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POTW Sludge Sampling And Analysis Guidance Document

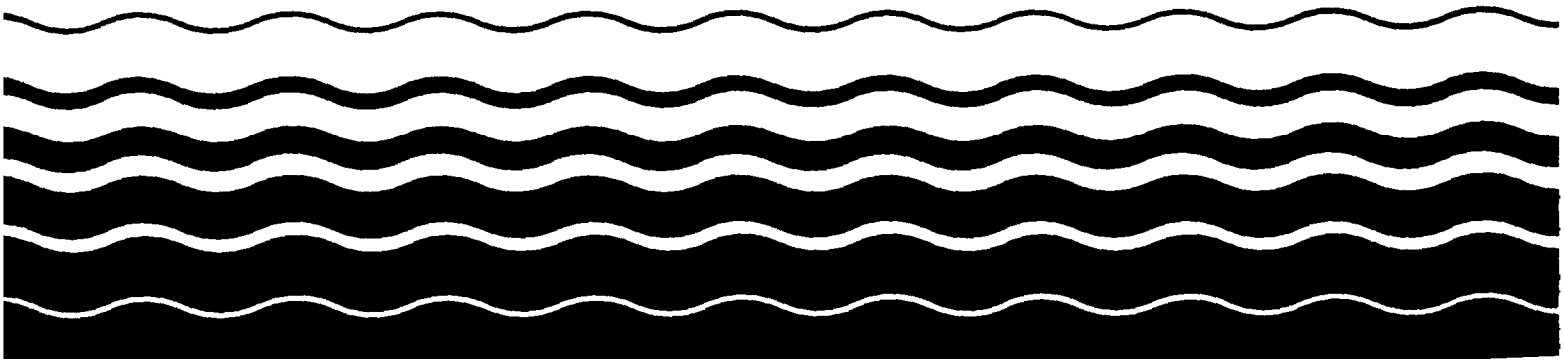

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

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1. INTRODUCTION

The passage of the 1987 amendments to the Clean Water Act brought about significant changes in the regulation of the use and disposal of municipal sewage sludge. Although the Clean Water Act had required since 1977 that EPA develop technical standards for sludge use and disposal, the 1987 amendments required that these standards, when promulgated, be implemented through permits. The amendments also state that prior to promulgation of the technical standards, EPA must include sludge conditions in NPDES permits issued to publicly-owned treatment works or take other appropriate measures to protect public health and the environment from pollutants in sewage sludge. This requirement has initiated a program for "case-by-case" permitting to ensure protection of the environment prior to the issuance of final sludge standards which are scheduled for promulgation in October 1991.

This focus on sludge permitting places increased emphasis on the need to assess sewage sludge quality. In policy and guidance documents that EPA has developed for implementing the sludge requirements of the Clean Water Act, the Agency has recommended that POTWs sample and analyze their sludge at least annually to determine if the sludge quality is such that the sludge may be safely reused and recycled or disposed. Accurate characterization of sludge composition spots operational problems at the treatment works and may also signal adverse environmental impacts. In addition, sludge sample and analysis is needed to assess compliance with current requirements (e.g., 40 CFR Part 257 requirements for cadmium and PCBs).

In view of the variability of municipal sludge quality, appropriate procedures must be followed to collect and analyze samples that accurately represent each POTW's sludge quality. This manual was developed to provide that guidance to POTW operators, engineers, managers, chemists and permit writers. It was intended to provide guidance in developing and implementing a sampling and analysis program, to gather information on sludge quality and determine compliance with permit conditions. This manual is based on current, state-of-the-art field and laboratory practices and therefore is recommended for all sludge sampling and analysis programs.

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 much higher solids content than most wastewaters. Solids content and solids settling characteristics determine whether a given sludge will separate into different fractions which increases the potential of obtaining a nonrepresentative sample.

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. Automatic samplers that rely on pumps may be useful only for liquid sludges with a solids content of less than 20 percent. However, sludge cakes require manual grab sampling. Other problems created by sludge

solids (see Section 2.3.1) generally preclude the use of automatic samplers.

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 and increase analytical accuracy, or carry away pollutants and decrease pollutant concentration and analytical accuracy. Analytical precision (repeatability) and accuracy (closeness to true value) may also decrease as the concentration of interfering compounds and matrix effects increase, due to higher solids content after dewatering.

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 dewaters easily and has a non-offensive odor. The addition of chemicals coagulates a digested sludge prior to mechanical dewatering. The dry residue of digested sludge contains 30 to 60 percent volatile solids. Depending on the mode of digester operation, the percent 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 depend on the type of sludge, chemical conditioning, and treatment processes employed. The percent solids content of dewatered cake ranges from 15 to >40 percent. Cake with a lower percent solids is similar to a wet manure, while cake with a higher percent solids 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 containing 75 to 80 percent solids. 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.

Incinerator ash is a product of the incineration of sewage sludge. Ash is therefore not covered under the sampling or analysis of sewage sludge. It is covered under RCRA Subtitle C if it is a hazardous waste and if not it falls under Subtitle D.

2.2 SAMPLE POINT SELECTION

2.2.1 General Considerations

NPDES, pretreatment and sludge 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:

- Does the sample point represent the entire sludge stream?
- Are the sludge stream flow or mass flux data available?

The following paragraphs examine both factors and present recommendations on means to address each factor.

2.2.1.1 Sample Point Representation of the Entire Sludge Stream

Often it is not possible to obtain a wholly representative sample of a given wastestream at any one time. Effort must be made, however, to ensure that a sample is obtained that is as representative as possible. Three concerns that need to be

addressed to ensure that the sample points selected will provide representative samples of the entire sludge stream are: obtaining samples that are representative of the cross-section of the entire flow; obtaining well mixed samples; and obtaining samples of multiple sludge streams.

A particular concern in any sampling program is to obtain samples which represent the entire flow past the sample point throughout the sample period. Each discrete sample should represent the cross-section of the entire flow at the sampling point. Each composite sample of multiple contributory streams should represent the cross-section of the entire flow of the combined stream.

Samples should be obtained from points where the sludge is well-mixed. While some pollutant parameters are predominantly associated with the solids fraction (particularly precipitated metals), others are more associated with the liquid-fraction (many dissolved organics). 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. Since turbulence ensures mixed samples, these recommendations should be followed:

- In sludge processing trains, samples from taps on the discharge side of sludge pumps are well mixed since flow at this point in the system is turbulent with no solids separation within the flow stream.
- If a sample is drawn from a tap on a pipe containing sludge which is distant from the sludge pumps, the average flow velocity through the pipe should be greater than 2 feet per second (fps). 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.

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.

Although it is preferable to sample sludge just prior to its exit from the treatment plant in a combined stream, sometimes that is not possible. Therefore, a consideration in many sludge sampling situations is the need to produce a composite sample from confluent streams. An example is the sampling of sludge flows from several parallel sources which later combine downstream in an unsafe or inaccessible location. Several options exist to accommodate multiple streams. The most appropriate choice depends on the sludge flow and solids flux 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 of the multiple sludge streams to create a 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. However, 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 application rates.

2.2.1.2 Availability of Flow Data and/or Solids Flux Data

The availability of accurate solids flux data (weight/time) or accurate flow data (volume/time) 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 solids flux of pollutant parameters found in sludge discharged from a POTW. The percent solids should be determined on sludge samples.

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. This data should be cross-checked against mass balance data. When ultimate use or disposal practices dictate monitoring sludge with

a high solids content, liquid flow meters are replaced by gross weight scales. Table 2.1 summarizes the types of flow measurement equipment employed to monitor various sludge flows.

2.2.2 Sludge Sample Points

The determination of the appropriate sludge sampling point is dependent on the rationale behind the sampling. For permits and regulation enforcement, sludge samples must come from the treatment unit process immediately preceding disposal or use. For example, if a POTW disposes of its dewatered filter cakes in a sanitary landfill, then sampling activity focuses on the output sludge stream from the dewatering device (i.e., vacuum filter, belt filter, etc.). The sludge treatment processes commonly employed are stabilization, dewatering, drying, composting, and thermal reduction. Table 2.2 summarizes sampling points for these processes. Other sludges sampling points may be necessary to examine the origin or fate of pollutants within a POTW, (i.e., additional sludge samples from influent and output of other processes may be needed).

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 safe, convenient and efficient.

TABLE 2.1. 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

TABLE 2.2. SLUDGE SAMPLING POINTS

Sludge Type	Sampling Point
Anaerobically Digested -	Sample from taps on the discharge side of positive displacement pumps.
Aerobically Digested -	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: (1) If aerated during sampling, air entrains in the sample. Volatile organic compounds may purge with escaping air. (2) When aeration is shut off, solids separate rapidly in well digested sludge.
Thickened Sludges -	Sample from taps on the discharge side of positive displacement pumps.

TABLE 2.2. SLUDGE SAMPLING POINTS
(continued)

Sludge Type	Sampling Point
Heat Treatment	Sample from taps on the discharge side of positive displacement pumps <u>after</u> decanting. Be careful when sampling heat treatment sludge because of: (1) High tendency for solids separation (2) High temperature of sample (frequently >60°C as sampled) can cause problems with certain sample containers due to cooling and subsequent contraction of entrained gases.
Dewatered, Dried, Composted, or Thermally Reduced various depths.	Sample from material collection conveyors and bulk containers. Sample from many locations within the sludge mass and at
Dewatered:	
Belt Filter Press, Centrifuge, Vacuum Filter Press	Sample from sludge discharge chute.
Sludge Press (plate and frame)	Sample from the storage bin; select four points within the storage bin, collect equal amount of sample from each point and combine.
Drying Beds	Divide bed into quarters, grab equal amounts of sample from the center of each quarter and combine to form a grab sample of the total bed. Each grab sample should include the entire depth of the sludge (down to the sand).
Compost piles	Sample directly from front-end loader as the sludge is being loaded into trucks to be hauled away.

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 two important considerations for selecting appropriate sludge sampling methods: sampling equipment and proper sampling practices.

2.3.1 Sampling Equipment

In general, automatic sampling devices, which are widely used for wastewater streams, do not work well for sludge streams because of the solids content and viscosity of sludges. 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 fouling of tubing and/or pump structure 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.

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, plastic, 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 into the sample.)

Graduated glass or plastic pitchers or cylinders are used to draw grabs for manually composted 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 that should be followed when sampling sludges:

- Clean all sampling equipment between each sample period to prevent cross-contamination. Cleaning consists of thorough washing with a laboratory detergent, thorough rinsing with tap water and then with at least three distilled water rinses.

- Sample aliquots should be composted 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 and 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.

- Sample collection procedures should be adequately documented, as discussed in Section 2.7.

- When collecting samples for organic volatiles or semi-volatiles, carefully pour liquid sludge into container so as to avoid entrapping air within sample. Fill container to overflowing and screw on lid. Check air bubbles by turning container upside down and tapping lid. If air bubbles rise, open container and fill with additional sample. For sludge cake, care-fully pack sludge into container so as to avoid air spaces. Fill the container to overflowing and screw on lid.

- When collecting samples for dioxin/furan, fill the container to 4/5 full to enable expansion of samples when they are frozen.

- When collecting samples for pesticides/PCBs/herbicides, metals and nonconventionals, fill container to within 1/2 inch of the top to provide room for expansion should there be any gas production during sample shipment.

When sampling liquid sludges:

- To draw a fresh representative sludge sample from a tap:

  a) Allow sufficient time following pump start up 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.

- To prevent solids separation in the sample, use glass, Teflon-coated stirring rods, or stainless steel spoons to mix the sample before splitting or transferring any portion of it to another container(s).

When sampling solid sludges:

- 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.

  a) To produce a sample from multiple sample locations (e.g., two or more dewatering units), combine the grab samples from each location (equal amounts or weighted based on flow or solids flux data) in a plastic or stainless steel pail and thoroughly mix the sample (with a scoop or spoon), then transfer it to sample containers. This is not appropriate for volatile or microbial samples.

b) When sampling drying beds, divide each bed into quarters. From the center of each quarter, collect a single core sample through the entire depth of the sludge using a coring device. Usually a small amount of sand will be collected; avoid large amounts of sand. Combine and thoroughly mix in plastic or stainless steel pail and transfer to sample containers.

2.4 SAMPLE SIZE, SAMPLE TYPE, AND SAMPLING FREQUENCY

Sample Size

A proper sample is small enough to transport conveniently and handle carefully in the laboratory, but large enough to accurately represent the characteristics of the whole material. Minimum sample sizes required for accurate analysis are specified in each analytical method. Table 2.3 lists minimum sample sizes for some common analytical methods. For methods not listed here, consult an analytical methods reference or the laboratory for further guidance.

Sample Type

A grab sample collected at a particular time and location can represent the composition of the source only at that time and location. 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. Although a 24-hour composite

TABLE 2.3

CONTAINERS, PRESERVATION, HOLDING TIMES, AND MINIMUM SAMPLE VOLUMES[1]

Parameter	Wide-mouthed Container	Preservative[2]	Maximum Holding Time[2]	Minimum Sample Volume[3]
Inorganic Compounds				
Asbestos	P,	None	None	2000 mL
Metals				
Chromium VI	P,G	Cool, 4°C	24 hours	300 mL
Mercury	P,G	HNO_3 to pH<2	28 days	500 mL
Metals except above	P,G	HNO_3 to pH<2	6 months	1000 mL
Organic Compounds				
Extractables (including phthalates, nitrosamines, nitroaromatics, isophorone, polynuclear aromatic HC, haloethers, chlorinated HC and TCDD)	G, teflon-lined cap P, for dioxin and furan only	Cool, 4°C 0.008% $Na_2S_2O_3$	7 days (u) 40 days (a)	1000 mL
Extractable (phenols)	G, teflon-lined cap	Cool, 4°C H2SO4 to pH<2 0.008% Na2S2O3	7 days (u) 40 days (a)	1000 mL
Purgeables (Halocarbons and Aromatics)	G, teflon lined septa	Cool 4°C 0.008% $Na_2S_2O_3$ 1:1HCl to pH 2	7 days (w/o) 14 days in darkness	>20 mL
Purgeables (Acrolein and Acrylonitrile)	G, teflon lined septa	Cool 4°C 0.008% $Na_2S_2O_3$ pH to 4 or 3	14 days	>20 mL

TABLE 2.3 (Continued)

CONTAINERS, PRESERVATION, HOLDING TIMES, AND MINIMUM SAMPLE VOLUMES[1]

Wide-mouthed Parameter	Container	Preservative[2]	Maximum Holding Time[2]	Minimum Sample Volume[3]
Pesticides & PCBs	G, teflon-lined septa	Cool 4°C 0.008% $Na_2S_2O_3$	7 days (u) 40 days (a)	1000 mL

(1) 40 CFR Part 136

(2) Preservatives should be added to sampling containers prior to actual sampling episodes. Holding times commence upon addition of sample to sampling container. Shipping of pre-preserved containers to the sample sites may be regulated under DOT hazardous materials regulations. Shipping of preserved samples to the laboratory is generally not regulated as a hazardous material.

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

P = Plastic (Polyethylene)

G = Glass (Non-etched Pyrex)

(a) After extraction

(u) Before extraction

(w/o) Without preservatives

sample (consisting of a number of time- or flow-weighted grab samples) is more representative than a grab sample, it can give a picture of only one day's sludge quality. Historical data is necessary to truly represent the sludge quality. A composite for volatile components analysis is produced in the lab from grab samples collected in the field.

Sampling Frequency

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 obtain representative data. Collection of representative sludge data is crucial because the permitting authority will use the resultant analytical data to establish permit monitoring parameters and frequencies, and thereafter, to assess compliance with the permit and to ascertain if there is a potential for adverse environmental impacts. POTW operators should be aware that EPA's "Strategy for Interim Implementation in Permits Issued to POTWs" (draft June 1988) to be finalized during the fourth quarter of 1989) sets forth minimum recommended monitoring frequencies to be included in the NPDES permit when it is reissued. The Interim Strategy is scheduled to be finalized in the summer of 1989. The NPDES permit writer may decide based on his/her best professional judgment (BPJ) that more frequent monitoring is needed. The sampling frequency will be set out in the POTW's permit.

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.

- Anticipated cyclical variation in pollutant loadings - although they are difficult to accurately predict, 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.

- **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.

Other factors that should be considered in determining sampling frequency include:

- **Size** - As influent flow increases, day-to-day sludge variability increases, as does outflow volume. Thus, where high volumes exist, the risk of adverse exposure is higher. Since variability and potential impact are major considerations, many sampling programs are based on size alone (e.g. 40 CFR Part 503 proposed rule). Size is also an easy factor to measure.

- **Percentage of industrial flow** - 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.

- **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 technologie , 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.

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.

2.5 SAMPLE PREPARATION AND PRESERVATION

There is the potential for errors of varying severity to be introduced during sample collection and storage which affect analytical determinations. 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 2.3 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 caps which can cause sample contamination (phenol, phthalate compounds). For organic parameters, these glass container caps should be fitted with Teflon liners; aluminum liners could be used but they must be fitted precisely within the circumference of the cap to prevent tearing and possible sample leakage.

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 detergent, thoroughly rinsed with tap water, and then rinsed at least 3 times with distilled water prior to air drying. Additional container preparations for analysis of particular parameters are described below:

- **Extractable Organics** - Use glass containers with Teflon-lined caps only. Wash containers as above and rinse with solvent (typically methylene chloride); air-dry.
- **Volatile Organics** - Prepare containers by washing and rinsing as described above, and then bake both vials and septums at 105°C until dry. Cool in an organic-free atmosphere.
- **Metals** - Wash and rinse as described above. Then rinse with dilute acid (1 part deionized, distilled water to 1 part nitric acid (HNO_3)), followed by two rinses with deionized, distilled water.

2.5.3 Sample Preservation

Table 2.3 presents U.S. EPA's 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. This does not apply to samples for analysis of volatile, semivolatile or microbial contaminants.

- If processing of microbial samples cannot occur within one hour of collection, iced coolers should be used for storage during transport to the lab. Samples should be held below 10°C during the maximum transport time of 6 hours. Note: these samples must be immediately refrigerated and processed at the lab within 2 hours of receipt.

- Whenever possible, sample containers should be pre-preserved. Thus, grab samples are preserved upon sampling and composite samples are preserved during compositing. This is not appropriate, however, when sampling for metals or pathogens.

- In general, all samples should be chilled (4°C) during compositing and holding.

- For solid sludge samples (cake), adding chemical preservative is generally not useful since the preservative usually does not penetrate the sludge matrix. Preservation consists of chilling to 4°C.

- When sampling and holding sludges, particularly biologically active sludges, gas production in the sealed container may cause an explosion unless the pressure is periodically released. This should not be

done however if volatile or semivolatile pollutants are to be analyzed.

2.5.4 Holding Time Prior to Analysis

Table 2.3 lists the maximum holding times for various pollutant samples. Table 2.4 lists some potential interferences that may affect samples during shipping and storage. There are many more interferences associated with particular analytical methods, which are discussed further in chapter 3 as well as in the particular methodology.

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 in order 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.

TABLE 2.4

POTENTIAL INTERFERENCES ASSOCIATED WITH
SAMPLE SHIPPING AND STORAGE

Parameter	Interferences[1]	Prevention
Acidity	Carbon dioxide loss	Fill container completely
Ammonia	Chlorine Volatilization	Sodium thiosulfate Fill container completely
Cyanide	Sulfides	Cadmium nitrate, tetrahydrate
Chromium VI	Reducing agents	Minimize holding time
Phenols	Hydrogen sulfide, Sulfur dioxide Oxidizing agents	Aerate Ferrous sulfate
Silica	---	Avoid freezing
Sulfide	Aeration, agitation	Fill container completely
Sulfite	Aeration, agitation	Fill container completely
Organic Chemicals	Photodegradation	Use brown glass container

1 Other than those addressed by protocols shown in Table 2.3

- When environmental samples are preserved as recommended (see Table 2.5), 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). A material is considered hazardous by DOT if it fails one of the four characteristic tests of: corrosivity, ignitability, reactivity and EP Toxicity [see "Test Methods for Evaluating Solid Waste, SW 846, 1986 for exact methods]. Municipal sewage sludges labeled as hazardous are usually from failed EP Toxicity tests and occasionally from reactivity tests.

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 procedures and a log book of sampling activities. The number of people in the chain of custody should be kept to a minimum to limit the possibility of contamination and to increase accountability.

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

TABLE 2.5

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	Hydrochloric acid	<2 ->1	2 ml of 1:1	0.04%
Nitrogen Species	Mercuric chloride	N.A.	40 mg	0.004%
Metals, Hardness**	Nitric acid	<2 - >1	5 ml of Conc. (70%)	0.35%
Nitrogen Species COD, Oil & Grease, P (hydrolyzable) Organic Carbon	Sulfuric acid	<2 - >1	2 ml of 36N	0.35%
Cyanides	Sodium hydroxide	>12 - <13	2 ml of 10N	0.080%
Phenolics	Ortho-phosphoric acid	<4 - >2	to yield desired pH	
Biological - Fish & Shellfish Tissue***	Freezing $0^{o}C$ (Dry Ice)	N.A.	N.A.	N.A.

* Sample dilution must be avoided. The volume of washings must be minimized and any dilution that does occur must be documented and the data corrected for the dilution.

** 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_3 to pH<2. At time of analysis, sample container should be thoroughly rinsed with 1:1HNO_3; 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.

- o Sample Number (specific to sampling event i.e. location)
- o Type of sample, i.e., grab, 24 hour composite, etc.
- o Date, Time (24 hour time is preferable, i.e., 1600 vs. 4:00 p.m.)
- o Sample Location
- o Preservatives
- o Analytical Parameter(s)
- o Collector
- o 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 shipment 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, the chain-of-custody procedure ensures an enforceable record of sample transfer which is necessary if the sample results are to be used in a judicial proceeding alleging violations of sludge standards. This document shall record each sample's collection and handling history from time of collection until analysis as well as the information listed on each sample bottle. 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 potential presence of toxic substances, 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.

Gas production from biologically active sludge samples may cause pressure build up, especially if the samples are not stored at 4°C as recommended in Table 2.3. Treating samples with the appropriate preservatives (e.g., acids for metals samples) as

well as refrigeration will significantly suppress biological activity and therefore gas evolution. However, except for volatile and semi-volatile analysis samples, pressure may need to be periodically released to prevent explosions of the sealed sampling containers. The field control sample should also be vented to expose it to the same potential contaminants.

There are several universal safety precautions that are applicable to sludge sampling as well. When sampling sludge in confined areas, particularly around anaerobic digesters, dangerous gases may be present. 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 detection meters and backup breathing apparatus. 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 is compositionally diverse, rich in organic matter, and highly variable in physical and chemical properties. Sewage sludge analysis is difficult because of the inherent complexity of sludge matrices. 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, which is exacerbated in sludges, 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. Often sludge samples must be diluted to attain analytical results. A tenfold sample dilution means a tenfold increase in the detection limit (e.g., 1 ppm to 10 ppm). This increases the complexity of attaining accurate, precise data.

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, inorganics, priority pollutant metals, priority pollutant organics, and pathogenic organisms are discussed.

3.1 CONVENTIONAL AND INORGANIC POLLUTANT PARAMETERS

Conventional pollutant parameters have historically been the focal point of sewage sludge analyses. The parameters normally associated with this group include total suspended solids, pH, oil and grease, BOD and fecal coliform. Inorganics, which have also been of concern, include 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.

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 background soil cation exchange capacity (CEC). Soil pH should be measured using a 1:1 solution of sludge-soil mixture and deionized water (see Table 3.1). For distinctly acid soils, CEC should be measured using the summation method (see Table 3.1). For neutral, saline, or calcareous soils, the sodium acetate method should be used (see Table 3.1).

Another inorganic of more recent concern is asbestos. Asbestos is a generic term which refers to naturally occurring, commercially useful fibrous silicate mineral. There are two types. Chrysotile, which comprises 93 percent of the current asbestos production, is a hydrated magnesium silicate which exhibits a much higher cancer risk for textile workers. Amphibole, which occurs in five forms, crocidolite, amosite, actinolite, tremolite and anthrophyllite, is a hydrated silica associated with various lung carcinogenic trace metals (nickel, chromium, aluminum and iron). Crocidolite poses the greatest health risk of all asbestos types and is the riskiest to miners and millers.

TABLE 3.1

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
Phosphorous (Ortho & Total)	Acidic Digestion Turbid samples must be filtered after digestion	C	B St Sp	0.001	- High iron concentration can cause precipitation and loss of phosphorous - Turbidity interference - 24 hr-holding time	(1) 365.3
Total Kjeldahl Nitrogen	H_2SO_4 digestion	C	B St	0.05	- Digestion solution 2 times for sludge - 24 hr-holding time - Fe + Cr catalyze; Cu inhibits reaction	(1) 351.2, 3
Ammonia	Colorimetric reaction	C ISE	Sp	0.05	- Hg can complex with NH_4 - Filter sample - Distillation required prior to analysis	(1) 350.1 350.2, 3 (2) 417A, B, D, E, G
Nitrate	Reaction to brucine sulfate or Nitrate-nitrite N minus Nitrite N	C		0.1	- Dissolved organic matter	(1) 352.1 (3) 9200
Nitrate-Nitrite	Hydrazine or Cd reduction	C		0.05	- Filter sample for Cd - Strong oxidizing or reducing agents - Suspended matter in reduction column - Samples which contain high conc. of metals or organics	(1) 353.1, or 353.2
Nitrite	Diazotization	S		0.5		(1) 354.1 (2) 419

TABLE 3.1 (Continued)

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
Cyanide	CN converted to HCN by reflux-distillation	C	B St Sp	0.02	- Fatty acids and sulfides interfere	(1) 335.2 (3) 9010, or 9012
Phenolics	Distillation and extraction	C	B St Sp	0.002	- 24 hr-holding time - Sulphur compounds and oxidizing agents interfere	(1) 420.1 (2) 510A or C (3) 9065, 9066, 9067
Total Organic Carbon	Inorganic carbon removal	Catalytic combustion & dispersive IR	B St Sp	1.0	- Carbonate + bicarbonate interfere	(1) 415.1 (2) 505A (3) 9060
Chemical Oxygen Demand	Oxidation to potassium dichromate and HCl	Titration	B St Sp	5.0	- Possible loss of volatiles - Chloride oxidation could be an interference	(1) 410.1, (Block digestion) (2) 1508 A or B
Biochemical Oxygen Demand	Incubation	Measurement of reduction in DO	B St Sp	2.0	- 5-day incubator	(1) 405.1 (2) 507
Oil and Grease	Solvent extraction	G	B Sp	5.0		(1) 413.1,2 (2) 503A, D (3) 9070, or 9071
pH	Solution in suspension with fluid	ISE	St	---	- Interference from solids and oily residues	(1) 150.1 (3) 9040 (4) p. 900, 57-4
CEC	$BaCl_2$/treatment (acid exchange) (base exchange)	T C	None cited in references		- Acid soils	(3) 9080 (4) Ibid.

TABLE 3.1 (Continued)

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
CEC	Na acetate sludge sol'n, isopropanol wash, NH_4 acetate exchange	Emission or absorption AAS	One B per batch	No data available	- Neutral, saline, or calcareous soils	(3) 9081 (4) p. 891
Solids	Filtration	Gravimetric	B	4.0-10.0		(1) 160.1 or .5
% Solids	Evaporation	Gravimetric	B	N/A		(1) 160.3 (2) 209A

(1) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.

(2) Standard Methods for the Examination of Water and Wastewater, 16th Edition, Mary Ann Franson, managing ed., American Public Health Association, Washington, DC, 1985.

(3) Test Methods for Evaluating Solid Waste, Third Edition, (SW-846), EPA, September 1986.

(4) "Methods of Soil Analysis", Agronomy Monograph Number 9, C.A. Black, ed., American Society of Agronomy, Madison, Wisconsin, 1965.

(a) C Colorimetric; DO - Dissolved Oxygen; G - Gravimetric; IR - Infrared; ISE - Ion Selective Electrode; S - Spectrophotometric; T - Titration

(b) B - Blank(s); St - Standards; Sp - Spike(s)

In certain cases, such as when large scale asbestos removal is/will occur during the permit term or in municipalities where asbestos industries are located, the permit writer or the permittee may feel that sampling the sewage sludge for asbestos is warranted. Consult Table 2.4 for the appropriate sample sizes, containers, preservatives and holding times. Unless sample preparation will be within 48 hours, the sample should be refrigerated or stored in the dark to prevent bacterial growth.

Although there are tests which differentiate between the various asbestos types, current research does not associate health risk with specific types. The risk from asbestos is directly proportional to the concentration of airborne respirable particles. Thus current recommended analytical detection methods count fibers per area. Respirable particles are those with a diameter (length in this case) of less than 2 microns, which can only be detected using transmission electron microscopy (TEM). The polarized light microscopy (PLM) method does not detect respirable particles.

3.2 METALS

There are several analytical techniques used for the 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 most frequently used approach involves determination of the total metal content or other materials of interest, without regard to chemical form. The analytical techniques for such determinations

are designed to solubilize all of the metal species (bound to organic particulates and mineralogically bound). In the other approach, often referred to as the "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 steps for sample preparation of metals in sewage sludge are (1) 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 <u>total</u> 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 (HNO_3), hydrofluoric acid (HF), hydrochloric acid (HCL), and perchloric acid ($HCLO_4$); while hydrogen peroxide and perchloric acid are

common oxidizing reagents. High temperature (550°0C) 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 techniques to estimate the amount of inorganic and organic contaminants which may be leached from the sludge after disposal in landfills or surface impoundments are the Extraction Procedure protocol and the Toxicity Characteristic Leachate Procedure. In both procedures the sludge is maintained in an aqueous slurry under a given set of conditions, after which contaminant levels are measured on the filtered aqueous media. The Extraction Procedure (EP) test developed by EPA (in response to RCRA legislation) to evaluate the impact of landfill waste disposal practices on subsurface and surface waters (40 CFR Part 261 Appendix II) evaluates criteria for 8 metals and 6 pesticides. The proposed Toxicity Characteristic Leaching Procedure (TCLP) 51 Federal Register 21648 is expected to be promulgated in August/September of 1989. The TCLP test which evaluates the same 8 metals and 6 pesticides and an additional 38 compounds will replace the EP test after promulgation.

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 (ICAP). Samples prepared by this method may be analyzed by ICAP for all the metals listed below, or by FLAA or GFAA as indicated:

FLAA		GFAA	
Aluminum	Lead	Arsenic	Manganese
Antimony	Magnesium	Beryllium	Nickel
Barium	Manganese	Cadmium	Selenium
Beryllium	Nickel	Chromium	Silver
Cadmium	Potassium	Cobalt	Zinc
Calcium	Silver	Copper	Thallium
Chromium	Sodium	Iron	Vanadium
Cobalt	Thallium	Lead	
Copper	Tin		
Iron	Vanadium		
	Zinc		

Method 3050 prepares samples for analysis of total metals (except mercury, silver and antimony) determination through vigorous digestion in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. This method is not appropriate for mercury, silver, and antimony because of potential for volatilization. For the digestion and analysis procedures for mercury, silver and antimony, 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 (ICAP). 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 (although not as low as AAS, and not strongly inhibited by matrix variation); costs are moderate since

TABLE 3.2.

RECOMMENDED PREPARATION TECHNIQUE
FOR ELEMENTAL ANALYSIS OF SLUDGE SAMPLES

METHOD 3050[1]

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 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 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% H_2O_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% H_2O_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% H_2O_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.

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 ICAP instruments (more than $100,000).

The basic principle behind atomic absorption spectroscopy is the opposite of the emission method, ICAP. In AAS, the analyte (metal) is dissociated into atoms in a flame or furnace, and passed through a light beam from the reference source. This reference source emits a beam of the characteristic atomic spectrum of the analyte. The analyte in the sample will absorb this energy thus decreasing the original signal to the detector from the reference beam. Since absorption is directly proportional to concentration, the analyte concentration can be determined. Selection of a specific wavelength which corresponds to one of the more intense characteristic line of the analyte's spectra allows for high element specificity. For this reason, AAS is more responsive than ICAP to lower concentrations of metals in sludge. However, this very precise nature of AAS is also the cause of its major drawback: only one elemental determination per sample is possible at a time. Thus, the total analysis time of AAS is significantly greater than that of ICAP 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, ICAP'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. 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 ICAP and AAS.

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	+	-
Spectral Interference	-	+
Matrix Interference	+	-

\- disadvantage
\+ advantage
++ extra advantage

ICAP Method 6010

EPA recommends Method 6010 for the determination of metals in solution by Inductively Coupled Argon Plasma atomic emission spectroscopy (ICAP). 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 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

EPA 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 complete set of procedures for each metal-specific method may be found on pages 7000-1 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. Ground water, aqueous samples other than drinking water, 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

[1] 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 3.4

RECOMMENDED INDUCTIVELY COUPLED WAVELENGTHS
AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Wastewater Estimated Detection Limit[b] (ug/L)	EMSL's Best SLUDGE Detection Limit[c] (ug/L)	EMSL's Estimate of Routine SLUDGE Limit (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	1	5
Calcium	317.933	10	--	--
Chromium	267.716	7	--	--
Cobalt	228.616	7	--	--
Copper	324.754	6	5	10
Iron	259.940	7	--	--
Lead	220.353	42	20	50
Magnesium	279.079	30	--	--
Manganese	257.610	2	--	--
Molybdenum	202.030	8	10	30
Nickel	231.604	15	--	--
Potassium	766.491	See note d	--	--

TABLE 3.4 (cont.)

RECOMMENDED INDUCTIVELY COUPLED WAVELENGTHS
AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Wastewater Estimated Detection Limit[b] (ug/L)	EMSL's Best SLUDGE Detection Limit[c] (ug/L)	EMSL's Estimate of Routine SLUDGE Limit (ug/L)
Selenium	196.026	75	75	100
Silicon	288.158	58	--	--
Silver	328.068	7	--	--
Sodium	588.995	29	--	--
Thallium	190.864	40	100	150
Vanadium	292.402	8	--	--
Zinc	213.856	2	5	15

Reference: Test Methods for Evaluating Solid Waste: SW-846.

a 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.

b The estimated instrumental detection limits are 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.

c EPA's Environmental Monitoring Support Laboratory detection limit ranges.

d Highly dependent on operating conditions and plasma position.

TABLE 3.5

ATOMIC ABSORPTION FLAME AND FURNACE INSTRUMENTAL DETECTION AND SENSITIVITY LIMITS FOR WASTEWATER SAMPLES

Metal	Direct Aspiration Detection Limit (mg/L)	Direct Aspiration Sensitivity (mg/L)	Furnace Procedure[a,c] Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	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	0.01	0.05	--
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel(p)	0.04	0.15	--
Potassium	0.01	0.04	--
Selenium[b]	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--

Reference: Test Methods for Evaluating Solid Waste: SW-846.

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

a For furnace sensitivity values, consult instrument operating manual.

b Gaseous hydride method.

c 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.

d Cold vapor technique.

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.

Antimony and Silver Analysis

The procedures for preparation of antimony and silver samples are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for antimony. It yields better recoveries than either Method 3010 or 3050. There is no hard digestion for antimony at this time (SW-846, Nov. 1986, 3rd Ed., p. 7041-2). Samples prepared by Method 3005 are amenable to determination by either ICAP Method 6010 or the atomic absorption furnace technique, Method 7041. (SW-846, 3rd Ed. - see pp 7041-1 through 7041-4). Detection limits for Method 7041 are 3 ug/L for antimony and 10 mg/l for silver.

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.

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 semi-volatile 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 (1624C, 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.

Semi-volatile 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. However,

sand, a fairly common constituent of sewage sludge, literally chews up high speed homogenizers.

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 for the listed applications include:

- Gel permeation resins - broad spectrum cleanup and higher molecular weight biogenic organics
- Activated carbon - fractionation and general purpose cleanup
- Alumina adsorbent - inorganic adsorbent
- Florisil adsorbent - inorganic adsorbent
- Silica gel adsorbent - inorganic adsorbent
- 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 1624C (EPA 1988a)
- Semi-Volatile Organics - 625-S (EPA 1984b) or 1625C (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 extract is vaporized quickly at an elevated temperature and carried by an inert gas (mobile phase) through a coated column (stationary phase). Separation of the extract components is effected 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 three to five 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 1624C and 1625C

Methods 1624C and 1625C are draft methods for analyzing volatile organics (Method 1624C) and base/neutral, non and semi-volatile organics (Method 1625C) 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 1624C/1625C (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 contaminant concentrations. Methods 1624C/1625C and 1624/1625 are similar in this respect but differ in sample preparation.

Method 1624C 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 1625c 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.

These methods are currently undergoing revision at EPA's Environmental Monitoring and Support Laboratory for problems relating to the sample preparation portions. They are the

methods used in the National Sewage Sludge Survey (which EPA is conducting to provide a current data base to be used to set pollutant limits, evaluate risks of use and disposal practices, and evaluate the impacts of the proposed rule) and also are discussed in the 40 CFR Part 503 regulation proposed on February 6, 1989 and now out for comment. Depending on the results of the comment period, the isotope dilution methods may be exclusively required for priority pollutant organics analysis when 40 CFR Part 503 is finalized.

3.3.2.2 Methods 624-S and 625-S

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

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 column GC/MS (HRGC/MS) is preferred since HRGC/MS allows easier data interpretation.

While Methods 1624C/1625C provide lower detection limits, in some cases, than Methods 624-S/625-S, these methods are also more costly. Presently, Methods 1624C/1625C 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.

Neither Methods 624-S/625-S or Methods 1624C/1625C 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 situations where lower detection limits are crucial such as in PCB or pesticide analysis, megabore column analysis is necessary.

3.4 PATHOGENIC MICROORGANISMS

A pathogen or pathogenic agent is any biological species that can cause disease in the host organism (primarily humans). These organisms fall into four broad categories: viruses,

bacteria, parasites, and fungi. From these categories, species commonly found in sewage sludge include fecal coliforms, fecal streptococci, salmonella, and ascaris (helminth). 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 under joint authority of Subtitle D of the Resource Conservation and Recovery Act (RCRA) and Section 405(d) of the Clean Water Act establish requirements for the disposal of solid waste which include pathogens in 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 process-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). Thus permit compliance is based on meeting process requirements, not pathogen reduction per se. Appendix II of 40 CFR Part 257 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 (of 40 CFR Part 257) does not prescribe the operation mode (i.e., batch or continuous) for digesters. The regulation also does not specify a method for calculating volatile solids reduction. For a comprehensive discussion of the ways that volatile solids reduction may be calculated and their limitations, refer to Appendix B of this guidance document.

Although the 40 CFR Part 257 regulations are based on specific processes rather than on meeting specific pathogen reduction levels, the regulations do provide that other processes "may be acceptable if pathogens are reduced to an extent equivalent to the listed processes." In order to provide guidance on the equivalence of these other methods EPA has a panel of experts, the Pathogen Equivalency Committee (PEC), which evaluates the acceptability of the process based on the level of pathogen reduction, as determined by standardized analytical tests. For more comprehensive information on pathogen and guidance on whether alternative processes provide equivalent levels of pathogen reduction consult the draft "Guidance for Controlling Pathogens in Municipal Wastewater Sludge" PEC/EPA May 1989 (to be finalized July/August 1989).

Sampling techniques for determining pathogens in sewage sludge are no different than for other tests except that no preservatives are used. In the absence of definitive sludge methods for determining bacteria concentrations, modified standard wastewater methods are often utilized. The analytical methods for analysis of pathogens and indicator organisms are provided in Table 3.6. Unfortunately no standardized methods exist for parasitic determinations.

TABLE 3.6

ANALYTICAL TECHNIQUES FOR DETERMINATION OF PATHOGENIC MICROORGANISMS IN SEWAGE SLUDGE

Pathogen	Preparation Technique	Culture Media	Reference
Fecal Coliform		---	A(908 or 909)
Fecal streptococcus/ enterococci		---	A(910A) or B
E. Coli	Centrifugation and filtration	M-PC broth membrane filters	A(912E)
Salmonella sp.	Filtration	Brilliant green-xylose lysine desoxycholate agars	A(912C.1) or C
Animal Viruses	Centrifugation, elutriation, filtration, and flocculation	Tissue culture	D
Helminth Ova	Filtration	---	A(917) or E
Protozoa	Filtration	---	A(917) or E

A) APHA-AWWA-WPCF Standard Methods for the Examination of Water and Wastewater. 16th Ed.

B) Slantely, L.W. and Bartley, "Numbers of enterococci in water, sewage, and feces determined by the membrane filter technique with an improved medium", J. Bacteriology 74: 591-595 (1957).

C) Kenner, B.A., and Clark, "Detection and enumeration of Salmonella and Pseudomonas aeruginosa", J. Water Pollution Control Federation 46(9): 2163-2171 (1974).

D) "The Manual of Methods for Virology", EPA/600/4-84/013 (February 1984) as revised.

E) Fox, J.C., Fitzgerald, and Lue-Hing, "Sewage Organisms: A Color Atlas", Lewis Publishers, Chelsea, Michigan (1981).

The effectiveness of many PSRPs and PFRPs for reducing pathogens can be estimated by measuring 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 and also provide good control data.

4. QUALITY ASSURANCE/QUALITY CONTROL

An essential part of a sampling and analysis program includes a well designed quality assurance/quality control (QA/QC) program. The extent of the QA/QC program should mirror the intent and purpose of the sampling effort. It should be noted that the facility is ultimately responsible for the quality of the data even if a contractor is used. Therefore, it behooves the POTW to have a good QA/QC program.

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/QC program should be extensive and be able to demonstrate the precision, accuracy, representativeness, comparability and completeness of the data. The determination of these QA/QC parameters and their definitions are as follows:

- QA is an overall program which guarantees the quality of the product. It includes a QC auditing process to prevent future defects. QA is synonymous with process control, continuous improvement and prevention of poor quality. QC is the examination of the product to determine if it meets the specifications of the QA program. QC is part of the overall QA program. QC is synonymous with appraisal after the fact. An example of QC is that lab duplicate results must be within a certain percentage of each other or else the whole batch must be redone.

- Laboratory QA includes prevention of data contamination during laboratory procedures. Contamination may be due to various other tests that are run in the lab at any given time. In order to assure that any sample contamination that does occur does not contaminate lab data, a lab QA sample, usually a deionized water "blank" (or other "clean" appropriate material), is run along with the actual field samples. Lab QA also includes doing duplicates and spikes of the actual samples. Field QA serves the same purpose, to prevent data from being erroneous. However, it is virtually

impossible to prevent contamination of the samples since the sampling environment is not controllable. Therefore, the field blanks are subject to the same conditions as the samples, i.e., the containers are exposed to the environment as long as the sample containers are open, the sample and field "blank" are transported together.

- Accuracy, which is closeness to actual values, of all sample testing and analyses should be evaluated at a minimum frequency of 5 percent of the samples tested (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 accuracy required in the quality assurance program for the analyses is 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, which is repeatability of results, 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 precision required in the quality assurance program for the analyses is 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 is calculated as the ratio of valid measurements obtained to the number of valid measurements needed to reach a predefined statistical level of confidence in the resulting data. Completeness is determined and evaluated on the basis of data sets for each specific measurement process. 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 which thus ensures 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/QC 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 operation and maintenance (O&M) decisions, a simplified QA program that 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:

Title Page

Table of Contents

Project Description

Project Organization and Responsibility

QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

Sampling Procedures and Frequency

Sample Custody

Calibration Procedures and Frequency

Analytical Procedures

Data Reduction, Validation and Reporting

Internal Quality Control Checks

Performance and System Audits

Preventive Maintenance

Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness

Corrective Action

Quality Assurance Reports to Management

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. There 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 American Society for Testing and Materials (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 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.

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
- Quality control sample analyses
- Serial dilution analyses (if applicable)
- Instrument detection limit determination
- Method of standard additions application.

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 1989.

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 24-hour composite sampling, a

minimum of two shifts (more likely three) are required. The actual time spent sampling during the shifts will depend on how frequently grab samples are collected (one per hour or once every 4 hours) during the 24-hour sampling period. In addition to the manpower required to actually collect the sample, additional time is required for sample preparation and handling. On-the-job training is generally acceptable for sampling procedures.

Estimates of some of these needs are presented below:

TABLE 5.1

Activity	Manpower
o Automatic Sampler Setup[1]	0.5 - 4 manhours
o Sample Container Preparation[2]	2 - 15 man-minutes / sample
o Sample Documentation[3]	2 - 15 man-minutes / sample
o Sample Handling[4]	2 - 60 man-minutes / sample

1 Depending on sample point characteristics.
2 Depending on parameter.
3 Depending on parameter, ultimate data use and number of points sampled simultaneously.
4 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 of this cost variability.

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, qualified (B.S. Chemistry or equivalent) 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 5.2 presents typical analytical costs for parameters commonly run on sludge samples. These cost estimates were obtained in a March 1988 and 1989 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 the 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 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).

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

TABLE 5.2

TYPICAL CONTRACT ANALYTICAL COSTS FOR
COMMONLY ANALYZED SLUDGE PARAMETERS

	ANALYSIS COST RANGE ($/SAMPLE)			
	Washington State	District of Columbia	California	Massachusetts
Priority Pollutants				
Organics Methods:				
1624C/1625C		2200-2400		
Office of Solid Waste #8240			250	
624-S/625-S		1800-2200	425	550
Acid Fraction Only		N/A	N/A	225
Base Neutral Only		N/A	N/A	325
Metals:				
ICAP or AAS		25-200/metal	240/(13)	290/(13)
Others:				
Cyanide		20-30	75	60
Phenols		20-30	75	50
Total PCBs		60-150	200	175
Pesticides			included in above	150
Total for Priority Scan without Dioxin		2225-5210	1265	1275
Other Non Priority Pollutants				
Oil & Grease		15-25		
" total grav.				60
" HC "				80
" HC & tot "				130
" IR method				100
Ammonia, as N		10-20		35
Tot Kjeldahl N		10-20		35
Tot Suspend Sol		10-20		15
Tot % Solids		10-20		15
Tot Phosphorus		10-20		35
Phosphate		10-50		35
Potassium		20-30		15
Tot Org Halides		50-100		80
EP Toxicity				
extraction		N/A	100	75
8 metals			140	185
2 pest.			100	150
4 herb.			150	175
TOTAL EP	$ 420		$490	$585

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 parameter(s) to be analyzed. The following are typical per-container prices for some commonly used containers:

Container	Size	Approx. Price
Teflon	1 liter	$ 35 - 40
Graduated Glass (w/Teflon-lined cap)	1 liter	$ 3 - 4
Polypropylene	1 liter	$ 2
Polypropylene	0.5 liter	$ 1.50
Polypropylene	10 liter	$ 15
Glass (w/Teflon lined cap)	0.5 liter	$ <1 - 2

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

- **Automatic Samplers** - In most sludge sampling programs the use of automatic sampling equipment will be precluded 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.

5.5 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 pollutant organics in sewage sludge, compositing samples provides an opportunity to substantially lower analytical costs. Field compositing is not an appropriate technique to use when the sample will be analyzed for volatile components. Lab personnel can composite grab samples in the lab.

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 2.3 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.

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APPENDIX A

CHAIN OF CUSTODY RECORD

Chain of Custody Record

W.O. No.	Project Name			Sample Type	Number and Type of Containers						Remarks
Samplers: (Signature)											
Sta. No.	Date	Time	Station Description								

Relinquished By: (Signature)	Date	Time	Received By: (Signature)	(Print)	Comments

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

APPENDIX B

DETERMINATION OF VOLATILE SOLIDS

DETERMINATION OF VOLATILE SOLIDS REDUCTION IN DIGESTION[1]

By J.B. Farrell

INTRODUCTION

When sewage sludge is utilized on land, Federal regulations require that it be treated by a "process to significantly reduce pathogens" (PSRP) or a "process to further reduce pathogens" (PFRP). A requirement of both of these steps is a reduction in "vector attraction" of the sludge. If the PSRP or PFRP is anaerobic or aerobic digestion, the requirement for vector attraction reduction is achieved if volatile solids are reduced by 38 percent. As Fischer[1] has noted, the Federal regulation[2] does not specify a method for calculating volatile solids reduction. Fischer observed that the United Kingdom has a similar requirement for volatile solids reduction for digestion (40 percent), but also failed to prescribe a method for calculating volatile solids reduction. Fischer has provided a comprehensive discussion of the ways that volatile solids reduction may be calculated and their limitations. He presents the following equations for determining volatile solids reduction:

1. Full mass balance equation
2. Approximate mass balance equation
3. "Constant ash" equation
4. Van Kleeck equation

The full mass balance equation is the least restricted but requires more information than is currently collected at a wastewater treatment plant. The approximate mass balance equation assumes steady state conditions. The "constant ash" equation requires the assumption of steady state conditions as well as the assumption that ash input rate equals ash output rate. The Van Kleeck equation, which is the equation generally suggested in publications originating in the United States[3] is equivalent to the "constant ash" equation. Fischer calculates volatile solids reduction using a number of

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[1] Source: "Control of Pathogens in Municipal Wastewater Sludge," EPA, to be published August, 1989.

examples of considerable complexity and illustrates that the different methods frequently yield different results. He closes with the recommendation, obviously directed to rulemakers, that "if it is necessary to specify a particular value for FVSR (fractional volatile solids reduction) then the specification should indicate the method of calculation of FVSR."

Fischer's paper is extremely thorough and is highly recommended for someone trying to develop a deep understanding of potential complexities in calculating volatile solids reduction. However, it was not written as a guidance document for field staff faced with the need to calculate volatile solids reduction in their own plant. The nomenclature is precise but so detailed that it makes comprehension difficult. In addition, two important troublesome situations that complicate the calculation of volatile solids reduction--grit deposition in digesters and decantate removal--are not explicitly discussed. Consequently, this presentation has been prepared to present guidance that describes the major pitfalls likely to be encountered in calculating volatile solids reduction and assists the practitioner of digestion to the best route to take for his situation.

The recommendation of this presentation is not the same as Fischer's. He suggests that the authorities should have provided a calculation method when they required specific volatile solids reductions. From a review of Fischer's results and this presentation, it will be clear that sometimes very simple calculations will give correct results and in other cases the simple methods will yield results seriously in error. Selecting one method and requiring that it be followed is excessively restrictive. The best solution is to require that the calculation be done correctly and then provide adequate guidance. This presentation attempts, belatedly, to provide that adequate guidance.

It is important to note that the calculations of volatile solids reduction will only be as accurate as the measurement of volatile solids content in the sludge streams. The principal cause of error is poor sampling. Samples should be representative, covering the entire charging and withdrawal periods. Averages should cover extended periods of time during which changes in process conditions are minimal. For some plants it is expected that

periodic checks of volatile solids reduction will produce results so erratic that no confidence can be placed in them. In this case, adequacy of stabilization can be verified by the method suggested in the text--periodically batch digest the product for 40 days. If VS reduction is less than 15%, the product is sufficiently stable.

The Equations for FVSR

The equations for fractional volatile solids reduction (FVSR) that will be discussed below are the same as developed by Fischer[1], except for omission of his "constant ash" equation. This equation gives identical results to the Van Kleek equation so it is not shown. Fischer's nomenclature has been avoided or replaced with simpler terms. The material balance approaches are called "methods" rather than "equations." The material balances are drawn to fit the circumstances. There is no need to formalize the method with a rigid set of equations.

In the derivations and calculations that follow, both VS (total volatile solids content of the sludge or decantate on dry solids basis) and FVSR are expressed throughout as fractions to avoid the frequent confusion that occurs when these terms are expressed as percentages. "Decantate" is used in place of the more commonly used "supernatant" to avoid the use of "s" in subscripts. Similarly, "bottoms" is used in place of "sludge" to avoid use of "s" in subscripts.

The "full mass balance" method

The "full mass balance" method must be used when steady conditions do not prevail over the time period chosen for the calculation. The chosen time period must be substantial, at least twice the nominal residence time in the digester (nominal residence time = average volume of sludge in the digester ÷ average volumetric flow rate. Note: when there is supernatant withdrawal, volume of sludge withdrawn should be used to calculate average volumetric flow rate). The reason for the long time period is to reduce the influence of short-term fluctuations in feed or product flow rates or compositions. If input compositions have been relatively constant for a long period of time, then the time period can be shortened.

An example where the full mass balance method would be needed is an aerobic digester operated as follows:

1. Started with the digester 1/4 full (Time zero).
2. Raw sludge is fed to the digester daily until digester is full.
3. Supernatant is periodically decanted and raw sludge is charged into the digester until not enough settling occurs to accommodate daily feeding. (Hopefully this will not occur until enough days have passed for adequate digestion.)
4. Draw down the digester to about 1/4 full (final time), discharging the sludge to sand beds.

The full mass balance is written as follows:

Sum of total volatile solids inputs in feed streams during the entire digestion period = sum of volatile solids outputs in withdrawals of decantate and bottoms + loss of volatile solids + accumulation of volatile solids in the digester. (1)

Loss of volatile solids is calculated from Equation 1. FVSR is calculated by Equation 2:

$$FVSR = \frac{\text{loss in volatile solids}}{\text{sum of volatile solids inputs}} \quad (2)$$

The accumulation of volatile solids in the digester is the final volume in the digester after the drawdowns times final volatile solids concentration less the initial volume at time zero times the initial volatile solids concentration.

To properly determine FVSR by the full mass balance method requires determination of all feed and withdrawal volumes, initial and final volumes in the digester and determination of volatile solids concentrations on all streams. In some cases, which will be discussed later, simplifications are possible.

The "approximate mass balance" method

If volumetric inputs and outputs are relatively constant on a daily basis, and there is no substantial accumulation of volatile solids in the digester over the time period of the test, an approximate mass balance (AMB) may be used. The basic relationship is stated simply:

volatile solids input rate = volatile solids output rate + loss of volatile solids. (3)

The FVSR is given by Equation 2.

No decantate, no grit accumulation - Calculation of FVSR is illustrated for Problem 1 in Table 1 which represents a simple situation with no decantate removal and no grit accumulation. An approximate mass balance is applied to the digester operated under constant flow conditions. Since no decantate is removed volumetric flow rate of sludge leaving the digester equals flow rate of sludge entering. Applying Equations 3 and 2,

$$FY_f = BY_b + \text{loss} \tag{4}$$

$$\text{Loss} = 100\ (50-30) = 2000 \tag{5}$$

$$FVSR = \frac{\text{Loss}}{FY_f} \tag{6}$$

$$FVSR = \frac{2000}{(100)(50)} = 0.40 \tag{7}$$

Nomenclature is given in Table 1. Note that the calculation did not require use of the fixed solids concentrations.

The calculation is so simple that one wonders why it is so seldom used. One possible reason is that the input and output volatile solids concentrations (Y_f and Y_b) may show greater coefficients of variation (standard deviation ÷ arithmetic average) than the fraction volatile solids (VS, fraction of the sludge solids that is volatile--note the difference between VS and Y).

Grit deposition - Grit deposition can be a serious problem in both aerobic and anaerobic digestion. The biological processes that occur in digestion dissolve or destroy the substances suspending the grit and it tends to settle. If agitation is inadequate to keep the grit particles in suspension they will accumulate in the digester. The approximate mass balance can be used to estimate accumulation of fixed solids.

For Problem 1, the balance yields the following:

$$FX_f = BX_b + \text{loss} \tag{8}$$

$$(100)(17) = (100)(17) + \text{Fixed Solids Loss} \tag{9}$$

$$\text{Fixed Solids Loss} = 0 \tag{10}$$

The material balance compares fixed solids in output with input. If some fixed solids are missing this loss term will be a positive number. Since we know that digestion does not consume fixed solids, we assume that the fixed solids are accumulating in the digester. As Equation 10 shows, the fixed solids loss equals zero. Note that for this case where input and output sludge flow rates are equal, the fixed solids concentrations are equal when there is no grit accumulation.

The calculation of fixed solids is repeated for Problem 2. Conditions in Problem 2 have been selected to show grit accumulation. Parameters are the same as in Problem 1 except for the fixed solids concentration (X_b) and parameters related to it. Fixed solids concentration in the digested sludge is lower than in Problem 1. Consequently, VS is higher and mass flow rate of solids (input rate = output rate + rate of loss of fixed solids) is presented in Equation 11-13.

$$FX_f = BX_b + \text{Fixed Solids Loss} \tag{11}$$

$$\text{Fixed Solids Loss} = FX_f - BX_b \tag{12}$$

$$\text{Fixed Solids Loss} = (100)(17) - (100)(15) = 200 \text{ kg/d} \tag{13}$$

The material balance, which only looks at inputs and outputs, informs us that 200 kg/d of fixed solids have not appeared in the outputs as expected. We know that fixed solids are not destroyed and conclude that they are accumulating in the bottom of the digester. The calculation of FVSR for Problem 2 is exactly the same as for Problem 1 (see Equations 4-7) and yields the same result. The accumulation of solids does not change the result.

Decantate withdrawal, no grit accumulation - In Problem 3, supernatant is withdrawn daily. Volatile and fixed solids concentrations are known for all streams but the volumetric flow rates are not known for decantate and bottoms. It is impossible to calculate FVSR without knowing the relative volume balance and a fixed solids balance, provided it can be assumed that loss of fixed solids (i.e., accumulation in the digester) is zero.

Selecting a basis for F of 100 m^3/d,

$$\text{Volume balance:} \quad 100 = B + D \tag{11}$$

$$\text{Fixed solids balance:} \quad 100\,X_f = BX_b + DX_d \tag{12}$$

Since the three Xs are known, B and D can be found.

Substituting 100-D for B and the values for the Xs from Problem 3 and solving for D and B.

$$(100)(17) = (100 - D)(23.50) + (D)(7.24) \tag{13}$$

$$D = 40.0\ m^3/d,\ B = 60.0\ m^3/d \tag{14}$$

The FVSR can now be calculated by drawing a volatile solids balance:

$$FY_f = BY_b + DY_d + \text{loss} \tag{15}$$

$$FVSR = \frac{\text{loss}}{FY_f} = \frac{FY_f - BY_b - DY_d}{FY_f} \tag{16}$$

$$FVSR = \frac{(100)(50) - (60)(41.42) - (40)(12.76)}{(100)(50)} = 0.40 \tag{17}$$

Unless information is available on actual volumes of decantate and sludge, there is no way to determine whether grit is accumulating in the digester. If it is accumulating, the calculated FVSR will be in error.

When we make the calculation shown in Equation 15-17, we assume that the volatile solids that are missing from the output streams are consumed by biological reactions that convert them to carbon dioxide and methane. We assume accumulation is negligible. Volatile solids are less likely to accumulate than fixed solids but it can happen. In poorly mixed digesters, the scum layer that collects at the surface is an accumulation of volatile solids. FVSR calculated by Equations 15-17 will be overestimated if volatile solids accumulation rate is substantial.

Decantate withdrawal and grit accumulation - In Problem 4, there is suspected grit accumulation. The quantity of B and D can no longer be calculated by Equations 11 and 12 because Equation 12 is no longer correct. The values of B and D must be measured. All parameters in Problem 4 are the same as Problem 3 except measured values for B and D are introduced into Problem 4. Values of B and D calculated assuming no grit accumulation (Problem 3--see previous section), and measured quantities are compared below:

	Calculated	Measured
B	60	49.57
D	40	50.43

The differences in the values of B and D are not large but they make a substantial change in the numerical value of FVSR. The FVSR for Problem 4 is calculated below:

$$FVSR = \frac{(100)(50) - (49.57)(41.42) - (50.43)(12.76)}{(100)(50)} = 0.461 \qquad (18)$$

If it had been assumed that there was no grit accumulation, FVSR would equal 0.40 (see Problem 3). It is possible to determine the amount of grit accumulation that has caused this change. A material balance on fixed solids is drawn:

$$FX_f = BX_b + DX_d + \text{Fixed Solids Loss} \qquad (19)$$

The fractional fixed solids loss due to grit accumulation is found by rearranging this equation:

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{FX_f - BX_6 - DX_d}{FX_f} \tag{20}$$

Substituting in the parameter values for Problem 4.

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{(100)(17) - (49.57)(23.50) - (50.43)(7.24)}{(100)(17)} \tag{21}$$

$$= 0.100$$

If this fixed solids loss of 10 percent had not been accounted for, the calculated FVSR would have been 13 percent lower than the correct value of 0.461. Note that if grit accumulation occurs and it is ignored, calculated FVSR will be lower than the actual value.

The Van Kleeck Equation

Van Kleeck first presented his equation without derivation in a footnote for a review paper on sludge treatment processing in 1945[4]. The equation is easily derived from total solids and volatile solids mass balances around the digestion system. Consider a digester operated under steady state conditions with decantate and bottom sludge removal. A total solids mass balance and a volatile solids mass balance are:

$$M_f = M_b + M_d + (\text{Loss of total solids}) \tag{22}$$

$$M_f \cdot VS_f = M_b \cdot VS_b + M_d \cdot VS_d + (\text{Loss of volatile solids}) \tag{23}$$

The masses must be mass of solids rather than total mass of liquid and solid because VS is an unusual type of concentration unit--it is "mass of volatile solids per unit mass of total solids."

It is now assumed that fixed solids are not destroyed and there is no grit deposition in the digester. The losses in Equations 22 and 23 then comprise only volatile solids so the losses are equal. It is also assumed that the VS of the decantate and of the bottoms are the same. This means that the bottoms may have a much higher solids content than the decantate but the

proportion of volatile solids to fixed solids is the same for both streams. Assuming then that VS_b equals VS_d and making this substitution in the defining equation for FVSR (Equation 2),

$$FVSR = \frac{\text{Loss of vol. solids}}{M_f \cdot VS_f} = 1 - \frac{(M_b + M_d)\, VS_b}{M_f \cdot VS_f} \tag{24}$$

From Equation 22, recalling that we have assumed that loss of total solids equals loss of volatile solids,

$$M_b + M_d = M_f - \text{loss of vol. solids} \tag{25}$$

Substituting for $M_b + M_d$ into Equation 24,

$$FRVS = 1 - \frac{(M_f - \text{Loss of vol. solids})}{M_f \cdot VS_f} \cdot VS_b \tag{26}$$

Simplifying further,

$$FRVS = 1 - \left(\frac{1}{VS_f} - FRVS\right) \cdot VS_b \tag{27}$$

Solving for FRVS,

$$FRVS = \frac{VS_f - VS_b}{VS_f - VS_f \cdot VS_b} \tag{28}$$

This is the form of the Van Kleeck Equation found in WPCF's Manual of Practice No. 16[3]. Van Kleeck[4] presented the equation in the following equivalent form:

$$FRVS = 1 - \frac{VS_b \cdot (1 - VS_f)}{VS_f \cdot (1 - VS_b)} \tag{29}$$

The Van Kleeck Equation is applied below to Problems 1-4 in Table 1 and compared to the approximate mass balance equation results:

	1	2	3	4
Approximate Mass Balance (AMB)	0.40	0.40	0.40	0.461
Van Kleeck (VK)	0.40	0.318	0.40	0.40

Problem 1: No decantate and no grit accumulation. Both methods give correct answers.

Problem 2: No decantate but grit accumulation. VK is invalid and incorrect.

Problem 3: Decantate but no grit accumulation. AMB method is valid VK method is valid only if $VS_b = VS_d$.

Problem 4: Decantate and grit acumulation. AMB method valid only if B and D are measured. VK method is invalid.

The Van Kleeck equation is seen to have serious shortcomings when applied to certain practical problems. The AMB method can be completely reliable whereas the Van Kleeck method is useless under some circumstances.

Review and Discussion of Calculation Methods and Results

Complete Mass Balance Method - The complete mass balance method allows calculation of volatile solids reduction of all approaches to digestion, even processes where final volumes in the digester does not equal initial volume and where daily flows are not steady. A serious drawback is the need for volatile solids concentration and volumes of all streams added to or withdrawn from the digester as well as initial and final volumes and concentrations in the digester. This can be a daunting task particularly for the small plants which are most likely to run their digesters in other than steady flow modes. For plants of this kind, an "equivalent" method that shows that the sludge has undergone the proper volatile solids reduction is likely to be a better choice than trying to demonstrate 38 percent volatile solids reduction. An aerobic sludge has received treatment equivalent to a 38 percent volatile solids reduction if specific oxygen uptake rate is below a specified maximum.

Anaerobically digested sludge has received treatment equivalent to a 38 percent volatile solids reduction if volatile solids reduction after batch digestion of the product sludge for 40 days is less than a specified maximum[5].

Approximate Mass Balance (AMB) Method - The approximate mass balance method assumes that daily flows are steady and reasonably uniform in composition, and that digester volume and composition does not vary substantially from day to day. Results of calculations and an appreciation of underlying assumptions show that the method is accurate for all cases, including withdrawal of decantate and deposition of grit, provided that in addition to composition of all streams the quantity of decantate and bottoms (the digested sludge) are known. If the quantities of decantate and bottoms are not known, the accumulation of grit cannot be determined. If accumulation of grit is substantial and FVSR is calculated assuming it to be negligible, FVSR will be lower than the true value. The result is conservative and could be used to show that minimum volatile solids reductons are being achieved.

The Van Kleeck Equation - The Van Kleeck Equation has underlying assumptions that should be made clear wherever the equation is presented. It is never valid when there is grit accumulation because it assumes the fixed solids input equals fixed solids output. Fortunately, it produces a conservative result in this case. Unlike the AMB method it does not provide a convenient way to check for accumulation of grit. It can be used when decantate is withdrawn provided VS_b equals VS_d. Just how big the difference between these VS values can be before an appreciable error in FVRS occurs is unknown, although it could be determined by making up a series of problems with increasing differences between the VS values, calculating FRVS using the AMB method and a Van Kleeck equation, and comparing results.

The shortcomings of the Van Kleeck equation are substantial and may eventually lead to a recommendation not to use it. However, it has one strong point. The VS of the various sludge and decantate streams are likely to show much lower coefficients of variation (standard deviation ÷ arithmetic average) than volatile solids and fixed solids concentration. Review of data are needed to determine how seriously the variation in concentrations affect the confidence interval of FVSR calculated by both methods. A hybrid approach may

turn out to be advantageous. The AMB method could be used first to determine if grit accumulation is occurring. If grit is not accumulating, the Van Kleeck equation could be used. If decantate is withdrawn, the Van Kleeck equation still cannot be used unless VS_b is nearly equal to VS_d.

Average Values - The concentrations and VS values used in the equations will all be averages. For the material balance methods, the averages should be weighted averages according to the mass of solids in the stream in question. The example below shows how to average the volatile solids concentration for four consecutive sludge additions.

Addition	Volume	Volatile Solids Concentration
1	10 m^3	50 kg/m^3
2	7 m^3	45 kg/m^3
3	15 m^3	40 kg/m^3
4	12 m^3	52 kg/m^3

$$Y_{av} = \frac{10 \times 50 + 7 \times 45 + 15 \times 40 + 12 \times 52}{10 + 7 + 15 + 12} = 46.3 \text{ kg/m}^3 \qquad (30)$$

For the Van Kleeck equation, the averages of VS are required. Properly they should be weighted averages based on the weight of the solids in each component of the average although an average weighted by the volume of the component or an arithmetic average may be sufficiently accurate if variation in VS is small. The following example demonstrates the calculation of all three averages.

Addition	Volume	Total Solids Concentration	VS
1	12 m^3	72 kg/m^3	0.75
2	8 m^3	50 kg/m^3	0.82
3	13 m^3	60 kg/m^3	0.80
4	10 m^3	55 kg/m^3	0.77

Weighted by Mass

$$VS\ av = \frac{12 \times 72 \times 0.75 + 8 \times 50 \times 0.82 + 13 \times 60 \times 0.80 + 10 \times 55 \times 0.77}{12 \times 72 + 8 \times 50 + 13 \times 60 + 10 \times 55} = 0.795 \quad (31)$$

Weighted by Volume

$$VS\ av = \frac{12 \times 0.75 + 8 \times 0.82 + 13 \times 0.80 + 10 \times 0.77}{12 + 8 + 13 + 10} = 0.783 \quad (32)$$

Arithmetic Average

$$VS\ av = \frac{0.75 + 0.82 + 0.80 + 0.77}{4} = 0.785 \quad (33)$$

In this example the arithmetic average was nearly as close as the volume-weighted average to the mass-weighted average, which is the correct value.

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3. Water Pollution Control Federation, Manual of Practice No. 16, "Anaerobic Sludge Digestion," pub. Water Pollution Control Federation, Washington, DC (1968).

4. Van Kleeck, L.W., Sewage Works J., 17 (6), 1240-1255 (1945), "Operation of sludge drying and gas utilization units," Refer to footnote on p 1241.

5. U.S. EPA, "Technical Support Document: Pathogens," pub. by EPA's Office of Water Regulation and Standards, Washington, DC (1989).

TABLE 1

QUANTITATIVE INFORMATION FOR EXAMPLE PROBLEMS [1,2,3]

Parameter	Symbol	Units	Problem Statement Number			
			1	2	3	4
Nominal residence time	Θ	d	20	20	20	20
Time period for averages		d	60	60	60	60
Feed Sludge						
Volumetric flow rate	F	m^3/d	100	100	100	100
Volatile solids concentration	Y_f	kg/m^3	50	50	50	50
Fixed solids concentration	X_f	kg/m^3	17	17	17	17
Fraction volatile solids	VS_f	kg/kg	0.746	0.746	0.746	0.746
Mass flow rate of solids	M_f	kg/d	6700	6700	6700	6700
Digested Sludge (Bottoms)						
Volumetric flow rate	B	m^3/d	100	100		49.57
Volatile solids concentration	Y_b	kg/m^3	30	30	41.42	41.42
Fixed solids concentration	X_b	kg/m^3	17	15	23.50	23.50
Fraction volatile solids	VS_b	kg/kg	0.638	0.667	0.638	0.638
Mass flow rate of solids	M_b	kg/d	4700	4500		
Decantate						
Volumetric flow rate	D	m^3/d	0	0		50.43
Volatile solids concentration	Y_d	kg/m^3	-	-	12.76	12.76
Fixed solids concentration	X_d	kg/m^3	-	-	7.24	7.24
Fraction volatile solids	VS_d	kg/kg	-	-	0.638	0.638
Mass flow rate of solids	M_d	kg/d	-	-		

1. Conditions are steady state; all daily flows are constant. Volatile solids are not accumulating in the digester, although grit may be settling out in the digester.

2. Numerical values are given at 3 or 4 significant figures. This is unrealistic considering the expected accuracy in measuring solids concentrations and sludge volumes. The purpose of extra significant figures is to allow more understandable comparisions to be made of the different calculation methods.

3. All volatile solids concentrations are based on the total solids, not merely on the suspended solids.