The aqueous digestate is now ready to be analyzed by an appropriate technique. The majority of metals analysis techniques fall into two categories: atomic emission, or atomic absorption spectrometry. The most common methods of analysis are inductively coupled plasma atomic emission spectrometry (ICP-AES, or ICP), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), cold vapor atomic absorption (CVAA), and hydride generation atomic absorption (HGAA).

1. Atomic Absorption (AA)

(For those who don't care, we know how much light is going into the sample, we measure what is coming out, and the difference tells us how much of the metal of interest is present.) There are four basic methods for Atomic Absorption analysis: Flame, Graphite Furnace, Cold Vapor, and Hydride Generation. All four methods use a hollow cathode lamp, a sample introduction system, a monochromator, and a detector. The sample is placed between the light source created by the hollow cathode lamp and the monochromator. Energy is added to the sample, which excites the atoms of interest, resulting in the atoms' absorption of a fraction of the light energy. The unabsorbed light energy is then passed through the monochromator, which isolates the wavelength of interest and directs the light energy into the detector. The absorption is measured and compared to standards of known concentrations, allowing us to determine the metal concentrations present within the prepared sample.

In *Flame Atomic Absorption (FLAA)*, the sample digestate is introduced into a flame, typically composed of air/acetylene or nitrous oxide/acetylene. The heat from the flame provides an excitation source for the metal atoms present. These excited atoms absorb light of known wavelengths, and by measuring the loss of this light as it is transmitted through the flame, we can determine the concentrations of the elements present. Advantages of FLAA include rapid single elemental analysis times, low cost of instrumentation, and ease of use. Disadvantages are the delays of switching the instrumentation settings between elements, a high degree of variability due to matrix interferences, and relative insensitivity (higher detection levels) for many elements.

Graphite Furnace Atomic Absorption (GFAA) uses an electrical current across a graphite cell, or furnace, to provide an excitation source for any atoms present. Typical furnaces heat the sample slowly through the boiling point of water to remove the aqueous portion of the digestate, then rapidly raise the temperature to 2000-3000 °C to volatilize any metals present. Light from a hollow cathode lamp is directed through the cloud of volatilized metals and absorbance is measured and quantified as with the flame procedure. The primary advantage to the GFAA method is its extremely high level of sensitivity for many elements (low detection levels). Disadvantages include a relatively small linear range, delays associated with switching the instrumentation settings between elements, and relatively high equipment cost.

Cold Vapor (CVAA) and *Hydride Generation (HGAA)* atomic absorption techniques use similar chemical reactions to liberate the metals present in the samples into gaseous states. This vapor is then carried through a cell, through which light from a hollow cathode lamp is directed. Absorbance is measured and quantified as with the FLAA and GFAA procedure. CVAA is most commonly used for mercury determinations, while HGAA is frequently used for arsenic and selenium. The primary advantages to the CVAA and HGAA techniques are sensitivity for their respective elements, and its ability to better isolate any matrix interferences. Disadvantages include a relatively small linear range, and delays associated with switching instrumentation settings between elements.

2. Inductively Coupled Plasma (ICP)

(For those who don't care, we measure the brightness and "colors" of light given off a sample when we superheat it.) The basis of ICP analysis is the introduction of the sample digestate into a region of high temperature (approximately 10,000 °C), resulting in the excitation ("heating up") of the atoms present. These atoms release energy in the form of photons (light) as they "cool down", or return to their normal atomic states. Each element releases photons of characteristic wavelengths, or "colors" when excited. The intensity of each wavelength of this emitted light is measured and compared to that of a known concentration for each element of interest.

One of the ICP's advantages over other elemental techniques is its ability to analyze multiple metals in the same analysis, without the delays most commonly associated with atomic absorption techniques (changing lamps, instrument recalibration, etc.). Under the operation of a knowledgeable and experienced operator, simultaneous analyses of up to twenty-five to thirty elements per analysis are possible. Another advantage is the nature of the instrument's linear range. Five, and in some cases six orders of magnitude are possible, as compared to AA's more typical one to two orders of magnitude. Disadvantages of the technique are its relatively high cost of instrumentation, and dependence upon the experience level of the analyst responsible for instrument operation.

3. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

(For those who don't care, we measure the atomic weights of the individual metals in a sample after we superheat it. The atomic weights of the metals are unique to each element.) The basis of ICP-MS is identical to ICP-AES regarding sample introduction into a region of high temperature. The excited atoms (or ions) then are then separated out by mass in the mass spectrometer and counted. The number of atoms are measured and compared to that of a known concentration for each element of interest.

One of the ICP-MS' advantages over ICP-AES is less prone to interferences resulting in better data quality and lower detection limits. A potential disadvantage of ICP-MS, is its' inability to handle samples with a high level of salt content - brine samples for example.

D. Inorganic Methods Summary

Element	ICP-AES	ICP-MS	Flame	Furnace	Hydride	Cold Vapor
Aluminum, Al	200.7/6010	200.8/6020	202.1/7020	202.2	N/A	N/A
Antimony, Sb	200.7/6010	200.8/6020	204.1/7040	204.2/7041	N/A	N/A
Arsenic, As	200.7/6010	200.8/6020	N/A	206.2/7060	206.3/7061	N/A
Barium, Ba	200.7/6010	200.8/6020	208.1/7080	208.2/7081	N/A	N/A
Beryllium, Be	200.7/6010	200.8/6020	210.1/7090	210.2/7091	N/A	N/A
Boron	200.7/6010	200.8/6020	N/A	N/A	N/A	N/A
Cadmium, Cd	200.7/6010	200.8/6020	213.1/7130	213.2/7131	N/A	N/A
Calcium, Ca	200.7/6010	200.8/6020	215.1/7140	N/A	N/A	N/A
Chromium, Cr	200.7/6010	200.8/6020	218.1/7190	218.2/7191	N/A	N/A
Cobalt, Co	200.7/6010	200.8/6020	219.1/7200	219.2/7201	N/A	N/A
Copper, Cu	200.7/6010	200.8/6020	220.1/7210	220.2/7211	N/A	N/A
Iron, Fe	200.7/6010	200.8/6020	236.1/7380	236.2/7381	N/A	N/A
Lead, Pb	200.7/6010	200.8/6020	239.1/7420	239.2/7421	N/A	N/A
Magnesium, Mg	200.7/6010	200.8/6020	242.1/7450	N/A	N/A	N/A
Manganese, Mn	200.7/6010	200.8/6020	243.1/7460	7461	N/A	N/A
Mercury, Hg	N/A		N/A	N/A	N/A	245.1/7470/7471
Molybdenum, Mo	200.7/6010	200.8/6020	246.1/7480	246.2/7481	N/A	N/A
Nickel, Ni	200.7/6010	200.8/6020	249.1/7520	249.2	N/A	N/A
Potassium, K	200.7/6010	200.8/6020	258.1/7610	N/A	N/A	N/A
Selenium Se	200.7/6010	200.8/6020	N/A	270.2/7740	270.3/7741	N/A
Silver, Ag	200.7/6010	200.8/6020	272.1/7760	272.2/7761	N/A	N/A
Sodium, Na	200.7/6010	200.8/6020	273.1/7770	273.2	N/A	N/A
Thallium, Tl	200.7/6010	200.8/6020	279.1/7840	279.2/7841	N/A	N/A
Tin, Sn	200.7/6010	200.8/6020	282.1/7870	282.2	N/A	N/A
Vanadium, V	200.7/6010	200.8/6020	286.1/7910	286.2/7911	N/A	N/A
Zinc, Zn	200.7/6010	200.8/6020	289.1/7950	289.2/7951	N/A	N/A

E. Inorganic Lists

Element	RCRA	PP	TAL	Appx. I	Appx. II	Appx. IX
Aluminum, Al			X			
Antimony, Sb		X	X	X	X	X
Arsenic, As	X	X	X	X	X	X
Barium, Ba	X		X	X	X	X
Beryllium, Be		X	X	X	X	X
Boron						
Cadmium, Cd	X	X	X	X	X	X
Calcium, Ca			X			
Chromium, Cr	X	X	X	X	X	X
Cobalt, Co			X	X	X	X
Copper, Cu		X	X	X	X	X
Iron, Fe			X			
Lead, Pb	X	X	X	X	X	X
Magnesium, Mg			X			
Manganese, Mn			X			
Mercury, Hg	X	X	X		X	X
Molybdenum, Mo						
Nickel, Ni		X	X	X	X	X
Potassium, K			X			
Selenium Se	X	X	X	X	X	X
Silver, Ag	X	X	X	X	X	X
Sodium, Na			X			
Thallium, Tl		X	X	X	X	X
Tin, Sn					X	X
Vanadium, V			X	X	X	X
Zinc, Zn		X	X	X	X	X

RCRA: Resource Conservation & Recovery Act

PP: Priority Pollutant

TAL: Target Analyte List