

POTW SLUDGE SAMPLING AND ANALYSIS  
GUIDANCE DOCUMENT

**DRAFT**

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This document has been reviewed by the Environmental Protection Agency and approved for distribution in order to provide guidance on the sampling and analysis of municipal sewage sludge. EPA assumes no responsibility for use of this information in a particular situation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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## 1. INTRODUCTION

The 1987 Water Quality Act requires EPA to immediately issue permits to POTWs for sludge use and disposal, or to take other appropriate measures to protect public health and the environment (PL100-4), February 1987. To fulfill this directive, EPA intends to require sludge monitoring in reissued POTW NPDES permits and, in some cases, EPA may write sludge quality limits into NPDES permits. (EPA's Strategy for Interim Implementation of Sludge Requirements in Permits Issued to POTWs, available from EPA's Office of Water Enforcement and Permits (EN-336, U.S. EPA, 401 M Street SW, Washington, D.C. 20460), provides additional information on EPA's interim sludge permitting program.) Thus, in addition to the reasons POTWs now have for sampling and analyzing their sludge (for example, to determine compliance with existing State or Federal requirements on sludge use and disposal, setting maximum headworks loadings for pollutants in the influent to the POTW, etc.), many POTWs will soon be asked to submit data on sludge quality to EPA or State NPDES permit writers and compliance monitoring staff.

POTWs currently use a variety of methods to sample sludges and to analyze them. The purpose of this manual is to provide guidance to POTW operators and EPA and State permit writers on which methods should be used when samples are drawn and analyzed in order to comply with NPDES permit program and pretreatment program requirements. The recommended methods are those used by EPA's Office of Water or Office of Solid Waste and Emergency Response, or methods specified in Federal Regulations.

Chapter Two provides guidance on sampling procedures for POTW sludges. Chapter Three provides guidance on which analytical methods should be used. Chapter Four presents information on sampling and analysis quality assurance. Chapter Five examines sampling and analysis costs.

EPA intends to revise this document as new information on POTW sludge sampling and analysis becomes available. Readers are invited to submit their comments to the Office of Water Enforcement and Permits (address provided above).

## 2. SLUDGE SAMPLING

### 2.1 BACKGROUND INFORMATION

Depending on the use or disposal practice, it may be necessary to sample various sludge types throughout a given POTW. In order to sample a sludge stream effectively, it is necessary for sampling personnel to be aware of the physical characteristics of the sludge stream(s) at intended sampling locations.

#### 2.1.1 Solids Content and Viscosity

Two important physical characteristics of sludge with respect to sampling and analysis are viscosity and solids content. Solids content is the percent, by weight, of solid material in a given volume of sludge. Sludges have a high solids content as compared to most wastewaters. Solids content and solids settling characteristics determine whether a given sludge will fractionate.

Viscosity is the degree to which a fluid resists flow under an applied force. The viscosity of a sludge is only somewhat proportional to solids content. This property affects the ability to automatically sample a liquid, since friction through pipes is proportional to liquid viscosity. In general sludges of up to 20 percent solids may be conveyed by means of a pump. Sludge with a greater solids content, often referred to as sludge cake, must be conveyed by mechanical means. Those automatic samplers which rely on pumps may be useful only for liquid sludges with a solids content of less than 20 percent while manual grab sampling is necessary for sludge cakes. However, other problems created by sludge solids generally preclude the use of automatic samplers. Table 2.1 summarizes the total solids concentrations of low and high viscosity sludges and dewatered sludges.

Solids content is also significant from an analytical standpoint. Increased solids content may require sample dilution and cause a corresponding increase in experimental error and detection limits. Also, water removal through dewatering can either concentrate parameters of interest in the sludge



TABLE 2.1. TOTAL SOLIDS CONCENTRATIONS OF VARIOUS  
LOW AND HIGH VISCOSITY SLUDGES

Sludge Source	Total Solids (%)
LOW VISCOSITY SLUDGES:	
Digested Sludges (Unthickened)	<4
HIGH VISCOSITY SLUDGES:	
Digested Sludges (Thickened)	4-10
SLUDGE CAKES:	
Raw Primary Plus Secondary	15-25
Secondary	8-25
Anaerobic Digested Primary Plus Secondary	15-30
Primary Plus Secondary Plus Alum	15-25
Primary Plus Secondary Plus Ferric Chloride	15-25
Primary Plus Secondary Plus Lime	20-35

and increase analytical accuracy, or carry away pollutants and decrease pollutant concentration and analytical accuracy. However analytical precision and accuracy may decrease as the concentration of interfering compounds and matrix effects increase.

#### 2.1.2 Processed Sludge Characteristics

The quantity and quality of sludge generated depends on raw wastewater characteristics and the sludge treatment practices. The sludge to be sampled may be in the form of a liquid, dewatered cake, compost product, or dried powder. Some of the physical characteristics of each sludge type are described below.

##### 2.1.2.1 Anaerobically Digested Sludge

Anaerobically digested sludge is a thick slurry of dark-colored particles and entrained gases. When well digested, it dewateres easily and has an inoffensive odor. The addition of chemicals coagulates a digested sludge

prior to mechanical dewatering. The dry residue of digested sludge contains 30 to 60 percent volatiles. Depending on the mode of digester operation, the percent of solids of digested sludges ranges from 4 to 8 percent.

#### 2.1.2.2 Aerobically Digested Sludge

Aerobically digested sludge is a dark-brown, flocculent, relatively inert waste produced by long-term aeration of sludge. The suspension is bulky and generally difficult to thicken. The odor of aerobically digested sludge is not offensive. The percent solids of aerobically digested sludge is less than that of the influent sludge (if not decanted), because approximately 50 percent of the volatile solids are converted to gaseous end products during aerobic digestion.

#### 2.1.2.3 Dewatered Sludges

Dewatering converts sludge from a flowing mixture of liquids and solids to a cake-like substance more readily handled as a solid. The characteristics of dewatered sludge depends on the type of sludge, chemical conditioning, and treatment processes employed. Density (% solids) of dewatered cake ranges from 15 to >40 percent. Thinner cake is similar to a wet manure, while higher solids cake is a chunky solid.

#### 2.1.2.4 Compost Product

Composting is a process in which organic material undergoes biological degradation to a stable end product. Properly composted sludge is a sanitary, nuisance-free, humus-like material. Approximately 20 to 30 percent of the volatile solids are converted to carbon dioxide and water.

#### 2.1.2.5 Dried Powder

Dried powder is the residue from heat drying processes. Sludge drying reduces water content by vaporization of water to permit sludge grinding, weight reduction, and to prevent continued biological action. The moisture content of dried sludge is less than 10 percent.

## 2.2 SAMPLE POINT SELECTION

### 2.2.1 General Considerations

NPDES and pretreatment program officials need sludge quality data in order to determine whether sludge use or disposal may pose a threat to public health or the environment. Thus, as a general rule, sludge samples should be drawn from an appropriate sampling point and in such a manner that the sample represents, as well as possible, the quality of the sludge as it will be disposed of or used.

When selecting a specific sample point, the following two factors should be carefully considered:

- Sample point representation of the entire sludge stream passing that point
- Supporting flow or mass flux data.

The following paragraphs examine both concerns and present recommendations on means to address each concern.

#### 2.2.1.1 Sample Point Representation of the Entire Sludge Stream

A particular concern in any sampling program is obtaining samples which represent the entire flow past the sample point, throughout the sample period. Each discrete sample should represent the entire flow cross-section at the sampling point. Each composite sample of multiple contributory streams should represent the entire flow cross-section of the combined stream. Ideally, a perfectly representative sample has the same pollutant concentration as the average of the flow at the time the sample was taken. In reality, it is not possible to obtain a wholly representative sample of any wastestream. Effort must be made, however, to ensure that a sample is obtained that is as representative as possible. Therefore, the sample should be from a point where the sludge is well-mixed. While some pollutant parameters are solids related (particularly precipitated metals), others are liquid-fraction related (many dissolved organics) and failure to acquire a sample with representative solid/liquid fractions can significantly affect the analytical results of a

given sample. This is particularly true of sludge streams with high percent solids and large floc particles. In order to ensure that representative samples are collected, these recommendations should be followed:

- In sludge processing trains, the most representative sample comes from taps on the discharge side of sludge pumps. Flow at this point in the system is turbulent and well mixed, with no solids separation within the flow stream.
- If a sample is drawn from a tap on a pipe containing sludge flow (distant from the sludge pumps), determine average flow velocity through the pipe. Average velocities of less than 2 fps result in solids separation and settling, and affect sample solids content, depending on the location of the tap (top, side or bottom of the pipe). Given a choice, a tap on the side of the pipe is preferable. In addition, the tap should be a large size to encourage draw from the entire cross-section of flow when fully open.

A second consideration in many sludge sampling situations is the need to sample multiple contributory streams. An example is the sampling of sludge flows from several parallel sources which later combine downstream. Several options exist to accommodate multiple streams. The most appropriate choice depends on the sludge flow information available, the parameters being sampled and the purpose of the generated data. Several options are as follows:

- The simplest option is to withdraw equal volumes of sample from each pump or sludge well to create a grab-composite sample. This approach is justified in the case of identical units receiving equal flow and generating equal sludge amounts.
- A second option is to weight the grab samples in each composite according to the wastewater flow to each unit (or in the case of filter cake, the thickened sludge flow to each unit). This approach recognizes that for different sized units with different design flows, the volume of sludge produced will theoretically be proportional to the influent flow to the unit. Note that factors such as unequal loading rates, differences in sludge collection mechanisms, etc. can affect solids removal rates and sludge generation rates by unequal, parallel treatment units. This option particularly applies to situations where no sludge flow or solids data exists for unequal parallel flow streams.
- The third option is to weight grabs from individual streams based on sludge flow data or solids flux data. Whether to use sludge flow or solids flux will depend on the sample streams, the parameters of interest, and the planned use of the resulting data. For example, if filter cake is being monitored for compliance with land application

limits, solids flux data would be used as the criteria for proportioning grabs from parallel dewatering systems, since most land application limits are based on dry weight applications rates.

#### 2.2.1.2 Availability of Flow Data and/or Solids Flux Data

The availability of accurate flow data (or solids flux data) is an important consideration in planning a sludge sampling program. Most information requirements relating to sludge characteristics involve, at least in part, the need for data on the mass flux (i.e., lbs/day) of pollutant parameters found in sludge discharged from a POTW.

Portable flow monitoring devices are not well suited to high-solids flow streams, and most sludge processing streams are not designed in a manner which is physically conducive to the use of these devices. Thus, in most cases, it is necessary to rely on existing integrated flow monitoring equipment. Due to difficulties in monitoring sludge flows, flow meters are high maintenance items. Frequent calibration of sludge flowmeters is necessary in order to ensure accurate flow measurement. When ultimate use or disposal practices dictate monitoring sludge with a high solids content, liquid flow meters are replaced by gross weight scales. Table 2.2 summarizes the types of flow measurement equipment employed to monitor various sludge flows.

TABLE 2.2. SLUDGE FLOW MEASUREMENT DEVICES

Application	Measurement Means
Stabilized Sludge	Venturi Flow Tube Magnetic Meter Positive Displacement Pump
Thickener	Magnetic Meter Positive Displacement Pump
Dewatering	Belt press scales
Drying Composting Thermal Reduction	Bulk container or truck scales

### 2.2.2 Sludge Sample Points

For permits and regulation enforcement, sludge samples must come from the treatment unit process immediately preceding disposal or use. For example, if a POTW discharges dewatered filter cakes to a sanitary landfill, then sampling activity focuses on the output sludge stream from the dewatering device (i.e., vacuum filter, belt filter, etc.). Treatment processes from which sludge is disposed or land applied are stabilization, dewatering, drying, composting, and thermal reduction. Table 2.3 summarizes sampling points used for different sludge streams.

To examine the origin or fate of pollutants within a POTW, additional sludge samples from influent and output of other processes may be needed. The rationale for these additional samples is entirely site-specific.

## 2.3 SAMPLE COLLECTION

Having selected appropriate sampling points for a sludge sampling program, it is then necessary to determine the method and equipment by which sampling will be carried out. In doing so, the following objectives should be considered:

- Each grab sample, or aliquot of a composite sample, must be as representative as possible of the total stream flow passing the sampling point
- Effort must be made to minimize the possibility of sample contamination
- The selected sampling method should be convenient and efficient.

Except for limitations on the use of automatic sampling devices, the actual sampling techniques for sludges are similar to those found in wastewater sampling. The following sections describe important considerations for selecting appropriate sludge sampling methods.

### 2.3.1 General Considerations

In general, automatic sampling devices do not work well for sludge streams because of the solids content and viscosity of sludges. Typical devices for automatically sampling wastewaters consist of a positive

TABLE 2.3. SLUDGE SAMPLING POINTS

Sludge Type	Sampling Point
Anaerobically Digested Sludge -	Sample from taps on the discharge side of positive displacement pumps.
Aerobically Digested Sludge -	<p>Sample from taps on discharge lines from pumps. If batch digestion is used, sample directly from the digester. Two cautions are in order concerning this practice:</p> <ol style="list-style-type: none"> <li>(1) If aerated during sampling, air entrains in the sample. Volatile organic compounds may purge with escaping air.</li> <li>(2) When aeration is shut off, solids separate rapidly in well digested sludge.</li> </ol>
Thickened Sludges -	Sample from taps on the discharge side of positive displacement pumps.
Heat Treatment Sludge - (e.g., Zimpro, Proteus)	<p>Sample from taps on the discharge side of positive displacement pumps <u>after</u> decanting. Be careful when sampling heat treatment sludge because of:</p> <ol style="list-style-type: none"> <li>(1) High tendency for solids separation, and</li> <li>(2) High temperature of sample (frequently &gt;60°C as sampled) can cause problems with certain sample containers due to cooling and subsequent contraction of entrained gases.</li> </ol>
Dewatered, Dried, - Composted, or Thermal Reduction Sludges	Sample from material collection conveyors and bulk containers. Sample from several locations within the sludge mass and at various depths.

displacement pump, a control module, and sample receptacle(s), and are widely used to sample wastewater streams. Models are either permanently installed or portable. Automatic samplers which use pumps to draw samples up a suction tube cause solids separation if flow velocity in the suction and discharge tube is too low. This increases pump head requirements and limits the range of tubing diameter. A second problem which occurs in the use of automatic samplers is tubing and/or pump structure fouled by sludge solids. This results in contamination of subsequent aliquots during composite sampling. Sludge particles may also plug the sample tube or pumping mechanism and interrupt sample collection. Therefore, it is preferable to sample liquid sludge streams manually, particularly if sample taps can be provided on pump discharge lines.

At times it may be necessary to sample a poorly mixed open channel flow. If this cannot be avoided, then each sample must be a composite consisting of grabs taken at several levels ( $1/4$ ,  $1/2$  and  $3/4$  depth, for example) in order to minimize sample bias caused by solids stratification. For sampling solid sludges (i.e. dewatered cake, compost, etc.), stratification can be avoided by not only sampling at various depths, but at numerous locations over the entire sludge pile.

Sampling equipment must be made of materials which will not contaminate or react with the sludge. The best material choices are Teflon, glass and stainless steel because they are relatively inert. When the cost of Teflon and stainless steel equipment prohibits or restricts their use, steel and/or aluminum may be substituted for most sampling activities. (If steel equipment is used, ensure that galvanized or zinc coated items are not used because these materials will readily release zinc in the sample.)

Graduated glass pitchers or cylinders are used to draw grabs for manually composited samples. Stainless steel pitchers are also commercially available, and are used to grab samples from taps and also can be affixed to lengths of conduit to sample from open channel flows. Only aluminum conduits should be used since most commercially available steel conduit is galvanized. In addition, only stainless steel clamps should be used to attach the sample container to the conduit.



### 2.3.2 Proper Sampling Practices

Listed below are practices followed when sampling liquid sludges:

- Clean all sampling equipment between each sample period to prevent cross-contamination. Cleaning consists of thorough washing with a laboratory soap, thorough rinsing with tap water and at least three distilled water rinses.
- To draw a fresh representative sludge sample from a tap:
  - a) Allow sufficient time following pump startup to clear line of stagnant sludge, and
  - b) Allow sludge to flow for several seconds from tap prior to sampling in order to flush out stagnant sludge and solids accumulated in the tap.
- Before drawing a sludge sample, rinse each piece of sampling equipment 3 times with sample to reduce the chance of contamination from the previous grab.
- In manually drawing sludge samples, to maintain uniform concentration throughout care must be taken to prevent solids separation in the sample if the entire sample is not to be added to the composite. Use Glass or Teflon-coated stirring rods to mix a grab sample being split between several composite containers.
- Sample aliquots should be composited directly into sample containers. Sample containers, preservation of sample and allowable holding time prior to analysis are discussed in Section 2.5.
- When collecting samples for oil & grease analysis, sample directly into the sample container since oil and grease tend to adhere to surfaces. Sample composites should be sent to the laboratory as a series of grab samples.
- For either dewatered cakes, dried powder or compost product, combine equal amounts collected at various locations/depths for each grab sample to obtain a more representative sample.
- Sampling activities should be adequately documented, as discussed in Section 2.7.

### 2.4 SAMPLE TYPE, SAMPLE NUMBER, AND SAMPLING FREQUENCY

A proper sample is small enough to transport conveniently and handle carefully in the laboratory, but large enough to still accurately represent the characteristics of the whole material. Minimum sample sizes required for accurate analysis are specified in each analytical method. Table 2.4 lists

TABLE 2.4. CONTAINERS, PRESERVATION, HOLDING TIMES, AND MINIMUM SAMPLE VOLUMES

Parameter	Container	Preservative	Maximum Holding Time	Minimum Sample Volume <sup>(*)</sup>
<b>Metals</b>				
Chromium VI	P,G	Cool, 4°C	48 hours	300 mL
Mercury	P,G	HNO <sub>3</sub> to pH<2	28 days	500 mL
Metals except above	P,G	HNO <sub>3</sub> to pH<2	6 months	1000 mL
<b>Organic Compounds</b>				
Extractables (including phthalates, nitrosamines organochlorine pesticides, PCBs, nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days (until extraction) 30 days (after extraction)	1000 mL
Extractable (phenols)	G, teflon-lined cap	Cool, 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days (until extraction) 30 days (after extraction)	1000 mL
Purgeables (Halocarbons and Aromatics)	G, teflon-lined septum	Cool 4°C 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	14 days	50 mL
Purgeables (Acrolein and Acrylonitrile)	G, teflon-lined septum	Cool 4°C 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	14 days	50 mL
Pesticides	G, teflon-lined septum	Cool 4°C 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days (until extraction) 30 days (after extraction)	1000 mL

(\*) Varies with analytical method. Consult 40 CFR Part 136.

P ■ Plastic

G ■ Glass

minimum sample sizes for some common analytical methods. For methods not listed here consult an analytical methods book or the laboratory for further guidance.

A grab sample collected at a particular time and point can represent the composition of the source only at that time and point. If through historical data a source is known to be constant in composition over a period of time, or over distances in all directions, then the sample can be considered to represent a longer period of time or a larger volume than the specific point of sampling. In the case of most sludges, single grab samples will adequately represent only the instantaneous composition of the material being sampled. The quality of a grab sample will be improved if it is comprised of several smaller samples taken over a period of a few minutes.

A composite sample gives a better reflection of the time- and location-weighted average concentrations that are found in the sludge flow stream. In most cases, the term composite sample refers to a mixture of grab samples collected at the same sampling point at different times. However, a 24-hour composite sample, consisting of a number of time- or flow-weighted grab samples will give a picture of only one day's sludge quality. As sludge quality is directly related to wastewater influent quality (which can vary from day to day and hour to hour), a POTW should sample and analyze its sludge frequently.

To the extent practicable, the POTW should have a sludge sampling program which adequately addresses random and cyclic variation within the system and the potential for human exposure to sludge once it is disposed of or used.

Important factors to consider in determining sludge monitoring frequency include:

- **Anticipated cyclical variation in pollutant loadings** - Anticipated cycles include daily industrial production cycles, weekly industrial production cycles, and other known or suspected production cycles, particularly those associated with intermittent batch discharges by significant industries. Longer-term production cycles, including seasonal and annual/multi-year production cycles (e.g., business cycles), do not need to be considered in determining monitoring frequency unless they are known to affect short-term variation in sludge quality.

- **Treatment plant characteristics** - As either detention time or mixing increases within a treatment plant, sampling frequency can be reduced since treatment processes will effectively composite sludge to a greater degree. For example, high rate digestion and storage/blending facilities will provide mechanical mixing of sludge. Other plant technologies, such as anaerobic digestion, aerobic digestion and storage, provide longer sludge detention times, enabling greater mixing through physical processes such as diffusion, convection, etc. For combined sewer systems, a sampling strategy may be designed to monitor the effects of storm events on sludge quality.
- **Risk of environmental exposures** - As the risk of environmental exposure from sludge use/disposal increases, a POTW should increase its sampling frequency to provide better information about potential variation in sludge quality. For example, a sludge that is applied to food-chain croplands should be sampled more frequently than sludge that is disposed of in a landfill that has an impermeable liner and a groundwater monitoring system.

Another factor to consider in determining monitoring frequency is the percentage of flow contributed to the POTW by commercial or industrial users. While sludge quality variability is directly related to the individual characteristics of each POTW, POTWs with little or no commercial/industrial contributors in the system can expect relatively small variation in sludge quality. POTWs with significant industrial contributions can expect to have monthly, weekly and even daily variation in sludge quality.

Another consideration is the type(s) of information a POTW wishes to collect. If, for example, a POTW desires to measure daily variation over a typical week, the POTW may collect and analyze seven or more 24-hour composite samples for the pollutant. Similarly, if a POTW wishes to measure variation within a single day, the POTW may collect and analyze several grab samples taken at different times during the day.

POTW operators should be aware that EPA's Draft Strategy for Interim Implementation of Sludge Requirements in Permits Issued to POTWs (June 1988) would require POTW operators with known or suspected sludge use or disposal problems to do a full priority pollutant scan on their sludge at least once per year. These operators would also have information on their sludge quality and use or disposal practices reviewed by NDPES permit writers when their

permits are renewed. Compliance with any limits on sludge quality placed into a POTW permit would have to be determined at least:

- Once a year for POTWs with less than 1 million gallons of flow per day (mgd)
- Quarterly for POTWs with flows between 1 mgd and 10 mgd
- Monthly for POTWs with flows greater than 10 mgd.

All other POTW operators would also be required to perform a full priority pollutant scan annually unless current sludge data, data on industrial users, or treatment/disposal information show no cause for concern considering the POTWs current use/disposal practices.

#### 2.4.1 Opportunities for Cost Savings

To provide a representation of sludge quality over a fixed duration, sewage sludge can be composited (i.e. mixed) reducing the number of samples to be analyzed. In light of the high costs associated with analysis of priority pollutants, especially organics in sewage sludge, compositing samples provides an opportunity to substantially lower analytical costs. Because sample compositing provides a representation of average sludge quality, it is not an appropriate technique to use when the entire range of sludge quality variation is of interest.

When interested in daily variation in sludge constituents, a POTW can collect and analyze 24-hour composite samples, each consisting of six or more grab samples. This represents a significant cost savings when compared to separately analyzing many individual, non-composited samples. Smaller POTWs, with less variation in sludge quality, may elect to composite samples over several days as opposed to 24-hour composites. The suitability of a multi-day compositing procedure will depend upon whether the specific sludge constituent can be adequately preserved in the sludge sample. Table 2-4 shows the recommended preservatives and maximum sample holding times for organic and metal pollutants.

Another way to reduce costs would be to sample more frequently for parameters that are relatively inexpensive to analyze such as metals, nitrogen, phosphorus, and potassium, and to test for organic pollutants (expensive) less frequently, so long as some data are available indicating that the levels of organic contaminants in the sludge are acceptable.

## 2.5 SAMPLE PREPARATION AND PRESERVATION

Errors of varying severity, which affect analytical determinations may be introduced during sample collection and storage. To avoid potential errors and maintain sample integrity, POTW operators should carefully consider the following:

- Sample Container Material
- Sample Container Preparation
- Sample Preservation
- Holding Time Prior to Analysis.

Table 2.4 lists recommended container materials, preservatives, holding times, and minimum sample volumes for the analysis of sludges. For method-specific details concerning all facets of sample preparation and preservation, consult the references cited in 40 CFR Part 136, "Guidelines for Establishing Test Procedures for the Analysis of Pollutants."

### 2.5.1 Sample Container Material

The requirements for sample containers are method specific, but containers are usually made of Teflon, glass or polyethylene. Sample containers should be wide-mouthed for sludge sampling, particularly for solids (cake) sampling. Teflon containers are typically supplied with Teflon caps. Glass containers frequently are supplied with phenolic caps. These containers should be fitted with Teflon liners for most parameters.

### 2.5.2 Sample Container Preparation

Proper sample container preparation is necessary to prevent contamination of the sample by material left from the container manufacturing process or that has otherwise been introduced into the unused sample containers. All containers should be washed with a good quality laboratory soap, thoroughly

rinsed with tap water, and then rinsed at least 3 times with distilled water prior to air drying. Additional container preparations are described below:

- **Extractable Organics** - Glass containers with Teflon-lined caps only. Containers are washed as above and solvent rinsed (typically methylene chloride) and air dried.
- **Volatile Organics** - Container preparation consists of wash and rinse as described above followed by baking at 105°C for both vials and septums. Cool in organic-free atmosphere.
- **Metals** - Wash and rinse as described above. Then rinse with dilute acid (1 part deionized and distilled water and 1 part HNO<sub>3</sub>) followed by a final rinse with deionized and distilled water; followed by redistilled water rinse.

### 2.5.3 Sample Preservation

Table 2.4 presents U.S. EPA recommended preservation protocols. These protocols are primarily intended for effluent monitoring; however, they are generally applicable to liquid sludge sampling.

The following are specific recommendations regarding sample preservation:

- In instances where it is desirable to split one composite sample into several fractions, each having incompatible preservation requirements, it is acceptable to chill the entire sample to 4°C during compositing. Following the sample period, the composite is then cautiously mixed and split into various fractions, each of which is appropriately preserved.
- Whenever possible, sample containers should be pre-preserved. Thus, grab samples are preserved upon sampling and composite samples are preserved during compositing.
- In general, all samples should be chilled (4°C) during compositing and holding.
- For solid sludge (cake), adding chemical preservative is generally not useful due to failure of the preservative to penetrate the sludge matrix. Preservation consists of chilling to 4°C and sampling as described in Section 2.3.
- From the standpoint of maximizing sample characterization, as large a sample as possible is desired. For manually composited samples, each grab should be of a substantial volume (i.e. 1-2 liters). Upon finishing the composite, the sample may be poured to a more conveniently sized, preserved container, following mixing.

#### 2.5.4 Holding Time Prior to Analysis

Table 2.4 lists the maximum holding times for various pollutant samples. Table 2.5 lists potential interferences that may affect samples during shipping and storage. There are many more interferences associated with analytical methods.

### 2.6 PACKAGING AND SHIPPING

When analysis will be performed away from the sampling locale, samples must be packaged and transported.

#### 2.6.1 Packaging

Sample containers must be packaged so as to protect them and to reduce the risk of leakage. Containers should be held upright and cushioned from shock. In addition, sufficient insulation and/or artificial refrigerant ("blue ice") should be provided to maintain a sample temperature of 4°C for the duration of transportation.

#### 2.6.2 Transportation Regulations

The following guidelines control the shipment of wastewater and sludge samples:

- Unpreserved normal (i.e., not heavily contaminated) environmental samples are not regulated under DOT Hazardous Material Regulations. These samples may be shipped following the packaging guidelines in Section 2.6.1., and using a commercial carrier, etc. To assure proper sample temperature, transit time should be held to less than 24 hours.
- When environmental samples are preserved as recommended, they may be shipped as non-hazardous samples.

The guidelines above assume no material is present in the samples at concentrations which would result in a "hazardous" DOT rating. Should hazardous material (as defined by DOT) be present, DOT regulations concerning packaging, transportation and labeling must be followed (see 49 CFR Parts 172, 173 and 178).



TABLE 2.5. POTENTIAL INTERFERENCES ASSOCIATED WITH  
SAMPLE SHIPPING AND STORAGE

Parameter	Interferences <sup>1</sup>	Preservative
Acidity	CO <sub>2</sub> loss	Fill container completely
Ammonia	Cl <sub>2</sub> Volatilization	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Fill container completely
Cyanide	Sulfides	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
Chromium VI	Reducing agents	Minimize holding time
Phenols	H <sub>2</sub> S, SO <sub>2</sub> Oxidizing agents	Aerate FeSO <sub>4</sub>
Silica	---	Avoid freezing
Sulfide	Aeration, agitation	Fill container completely
Sulfite	Aeration, agitation	Fill container completely
Organic Chemicals	Photodegradation	Brown glass container

<sup>1</sup>Other than those addressed by protocols shown in Table 2.4

TABLE 2.6. STANDARD PRESERVATIVES LISTED IN THE HAZARDOUS MATERIALS TABLE  
(49 CFR 172.101) USED BY EPA FOR PRESERVATION OF WATER, EFFLUENT  
BIOLOGICAL, SEDIMENT, AND SLUDGE SAMPLES

Sample Type/ Parameter	Preservative	pH Recommendation	Quantity of Preservative Added Per Liter	WT. % of Preservative
Organic Carbon	HCl	<2 - ≥1	2 ml of 1:1	0.04%
Nitrogen Species	HgCl <sub>2</sub>	N.A.	40 mg	0.004%
Metals, Hardness*	HNO <sub>3</sub>	<2 - ≥1	5 ml of Conc. (70%)	0.35%
Nitrogen Species COD, Oil & Grease P (hydrolyzable) Organic Carbon	H <sub>2</sub> SO <sub>4</sub>	<2 - ≥1	2 ml of 36N	0.35%
Cyanides	NaOH	>12 - ≤13	2 ml of 10N	0.080%
Phenolics	H <sub>3</sub> PO <sub>4</sub>	<4 - ≥2	Sufficient to yield desired pH	
Biological - Fish & Shellfish Tissue**	Freezing 0°C (Dry Ice)	N.A.	N.A.	N.A.

\*The sample may be initially preserved by cooling and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with conc. HNO<sub>3</sub> to pH<2. At time of analysis, sample container should be thoroughly rinsed with 1:1 HNO<sub>3</sub>; washings should be added to sample.

\*\*Dry ice is classified as an ORM-A hazard by DOT. There is no labeling requirement for samples preserved with dry ice, but each package must be plainly and durably marked on at least one side or edge with the designation ORM-A. Advance arrangements which must be met to ship dry ice are found in DOT regulation 49 CFR 173.616.

## 2.7 DOCUMENTATION

Adequate documentation of sludge sampling activities (1) is important for general program Quality Assurance/Quality Control, and (2) is required by most monitoring regulations. Proper sampling activity documentation includes proper sample labeling, chain-of-custody inventory for each sample lot and a log book of sampling activities.

### 2.7.1 Sample Labeling

It is important that each sample label include the following information (items in bold text are minimum elements):

- Sampling Organization Name
- **Facility Name (being sampled)**
- Bottle Number (specific to container)
- Sample Number (specific to all containers comprising one sample)
- **Type of sample, i.e., grab, 24 hour composite, etc.**
- **Date, Time (24 hour time is preferable, i.e., 1600 vs. 4:00 p.m.)**
- **Sample Location**
- **Preservatives**
- Analytical Parameter(s)
- **Collector**
- Special Conditions or Remarks.

Labels and ink should be waterproof. Fix labels to containers with clear waterproof tape. Tape completely around container and over label to prevent accidental label loss or ink smear during shipping and handling.

### 2.7.2 Chain-of-Custody

Each sample lot requires a chain-of-custody record. A chain-of-custody document provides a record of sample transfer from person to person. This document helps protect the integrity of the sample by ensuring that only authorized persons have custody of the sample. In addition to the information listed on each sample bottle, this document shall record each sample's collection and handling history from time of collection until analysis. All personnel handling the sample shall sign, date and note the time of day on the chain-of-custody document. A sample chain-of-custody document is provided in Appendix A.

### 2.7.3 Sampling Log Book

All sampling activities should also be documented in a bound log book. This book duplicates all information recommended for the chain-of-custody document above, and notes all relevant observations regarding sample stream conditions.

## 2.8 SAFETY CONSIDERATIONS

Safety is important in sludge sampling, especially since many sampling points preclude direct collection of grab samples. Several safety considerations are noteworthy given the potential health-related effects of sewage and sludge, and the hazards associated with treatment plant equipment (water, electricity, moving components, etc.).

Personal hygiene is important for all personnel involved in sludge sampling efforts. Sludge presents a unique health hazard, not only because of the toxic substances present, but also because of the abundance of pathogens (bacteria, viruses and worms). As a precautionary measure, inoculations are recommended for all personnel who have direct contact with sludge (as well as any wastewater) samples. As a minimum, inoculation should include diseases such as typhoid and tetanus. Avoidance of direct sludge contact is preferred and is possible if proper precautions are taken. Wear rubber or latex gloves at all times, especially while collecting or handling samples, and use waterproof garments when the risk of splashing exists. Wash any cuts or scrapes thoroughly and treat immediately.

When sampling sludge in confined areas, particularly around anaerobic digesters, a possibility exists for the presence of dangerous gases. These gases may include either explosive vapors (methane), poisonous mixtures (including hydrogen sulfide), or oxygen-deprived atmospheres (carbon dioxide). Explosive vapors require care to avoid sparks and possible ignition. These situations necessitate adequately ventilated equipment, gas meters and backup breathing apparatus.

There are several universal safety precautions that are applicable to sludge sampling as well. Exercise care around open pits or uncovered holes. Proper lighting increases the visibility of such hazards. Loose or dangling garments (ties, scarves, etc.) should not be worn around equipment with moving parts, especially pumps. Exercise extra awareness around pumps controlled by intermittent timers. Finally, be very careful when sampling high pressure sludge lines or lines containing high temperature, thermally-conditioned sludges (i.e., Zimpro or Porteus) in order to avoid injury by either high pressure streams or burns.

### 3. ANALYTICAL PROCEDURES

Sewage sludge analysis is difficult because of the inherent complexity of sludge matrices. Sewage sludge is compositionally diverse, rich in organic matter, and highly variable in physical and chemical properties. Matrix complexity often results in significant analytical interference which can lead to poor analytical accuracy and precision with a resultant loss of data reliability. For example, matrix interference can both mask the identity of analytes by suppressing instrumental response, or falsely contribute to a positive response. Variations in the physical and chemical properties of sewage sludge often make it difficult to obtain samples which represent the material as a whole. The diversity of sludge characteristics, coupled with the heterogeneous nature of sludges, presents a considerable challenge to precise and accurate determinations of trace levels of pollutants in sludges.

The following sections provide a summary of the analytical techniques available for characterization of the sewage sludge and soil constituents considered important in the selection of use or disposal options. Analytical techniques for conventional pollutants, priority pollutant metals, priority pollutant organics, and pathogenic organisms are discussed.

#### 3.1 CONVENTIONAL POLLUTANT PARAMETERS

Conventional pollutant parameters have historically been the focal point of sewage sludge analyses. The parameters normally associated with this group include solids, pH, oil and grease, phosphorus species, nitrogen species, phenolics, and total cyanide. As Table 3.1 indicates, the analytical protocols commonly employed for these analyses are adaptations of gravimetric or colorimetric techniques developed for aqueous samples. Total cyanide, oil and grease, pH, and solids analyses adapt readily to sludge matrices.

Existing Federal regulations (40 CFR Part 257) require POTWs that apply sludge to food-chain croplands to measure the pH of the sludge-soil mixture and soil cation exchange capacity (CEC). Soil pH should be measured using a 1:1 solution of soil and deionized water (see Table 3.1). For distinctly acid soils, CEC should be measured using the summation method (see Table 3.1). For

TABLE 3.1 ANALYTICAL TECHNIQUES FOR CONVENTIONAL POLLUTANTS

Parameter	Preparation Techniques	Analytical Technique	Recommended QA/QC	Aqueous Detection Limit (mg/l)	Comments	Reference
Phosphorous (Ortho Phos) (Total Phos)	Acidic Digestion Turbid samples must be filtered after digestion	Colorimetric	Blanks Standards Spike	0.001	- High iron concentration can cause precipitation and loss of phosphorous - Turbidity interference - 24 hr. holding time	EPA600/4-79-020 365.1
Nitrogen (Tot. Kjeldahl N)	H <sub>2</sub> SO <sub>4</sub> digestion	Colorimetric	Blanks Standards	0.05	- 24 Hr. holding time - Fe + Cr catalyze; Cu inhibits reaction	EPA 600/4-79-020 351.1
Ammonia	Colorimetric reaction	Colorimetric, ion specific electrode	Spike	0.05	- Hg can cause complex to NH <sub>4</sub>	350.1, 350.2, 350.3
Nitrate	Reaction to brueline sulfate	Colorimetric		0.1	- Dissolved organic matter	352.1
Nitrite	Hydrazine or Cd reaction	Colorimetric		0.05	- Strong oxidizing or reducing agents - Suspended matter in reduction column - Samples which contain high conc. of metals or organics	353.1, 353.2
Cyanide	CN converted to HCN by reflux- distillation	Colorimetric	Blanks Standards Spike	0.02	- Fatty acids and sulfides interfere	EPA 600/4-79-020 335.2
Phenolics	Distillation and extraction	Colorimetric	Blanks Standards Spike	0.002	- 24 hr. holding time - Sulphur compounds and oxidizing agents interfere	EPA 600/4-79-020 420.1
Total Organic Carbon	Inorganic carbon removal	Catalytic com- bustion & non- dispersive IR	Blanks Standard Spike	1.0	- Carbonate + bicarbonate carbon interfere	EPA 600/4-79-020 415.1
Chemical Oxygen Demand	Oxidation to potassium dichro- mate and HCl	Titration	Blanks Standard Spike	5.0	- Possible loss of volatiles - Chloride oxidation could be an interference	EPA 600/4-79-020 410.1 and 410.2

TABLE 3.1 ANALYTICAL TECHNIQUES FOR CONVENTIONAL POLLUTANTS (Continued)

Parameter	Preparation Techniques	Analytical Technique	Recommended OA/OC	Aqueous Detection Limit (mg/l)	Comments	Reference
Biochemical Oxygen Demand	Incubation	Measurement of reduction in dissolved oxygen	Blanks Standards Spikes	1.0	5 day incubator	EPA 600/4-79-020 405.1
Oil and Grease	Solvent extraction	Gravimetric IR Analysis	Blanks Spike	0.2		EPA 600/4-79-020 413.1, 413.2
pH	Solution in suspension with DI water	Ion selective electrode	Standards	—	Interference from solids and oily residues	EPA 600/4-79-020 150.1 Black 1965
CEC	BaCl <sub>2</sub> /treatment amine extraction (acid exchange) Ammonium acetate ester action, ignition (base exchange)	Titration, Colorimetric	None cited in Ref.	None cited in Ref.	Acid soils	Black, 1965 p. 900, 57-4
CEC	Sodium acetate-sludge solution, isopropylalcohol wash, ammonium acetate exchange	Emission, or absorption spectroscopy, or equivalent	One blank per sample batch	No data available	Neutral, saline, or calcareous soils	Black, 1965 pp. 891-900 SW-846 Method 9081
Solids	Filtration	Gravimetric	Blanks	4.0-10.0		EPA 600/4-79-020 160.1-160.5
Solids % (total)	Evaporation	Gravimetric	Blanks	N/A		160.3



neutral, saline, or calcareous soils, the sodium acetate method should be used (see Table 3.1).

## 3.2 METALS

There are several analytical techniques used for determination of metals in sewage sludge, with variations in both the sample preparation and analysis steps. A discussion of these techniques follows.

### 3.2.1 Analyte Isolation/Preparation Overview

Two approaches are currently used to evaluate the concentrations of metal contaminants in sludges. The first involves determination of the total metal content or other materials of interest, without regard for chemical form. This approach has been used most frequently, and the analytical techniques for such determinations are designed to solubilize all of the metal species (bound to organic particulates and mineralogically bound). In the second approach often referred to as "leachate approach," the proportion of the total contaminant loading which will become available or mobilized under environmental conditions is determined. Thus, leachate techniques are designed to mimic a given environmental scenario. With either approach, the complexity and variability of sludge matrices has made the development of sample preparation techniques a great analytical challenge.

The two primary aspects of metal determination in sewage sludge are 1) affecting the desired level of dissolution of the sample portion containing the metal components of interest, and (2) elimination of inorganic and organic interferences. The preparation procedure must be capable of effectively liberating the analytes from the solid constituents, solubilizing the elemental species, homogenizing the sample phase(s) of interest, as well as completely oxidizing the associated organics. Sludge matrices are challenging in this regard because of the high organic levels and solids loadings characteristics.

All state-of-the-art sample preparation procedures for total metal determinations depend on acid-mediated digestions and chemical or physical oxidation techniques. The approach involves the use of strong acid and

elevated temperature digestion procedures in combination with chemical or physical oxidants. The modifications which have been used include variations in acids, oxidation reagents, physical oxidation techniques, reaction conditions, and/or the sequence in which components are employed. Acids used most frequently include nitric acid ( $\text{HNO}_3$ ), hydrofluoric acid ( $\text{HF}$ ), hydrochloric acid ( $\text{HCL}$ ), and perchloric acid ( $\text{HClO}_4$ ); while hydrogen peroxide and perchloric acid are common oxidizing reagents. High temperature ( $550^\circ\text{C}$ ) combustion and low temperature plasma ashing (LTPA) have been used successfully as physical oxidants. Closed system digestion procedures are also used successfully.

Two closely related approaches have been used to estimate the amount of inorganic and organic contaminants which may be released after disposal of contaminated material. Both involve the leachate approach. The contaminated material is maintained in an aqueous slurry under a given set of conditions, after which contaminant levels are measured on the filtered aqueous media. The first approach, called the elutriate test, was developed by the Army Corps of Engineers to evaluate the impact of dredge disposal activities on the aquatic environment. The second is part of the Extraction Procedure (EP) toxicity procedure developed by EPA (in response to RCRA legislation) to evaluate the impact of landfill waste disposal practices on subsurface and surface waters (Federal Register 45: 5/19/80).

### 3.2.2 Analytical Techniques for Metals

#### 3.2.2.1 Sample Preparation/Digestion

Table 3.2 shows the sample preparation/digestion technique recommended by the USEPA. Method 3050 (SW-846, 3rd ed.) is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this

TABLE 3.2. RECOMMENDED PREPARATION TECHNIQUE  
FOR ELEMENTAL ANALYSIS OF SLUDGE SAMPLES

Method 3050<sup>(1)</sup>

- 1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.
  - 2) Add 10 ml of 1:1  $\text{HNO}_3$ , mix the slurry, and cover with a watch glass. Heat the sample to 95° C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 ml of concentrated  $\text{HNO}_3$ , replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 ml without boiling, while maintaining a layer of solution over the bottom of the beaker.
  - 3) After Step 2 has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30%  $\text{H}_2\text{O}_2$ . Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.
  - 4) Continue to add 30%  $\text{H}_2\text{O}_2$  in 1-ml aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged.
- NOTE: Do not add more than a total of 10 ml 30%  $\text{H}_2\text{O}_2$ .

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(1) USEPA "TEST METHODS FOR EVALUATING SOLID WASTE: VOLUME 1A"  
SW-846 3rd EDITION, NOVEMBER 1986. CHAPTER 3, PP. 3050-1,5.

method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below:

<u>FLAA</u>		<u>GFAA</u>
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Thallium	Molybdenum	Selenium
Copper	Vanadium	Thallium
Iron	Zinc	Vanadium
Lead		

Method 3050 prepares samples for analysis total metals (except mercury) determination through vigorous digestion in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid.

For the digestion and analysis procedures for mercury, see section 3.2.2.2.

#### 3.2.2.2 Analytical Detection Methods

Metals should be analyzed using either Atomic Absorption Spectrometry (AAS) or Inductively Coupled Argon Plasma (ICP). The following discussion generally describes both methods.

Inductively Coupled Argon Plasma is a form of optical emission spectroscopy which uses an argon plasma to excite ions and atoms. This process causes the ions and atoms to emit light which is measured as a signal. The signal response is proportional to concentration level, and each element emits a uniquely characteristic light. This technique poses several advantages. A linear relationship between concentration and signal response can be expected over 4-6 orders of magnitude, detection limits are low and not strongly inhibited by matrix variation, costs are moderate since many elements may be determined at once, and analysis time is fairly rapid. The primary drawbacks are matrix interferences (as with all analyses), the fact that solid samples cannot be analyzed directly as in AAS, and the high cost of purchasing ICP instruments (more than \$100,000).

The basic principle behind atomic absorption spectroscopy is the opposite of the emission method, ICP. In AAS the element (metal) being analyzed is dissociated from its chemical bonds by heating the sample. It is then capable of absorbing radiation until it reaches the excited state at a characteristic wavelength. This affects the sensitivity in analyzing for elements via atomic absorption because under optimum conditions, for every atom available in an excited state there are many more available in a dissociated condition. For this reason, AAS is more responsive than ICP to lower concentrations of metals in sludge. However, this very precise nature of AAS is also the cause of its major flaw--only one elemental determination per sample is possible at a time. Thus, the total analysis time of AAS is significantly greater than that of ICP when many metals are present in the sample.

In sewage sludge applications, it is important to realize that both of these analytical techniques are reliable tools and neither offers a significant technical advantage over the other. However, ICP's capability to simultaneously analyze multiple elements is a tremendous advantage in terms of sample throughput and labor savings, which may outweigh the noted limitations.<sup>1</sup> For sludge applications, EPA recommends either method and leaves the final decision to individual POTWs.

Table 3.3 summarizes the relative advantages and disadvantages of ICP and AAS.

#### ICP Method 6010

EPA recommends Method 6010 for the determination of metals in solution by Inductively Coupled Plasma atomic emission spectroscopy (ICP). This method can be found in the USEPA manual "Test Methods for Evaluating Solid Waste," (SW-846, Nov. 1986, 3rd Ed., Vol 1A, pp. 6010-1,17). The method is applicable

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<sup>1</sup>For drinking water and other non-sludge applications, priority pollutant scans may require very low contaminant detection levels. Therefore, there may be no choice except to rely on the lower detection limit capability of graphite furnace AAS. This, in turn, will determine the digestion method used.

TABLE 3.3 COMPARISON SUMMARY OF ICAP AND AAS

	ICAP	AAS
Cost for Instrument	-	+
Cost per sample	+	+
Detection Limits	+	+
Precision	+	+
Linear Working Range	+	-
Sensitivity	+	++
Number of Elements/Sample	+	-
Analysis Time	+	-

- disadvantage

+ advantage

++extra advantage

to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. EPA recommends digestion Method 3050 (SW-846, 3rd Ed. - see Section 3.2.2.1).

Elements for which Method 6010 is applicable are listed in Table 3-4. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 3-4 provide concentration ranges for clean (interference-free) aqueous samples. Due to matrix interferences, the detection limits in typical sludge samples will be somewhat higher. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

#### Atomic Absorption Methods

The USEPA recommends use of the methods listed in the manual "Test Methods for Evaluating Solid Waste," (SW-846, Nov. 1986, 3rd Ed., Vol 1A) for the determination of metals in solution by atomic absorption spectroscopy. A

TABLE 3.4. RECOMMENDED INDUCTIVELY COUPLED WAVELENGTHS AND  
ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength <sup>a</sup> (nm)	Estimated Detection Limit <sup>b</sup> (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See note c
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

<sup>a</sup>The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. In time, other elements may be added as more information becomes available and as required.

<sup>b</sup>The estimated instrumental detection limits shown. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

<sup>c</sup>Highly dependent on operating conditions and plasma position.

complete set of procedures for each metal-specific method may be found on pages 7020-1 to 7950-3. These methods are simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters as well as domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other wastes require digestion prior to analysis. EPA recommends digestion Method 3050 (SW-846, 3rd Ed. - see section 3.2.2.1).

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrometers. The data shown in Table 3.5 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. Due to the matrix interferences, the detection limits for typical sludge samples will be somewhat higher.

#### Mercury Analysis

The physical-chemical characteristics of mercury are not amenable to digestion by the generally recommended technique, Method 3050. For the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge material, EPA recommends using Method 7471, a cold-vapor atomic absorption spectrometry. This method appears in the EPA manual "Test Methods for Evaluating Solid Waste." (SW-846, Nov. 1986, 3rd Ed., pp. 7471-1,10). Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method. The typical detection limit for this method is 0.0002 mg/L.

### 3.3 ORGANICS

The evolution of analytical techniques for organic contaminants has involved a number of modifications to a basic method in order to widen potential applications. Because the instrumentation is complex and the number of possible analytes is large, quality control is difficult to monitor and several analytical techniques are required. As with analyses for metals and other elements, the organic-rich complex matrices characteristic of sewage sludges often mean that analyte extraction/isolation procedures play a significant role in the reliability of the resultant analytical data.



TABLE 3.5. ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure <sup>a, c</sup> Detection Limit (ug/L)
	Detection Limit (mg/L)	Sensitivity (mg/L)	
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic <sup>b</sup>	0.002	--	1
Barium(p)	0.1	0.4	--
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	--
Iron	0.03	0.12	--
Lead	0.1	0.5	1
Magnesium	0.001	0.007	--
Manganese <sup>d</sup>	0.01	0.05	--
Mercury <sup>a</sup>	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel(p)	0.04	0.15	--
Potassium <sup>b</sup>	0.01	0.04	--
Selenium <sup>b</sup>	0.002	--	2
Silver	0.01	0.06	--
Sodium	0.002	0.015	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	--

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

<sup>a</sup> For furnace sensitivity values, consult instrument operating manual.

<sup>b</sup> Gaseous hydride method.

<sup>c</sup> The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

<sup>d</sup> Cold vapor technique.

### 3.3.1 Overview of Analyte Extraction and Isolation

For a number of reasons, EPA has focused regulatory attention on two categories of contaminants: volatile organics and extractable organics. While the classification of these groups is founded upon inherent physical/chemical properties, extraction and isolation techniques are the functional basis for the distinction.

#### Volatile Organics

Two methods are available for extraction and isolation of volatile organics in aqueous and solid matrices: headspace techniques and purge and trap techniques. Several versions of these procedures have been sanctioned by regulatory agencies and/or developed for use in specific applications. For POTW sludge sampling and analysis, EPA recommends two analytical methods (1634, 624-S) which both extract via purge and trap (see Section 3.3.2.).

Purge and trap requires moderate sample preparation. The method relies upon a stripping process in which an inert gas is bubbled through the sample to remove the volatile organics. The volatilized organics are transferred from the aqueous/solid phase to the gaseous phase and subsequently trapped on a solid adsorbent column. The adsorbent column is then heated and the trapped organics are thermally desorbed and swept into the analytical instrument.

#### Extractable Organics

The first step in all procedures for determination of semi-volatile organics is solvent extraction. (Note: For extraction procedures recommended by EPA for sludge analysis see Section 3.3.2). The sample material is mixed and agitated with a solvent, causing the organic analytes to be preferentially partitioned into the solvent phase. Extractions are typically performed at both acidic and basic pH ranges to facilitate extraction of ionizable organics. Modifications to the extraction method are usually based upon the manner in which the sample-solvent mixture is agitated and post-extraction cleanup procedures.

The organic solvent used most frequently for extraction of semi-volatile analytes is methylene chloride, either singly or in combination with a more

polar solvent. Extraction techniques which are applicable to sludge and solid matrices include:

- Sonication extraction
- Continuous liquid-liquid extractors
- Soxhlet extraction
- Mechanical agitation (shaker table, homogenization, or wrist-action shaker).

Sonication relies on the mechanical energy developed from ultra-sonic devices to affect agitation and solvent-solid contact. The best approach involves the use of a sonication horn which is immersed into the solvent-sample mixture, rather than a sonication bath. This technique has also been proven effective in sludge and sediment applications.

Continuous liquid-liquid extractors and Soxhlet extractors employ the same basic principle of operation. The extraction solvent is distilled from a reservoir, condensed above the sample material, and subsequently rains down through the sample. The distillation-condensation process continues until a volume of solvent has collected sufficient force to establish a siphon, at which point the extraction solvent is siphoned back into the reservoir. The cycle is repeated with freshly distilled solvent and is generally allowed to occur for 12-24 hours. The continuous liquid-liquid extraction procedure can only be used on low solids (<5%) sludges, while the Soxhlet technique is most useful for materials with low water content.

A variety of mechanical agitation techniques have been used for extractable organics determinations including homogenization, wrist-action shakers and platform shakers (shaker tables). The objective of each technique is to maximize the contact between the extraction solvent and the solid particles. Wrist-action and platform shakers have both proven adequate, with wrist-action shakers generally preferable for smaller sample containers and platform shakers preferable for larger extraction vessels. Homogenization relies on agitation of the solvent-solid mixture, rather than agitation of the entire extraction vessel. This technique has been used quite successfully in sludge applications as a result of its superior agitation.

As a result of the complexity of sludge matrices, fractionation and/or cleanup procedures are often required after sample extraction to minimize interference. The basic concept used in virtually all cleanup techniques is selective adsorption of the interfering components. Although a variety of cleanup procedures have been developed for specific analytes, the techniques commonly employed in broad spectrum applications include:

- Silica gel adsorbent resins - fractionation and general purpose cleanup
- Florisil adsorbent resins - fractionation and general purpose cleanup
- Alumina adsorbent resins - fractionation and general purpose cleanup
- Activated carbon - fractionation and general purpose cleanup
- Gel permeation resins - higher molecular weight biogenic organics
- Copper and mercury - removal of sulfur-containing compounds.

Cleanup procedures can be used individually or in combination with other procedures, depending upon the need of the particular application and the complexity of the sample.

For more detail regarding extraction and isolation techniques, consult the references cited in 40 CFR Part 136, "Guidelines for Establishing Test Procedures for the Analysis of Pollutants."

### 3.3.2 Recommended Analytical Techniques for Organics

For determining concentrations of organic pollutants in sludge, EPA recommends two methods designed for qualitative and quantitative analysis of municipal and industrial wastewater treatment sludges:

- **Volatile Organics** - 624-S (EPA 1984b) or 1634 (EPA 1988a).
- **Semi-volatile Organics** - 625-S (EPA 1984b) or 1635 (EPA 1988a).

Each of these two methods employ gas chromatography/mass spectrometry (GC/MS).

GC/MS is a combination of two microanalytical techniques: gas chromatography (a separation technique) and mass spectrometry (an identification technique). A sample aliquot is prepared for extraction, extracted,

then introduced to the GC/MS system. The sample is vaporized quickly at an elevated temperature and carried by an inert gas (mobile phase). The vaporized sample is forced through a lined column (stationary phase). Separation of the sample components is affected by their differential partitioning between stationary and mobile phases. The separated components exit the column and enter the mass spectrometer (MS) where they are decomposed to specific unimolecular species. The manner in which a component fragments is characteristic of that component and is the basis for identification. The MS detector quantifies a compound by responding with a signal proportional to the detected amount of the compound.

The GC/MS system is calibrated by measuring signal response to several (3-5) analyte standard solutions of various concentrations (e.g., 20-160 ng/ml). The solutions are carefully prepared mixtures of pollutants suspected to be present in the sample, as well as a few labeled pollutant analogs known as internal standards. The accumulated measurements form an instrument response curve. Samples are spiked with the same internal standards at a fixed concentration immediately prior to analysis. If the MS detects any sample-originated pollutants, the generated signal for each pollutant is measured against both the internal standard and the response curve.

GC/MS analysis affords several advantages over other techniques:

- Provides qualitative and quantitative information about a wide range of organic compounds.
- Confirms specific information from a small sample size.
- Produces a spectrum with a fragmentation pattern, or fingerprint, which can be used to identify an unknown.

#### 3.3.2.1 Methods 1634 and 1635

Methods 1634 and 1635 are draft methods for analyzing volatile organics (Method 1634) and base/neutral organics (Method 1635) in sludge. These methods were developed by the USEPA Office of Water Industrial Technology Division, and are derived from previous methods 1624 and 1625 (see 40 CFR Part 136) for analyzing wastewaters.

The 1634/1635 (and 1624/1625) test procedures are isotope dilution techniques. In conventional GC/MS, up to six internal standards are used to quantify the response of perhaps several dozen analytes. Isotope dilution GC/MS employs stable, isotopically labeled analogs of the compounds of interest, which is analogous to providing a separate internal standard for each analyte. The result is that isotope dilution GC/MS is sensitive to even minute amounts. Methods 1634/1635 and 1624/1625 are similar in this respect but differ in sample preparation.

Method 1634 sample preparation for sludge samples consists of the following three routes, depending on the percent (%) solids content of the sludge. If the solids content is less than one percent, stable isotopically labeled analogs of the compounds of interest are added to a 5 gram sample and the sample is purged in a chamber designed for soil or water samples. If the solids content is 30 percent or less, the sample is diluted to one percent solids with reagent water and labeled compounds are added to a 5 gram aliquot of the sludge/water mixture. The mixture is then purged. If the solids content is greater than 30 percent, five ml of reagent water and the labeled compounds are added to a 5 gram aliquot of sample. The mixture is then purged.

Method 1635 sample preparation for sludge samples consists of the following three routes, depending on the percent (%) solids content of the sludge. If the solids content is less than one percent, a one liter sample is extracted with methylene chloride using continuous extraction techniques. If the solids content is 30 percent or less, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted. If the solids content is greater than 30 percent, the sample is extracted using ultrasonic techniques. Each extract is subjected to a gel permeation chromatography (GPC) cleanup.

#### 3.3.2.2 Methods 624-S and 625-S

Methods 624-S and 625-S are interim methods for the measurement of organic priority pollutants in sludges. Method 624-S is used to analyze for volatile organic compounds. Method 625-S is used for semi-volatile or

nonvolatile organics. These test procedures were derived from previously developed methods 624 and 625 for analyzing wastewaters (see 40 CFR Part 136). The 624-S/625-S techniques are conventional GC/MS and operate as described in Section 3.3.2.

In Method 624-S, an inert gas is bubbled through a 10-ml sludge aliquot contained in a purging chamber at ambient temperature. The purgeable compounds are transferred from the aqueous phase to the vapor phase. The vapor is carried through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables into a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

Method 625-S uses repetitive solvent extraction (see section 3.3.1) aided by a high-speed homogenizer. The extract is separated by centrifugation and removed with a pipette or syringe. Extracts containing base/neutral compounds are cleaned by silica gel or florisil chromatography or by gel permeation chromatography (GPC). Extracts containing the acidic compounds are cleaned by GPC. The organic priority pollutants are determined in the cleaned extracts by capillary column or packed column GC/MS. Option A, i.e., extract cleanup by silica gel or florisil chromatography and analysis by capillary GC/MS (HRGC/MS) is preferred since HRGC/MS allows easier data interpretation.

While Methods 1634/1635 provide lower detection limits than Methods 624-S/625-S, these methods are also more costly. Presently, Methods 1634/1635 cost about \$2,200-\$2,400 per sample, which is approximately \$200-\$400 more than a similar analysis by Methods 624-S/625-S. The extra cost reflects the Method 1634/1635 isotope spikes and approximately two weeks of work necessary to prepare additional spectral libraries. At this time, EPA recommends using either set of methods.

Neither Methods 624-S/625-S or Methods 1634/1635 detect pesticides at very low concentrations. Without megabore column analysis, which may cost an additional \$1,000, none of these methods will do better than the detection limits, 20-50 ppb. For some highly mixed pesticides such as chlordane, these methods can only detect 200-300 ppb. At this time, EPA is not recommending

megabore column pesticide analysis nationally. However, in particular situations, megabore column analysis may be appropriate.

### 3.4 PATHOGENIC MICROORGANISMS

A pathogen or pathogenic agent is any biological species that can cause disease in the host organism (primarily man). These organisms fall into four broad categories: viri, bacteria, parasites, and fungi. From these categories, species commonly found in sewage sludge include fecal coliforms, fecal streptococci, salmonella, and ascaris. Wastewater sludge disinfection, the destruction or inactivation of pathogenic organisms in the sludge, is carried out to minimize public health concerns regarding these and other microbial agents.

The 40 CFR Part 257 regulations issued on September 13, 1979 (44 FR 53438-53468) under joint authority of Subtitle D of the Resource Conservation and Recovery Act (RCRA) and Section 405(d) of the Clean Water Act establish acceptable practices for the disposal of solid waste which include sewage sludge. The regulations (40 CFR Part 257.3-6) require that sewage sludges applied to the land surface or incorporated into the soil be treated by a Process to Significantly Reduce Pathogens (PSRP). Public access must be controlled for at least twelve months after sludge applications and grazing by animals whose products are consumed by humans must be prevented for at least one month after application. Treatment by a Process to Further Reduce Pathogens (PFRP) is required for sewage sludge applied to the land surface or incorporated into the soil if crops for direct human consumption are grown within eighteen months after application, if the edible portion of the crop will touch the sludge.

Rather than requiring a specific reduction or concentration for given pathogens, the technology-based regulation (see Appendix II of 40 CFR Part 257) describes and sets numerical requirements for unit processes and operating conditions that qualify as PSRP and PFRP (e.g., criteria for process time and temperature and for volatile solids reduction). Appendix II allows methods or operating conditions other than those listed under PSRP or PFRP if



pathogens and vector attraction are reduced commensurate with the reductions attainable from listed methods. Appendix II does not prescribe the operation mode (i.e., batch or continuous) for digesters.

Analytical techniques which have been used in sewage sludge applications are summarized in Table 3.6. It should be noted that bacteria are tested for (usually) via modified standard wastewater methods because there are no definitive sludge methods. In addition, there are no standardized methods of any kind for parasitic determinations.

The effectiveness of many PSRPs and PFRPs for reducing pathogens can be estimated by the effects on fecal indicator organism densities (e.g., fecal coliform and/or fecal streptococcus). These tests are less expensive and easier to run than tests for specific pathogens. They make good control tests.

TABLE 3.6 ANALYTICAL TECHNIQUES FOR DETERMINATION OF PATHOGENIC MICROORGANISMS IN SEWAGE SLUDGE

Pathogen	Preparation Technique	Culture Media	Comments	Reference <sup>(1)</sup>
Fecal Coliform and Fecal Streptococcus Indicator Organisms	—	—	most practical method	A,B
Klebsiella	—	eosine - methylene blue agar	—	C
Staphylococcus	—	mannitol salt agar	—	C
Salmonella	—	selenite-brilliant green agar	—	C
Mycobacterium	Sludge is vortex mixed, sonicated, or homogenized serial dilution in appropriate media	Middlebrooks 7H11 agar	—	C
Pseudomonas	appropriate media	acetamide agar	—	C
Clostridium	—	differential reinforced clostridia media	—	C
Shigella	—	xylose lysine desoxycholate agar	—	C
Gram negative enteric bacteria	—	xylose lipine desoxycholate agar	—	C
Polio/Echo/Coxsackie viruses	Sludge is mixed at pH 3.5 (HCl) with AlCl <sub>3</sub> , centrifuged; viruses eluted with 10% beef extract (pH 7.0). Eluted viruses filtered flocculated in 3% beef extract of pH 3.5 to concentrate.	tissue culture	tests with activated sludge yield recoveries of 68-80%	D,E
E. coli	centrifugation and filtration	M-FC broth membrane filters	—	B (912E)
Leptospirae	filtration	Fletchers semi-solid media	incubation at 30°C for six weeks	B (912F)
Vibrio Cholerae	filtration	serial dilution in alkaline peptone water (pH 9.0)	incubation at 35°C for 6-18 hours	B (912G)

- <sup>(1)</sup> References: A) Bordner and Winter (eds.) (1978) "Microbiologic Methods for Monitoring the Environment—Water and Waste," EPA-600/8-78-017  
 B) APHA-AWWA-WPCF (1980) Standard Methods for the Examination of Water and Wastewater. 15th edition.  
 C) Dudley, D.J. et. al. (1980) "Enumeration of Potentially Pathogenic Bacteria from Sewage Sludges" *Applied and Environmental Microbiology* 39:(1) p. 118-126.  
 D) Hurst, C.J. et al. (1978) "Development of Quantitative Methods for the Detection of Enteroviruses in Sewage Sludge During Activation and Following Land Disposal" *Applied and Environmental Microbiology* 36:(1) p. 81-89.  
 E) "U.S. EPA Manual of Methods for Virology," EPA-600/4-84-013, February 1984, EMSL, Cincinnati, OH.

#### 4. QUALITY ASSURANCE

An essential part of a good sampling and analysis program is a well designed quality assurance (QA) program. The extent of the QA program should mirror the intent and purpose of the sampling effort.

If the purpose of the sampling and analysis program is to determine compliance with permit conditions, or to provide critical data for making a major cost decision, then the QA program should be extensive and be able to demonstrate the precision, accuracy, representativeness, comparability and completeness of the data. The determination of these QA parameters and their definitions are:

- Accuracy of all sample testing and analyses should be evaluated at a minimum frequency of 5 percent (i.e., at least one in every 20 samples), using spiked samples. Accuracy is calculated from the known and analytically derived values of spiked parameters, and expressed as percent recovery.

The quality control limits for accuracy of the analyses will be those specified in each of the EPA methods (e.g., EPA 600 or 1600 Series or EPA Methods for Chemical Analysis of Water and Wastes).

- Precision of sample analyses should be evaluated at a minimum frequency of 5 percent (i.e., at least one in every 20 samples), using spiked samples in duplicate. Precision is calculated from the analytical results of the spiked analytes in each set of duplicate samples, and expressed as percent relative standard deviation.

The quality control limits for the precision of the analyses will be those specified in each of the EPA Methods (e.g., EPA 600 or 1600 series or EPA Methods for Chemical Analysis of Water and Wastes).

- Completeness should be determined and evaluated on the basis of data sets for each measurement process. Completeness is calculated as a percentage, based on the number of valid values obtained for each measurement process relative to the number of valid values originally anticipated. Data are considered to be valid if both the accuracy and precision of the measurements meet the Data Quality Objective (i.e., accuracy, precision, and compliance with analysis method protocol).
- All sampling should be performed using methods, procedures, and controls that ensure the collection of representative samples for analysis. All sampling will be conducted to ensure that the analytical results are representative of the media and the conditions being measured.

- Comparability is a more qualitative QA measurement. All analytical data must be calculated and reported in units consistent with those specified in the applicable permit. Previously developed data generated for each facility about to be inspected is reviewed to ensure that no difficulties of data comparability will be encountered by following the specifications of the permit. If no previous data exist and the permit requirements are incomplete or ambiguous, data should be reported in the standard units prescribed in the appropriate EPA Methods (e.g., EPA 600 or 1600 series or EPA Methods for Chemical Analysis of Water and Wastes).

These QA procedures are necessary for ensuring data quality. On the other hand, if the purpose of the sampling effort is to monitor plant performance for routine O&M decisions, a simplified QA program which includes sample replicates and a field blank might suffice.

Sludge sampling and analysis programs for determining compliance with permit conditions should include a written QA Plan. EPA guidance for the development of a QA Program (EPA Quality Assurance Project Plans (QAPP), 1983) identifies 16 elements which should be addressed in a QA plan:

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In preparing a QAPP, the QA parameters and specifications of the analytical program, should be dictated by the analytical parameters. The QA parameters are specified in each analytical protocol. These are situations (particularly for enforcement actions) in which more stringent protocols will be desired.

In preparing the QA plans, the collection of field blanks (blanks to reflect sample handling effects) and sample replicates should be addressed. At a minimum, field blanks should be collected every day that sampling is performed. Field blanks should be prepared at the beginning of each sampling event, at each discrete sampling site, by pouring ASTM Type II reagent water into prepared sample bottles. These sample bottles are randomly selected from the supply of prepared sample bottles; a sample container should be selected that is appropriate for each type of analysis for which environmental samples are being collected (see Table 2.4). The field blanks should be handled and analyzed in the same manner as environmental samples. Because field blanks and environmental samples are collected under the same conditions, field blanks analyses should be used to indicate the presence of external contaminants that may have been introduced into samples during collection.

One field replicate for every 20 samples or less should be collected at a preselected POTW monitoring point. Field replicates should be collected at the same time and in the same manner as the other environmental samples. Results of the field replicate analyses should be used primarily to assess the precision of the field sampling methods.

In preparing and evaluating the analytical report, attention should be given to the data quality, and the impact of both the sampling and analysis data quality to the overall interpretation of the analytical results. Both the data from the field QA samples and the laboratory QA samples should be evaluated for the presence of contaminants. Additionally, statistical

procedures should be used for the determination of precision, accuracy and completeness. The QAPP 1983 document provides a description of the statistical procedures and their applications. All reports of analytical data should contain a separate section which assesses the quality of the reported data.

The section of the quality assurance plan on internal quality control checks specifically discuss how the following activities will be addressed:

#### Organic Priority Pollutants

- Instrument tuning and calibration
- Method blank analysis
- Surrogate spike analysis
- Matrix spike/matrix spike duplicate analysis
- Internal standards analysis

#### Inorganic Priority Pollutants

- Initial calibration verification
- Continuing calibration verification
- Instrument response and linearity verification
- Calibration and preparation blank analyses
- Interference check sample analyses
- Spike sample analyses
- Duplicate sample analyses
- Laboratory control sample analyses
- Serial dilution analyses (if applicable)
- Instrument detection limit determination
- Method of standard additions application.

The sample procedures and frequency section of the quality assurance plans should address, among other elements, sample holding times, sample preservation procedures, and sample chain-of-custody. Maximum sample holding times are presented in Table 2.4. Section 2.5.3 addresses sample preparation. Section 2.7.2 addresses sample chain-of-custody.

## 5. SAMPLING AND ANALYTICAL COSTS

The cost of carrying out a sludge sampling program can vary depending on the number and type of samples, parameters analyzed, and whether analytical services are contracted out. The following discussion examines sampling and analytical costs as of April 1988.

### 5.1 MANPOWER REQUIREMENTS

Manpower requirements fall into two categories: (1) supervisory and program development, and (2) sampling/analytical. All sampling programs should be designed and supervised by qualified personnel. Developmental and supervisory needs will vary according to the following factors:

- Type and Number of Samples
- Number of Streams to be Sampled
- Number of Facilities/Locations
- Availability of Suitable Sample Points
- Parameters to be Analyzed
- Experience and Qualifications of Field and Laboratory Personnel.

The number of factors influencing supervisory needs makes estimating average costs for these needs impractical. Costs will vary according to the hours needed for each program and according to the salary range of qualified personnel within a given organization.

Sampling manpower needs will also vary widely depending on the conditions listed above. For twenty-four hour composite sampling, a minimum of two shifts (more likely three) are required when automatic sampling devices cannot be used. In addition to the manpower required to actually collect the sample, additional time is required for sample preparation and handling.

Estimates of some of these needs are presented below:

<u>Activity</u>	<u>Manpower</u>
● Automatic Sampler Setup <sup>1</sup>	.5 - 4 manhours
● Sample Container Preparation <sup>2</sup>	2 - 15 <u>man-minutes</u> sample
● Sample Documentation <sup>3</sup>	2 - 15 <u>man-minutes</u> sample
● Sample Handling <sup>4</sup>	2 - 60 <u>man-minutes</u> sample

<sup>1</sup> Depending on sample point characteristics

<sup>2</sup> Depending on parameter

<sup>3</sup> Depending on parameter, ultimate data use and number of points sampled simultaneously.

<sup>4</sup> Depending on parameters sampled and whether samples are analyzed on site, are delivered or shipped.

## 5.2 IN-HOUSE ANALYTICAL COSTS

If any analytical work is done in-house, manpower, equipment/facility and operating (i.e., electrical, chemical supplies, etc.) costs will be incurred. Real costs will vary according to what extent the analytical load imposed by the sludge sampling is marginal to the laboratory's operational capacity. Two extremes serve as examples:

A plant electing to do in-house analysis which has no laboratory would need to make a sizable expenditure for an adequate facility and the necessary analytical equipment and supplies. In addition, laboratory personnel must be put on the payroll. Given these circumstances, it would generally not be practical to do in-house analysis. Instead, it is likely that this plant would contract out for analytical services.

A second plant, conducting a similar sludge sampling program, also elects to do all related analytical work in-house. This plant, however, has an analytical laboratory in place which is capable of performing all analyses required. In addition, the laboratory is presently operating below capacity. The additional load imposed by the sludge sampling program will not require any capital expenditure, and will require little, if any, additional laboratory manpower (any additional manpower needs can be accommodated by limited



overtime rather than new employee hires). In the case of this plant, in-house analysis for a sludge sampling program can be accomplished at a very low real cost.

Because of the wide range of real costs possible for sampling and in-house analytical work, no attempt is made herein to quantify these costs on a dollars per sample basis. Rather, each sampling program must be analyzed in light of applicable salary scales, sampling program complexity and in-house analytical capabilities.

### 5.3 CONTRACT ANALYTICAL COSTS

Many sludge sampling programs, particularly those conducted by small municipalities or authorities, will utilize contract laboratories for analytical work. In contrast to sampling costs, which vary greatly due to a wide variety of factors, contract analytical costs fall within a relatively narrow range. Table 5.1 presents typical analytical costs for parameters commonly run on sludge samples. These cost estimates were obtained in a March 1988 telephone survey of analytical laboratories.

Two factors must be considered in estimating contract analytical costs for sludge sampling programs. The first is the need, depending on parameters, for additional preparation of sludge samples prior to analysis. Many laboratories charge an additional fee for this preparation, which can be as much as \$100, depending on parameters to be run.

The second factor impacting analytical costs is the practice by most laboratories of offering discounts on per sample prices for multiple sample analysis. These discounts vary from laboratory to laboratory, and can be substantial (20% or more) depending on the number of samples involved. Of particular importance is the number of samples being received simultaneously by the laboratory (i.e., a greater discount will typically be offered for 10 samples if all are to be analyzed at one time rather than if one is to be delivered to the lab each week for 10 weeks).

TABLE 5.1 TYPICAL CONTRACT ANALYTICAL COSTS FOR  
COMMONLY ANALYZED PARAMETERS

<u>Priority Pollutant Organics</u>	<u>Sample Cost Range (\$/Sample)</u>
1634/1635	2200 - 2400 <sup>1</sup>
624-S/625-S	1800 - 2200 <sup>1</sup>
<u>Priority Pollutant Metals</u>	
ICAP or AAS	25 - 200 <sup>2</sup>
<u>Conventional Pollutants</u>	
Oil & Grease	15 - 25
Nitrates, Nitrites	10 - 20
Ammonia, as Nitrogen	10 - 20
Total Kjeldahl Nitrogen	10 - 20
Total Suspended Solids, Total % Solids	10 - 20
Total Phosphorus	10 - 20
Digested Phosphate	10 - 50
<u>Pathogenic Pollutants</u>	
Total Coliforms	20 - 45
Fecal Coliforms	20 - 45
Fecal Streptococci	20 - 45
Salmonella	20 - 45
<u>Other</u>	
Cyanide	20 - 30
Phenols	20 - 30
Potassium	20 - 30
Total Organic Halides	50 - 100
Total PCBs	60 - 150

<sup>1</sup>Costs are for complete priority pollutant analysis for organic pollutant

<sup>2</sup>Cost is per metal and will vary depending on number of metals analyzed per sample.

#### 5.4 SAMPLING EQUIPMENT COSTS

The cost of sampling equipment and containers is typically a relatively small fraction of the overall cost of a sludge sampling program. In general, the manual collection methods used for sludge sampling require only simple, relatively inexpensive equipment. The following paragraphs highlight the primary equipment cost items in a typical sludge sampling program.

- **Sample Containers** - Sample container costs are related to: (1) the number of containers needed, and (2) the type of container needed, depending on parameters(s) to be analyzed. The following are typical per-container prices for some commonly used containers:

<u>Container</u>	<u>Size</u>	<u>Approx. Price Per</u>
Teflon	1 liter	\$ 35 - \$40
Graduated Glass		
(w/Teflon-lined cap)	1 liter	\$3.00 - \$4.00
Polypropylene	1 liter	\$2.00
Polypropylene	0.5 liter	\$1.50
Polypropylene	10 liter	\$15.00
Glass		
(w/Teflon lined cap)	0.5 liter	<\$1.00 - \$2.00

As with analytical costs, suppliers of containers often offer substantial discounts for volume purchases.

- **Automatic Samplers** - In most sludge sampling programs automatic sampling equipment will be found to be unsatisfactory due to sample characteristics. If automatic sampling is utilized in a given sampling program, automatic sampler costs will typically constitute the majority of sampling equipment costs. Portable, battery-powered peristaltic-type samplers typically cost from \$1000 to \$3000, depending on features such as computerized controls, etc. Pneumatically operated plunger-type samplers will vary in price according to application and capacity.
- **Manual Sampling Equipment** - In general, equipment costs for manual sludge sampling are minimal. Stainless steel pitchers (2 liter), which are useful for sampling from either a tap or an open channel flow, are available for approximately \$20. Polypropylene pitchers typically cost about 1/2 of the price of stainless steel. Stainless steel scoops used for sludge cake sampling cost approximately \$40 (depending on size), while aluminum scoops of similar size are available for less than \$10.
- **Preservatives** - Reagent grade chemicals should be used as preservatives. Since each sample will typically require very small amounts of preservatives, cost on a per sample basis is negligible.

## 6. REFERENCES

- APHA-AWWA-WPCF. 1976. Standard Methods for the Examination of Water and Wastewater. Washington, D.C.: APHA-AWWA-WPCF.
- Black, C.A. (ed.). 1965. "Methods of Soil Analysis, Agronomy Monograph No. 9." Madison, Wisconsin: American Society of Agronomy.
- Colby, Bruce N., and Ryan, Philip W. 1986. Initial Evaluation of Methods 1634 and 1635 for the Analysis of Municipal Wastewater Treatment Sludges by Isotope Dilution GC/MS. Washington, D.C.: U.S. Environmental Protection Agency, Office of Water Regulations and Standards.
- "Criteria for Classification of Solid Waste Disposal Facilities and Practices," 40 CFR Part 257. Washington, D.C.: National Archives and Records Administration, Office of the Federal Register.
- EPA. 1974. Process Design Manual for Sludge Treatment and Disposal, EPA625/1-74-006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Technology Transfer.
- EPA. 1976. Analytical Methods for Trace Metals, EPA-430/1-76-002. Cincinnati, OH: U.S. Environmental Protection Agency, National Training and Operational Technology Center.
- EPA. 1977. The Sources and Behavior of Heavy Metals in Wastewater and Sludges, EPA-600/2-77-070. Cincinnati, OH: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory.
- EPA. 1978a. Microbiological Methods for Monitoring the Environment, Water and Wastes, EPA-600/8-78-017. Cincinnati, OH: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory.
- EPA. 1978b. Validity of Fecal Coliforms, Total Coliforms, and Fecal Streptococci as Indicators of Viruses in Chlorinated Primary Sewage Sludge Effluents, EPA-600/J-78-175. Cincinnati, OH: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory.
- EPA. 1979. Process Design Manual - Sludge Treatment and Disposal, EPA 625/1-79-011. Cincinnati, OH: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory.
- EPA. 1981. Parasites in Southern Sludges and Disinfection by Standard Sludge Treatment, EPA-600/2-81-166. Cincinnati, OH: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory.
- EPA. 1983a. Process Design Manual - Land Application of Municipal Sludge, EPA-625/1-83-016. Cincinnati, OH: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory.
- EPA. 1983b. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. PB83-170514, QAMS-005/80. Office of Research and Development.

- EPA. 1984a. Multielemental Analytical Techniques for Hazardous Waste Analysis: The State-of-the-Art, EPA-600/4-84-028. Las Vegas, NV: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory.
- EPA. 1984b. Interim Methods for the Measurement of Organic Priority Pollutants in Sludges. Cincinnati, OH: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory.
- EPA. 1984c. Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants in Sludge, EPA-600/4-84-001. Cincinnati, OH: Environmental Monitoring and Support Laboratory.
- EPA. 1984d. USEPA Manual of Methods of Virology, EPA-600/4-84-013. Cincinnati, OH: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory.
- EPA. 1986a. Proceedings: Workshop on Effects of Sewage Sludge Quality and Soil Properties on Plant Uptake of Sludge - Applied Trace Constituents. Las Vegas, NV: U.S. Environmental Protection Agency, Office of Research and Development.
- EPA. 1986b. Test Methods for Evaluating Solid Waste, SW-846. Washington, D.C. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.
- EPA. 1987. Preparation Aid for HWERL's Category II Quality Assurance Project Plans. Cincinnati, OH: U.S. Environmental Protection Agency, Office of Research and Development.
- EPA. 1988a. Analytical Methods for the National Sewage Sludge Survey. Washington, D.C.: U.S. Environmental Protection Agency, Office of Water Regulations and Standards.
- EPA. 1988b. Draft Guidance for Writing Case-by-Case Permit Requirements for Sludge. Washington, D.C.: U.S. Environmental Protection Agency, Office of Water Enforcement and Permits.
- "Guidelines for Establishing Test Procedures for the Analysis of Pollutants," 40 CFR Part 136 . Washington, D.C.: National Archives and Records Administration, Office of the Federal Register.
- "Memorandum: Pathogen Equivalency Committee," U.S. Environmental Protection Agency, Office of Water, November 2, 1987.
- Metcalf and Eddy, Inc. 1979. Wastewater Engineering. Treatment, Disposal, Reuse. New York: McGraw-Hill Book Company.

## APPENDIX A

# Chain of Custody Record

W.O. No.		Project Name:		Sample Type	Number and Type of Containers						Remarks
Sampler: (Signature)											
Sa. No.	Date	Time	Station Description								
Relinquished By: (Signature)		Date	Time	Received By: (Signature)		(Print)		Comments			

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Source: 1987 EPA Document  
 "Preparation Aid for HWERL's Category II  
 Quality Assurance Project Plans"