Guidelines for Flue Gas Desulfurization (FGD) Water Sampling and Analysis

Trace Metals

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PRODUCT DESCRIPTION

Flue gas desulfurization (FGD) scrubbers are being installed on coal-fired power plants in response to federal and state air pollution regulations limiting sulfur dioxide emissions. FGD scrubbers produce an aqueous waste stream that contains metals adsorbed from flue gas. At the same time, the U.S. Environmental Protection Agency (EPA) is reviewing, and may tighten, water discharge limits on trace metals. Collection of accurate data on the trace metal composition of FGD water discharges is therefore essential to respond to current and future regulations. The purpose of this report is to summarize the state-of-the-art for sampling and analysis of trace metals in FGD waters.

Results and Findings

Recent studies of the chemical composition of FGD waters have noted significant barriers to obtaining accurate, representative measurements of trace metals. Challenges include temporal and spatial variability in wastewater composition, high solids content, and the presence of high levels of dissolved salts that interfere with many analytical methods. This report summarizes the best currently available practices for sampling and analysis that can be used to produce accurate measurements of mercury, selenium, and other metals in FGD waters. The report also describes clean sampling and analysis procedures that can be used when low concentrations of trace metals are of interest.

Challenges and Objective(s)

Power plant staff responsible for monitoring trace metals concentrations in FGD waters will often encounter challenges in collecting representative samples and identifying appropriate analytical techniques for this complex and difficult water matrix. The objective of this report is to provide guidance on the current knowledge and best available practices for sampling and analyzing FGD waters.

Applications, Values, and Use

This report will help coal-fired power plants to better characterize FGD wastewater and avoid reporting inaccurate data to treatment system design engineers and water permitting authorities. The report provides guidance to help in the design of a sampling and analysis plan, selection of sampling equipment, identification of appropriate analytical methods, and evaluation of sampling equipment suppliers and contract analytical laboratories.

EPRI Perspective

EPRI has conducted numerous studies of FGD waters that have led to an appreciation of the difficulty of obtaining a representative sample of a waste stream that varies greatly over time and between sampling locations. Measuring low levels of trace metals in FGD waters with accuracy is challenging. Comparability of results using different analytical methods can be poor due to chemical interferences and differing method sensitivities. At present, unresolved analytical issues remain in the analysis of mercury, selenium, and other trace metals in FGD waters. EPRI is studying these issues and is participating in method development efforts to resolve them. This report provides guidance available based on present industry knowledge. EPRI will update these guidelines as more information becomes available. Related EPRI reports include 1014073 and

1015588, which are 2007 and 2008 updates, respectively, on FGD wastewater characterization and management.

Approach

Recommendations for sampling and analyzing trace metals in FGD waters were developed based on past studies conducted by EPRI and others as well as the principal investigator's personal experience.

Keywords

Flue Gas Desulfurization (FGD)
FGD Wastewater
Sampling and Analysis
Trace Metals
Mercury
Selenium

ACRONYMS AND ABBREVIATIONS

As	Arsenic
CRC	Collision/reaction cell
CRM	Certified reference material
CVAFS	Cold vapor atomic fluorescence spectrometry
CWA	U.S. Clean Water Act (40CFR Part 136)
DQO	Data quality objective
DRC	Dynamic reaction cell
EDD	Electronic data deliverable
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
FEP	Fluorinated ethylene propylene resin
gpm	Gallons per minute
Hg	Mercury
HGAFS	Hydride-generation atomic fluorescence spectrometry
ICP-AES	Inductively coupled plasma - atomic emission spectroscopy
ICP-MS	Inductively coupled plasma - mass spectrometry
ID	Inside diameter, usually in reference to tubing size
IDL	Instrument detection limit
IRL	Instrument reporting limit
L	Liter
MDL	Method detection limit
MDL	Method detection limit
mg	Milligram
ML	Minimum level
MQL	Minimum Quantification Limit
MQL	Method quantitation limit

MS/MSD	Matrix spike/matrix spike duplicate
MUR	EPA Method Update Rule
NPDES	National Pollutant Discharge Elimination System
OD	Outside diameter, usually in reference to tubing size
POTW	Publicly owned treatment works
ppb	Micrograms per liter as an aqueous concentration (parts per billion)
ppm	Milligrams per liter as an aqueous concentration (parts per million)
pptr	Nanograms per liter as an aqueous concentration (parts per trillion)
QA	Quality assurance
QC	Quality control
RL	Reporting limit
Se	Selenium
SP	Sampling point (i.e. each individual location where a sample is collected)
TAT	Laboratory turn-around time
TDS	Total dissolved solids
TSS	Total suspended solids
WWTP	Wastewater treatment plant

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- Nicolas Bloom for his expert input.

Their participation materially enhanced the quality and informational content of the final technical report.

EXECUTIVE SUMMARY

Flue gas desulfurization (FGD) systems are being installed on coal-fired power plants in response to federal and state air pollution regulations limiting sulfur dioxide emissions. FGD systems produce an aqueous waste stream that contains metals adsorbed from flue gas. At the same time, the U.S. Environmental Protection Agency (EPA) is reviewing, and may tighten, water discharge limits on trace metals. Collection of accurate data on the trace metal composition of FGD water discharges is therefore essential to respond to current and future regulations. The purpose of this report is to summarize the current state-of-the-art for sampling and analysis of trace metals in FGD waters. The report provides practical and detailed guidance to power plant personnel on considerations for collecting representative, contamination-free FGD water samples, and to analytical chemists tasked with accurately measuring trace metals such as selenium (Se) and mercury (Hg) in FGD waters.

FGD units remove sulfur dioxide from the gas stream by reacting it with a limestone or lime slurry. Most of the water and slurry solids are retained or recycled within the FGD scrubber system by separating the solids from the liquids with hydroclones or filters. However, to control buildup of chlorides and fines in the system, a portion of the liquid is removed for treatment and disposal. This water stream is variously referred to as chloride purge stream, FGD purge water or FGD blowdown. Since this stream has not yet undergone removal of suspended solids, the term untreated FGD water is used in this report. FGD water treatment processes vary greatly from one facility to the next. At some facilities, clarification and settling is the primary treatment. At other facilities, treatments may include ferric chloride and organosulfide addition, primary clarification, pH adjustment, polymer addition, secondary clarification, sand filtration, and biological treatment.

FGD waters from different facilities vary in trace metal composition due to variations in design, fuels burned, lime or limestone composition, operational factors such as the degree of water recirculation, and the use of FGD performance additives. Past studies conducted by EPRI and others observed a very large range of trace metal concentrations (1 to 3 orders of magnitude) in both untreated and treated FGD water across multiple FGD systems. However, even the effluent from a single FGD unit can exhibit large temporal and spatial changes in composition due to purge cycles, fuel changes, plant load, and other operational factors. This variability increases the challenge of obtaining a representative sample.

To collect representative samples of FGD water, it is necessary to fully understand the operation of the specific FGD system being studied. The objectives of the study and the specific questions to be answered should be clearly defined in the sampling plan. The data requirements for compliance monitoring may be very different from those for process control monitoring. Each sampling point should be characterized as to the temporal and spatial variability of the flow volume and mixing. The logistics of sample collection at each sampling point should be addressed in the sampling plan.

A critical planning step in the study is to define the target analytes, the ancillary data needs (e.g., mass flows), and the number and type of samples (e.g., grab, composite) to be collected. The number of samples and the frequency of collection will depend on the variability of the FGD water stream and the study objectives. The decision to collect total recoverable (unfiltered) or dissolved samples or both will be dictated by the goals of the sampling effort and any regulatory requirements. The analytical methods selected should have adequate sensitivity for the expected levels of analytes in FGD water and should be free of known biases, or at least incorporate quality control measures to minimize and account for biases. Finally, acceptance criteria should be specified in the sampling plan to insure that the analytical data obtained will be sufficiently accurate to meet study objectives.

It is important to avoid introducing contamination during sampling. Sample contamination is of particular concern for mercury, but may also be an issue for other trace metals in treated FGD water if the level of a trace metal in the FGD water approaches the regulatory limit or other decision point. A tiered approach can be used to tailor clean sampling procedures to the needs of a given monitoring study. This approach involves identifying the target analytes that require the greatest degree of cleanliness (due to low regulatory levels or method quantitation limits - MQLs) and selecting field equipment and procedures that will provide that level of cleanliness. In practice, the clean sampling tier is chosen to accommodate the analyte with the lowest MQL. Clean techniques are discussed for various sampling scenarios, including manual grab sampling, pumped grab sampling, field-filtered samples, composites and split samples.

Analyzing a FGD water sample for many metals at once is difficult because some metals of interest are commonly found at ppb levels while others are thousands of times more concentrated. Multiple dilutions of the sample may be required to measure all of the metals accurately. In addition, high levels of total dissolved solids (TDS) such as calcium and sulfur cause analytical interferences that most laboratories have little experience controlling. The routine implementation of EPA multi-element methods (for example, EPA Methods 200.7 and 200.8) is not robust enough to accommodate the challenging FGD sample matrices without additional method development/optimization. Analytical methods that are applicable to the analysis of non-mercury trace metals in FGD waters include:

- EPA Method 200.7-- Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES: large dynamic range but not sensitive enough to quantify some trace metals in FGD waters. Subject to interferences for some metals in FGD waters.
- EPA Method 200.8 or Method 1638-- Inductively Coupled Plasma- Mass Spectrometry (ICP-MS): good sensitivity, but subject to interferences for arsenic, selenium and certain other metals in FGD waters.
- EPA Methods 200.8 or 1638 modified for dynamic reaction cell or collision cell ICP-MS: low detection limits and the ability to control interferences for arsenic, selenium and some other metals in FGD waters.
- EPA Method 1632-- Hydride Generation Quartz Furnace Atomic Absorption Spectrometry, modified for use with atomic fluorescence spectrometry: very low reporting limits for arsenic and selenium in FGD waters, with some concerns about the effects of selenium speciation on the determination of total selenium.

Sample digestion procedures have been shown to have a major impact on the results of total metal analyses. The use of closed vessel digestions for aqueous samples should be considered to eliminate the possible loss of volatile species of selenium and other metals. For FGD water samples with total suspended solids (TSS) levels greater than 1%, a biphasic separation procedure should be considered to optimize the separate analysis of the liquid and solids components. The metals concentration in the original whole sample is then calculated based on metals levels in the two components.

FGD sampling plans may require more extensive quality control measures than are generally included in a monitoring effort. The recommended quality control samples include a matrix spike and matrix spike duplicate for every distinct sample matrix, to detect incomplete recovery of the target analytes. In some cases, every sampling point may be considered a distinct matrix, due to the changes in TSS that occur through the treatment process. It may be necessary, at least for the first samples from a facility, to pre-screen each sample using a less sensitive method in order to select an appropriate matrix spike concentration and to determine the most appropriate sample dilution for use with a more accurate and sensitive method. These measures add to the cost of a FGD sampling effort, but avoid more significant costs that may be incurred from relying on potentially inaccurate data.

Mercury is typically an element of interest in FGD water monitoring studies due to extremely low discharge limits. "Clean" analytical methods with extremely low (low parts-per-trillion) quantitation limits are available. Less sensitive methods may be appropriate for process monitoring studies where the study objectives due not require quantitation to these low levels. Compliance monitoring for mercury in permitted discharges will generally require the most sensitive methods. EPA Methods 1631E and 245.7 are highly sensitive methods; both methods use cold vapor atomic fluorescence spectrometry (CVAFS) but differ in the technique used to introduce the sample into the detector. EPA Method 1631E is the method of choice for FGD waters. EPA Method 245.7 is problematic for mercury analyses in FGD waters due to the tendency of the method to underestimate mercury concentrations in complex sample matrices.

Whenever clean analytical methods are used, compatible clean sample collection procedures should also be used to avoid contamination at the levels achievable using these techniques. Clean sampling equipment and analytical laboratories should be selected based on the level of data accuracy and quality needed for a specific FGD study. In selecting a clean sampling equipment vendor, the best success will come from using a supplier with specific experience in certifying and providing clean sampling equipment for industrial monitoring studies.

At the present time, there are few commercial laboratories with the necessary equipment and experience to support state-of-the-art FGD water monitoring studies. Many laboratories that provide routine metals analyses lack the required expertise and specialized equipment to resolve interferences for trace metals. Laboratories performing Method 1631E analyses must pay scrupulous attention to minimizing background mercury contamination and to cleaning and certifying their solvents and glassware. It is important to evaluate a candidate laboratory's experience in analyzing complex matrices, and to specify all requirements for analyzing the sample in a detailed Request for Proposal. This document should specify the quality control samples to be analyzed, the required method quantitation limits, the acceptance criteria for each method and analyte, the procedures to be followed in case those criteria are not met, and any additional repeat analyses that the laboratory will be expected to perform in case data are not acceptable. It is helpful to submit familiarization samples of the specific FGD water to a new laboratory before sending actual samples that require timely completion or regulatory reporting. This will allow the laboratory to perform any needed method optimization without impacting the project schedule. Finally, splitting samples with a second, qualified laboratory can help to identify any analytical problems and aid in resolving data quality issues.

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INTRODUCTION

Flue gas desulfurization (FGD) systems are being installed throughout the power industry in response to federal and state air pollution regulations. FGD systems produce a highly variable and complex aqueous waste stream that contains metals absorbed from flue gas. At the same time, the U.S. Environmental Protection Agency (EPA) is reviewing, and may tighten, wastewater discharge limits on trace metals and salts [1]. The purpose of this report is to summarize the current state-of-the-art for the collection, processing and analysis of FGD waters. The report provides practical and detailed guidance to power plant personnel on considerations for collecting representative, contamination-free FGD water samples, and to analytical chemists tasked with accurately measuring trace metals and mercury (Hg) in FGD waters.

Section 2 of this report summarizes the composition and variability of FGD waters. The aqueous matrix produced by blowing down the FGD scrubber is highly complex. FGD waters can contain over one percent total suspended solids (TSS) as well as percent levels of total dissolved solids (TDS) including high concentrations (thousands of parts per million) of calcium, chloride, magnesium, sodium and sulfate and significantly elevated levels (hundreds of ppm) of boron, iron and potassium. Concentrations of trace metals are typically in the parts per billion (ppb) range.

Section 3 presents guidance on the collection of FGD water samples using a tiered approach to clean metals and Hg sampling procedures that can be tailored to the data usability needs of a given monitoring study. Various sampling scenarios are discussed, including manual grab sampling, pumped grab sampling, composites and split samples. Procedures for both total recoverable and dissolved metals and Hg sample collection are covered. The collection and analysis of samples for metals speciation analysis is beyond the scope of this report and is not covered.

Section 4 provides guidance on the selection of methods for analysis of trace metals (other than Hg) in FGD waters. Trace metals concentrations in FGD waters, although variable by element, are usually orders of magnitude lower than the major constituents, typically less than 100 ppb. This difference highlights the challenge of making accurate trace metals and Hg measurements in such variable and complex sample matrices.

Section 5 provides guidance on the analysis of Hg in FGD waters, with an emphasis on low-level, "clean" analytical methods. Alternative, higher detection limit, Hg analytical methods are briefly discussed.

Finally, Section 6 provides guidance for selecting qualified suppliers of both equipment and analytical services for the sampling and analysis of FGD waters. The guidance is based on a two-step approach. First, the data usability needs of a given project are defined. Second, guidance is given for selecting qualified suppliers to meet the specified data usability needs.

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FGD WATER COMPOSITION AND VARIABILITY

Planning a sampling and analytical effort for an FGD system is challenging because FGD systems and FGD water treatment processes vary from one system to the next. The sampling procedures and locations should be tailored to the situation. In addition, an FGD purge stream is highly variable spatially and temporally and is an extremely challenging matrix to analyze for trace metals. To obtain accurate and representative results, it is essential to understand the sources of variability. It is also helpful to predict the approximate concentrations of major and minor constituents in the water, to assist the laboratory in overcoming interferences. Submitting samples for analysis without this information will require the laboratory to perform extensive pre-analysis work to identify appropriate dilutions and quality control samples. This section discusses factors contributing to FGD water variability.

Effluent from wet FGD scrubber systems represents a new liquid waste stream at many coal-fired power plants. Although scrubbers have been in place at a few facilities for many years, the majority of FGD systems have been installed since 2006 in response to EPA requirements to reduce sulfur dioxide (SO_2) in flue gas. The FGD process involves contacting flue gas with an alkaline material (usually lime or limestone) that absorbs the SO_2 to form a solid product that can be separated from the flue gas.

Figure 2-1 shows an example system process flow diagram for a newer FGD scrubber. Wet FGD scrubber systems periodically blow down or purge a portion of the absorber slurry to limit buildup of chlorides and suspended solids. The purge stream is a slurry of water, dissolved solids and suspended solids [principally calcium sulfate (gypsum) or calcium sulfite solids], flyash and inert constituents from limestone. The purge is separated into coarse (> 0.1 mm) and fine solid fractions (< 0.1 mm), usually using hydroclones, and the coarse fraction is dewatered by vacuum belt filters. Most of the hydroclone overflow (fines) and the vacuum filter filtrate are returned to the FGD. However, to control buildup of chlorides and fines in the FGD scrubber system, a portion of the hydroclone overflow and/or vacuum filter filtrate is removed by pumping for disposal. This liquid stream is variously referred to as chloride purge stream, FGD purge water or FGD blowdown. Since this stream has not yet undergone solids removal, the term untreated FGD water will be used in this report. Liquid samples collected after primary solids removal by a clarifier or thickener will be referred to as treated FGD water.

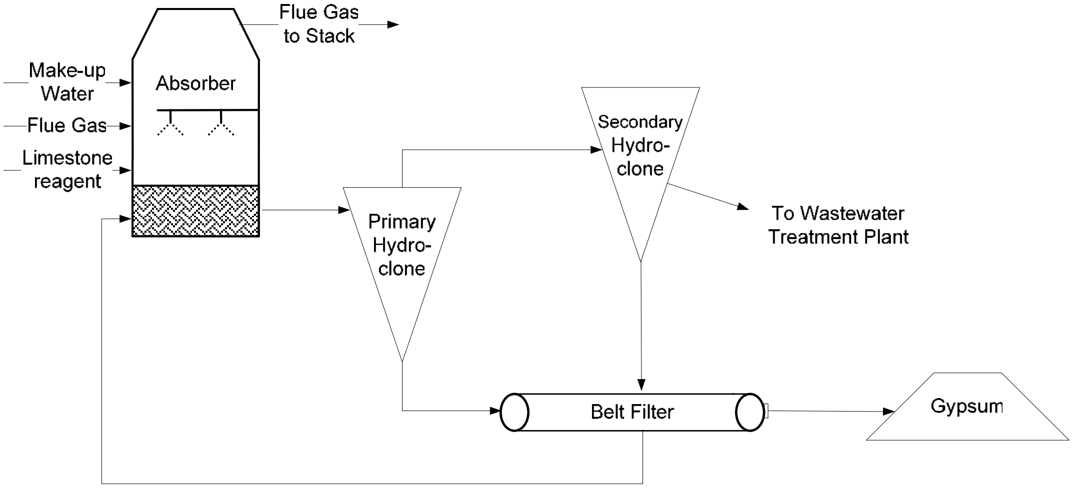


Figure 2-1
Solids Separation Processes in a Newer FGD System

Some facilities have installed treatment systems to remove solids and metals prior to discharging the FGD water, while others send the untreated water to an on-site detention pond to settle out the solids. Figure 2-2 shows a typical process diagram for a wastewater treatment plant (WWTP) receiving untreated FGD water. FGD treatment processes vary greatly from one facility to the next, but generally include ferric chloride addition, primary clarification, pH adjustment, and may include ferric chloride and organosulfide addition, primary clarification, pH adjustment, polymer addition, secondary clarification, sand filtration, and biological treatment.

Sampling of untreated FGD waters can be required for process control or to aid in water treatment system design. Various intermediate sampling points within the FGD WWTP may be sampled in order to optimize FGD water treatment processes. Samples are frequently taken at the outlet of an FGD WWTP and at National Pollutant Discharge Elimination System (NPDES) compliance monitoring locations (outlets), in accordance with requirements specified in the Clean Water Act (CWA).

Previous EPRI reports [1,2] have characterized the variability in FGD systems and water characteristics in considerable detail. In the current report, these topics are summarized in order to provide an understanding of factors that should be considered in planning a sampling and analysis effort for FGD waters.

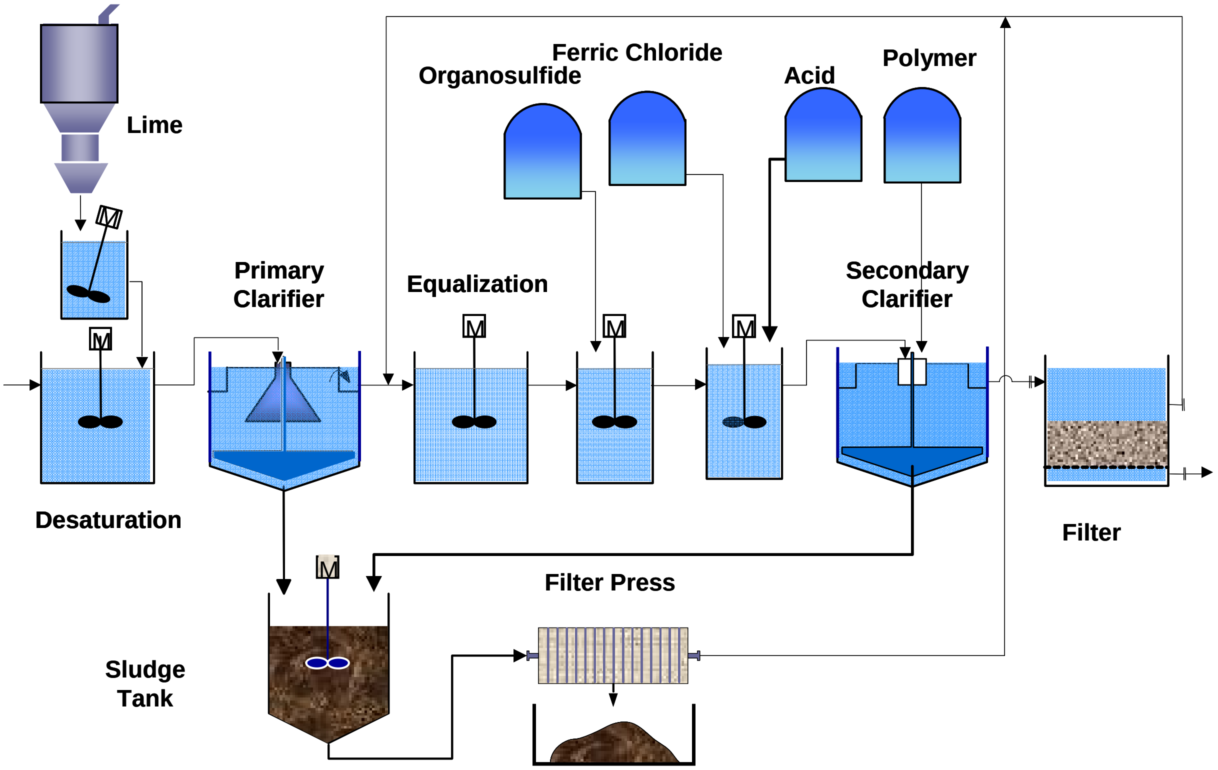


Figure 2-2
Example FGD Water Treatment Process Diagram

Untreated FGD water is a highly variable in composition even within a single power plant facility. Understanding the sources and magnitude of variability is important when designing monitoring studies, to insure the collection of samples that are truly representative of the FGD water streams being studied. Variables that can impact the composition of untreated FGD water include coal rank and elemental composition, FGD reagent chemicals (primarily limestone), temporal variability related to FGD system operations, and spatial variability related to solids removal and channelized flow. Intermediate sampling locations within a WWTP can also be impacted by temporal and spatial variability, particularly if the system lacks an equalization basin. Treated FGD water quality can also vary over time due to changes in the FGD scrubber operation (e.g., purge cycles) and difficulties in adjusting the treatment chemical load to changing influent composition. These factors contributing to FGD water variability are discussed below, while Section 3 recommends sampling techniques to obtain representative samples under these conditions.

Factors Influencing the Variability of FGD Waters

Coal is the largest source of trace metals mass loading in an FGD system liquid. For those metals that tend to partition from flue gas into the FGD liquid (e.g. Hg and Se), the higher the metals concentration in the coal, the higher the metals load in the FGD system. Changes in the type or blend of coal used will affect both metals and other constituent mass loadings to FGD water. The chloride and sulfur content of coal as well as the FGD equipment metallurgy determines the number of times that water can be cycled through the FGD system absorber. The more cycles, the more trace metals are concentrated in the FGD liquid, but the mass loading rate of metals remains constant. Use of higher chloride coal may lead to less cycling and lower trace metals concentrations.

FGD reagents can also affect untreated FGD water composition. Lime, limestone and other FGD system reagents introduce varying amounts of solids and trace metals. However, the contribution of metals from reagent chemicals is much less than the amount from coal (via flue gas). Limestone contains fine-grained clay impurities that are rich in aluminum and silicon and are difficult to remove by settling. Measurement of metal concentrations in limestone and other reagent chemicals could be useful in predicting metals loading in untreated FGD waters. However, making accurate metal measurements in such a high calcium matrix is analytically very difficult.

Temporal variability related to changes in flow rate and intermittent flows caused by FGD system operations should also be considered when evaluating FGD water variability. Much of the temporal variability is related to corrosion control practices which determine the flow of the purge stream diverted to the FGD WWTP. These factors are discussed later in this Section.

Spatial variability can be an important factor especially for sampling untreated FGD water (influent) and FGD water at intermittent sampling points (SP) in the treatment process (e.g. primary clarifier, secondary clarifier, etc.). The spatial variability is largely related to variations in the TSS loading and settling dynamics at the SPs being studied. Since many metals (e.g. Hg, Pb) are associated with particulates, the concentrations are directly related to the TSS in the sample. Spatially heterogeneous, channelized flows occur in ash and other treatment ponds and can make selection of a representative pond inlet sample difficult.

Composition of FGD Waters

The compositional variability in both untreated FGD water (influent), primary solids removal effluent, and WWTP effluent have been characterized in previous EPRI studies [1,2]. Four additional sites were characterized by the EPA in 2007 [3-6]. Figures 2-3 and 2-4 present data for hydroclone effluent or FGD blowdown collected before any solids removal treatment employing a primary clarifier/thickener or settling pond. Figure 2-3 shows 5th and 95th percentiles and median concentrations from these studies for major elements in untreated, unfiltered FGD water (primary solids removal influent). Figure 2-4 shows ranges of concentrations for trace metals. The concentrations (in mg/L for major elements and µg/L for trace metals) are plotted on a logarithmic scale due to the large range of measured values. These plots include samples of FGD pond influent for systems without clarifiers. The black rectangles in Figure 2-4 indicate the range of detected trace metals; The red lines indicate the range of nondetects (if any were reported for that element). As can be seen in Figure 2-4, detection limits for these elements were also highly variable, and there is a significant overlap of detected and nondetected values.

Figures 2-5 and 2-6 show the same information for major elements and trace metals, respectively, in unfiltered samples of solids removal effluent. These plots include samples taken after primary clarification/thickening and from the effluent of FGD water holding ponds, for those facilities that use settling in a pond as the solids removal system.

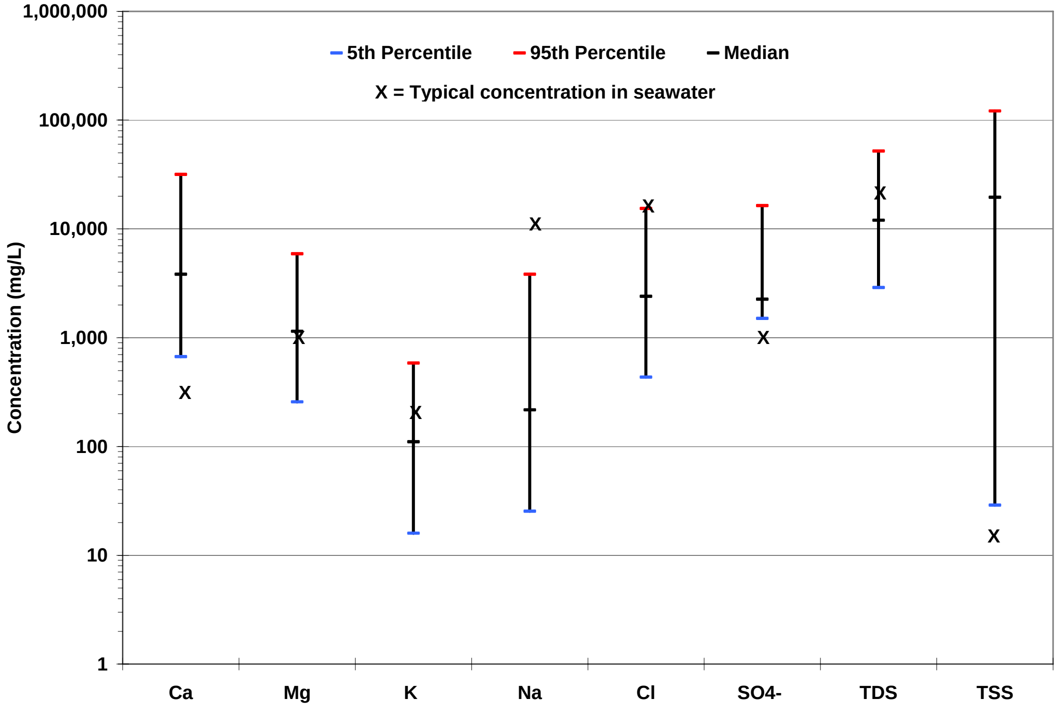


Figure 2-3
Major Constituents in Untreated, Unfiltered FGD Water (before Solids Removal)

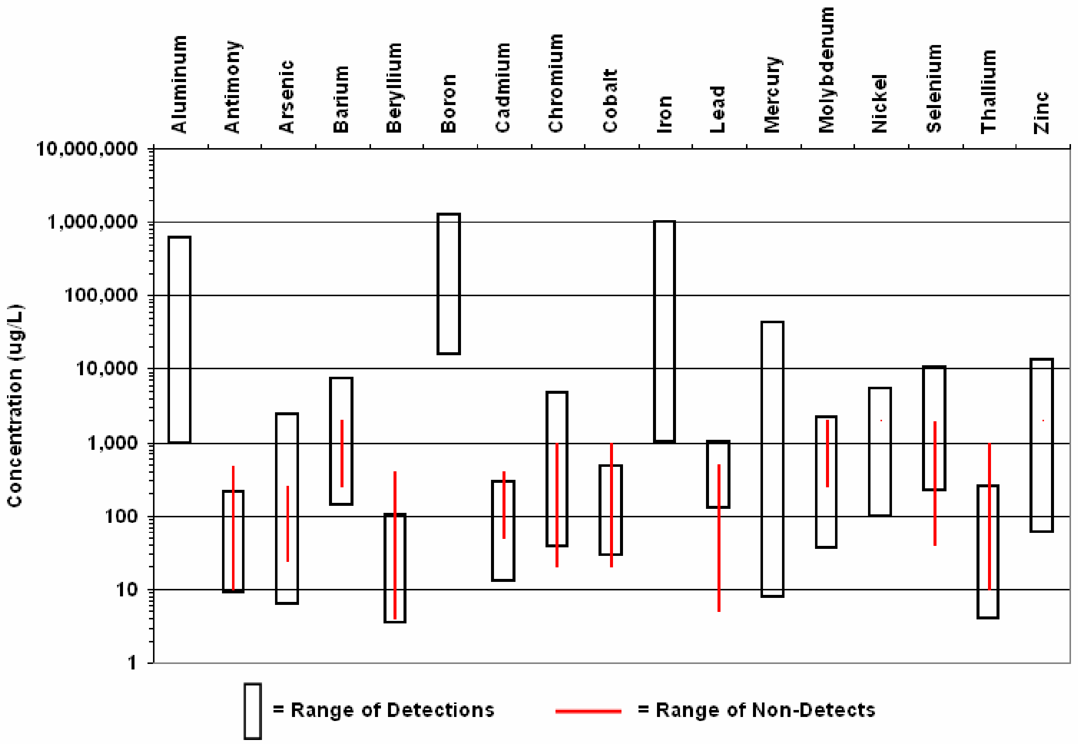


Figure 2-4
Ranges of Trace Metals in Untreated, Unfiltered FGD Water (before Solids Removal)

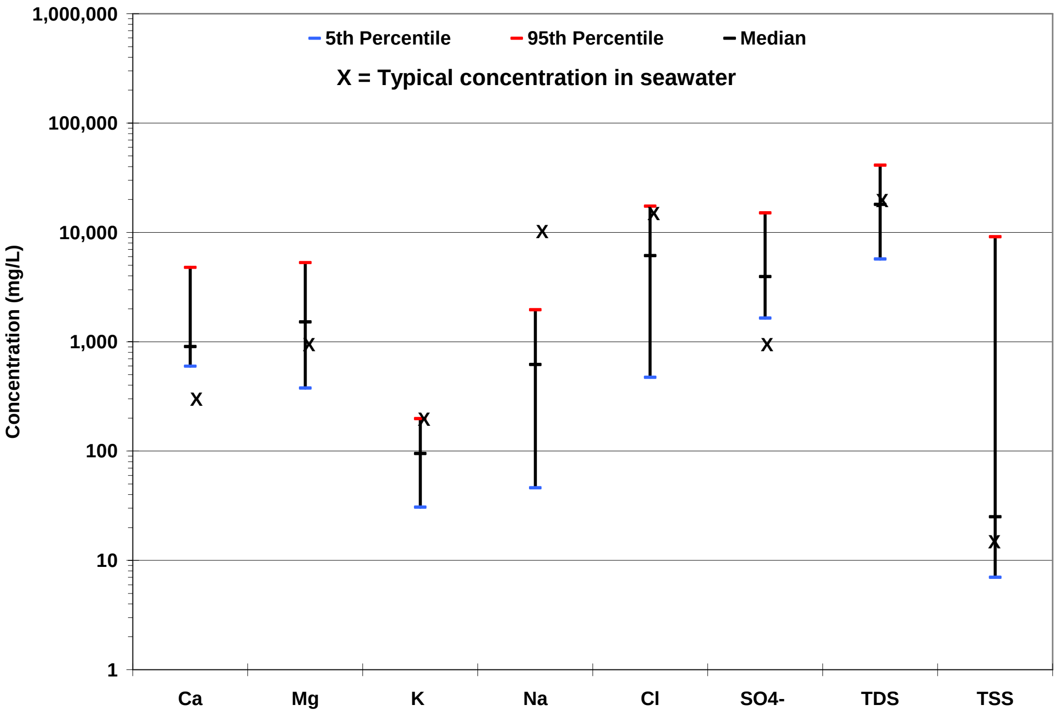


Figure 2-5
Major Constituents in Unfiltered FGD Water (after Solids Removal)

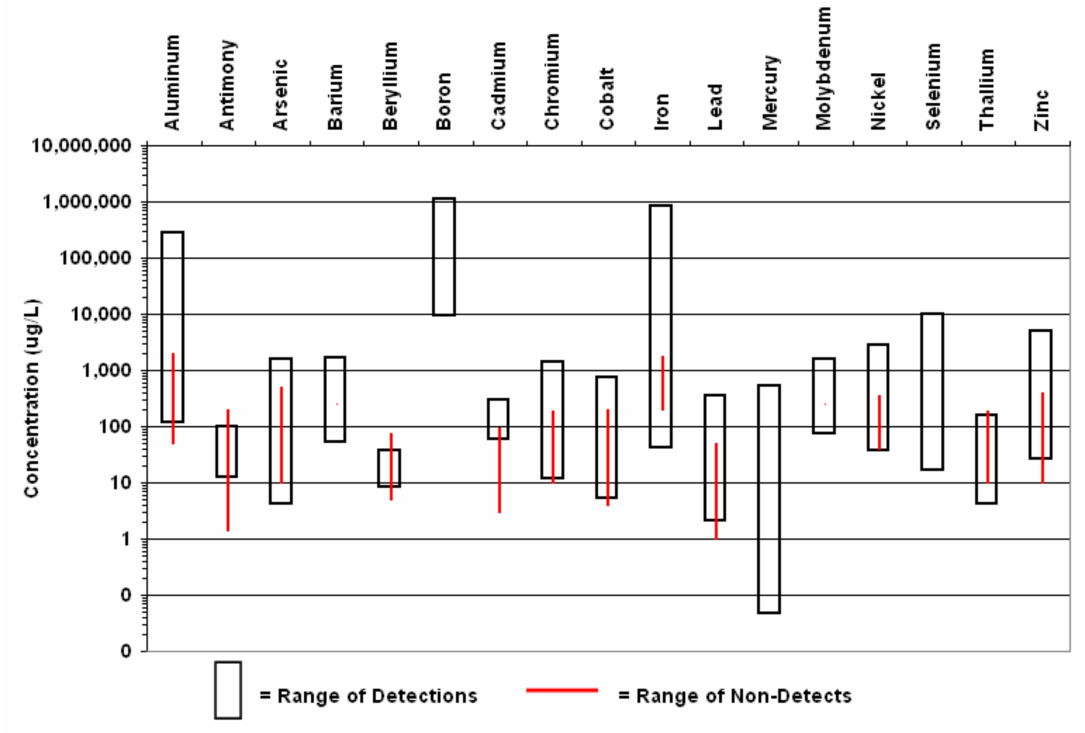


Figure 2-6
Ranges of Trace Metals in Unfiltered FGD Water (after Solids Removal)

The data in these figures are taken from studies conducted from the late 1990s to the present, using a variety of analytical methods, some of which have been determined not to produce accurate measurements of the target species. Even recent studies have been found to produce inaccurate concentrations for some elements. These ranges should therefore be viewed only as a general indicator of elemental composition. Finally, due to the small number of samples in the data set (9 samples of untreated and 18 of treated water) and the limited number of plant sites studied, the concentration ranges should not be considered representative of all FGD water systems.

The figures demonstrate the large variability (1 to 3 orders of magnitude) in both untreated and treated FGD water composition across multiple FGD systems, and illustrate that there is no such thing as a "typical FGD water". However, the plots also exhibit far more variability than would be found at a single FGD facility. First, numerous FGD system configurations and water reuse scenarios are represented in the data. The plots include data from FGD systems with various system types (inhibited and forced oxidation), primary solids removal (clarifiers, vacuum belt filters), and water treatments. Second, the trace element ranges shown in the figures include some extremely high outliers. For example, Hg was detected at 44 mg/l in one influent sample while the next highest detection was 496 µg/l. Third, evaluating ranges of total recoverable (unfiltered) metals concentrations in FGD water is complicated by the widely varying TSS present in the source samples. TSS varies greatly prior to settling (in a pond or treatment plant) and the extremely wide range of TSS values (and associated particulate metals) in these plots is characteristic of FGD waters collected from multiple sampling locations and systems.

How to best characterize high-TSS FGD waters is an important consideration in planning a sampling effort. Many metals are present predominantly in the particulate phase in FGD waters. Depending on the specific objectives of a given monitoring study, trying to characterize untreated (whole) FGD water for total recoverable metals, which is a challenging task, may not be needed. For example, if the goal is to understand what effect adding FGD water will have on a treatment pond effluent, then the optimal approach would be to let the influent to the pond settle (or even filter the influent) prior to taking a sample for metals analysis. However, if a total metals mass balance is needed, then characterizing total recoverable metals in the whole, untreated FGD water would be needed.

In addition to the inherent variability in constituent concentrations in FGD waters, the sample matrix is very difficult to analyze due to high levels of total dissolved solids (TDS), which increases the measurement variability of repeated samples. Most commercial laboratories have little experience making accurate measurements of trace metal levels in elevated TDS matrices. The elevated TDS levels create many potential interferences related to physical transport (viscosity) in instrument sample introduction systems as well as spectral overlaps or elevated background signals (see also Section 4). In addition, many elements (e.g. calcium, sulfur, boron, iron, aluminum) are unusually elevated in FGD waters, leading to unusual and novel interferences that most analytical laboratories have little experience controlling. Figures 2-3 and 2-5 compare constituent levels in FGD waters with typical levels in seawater (indicated by an "X"). The difficulty of accurately measuring metal levels in seawater is well documented in the oceanographic research literature. The comparison shows that FGD waters present even more analytical challenges than seawater:

- Although TDS levels are similar in seawater and FGD water, calcium and sulfate concentrations are significantly elevated in FGD waters.
- TSS levels in many FGD waters are orders of magnitude greater than those typically present in even estuarine seawater.

FGD Water Composition as a Function of FGD Scrubber and Treatment

In addition to coal and reagent chemical composition, FGD water composition is also affected by the FGD system type (both scrubber and water treatment configuration) and FGD system operation. FGD system variables that should be considered include:

- FGD absorber type
- Coal, boiler, and FGD performance additives
- FGD system liquid/solid separation
- FGD system purge cycle management
- Water treatment design and processes

Some metals, including selenium, are affected by the oxidation design of FGD scrubbers. Particularly for older FGD installations, systems vary greatly because scrubber technology was undergoing rapid change. In inhibited oxidation FGD systems, as the name implies, metals including selenium stay in a more reduced state (i.e. selenite (+ IV valence state). In forced oxidation scrubbers in which air is added to enhance sulfate production, conversion of selenite to selenate (+VI valence state, the most oxidized form of selenium) is enhanced, which complicates treatment (i.e. metals removal) using normal iron co-precipitation. Also the type of forced oxidation scrubber (i.e. spray tower and jet bubble absorbers) can affect metal levels in FGD water. For example, jet bubble absorbers allow higher cycles of concentration (lower purge flows) resulting in higher metals concentrations in the untreated FGD water.

Reagents added at any point in the coal combustion or flue gas treatment process have the potential to impact FGD water quality and/or the accuracy of metals analyses. The impacts of these additives are not fully understood, but should be considered in planning a FGD water sampling and analysis effort.

- A few plants are experimenting with addition of additives to coal or to the boiler to reduce mercury emissions in the flue gas. One additive that has been used is bromine. This element can partition into the FGD liquid and pose an interference for metals analysis.
- In some FGD systems, reagents are added to the absorber to improve SO_2 absorption efficiency (e.g. dibasic acid (DBA), formic acid). EPRI studies have shown that these additives may affect the concentration and speciation of selenium in the scrubber liquid. Speciation in turn affects the removal of selenium by water treatment processes [7]. The impact of additives on other metals has not been evaluated in detail.

Hydroclones are typically used to separate solids from FGD absorber liquid. Hydroclone overflow is the typical source of untreated FGD water. If a single hydroclone is used, and this is the only source of untreated FGD water, then TSS concentrations as high as 3-6 percent can be observed. If a secondary hydroclone is used, the purge solids content is lower (•1-2%). Lower TSS levels can also result when gypsum dewatering filtrate is added to the hydroclone purge stream. If settling ponds or thickeners (instead of hydroclones) are used for solids control, purge water TSS levels may also be low. Many metals (e.g. Hg, Pb) are associated with particulates, and their concentration in the purge stream (FGD WWTP influent) is directly related to TSS level.

The purge of untreated FGD water to the FGD water treatment system controls the concentration of chlorides in the absorber reaction tank slurry to an acceptable maximum. This typically ranges from 12,000 ppm (spray tower absorbers) to as high as 35,000 ppm (jet bubbler absorbers) depending on the corrosion resistance (metallurgy) of the FGD system. The flow rate of untreated FGD water (i.e. typical range of 75-1,200 gpm) varies among different facilities and over time at the same plant. The flow rate is typically based on controlling chlorides (corrosion control) and fines in the FGD absorber liquid. Use of high chloride coal will lead to higher flow rates to control chloride levels. Conversely, use of lower chloride coal reduces the blowdown flow rate to the FGD WWTP. These corrosion (chloride) control procedures directly affect trace metal levels in FGD waters. The more reuse cycles a scrubber can accommodate before diverting the purge stream to the FGD water treatment process, the higher (more concentrated) the trace metals levels become in the untreated FGD water (purge stream).

FGD water treatment systems and FGD ponds are designed to remove TSS and most associated particulate metals via solids removal (settling). The metals content of the FGD water depends on whether a metal is particulate or soluble in the recirculating scrubber (absorber) slurry, because most solids (90-95%) are removed in the gypsum stream and are not purged in the FGD water [2]. If a metal is associated primarily with particulate material in the scrubber slurry, then most (e.g. ~90% or more) will be removed to the gypsum. Due to their presence in coal and their volatility, two metals of primary concern for FGD treatment are selenium and mercury. Selenium is soluble and is relatively volatile in flue gas, and thus a significant fraction of the selenium from coal partitions into FGD water. Mercury is also volatile in the flue gas but is more particle-reactive. As a result more of the mercury in coal ends up in the gypsum, and the mercury that is present in the untreated FGD water is associated primarily with the particulate phase. Because of these processes, the composition of FGD water can vary as a function of the WWTP design.

Reagents are added in a WWTP to promote precipitation of metals (ferric iron and pH adjustment) and coagulation of the suspended particulate (polymers). Other treatment chemicals or processes may be added to meet specific discharge criteria. Describing these treatments and their impact on the FGD discharge is beyond the scope of this report, but the reagent inputs and characteristics of the treated water should be taken into account in planning the sampling and analytical effort. In particular, the concentrations of target species in the water will determine the need for clean sampling techniques and trace-level metals analysis.

3

COLLECTING REPRESENTATIVE FGD WATER SAMPLES

The purpose of this Section is to provide practical information for collecting representative and contamination-free FGD water samples. The focus of the discussion is on compliance monitoring because of the need for highly accurate data for permit compliance reporting. However, other types of sample collection (e.g. process monitoring) where highly accurate, low detection limit data may not be required, will also be discussed. Much of the information provided here is drawn from the latest EPA Method update final rule (MUR), which became effective 12 April 2007 [8].

Designing a FGD Water Sampling Plan

Collecting a representative sample of a variable matrix is challenging but necessary to accurately characterize FGD water composition. Because of the large number of potential variables and sampling scenarios, there is no single sampling approach that will work for all situations. However, to design an effective sampling strategy, the following steps should always be followed:

1. Review the FGD system and water treatment system characteristics
2. Define the specific objectives of the sampling plan
3. Identify and characterize the sampling points (SP)
4. Define the analytes and analytical methods needed to meet study objectives
5. Determine the number and type of samples to be collected
6. Determine if dissolved (filtered) samples are needed
7. Select appropriate sampling equipment and procedures
8. Specify data acceptance, validation and usability criteria

It is imperative to understand the operation of the FGD system to be able to collect representative water samples. A flow diagram of the FGD system and WWTP should be obtained for each unit and the operations reviewed with plant engineers. Questions that should be answered include:

- Which waste streams have continuous, uniform flows and which ones have intermittent flows?
- How many recirculation (concentration) cycles are representative of normal operations, or is the number of cycles continually varying due to changes in coal sources or other factors?
- Are metal levels in the coal and FGD reagent (e.g. limestone) consistent over time? How often do the source lots of coal and reagent change? What is the lag time between a change in coal burned and the time when the combustion byproducts would enter the WWTP?
- Are source solids (i.e. coal, reagent chemicals) and air measurements needed in addition to aqueous determinations to provide a complete system mass balance to meet study objectives?

- How variable is the operation of the scrubber and the FGD WWTP in terms of the use and volume of process chemicals?
- What is the detention time of the water in the treatment plant?
- Are there regulatory reporting requirements that must be considered in selecting the SPs?

The answers to these questions must be taken into consideration to design the sampling plan and schedule sampling events. The sampling plan should include provisions to monitor and record critical operational parameters immediately prior to and during the sampling event.

The goals of the sampling plan and specific questions to be answered must be clearly defined. Is the sampling required to support NPDES permit compliance monitoring or is it a process oriented study aimed at optimizing water treatment? Based on expected temporal variability, how many samples will be needed and how often should they be collected to obtain representative data? Is mass loading data needed to address specific project goals? Do plant operations have to be modified during the sampling event to answer specific project questions? Do treatment processes such as solids removal need to be monitored for the project? What other ancillary data (e.g. flow rates, coal and limestone sources and usage rates, etc.) need to be collected prior to or during the sampling event to meet study objectives?

Each of the SPs to be sampled must be specified and characterized. What means of access is there to the waste stream at each SP? Are modifications needed such as the installation of a special sampling tap or making modifications to facilitate access to the SP? If mass loadings are to be determined, flows must be measured during sampling. Not all reagent and waste streams are metered; flow meters may have to be installed to support the sampling plan. What are the flow characteristics at each SP that affect the timing of sample collection? Is there spatial heterogeneity in the waste stream that must be accommodated during sample collection? For example, in clarifiers the TSS level in the water is significantly affected by the location of the SP in relation to the inlet and outlet and the settling dynamics of the clarifier. Are there operations in the vicinity of a SP (e.g. coal pile management, generator operation, motor vehicle traffic, etc.) that generate dusts or vapors and should be halted during the sampling event to avoid contaminating the samples?

The next step in designing a sampling plan is to define the target analytes and ancillary data to be collected. What analytes must be measured to meet project objectives? Are there any process monitoring measurements (e.g. flow, rate of chemical addition, temperature, conductivity, etc.) that must be recorded to support each sampling event? Which metals will be determined, and what are the minimum quantification limits (MQL, also referred to as the minimum reporting limit) needed to meet study objectives? What levels of TDS (or specific conductance), TSS and other major constituents are expected in the FGD water at each SP. This information will assist in selecting appropriate analytical methods, as described in Sections 4 and 5.

The number of samples and the frequency of collection should take into consideration the variability of the waste streams and the study objectives. The more variable the waste stream, the higher the frequency (temporal and/or spatial) of sampling required to accurately capture that variability. For example, if the project objective is to collect a sample representative of water quality over a 24-hour period, there is a continuum in representativeness from a single grab sample (least representative) up to a 24-hour composite from an automated pump capable of collecting a sample every few minutes (most representative). A SP that has only variable and intermittent flows (temporal variability) requires special consideration about how best to collect a truly representative sample. At SP's with spatial heterogeneity (e.g. clarifiers, pond channels, etc.) pre-sampling using an easily measured surrogate such as TSS or TDS may be required to identify the sampling location that is most representative of the waste stream.

The decision to collect total recoverable (unfiltered) or dissolved samples (or both) will be dictated by the goals of the sampling effort. NPDES permits may specify collection of either or both types of sample, as dictated by the state or federal permitting authority. If the objective is to obtain a mass balance for a treatment process, a total metals measurement will be needed. Dissolved measurements can be used as a surrogate for determining which metals can be settled out by solids removal and which metals remain soluble and may require additional treatment processes. Considerations for filtration procedures include:

- The sampling plan should specify when and how dissolved samples will be filtered. EPA guidance specifies that dissolved metals samples be filtered onsite within 15 minutes of collection [9], and this approach is recommended for FGD water samples. EPA guidance does allow dissolved Hg samples only to be filtered at a laboratory within 24 hours of collection, if onsite filtration is not feasible [9].
- Normally, 0.45 µm pore size filters are used, which is the EPA operational definition of dissolved constituents. However, depending on the amount and importance to the study of small (colloidal) particulates (< 1 µm), the type of filter used can make a difference. Capsule filters tend to retain a larger fraction of the < 0.45 µm colloids than do flat filters.
- If a dissolved composite sample is required, gravimetric compositing of individual dissolved grab samples is preferred to collection of a single composite sample. Filtering composite samples at the end of a 24-hour collection period is problematic for potentially reactive FGD waters. If composite sampling is needed, the flow rates of the waste stream must be monitored to permit flow proportioned compositing.
- Depending on the specific objectives of the study, it may be advisable to allow high solids samples to settle for a set period of time (e.g. typically one hour) prior to filtration from the "cleared" liquid. For example, this approach would be appropriate if you are trying to determine the effectiveness of a settling pond or simple clarifier.

The types of sampling equipment and the procedures needed to support the sampling plan are a logical extension of the factors discussed above. If low MQLs are needed for metals analysis then the use of clean sampling equipment and procedures (including field blanks) would be prudent to minimize the chance of contamination (false positives) during sample collection. If high MQLs are acceptable then conventional sampling procedures with no field blanks or specially pre-cleaned sampling equipment may suffice. If a mixture of high and low MQLs are required, then clean sampling procedures should be used to collect all metals and mercury samples.

At a SP with easy physical access and low water variability, a single grab sample (i.e. submerged grab or sampling tap) may be appropriate. If dissolved (filtered) samples must be collected, pumped grab sampling is preferred to allow real time filtration. At a SP with highly variable water (as indicated by high TSS or intermittent flows), some type of composite sampling, either individual grabs gravimetrically composited or pumped composite sampling, will be needed.

For high TSS waters, the location of the sampling point must be selected carefully to obtain a representative sample. If a pump is used for sample collection, care must be taken to avoid the solids settling or accumulating in the pump tubing during extended composite sampling periods. Special procedures must be used to collect replicate samples for high-TSS waters, to avoid unequal distribution of settled solids. Procedures for splitting these types of samples are discussed later in this section.

Acceptance criteria must be specified in the sampling plan to insure that the data obtained will be sufficiently accurate and usable to meet study objectives. Valid data are typically defined in terms of acceptable performance for both field quality control samples [e.g. equipment blanks (prepared and analyzed in the laboratory to certify sampling equipment as clean prior to shipment for use in the field), field blanks and field duplicates) and laboratory QC samples such as certified reference materials, matrix spikes, digestion and laboratory duplicates, blank spikes and method blanks. The level at which acceptance criteria are set is a compromise between the importance of detecting matrix interferences (inaccurate data) and the cost of excluding data and having to re-sample. For example, a percent recovery of analyte from a matrix spike (MS) sample of ±15-20% is considered a stringent acceptance criterion, and a percent recovery of ±30-35% a much less stringent criterion. It is important to state in the sampling plan the criteria for rejecting non-usable data which will be excluded from consideration, as well specifying the flags or qualifiers to be assigned to data of limited usability that may be used but is considered an estimate. In addition to QC acceptance criteria, decisions on the usability of data should consider other factors. For example, were plant operations in an upset condition during sampling which would render the data unusable in meeting study objectives? Specifying acceptance criteria up front will facilitate the decision to resample if it is determined that insufficient usable data have been collected.

Clean Versus Conventional Sampling for FGD Waters

Clean sampling refers to procedures that are used to reduce or eliminate introduction of contaminants into environmental samples. Sources of contaminants that clean sampling is designed to control include ambient air, dust from nearby industrial processes, sampling equipment, sample bottles, skin and clothing. Numerous studies have shown that the use of clean sampling for surface waters can reduce the observed levels of metals by an order of magnitude. Clean sampling is particularly important for mercury, due to its volatility and the extremely low detection limits required for compliance monitoring.

The decision whether to incorporate clean sampling into a specific FGD water sampling plan will depend on the objectives of the project. The planner must balance the data quality requirements with the additional cost of clean sampling equipment and the additional time and effort needed to perform the clean sampling procedures. The risk of having to repeat sampling and analysis if unacceptable levels of contamination are found must also be considered. In this report, we present a tiered approach to the use of clean metals and mercury sample collection (i.e. "clean hands-dirty hands" procedures) based on target reporting limits (RL). This approach should facilitate tailoring the sampling techniques to a specific FGD water sampling effort.

Developments within the regulatory community suggest that clean metals and Hg sampling procedures may be needed in the future for NPDES compliance monitoring. EPA Region 6 recently proposed new MQLs that are far lower than those in use in other Regions [10]. Permittees should ascertain the applicable NPDES MQLs for their permitting authority and determine if plans are underway to change (lower) any of the relevant MQLs. Achieving the proposed Region 6 MQLs will likely require clean collection techniques. States in this Region

[Arkansas, Louisiana, New Mexico (non-delegated), Oklahoma and Texas] have been requested to adopt the proposed MQLs. Of the ten MQLs that were changed, all were lowered by a range of 4 to 400 fold. The selenium (Se) MQL was unchanged at 5 µg/L and Hg was lowered by 40 or 400 fold, depending on the analytical method used. Particularly for mercury, the proposed MQLs cannot be achieved without the use of clean procedures to minimize the occurrence of false positives due to contamination during both sample collection and analysis. In addition, at such low MQLs, the potentially significant impact of sampling contamination cannot be evaluated without the use of field blanks required by clean procedures.

Table 3-1
EPA Region 6 Minimum Quantification Limits (MQL)

Element	Existing MQL (µg/L)	Revised MQL (µg/L)	Analytical Method
Ag	2	0.50	EPA 200.8
Al	100	2.5	EPA 200.8
As	10	0.50	EPA 200.8
B	100	100	EPA 200.7
Ba	100	100	EPA 200.7 or EPA 200.8
Be	5	0.50	EPA 200.8
Cd	1	1	EPA 200.8
Co	50	50	EPA 200.7 or EPA 200.8
Cr (Total)	10	10	EPA 200.8
Cu	10	0.50	EPA 200.8
Hg	0.2	0.005 / 0.0005	EPA 245.7 / 1631E
Mo	10	10	EPA 200.8
Ni	40	0.50	EPA 200.8
Pb	5	0.50	EPA 200.8
Sb	60	60	EPA 200.7 or EPA 200.8
Se	5	5	EPA 200.8
Tl	10	0.50	EPA 200.8
U	10	0.1	EPA 200.8
V	50	50	EPA 200.7 or EPA 200.8
Zn	20	20	EPA 200.8

Clean metals and Hg sampling procedures were introduced by the EPA in the mid-1990's to support the lower metals and Hg monitoring requirements of NPDES permitting. The primary guidance document for clean sampling procedures is EPA Method 1669 [11]. This method was written with low-level Hg monitoring in mind and can be intimidating to a first time reader. Method 1669 provides a detailed description of the two-person approach (i.e. clean hands-dirty hands) recommended for clean sampling, and should be consulted before starting a clean sampling program. Such detailed descriptions of clean sampling procedures are beyond the scope of this report. However, clean sampling procedures are largely based on a common sense approach to minimize contamination during sample collection. Basically, clean sampling procedures can be distilled down to a few simple principles:

- Use only carefully pre-cleaned sampling bottles and equipment (e.g. tubing sets, filters, etc.) that have been pre-analyzed in the laboratory (i.e. equipment blanks) down to the lowest reporting limit needed for each element of interest.
- Collect at least one field blank for each set of up to ten samples collected at a given site (SP) at the same time, to document the presence or absence of contamination introduced during sample collection. Insure that the field blank is collected, to the greatest extent possible, in exactly the same manner as the associated field samples.
- Collect samples carefully to minimize the possibility of any airborne particulates entering the sampling equipment or sample bottle. In many cases, this means simply wearing powder-free gloves and opening a pre-cleaned bottle only long enough to collect the representative sample of interest. Also, it is often prudent to start with more stringent clean sampling procedures (e.g. special outer garments, etc.) and then relax them using non-detectable field blank performance as the determining factor.

Obviously, the most carefully collected field sample can be compromised (contaminated) during laboratory analysis. Because of this situation, the EPA also introduced the so-called “1600 series” clean analytical methods of which EPA method 1631E [12] and method 1638 [13] are the most widely used. These clean methods provided sufficient sensitivity to make accurate measurements at low water quality criteria concentrations and included required field QC samples (i.e. field blanks and field duplicates) and extensive guidance on contamination control in analytical laboratories.

Tiered Use of Clean Sampling Procedures

The use of clean sampling procedures can add to the complexity and cost of a monitoring study. A tiered approach can be used to allow tailor the level of clean sampling to the data usability needs of a given monitoring study [14]. Table 3-2 describes in detail a four-tiered approach to consider in designing the sample collection protocols. The term original equipment manufacture (OEM) in the table refers to equipment that can generally be used right out of the manufacturer’s box for sample collection without any additional pre-cleaning steps by the end user.

The EPA does not recognize or distinguish between the terms clean and ultra-clean. However, these terms are generally recognized by the environmental monitoring community as indicating different levels of effort in clean sampling and are used for this discussion. Tier 1 assumes basic metals and Hg sampling practices (i.e. no smoking, care to avoid sampling in the rain, blowing dust, vehicle or machinery exhausts, etc.). Progressively higher tiers incrementally add more contamination control and avoidance procedures until Tier 3, at which all feasible clean sampling procedures are employed. Figure 3-1 shows a typical Tier 3 clean sampling set-up in an industrial setting, complete with full Tyvek suits, face masks and CleanBox® portable clean sampling enclosures.

Table 3-2
Tiered Approach to Clean Metals and Hg Sampling

Sampling Item	**Tier 1**	**Tier 2A**	**Tier 2B**	**Tier 3**
General description	Conventional	Clean	Cleaner	Ultra-Clean
Lowest expected reporting limit (µg/L)	> 100	• 10	• 1	< 1
Field blanks	Recommended	Yes	Yes	Yes
Sample containers (bottle blanks)	OEM	OEM	Special	Special
Pump tubing (sampler blanks)	Installed	New	Special	Special
Filters (sampler blanks)	OEM	New	Special	Special
Powder-free gloves	Recommended	Yes	Yes	Yes
Plastic ground cover	NA	Recommended	Yes	Yes
Portable "CleanBox"	NA	Recommended	Yes	Yes
Normal work clothes	Yes	No	No	No
Clean outer garments	NA	Yes	Yes	No
Special outer garments incl. Tyvek	NA	NA	As needed	Yes
Full Tyvek outer garments	NA	NA	As needed	Yes

NA - Not applicable ; OEM – original equipment manufacture Adapted from Boothe (2000) [14]

The key deciding factors in selecting the level of clean sampling effort (tier) to be used are:

1. The lowest MQL or reporting limit required for any analyte of interest in the samples to be collected.
2. The expected analyte concentrations in the waste stream to be sampled. For example, selenium is generally found in FGD waters at levels well above reporting limits, and blank contamination is not a significant issue. For this element, the level of clean sampling effort needed to avoid significant contamination is less than for other metals present at lower concentrations.
3. The general sampling environment. For example, sampling outside near a coal or ash pile on a windy day will require a higher level of clean sampling effort than sampling from a sampling tap inside a building.

It is best to err on the side of caution; beginning with a higher (cleaner) tier and then moving to a lower tier based on the continuing ability to achieve acceptable field blanks. The criterion for an acceptable field blank will depend on the target levels and data quality objectives. In general, for Hg, the blanks should be below detection. This recommendation for Hg can be relaxed for those FGD water samples and SPs with known higher (e.g. parts per billion) Hg concentrations. For other metals, the concentration in the blank should be less than the reporting limit for each element. However, for process monitoring and other applications with high concentration waters, higher blank levels may be acceptable.

Figure 3-1
Clean Sampling Operation

Specific considerations that apply to the tiered approach to clean and ultraclean sampling described in Table 3-2 are summarized below:

- **Field blanks:** For Tiers 2A, 2B and 3, field blanks are required. For Tier 2A an approach can be considered where a field blank at one sampling point (SP) is used to satisfy the field blank requirement for all samples collected during the same sampling event on the same day at the same facility but at different SP's. For Tiers 2B and 3, EPA guidance should be followed explicitly, meaning that one field blank is collected for each set of samples collected at a given SP at the same time, to a maximum of 10 samples.
- **Sample containers:** Tiers 1 and 2A can use commercially available, trace metal grade plastic (metals) or glass (Hg) bottles. For Tier 2A the use of series "200" bottles should be sufficient. Be sure to confirm that the series "200" bottles are pre-cleaned and certified for the lowest trace metal or Hg detection limit needed for the monitoring study. Series "300" bottles with a certificate of analysis should not be needed for Tiers 1 and 2A sampling. For Tiers 2B and 3, specially pre-cleaned bottles should be used and low-density polyethylene (LDPE) is preferred for metals and borosilicate glass for Hg. Bottle supplier must provide equipment (bottle) blank data for each cleaning batch of bottles supplied. Bottle blank data should certify that the LDPE and glass bottles are clean down to the lowest trace metal and Hg detection limit needed for the monitoring study. For Tier 3 bottles, the bottle blank data detection limits may need to be much less than.1 ppb for certain elements.

- **Pump tubing:** For Tier 1 sampling, using existing installed pump tubing that has been flushed with deionized water to remove adhering particulates and then flushed with several liters of sample water should be satisfactory. However, the efficacy of reusing the same installed pump tubing to collect samples at the same SP for a prolonged period of time should be evaluated on a case by case basis. For Tier 2A sampling, new or re-used tubing that has been acid pre-cleaned and is configured for the SP should be used. It is recommended that a sampler blank (i.e. deionized water passed through the pre-cleaned tubing) be taken and analyzed to confirm that the tubing set is clean to below the lowest trace metal or Hg detection limit needed for the monitoring study. For Tiers 2B and 3, specially pre-cleaned tubing sets (i.e. FEP inlet tubing and Cole Parmer C-flex pump tubing) specifically configured for the SP should be used. The tubing set supplier must provide equipment (sampler) blank data for each cleaning batch supplied. Sampler blank data should certify that the tubing set is clean down to the lowest trace metal or Hg detection limit needed for the monitoring study. For Tier 3 tubing sets, the sampler blank data detection limits may need to be << 0.1 µg/L for certain elements.
- **Filters:** EPA guidance requires that dissolved metals filtration (0.45 µm) be performed within 15 minutes of sample collection [9]. Tier 1 sampling can use commercially available filters certified for trace metals use. For Tier 2A, use new filters taken from the original equipment manufacturer's packaging that are certified for metals and Hg use and are certified clean (usually on package) below the lowest trace metal or Hg detection limit needed for the monitoring study. A sampler blank (i.e. deionized water passed through the filter) should be taken and analyzed to confirm that the filter is clean below the lowest trace metal and Hg detection limit needed for the monitoring study. For Tiers 2B and 3 sampling, specially pre-cleaned 0.45 µm filters should be used. The filter supplier must provide equipment (sampler) blank data for cleaning batch of filters supplied. Sampler blank data should certify that the filter is clean down to the lowest trace metal detection limit needed for the monitoring study. For Tier 3 filters, special additional cleaning may be needed and the filter sampler blank data detection limits may need to be << 0.1 µg/L for certain elements.
- **Powder-free gloves:** Use of powder-free gloves is recommended for Tier 1 and required for Tiers 2A, 2B and 3. Sampling personnel may don multiple pairs of powder-free gloves and peel each pair off when it is considered to have become contaminated.
- **Plastic ground covers:** Ground covers are recommended for Tier 2A sampling and required for Tier 2B and 3 sampling. New plastic ground covers not contaminated with dust, etc. during storage should be used to control particle generation at a SP and discarded after each use.
- **Clean enclosure:** For Tier 2A, a portable, clean sample handling enclosure is recommended to minimize the chance of airborne contamination during sample processing. Such enclosures are especially useful when dissolved metals filtrations are being performed in the field or when airborne particulates are a concern. For Tiers 2B and 3 a portable enclosure should be used.
- **Outer garments:** For Tier 1, normal work clothes can be used but care should be taken that the clothes are not excessively dusty or dirty. For Tier 2A and 2B sampling, clean work clothes should be worn by sampling personnel and an effort should be made to remove loose particulates (e.g. using a masking tape delinter roll or similar device) at each SP prior to sample collection. This approach may be sufficient for Tier 2B sampling. Typical sampling conditions and the ability to obtain acceptable field blank data should be used to make this

decision. For Tier 3 sampling, a continuum from a Tyvek apron to full Tyvek overalls to full Tyvek head covering, booties and mask (to avoid mercury contamination from dental fillings) should be considered. Typical sampling conditions and the ability to obtain acceptable field blank data should be the determining factors in this decision. With experienced sampling personnel, it is usually possible over time to back-off from total Tyvek outer garments.

- **Sampling personnel:** The use of trained local sampling personnel familiar with typical conditions at each SP and interested in collecting contamination-free samples is always recommended. For Tiers 2A, 2B and 3 sampling, training of local personnel by experienced personnel (e.g., an outside subcontractor) should be considered. After initial training and follow-up (e.g. phone or e-mail to answer follow-up questions), local personnel should be able to successfully conduct all tiers of clean metals sampling.

Conventional (Process) versus Clean Sampling Procedures

Conventional sampling procedures (Tier 1) are widely used at most power plants and FGD systems. For process control sampling or monitoring where data are used only internally, this approach can be recommended. Conventional procedures are familiar to plant personnel and usually provide adequate data quality to meet process control needs at an acceptable cost for sampling and analysis. Deciding when to move to clean sampling and analysis procedures and how to tailor the level of clean sampling effort is not a precise process. Table 3-2 listed reporting limits (RLs) for which various tiers might be appropriate. These concentrations take into account the potential contamination balanced against the target RL needed for a study.

In practice, the tier is usually chosen (defaults) to accommodate the analyte with the lowest target RL. It is not efficient or desirable to mix tiers in the same study. If samplers have to collect Tier 3 Hg samples, it is usually not worth the time and effort (except for safety or other logistical reasons) to remove Tyvek outer garments in order to collect higher level or conventional parameter samples. As suggested above, the best approach is to start with a more stringent tier for the initial sampling events and then move to less stringent tiers if field blanks are acceptable. This is the optimal approach for low detection limit compliance monitoring. The author’s experience is that with properly trained and motivated local personnel, Tier 2B without Tyvek outer garments is usually sufficient to collect both low-level metal (compliant with MQLs at or below those listed in Table 3-1) and Hg samples (to an MDL/RL of 0.2/0.5 ng/liter) with acceptable field blanks.

Clean Sampling Equipment

Clean sampling methods are generally common sense based procedures aimed at minimizing the possibility of airborne contaminants (i.e. from blowing dust, clothes bound particulates, etc.) from entering carefully pre-cleaned sampling equipment during sample collection. The focus of this section is to summarize important considerations for selecting equipment to be used when employing clean sampling techniques. EPA Method 1669 should be consulted for detailed descriptions of equipment cleaning and certification procedures.

Table 3-3 summarizes the latest EPA guidance and requirements for collecting and processing clean metals and Hg samples in the field. Current EPA guidance requires that metals and Hg sample not be refrigerated or iced after collection or during shipment (to avoid potential melt water contamination). EPA guidance also allows metals and Hg samples to be preserved at the receiving laboratory under clean room conditions rather than in the field. All considerations being equal, preservation in the laboratory is the preferred approach. Any precipitation that may occur between sample collection and laboratory preservation should be reversible upon addition of the preservation acid.

FGD waters may require more acid preservative than a typical sample to achieve the required pH < 2. In some cases, the samples are so alkaline (or have so much buffer capacity) that the required pH cannot be obtained without excessive sample dilution. In this case, pH adjustment in the laboratory will be required. Also, the pH of FGD water samples should be checked prior to any processing in case any changes in the original preservation status.

The current EPA sampling guidance [12, 15] has greatly simplified the processing and shipment of clean metals and Hg samples compared to earlier requirements. Field sampling personnel can simply collect the sample and return the bottle to the original double bags. At this point, the clean samples are ready for shipment without ice and with no need for expedited overnight shipment unless dissolved Hg samples are to be filtered at the receiving laboratory.

All equipment used in clean sampling (i.e. bottles, tubing sets, filters, etc.) that will come in contact with the FGD water being sampled must be rigorously pre-cleaned and verified by analysis of a bottle blank to be below the MDL of the method to be used to analyze the sample. Table 3-3 lists the types of sample containers required for metals and Hg sampling. Although Table 3-3 focuses on aqueous samples, the information is also generally applicable to related solids sampling except for different solids preservation and digestion requirements as outlined in the applicable methods.

For pumped sampling, pre-cleaned and blank-tested tubing sets pre-configured to a given SP are needed. A typical tubing set configuration incorporates a 25 foot FEP Teflon inlet tubing (0.31 inch OD and 0.25 inch ID) mated to an appropriately sized peristaltic pump tubing. The length of inlet tubing can be more precisely tailored to a given SP but, depending on the supplier, may not reduce costs because a shorter length may be considered a custom configuration. Automated composite peristaltic pump samplers are often used for pumped sampling. The standard pump tubing size for these sampling pumps is 0.375 in ID and 0.625 inch OD. Consistently acceptable (non-detectable) equipment (sampler) blanks have been achieved using Cole-Parmer c-flex type pump tubing. Polypropylene or high density polyethylene tubing fittings (e.g. couplers, “Y” splitters, etc.) can be used to construct tubing set configurations to meet any sampling scenario. Each tubing/fitting connection should be secured using a plastic cable tie to avoid leakage during field sampling. Each tubing set configuration used for clean sampling must be pre-cleaned and blank-tested.

Of the other clean sampling equipment listed in Table 3-2, powder-free gloves are the most important aside from the actual sample bottles and tubing sets. The powder-free specification is important because of the high trace metal levels present in talc powder. For Tiers 2B and 3, the powder-free gloves selected (i.e. vinyl, latex, etc.) should be pre-tested for metal and Hg levels by dipping the gloves into a ~ 1% nitric acidic solution and then analyzing the solution for the elements of interest. This approach will identify the potential metal contaminants associated with the gloves, which will be helpful in selecting the supply of powder-free gloves best suited to a given monitoring study. Any plastic bags used in clean sampling (except ground covers) should be food grade but typically do not have to be pre-cleaned and blanked.

Clean Sampling Procedures

For many FGD water monitoring studies, project requirements will necessitate the use of clean sampling procedures (see Table 3-1, Tiers 2A, 2B and 3). The focus of this section is to summarize important considerations when employing clean sampling techniques. EPA Method 1669 should be consulted for detailed descriptions of clean sampling procedures (i.e. “clean hands and dirty hands”).

Table 3-3
Clean Metals And Mercury Collection Requirements for Water[1]

Sampling Parameter	**Trace Metals**	**Low-Level Mercury[2]**	**Conventional Mercury[3]**	**Boron**	**Cr (VI)**
Analytical method	EPA 200.8/1638	EPA 1631E, EPA 245.7	EPA 245	EPA 200.8 modified for clean use, EPA Method 1638	EPA 218.6
Method description	ICP-MS	CVAFS	CVAA	ICP-MS	Ion chromatography /colorimetric
Sample containers	Polyethylene or FP	Glass (4) or fluoropolymer (FP)	Polyethylene, FP or glass[4]	Polyethylene, FP or quartz	Polyethylene, FP or glass
Refrigeration / icing during composite sampling (5)	Not required	Not required	Not Required	Probably not required[5]	Refrigerate/ice composite at •6 °C during collection
Dissolved metals filtration- grab samples[6,7]	•15 minutes of sample collection	• 24 hours of sample collection	•15 minutes of sample collection	•15 minutes of sample collection	•15 minutes of sample collection
Dissolved metals filtration - composite samples[6,7]	•15 minutes of sample collection or individual grabs	• 24 hours of sample collection or individual grabs	•15 minutes of sample collection	•15 minutes of sample collection	•15 minutes of sample collection
Preservation	HNO_3 pH < 2	pH < 2 Bromine monochloride & Yellow color[8]	HNO_3 pH < 2	HNO_3 pH < 2	Ammonium sulfate buffer
Field preservation	No. Preserve at laboratory[9]	No. Preserve at laboratory[9]	No. Preserve at laboratory[9]	No. Preserve at laboratory[10]	Cool, •6 °C, pH = 9.3– 9.7
Post collection refrigeration / icing	No[9]	No[9]	No[9]	No[9]	Maintain •6 °C until analyzed
Preservation holding time (oxidized or digested in original sample bottle)	24 hours prior to analysis	28 days	Preserve immediately upon receipt at lab.[11]	Preserve immediately upon receipt at lab.[11]	15 minutes

Table 3-3 (continued)
Clean Metals And Mercury Collection Requirements (1)

Sampling Parameter	Trace Metals	Low-Level Mercury[2]	Routine Mercury[3]	Boron	Cr (VI)
Preservation holding time (not in original sample bottle)	NA	48 hours	NA	NA	NA
Analytical holding time	180 days	90 days	28 Days	180 days	28 Days

1. Based on Table II and footnotes in EPA Method Update Rule (MUR) [8]

2. Hg by cold-vapor atomic fluorescence spectrometry (CVAFS, EPA Methods 1631E and 245.7).

3. Conventional (routine) Hg by cold-vapor atomic absorption spectrometry (CVAAS, EPA Method 245.2).

4. Low-level Hg samples require a FP (Teflon) lined cap.

5. This interpretation is based on MUR Table II, footnotes 2 and 19. Trace metals and low-level Hg samples do not have to be refrigerated or iced after collection (see also note 9 here). However, if some other analyte (e.g. TSS) is to be collected from the same composite sample used for metals and Hg then refrigerating/icing the automated composite sampler during actual sample collection would be necessary. EPA guidance for boron is ambiguous and the conservative approach would be the refrigerate/ice the composite sample during collection if boron is one of the analytes of interest.

6. Based on MUR Table II, footnotes 7 and 17. For low-level dissolved Hg, if circumstances preclude overnight shipment of if sample integrity will not be maintained by shipment to and filtration in the laboratory , the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. Field filtration should occur as soon as possible after collection to maintain sample integrity.

7. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (MUR Table II, footnote 2) in place of a composite sample collected automatically. Four grab samples over the course of a day, at 6-hour intervals is stated in footnote 2.

8. EPA Method 245.7 preservation involves adding 5 mL/L of pretested 12 N HCl followed by $KBrO_3/KBr$ directly to the sample bottle at least 24 hours before analysis.

9. Based on MUR table II footnote 19 (trace metals) and EPA Method 1631E (low-level Hg). Because routine Hg is collected in the same bottles as routine trace metals then the interpretation here is that MUR table II footnote 19 (not footnote 2) also applies to routine Hg samples. The reasoning for no icing is to avoid melt water contamination of samples during storage and shipment.

10. Again, because other trace metals are collected in the same bottles as boron then the interpretation here is that MUR table II footnote 19 (not footnote 2) also applies to boron.

11. Interpretation here is compromise due to ambiguity between applicability of MUR Table II footnotes 2 and 19 to routine Hg and boron samples which are often collected as normal trace metals samples.

Closed Pipe With a Sampling Tap

For SPs with a sampling tap, the primary considerations are to purge the tap prior to sampling and to shroud the tap to minimize airborne contamination. Figure 3-2 shows an installed polyvinyl chloride (pvc)-valved tap configured with three outlets for split sampling. For the tap configuration shown, pre-cleaned tubing was attached to the tap to direct the split samples into CleanBoxes® for sample processing. The tap itself should be cleaned to remove loose particulates. The tap should also be shrouded with a gallon size, food grade plastic bag with a small slit opposite the bag opening. The bag shroud is held in place using a plastic cable tie. When split samples are not needed, a normal sample tap can be used in the same way.

After the shroud is in place, the sequence of actions to sample at the tap is as follows:

1. A field blank is taken by pouring blank water from one bottle to another inside the shroud.
2. The tap should then be opened and allowed to purge for several minutes to insure a representative sample will be collected.
3. The pre-cleaned sample bottle is opened inside the shroud, filled and immediately recapped.
4. The filled container is placed back into the original double bags.

An alternative is to attached a pre-cleaned piece of tubing onto the tap, perform the same purging step, then fill the sample bottle inside a portable CleanBox® type clean sampling enclosure. Before installing the tubing on the tap, a field blank should be taken by pouring blank water through the tubing into the field blank bottle.

Automated composite pump sampling is potentially feasible from a low-pressure tap. However, special equipment has to be installed that can be costly. A good approach is to take four individual tap grabs (as describe above) over a 24 hour period and request the laboratory to prepare a gravimetrically flow-proportioned composite from the grab samples (see MUR Table II footnote 2).

If dissolved metals or Hg are to be collected, a larger volume grab would be collected from which the dissolved sample will be taken. Again, a dissolved field blank should be taken before the dissolved FGD sample using the same pump tubing set and filter.

Figure 3-2
Using a Splitter to Collect Replicate Samples

Direct Access To Water Surface

Several clean sampling options are feasible when there is direct access to the surface of the water being sampled. Manual submersion grab sampling is the "gold standard" and safest way to take a contamination-free grab sample. The steps to be used are as follows:

1. A pour field blank is taken by pouring blank water from one bottle to another near the surface of the water where the submersion grab sample will be collected.
2. The sample bottle (still capped) is submerged, uncapped facing upstream, filled and recapped underwater.

For a pumped grab, the procedure is similar. Whenever the open ends of a tubing set are open to the atmosphere they should be covered with a food grade plastic bag to avoid airborne contaminants getting into the interior of the pre-cleaned tubing set. Figure 3-3 shows a typical Tier 2B pumped grab sampling set-up for surface water monitoring. Steps used in pumped grab sampling include:

1. The field blank is taken by pumping blank water through the tubing set and into the field blank sample bottle.
2. The same tubing set is attached to a pvc pole with plastic cable ties and positioned in the FGD water being sampled. Prior to use the pvc pole should be wiped clean of any adhering particulates that could inadvertently become dislodged and enter a sample bottle during collection.

3. The tubing set is purged with the FGD water and the sample aliquot is pumped into the sample bottle. Again, pumped sample processing is best done inside a portable clean sampling enclosure.

A pumped grab sample for dissolved metals or Hg would be collected in the same manner, using an inline membrane filter (not a cartridge) or a syringe filter. A similar procedure can be used for automated composite pump sampling of the FGD water.

Figure 3-3
Clean Setup for Surface Water Grab Sampling

Figure 3-4 shows a typical clean pumped composite sampling setup. A “Y” splitter is being used to deliver a sample of the pumped waste stream to two composite samplers. The composite bottles (inside the plastic tubs) are iced because other analytes requiring icing were being sampled from the composites. The large volume composite sample bottle should be shrouded from the outside environment during the 24 hour collection period. Sub-sampling a representative aliquot from a large volume composite bottle must be done carefully, with the composite sample bottle being thoroughly shaken during the entire “multi-pour” sub-sampling procedure (i.e. described below under split sampling). Dissolved metals or Hg samples can be filtered directly out of the composite bottle at the end of the 24 hour sampling period (see MUR Table II, footnote 7). Taking four or more individual grabs to be gravimetrically composited in the laboratory is another alternative for composite sampling. To flow-proportion individual grabs, flow rates at the SP would have to be monitored during the sampling period covered by the four or more grab samples.

Figure 3-4
Clean Setup for Surface Water Composite Sampling

Dissolved Metals or Hg Sampling

For compositionally complex and changeable FGD waters, it is preferable to filter dissolved metals or Hg samples in the field within 15 minutes of collection, as required by EPA guidance (MUR Table II, footnote 7). The only exception to the “15-minute rule” is for dissolved low-level Hg, which can be filtered in the laboratory within 24 hours of sample collection (MUR Table II, footnote 17). Research to date has shown no clear trend concerning dissolved Hg filtered immediately in the field or filtered within 24 hours in the laboratory [1]. Metals and Hg in FGD waters can be in the form of colloids (i.e. particles size • ~ 1 micrometer). Research has shown that capsule (cartridge) inline filters can over-sample (retain) colloidal metals and Hg particles smaller than 0.45 µm, giving a lower dissolved (i.e. EPA definition of < 0.45 micrometers) concentration than flat filters, including syringe filters.

Clean sampling procedures require that a dissolved field (filtration) blank be collected for each set of up to 10 dissolved samples collected at a given site (SP) at the same time. Filters for clean sampling must be pre-cleaned and blank-tested. Depending on the MQLs needed for a given study, it may be possible to use filters without pre-cleaning if filter blank data provided by the manufacturer certifies that the filters are free from contamination at or below the study required MQL. Acid cleaning of filters should be avoided if possible because of the potential for residual low pH conditions in the filter that can result in overestimating the dissolved metals or Hg due to leaching of particles retained on the filter.

Split Sample Collection

EPA clean metals and Hg guidance have no requirement for split sample analysis. However, collecting identical split samples can be an important means to ascertain data quality, by sending the splits to multiple laboratories for confirming (consensus) analyses. Split sampling and confirmation analysis is especially important for complex FGD waters with substantial analytical uncertainties. Collecting identical splits can be a challenge especially in higher-TSS samples. The best approach is to collect a representative large-volume grab sample from which the splits are sub-sampled. The optimal sub-sampling approach is the so-called “multi-pour” method. The large-volume grab is thoroughly homogenized (shaken) before each aliquot is poured. An aliquot comprising approximately 25-33% of the total desired split sample volume is poured into the first sample bottle. The parent large-volume sample is re-shaken and a similar sized aliquot is poured into the second split sample bottle. This procedure is repeated for each additional split sample. Once all split samples have received one aliquot, the process is repeated for each split in sequence until the total volume is achieved. Another approach is to use a pre-cleaned tubing set with a “Y” splitter to collect two split samples simultaneously.

Sampling High Solids FGD Waters and FGD Blowdown

FGD waters, especially influents to FGD treatment systems prior to primary clarification or a pond, often have TSS levels greater than 1%. Collecting a representative sample of such a high-solids sample can be challenging. A key consideration is whether or not the FGD water is homogeneous at the SP. Collecting a series of TSS samples over a 24 hour period is one way to evaluate homogeneity. Once a well mixed SP is established, the main concern is not to allow the FGD water to fractionate by settling during the sampling process. This may be a concern during pumped grab sampling. The best approach is probably grab sampling of a well mixed SP.

Sampling FGD slurry or blowdown can be especially challenging due to the potentially very high and variable solids and other factors such as high sample temperatures. The solids may be present at such high levels that a visible layer of sediment will accumulate on the bottom of a sampling container. To collect a representative sample of the matrix will require some type of composite sampling, probably a flow-weighted composite of individual grabs taken over the sampling period chosen. The grab samples must be allowed to cool and then thoroughly shaken or mixed to resuspend solids before being composited. However, in some FGD systems with continually circulating, well-mixed slurries, grab (not composite) sampling may be adequate for collecting representative samples.

Clean Sampling Field QC

Field QC samples are an integral part of clean metals and Hg sampling methodology. Clean metals and Hg data are not considered valid or usable for compliance reporting purposes without the appropriate associated field QC data. EPA Methods 1631E (Hg) and 1638 (metals) are the two most widely used clean analytical methods. The field QC requirements in EPA Method 1669 (sampling) and the two clean analytical methods are used as the basis for this discussion. The conventional EPA metals methods 200.7 and 200.8 have no field QC requirements, but depending on the data quality objectives of the project, it is generally desirable to collect field QC samples for use with those methods. Table 3-4 summarizes the field QC sample requirements for clean metals and Hg sampling.

Acceptable equipment blanks (i.e. bottle and sampling equipment that will contact the sample) are required before the equipment can be shipped for use in the field. Depending on the MDL/RL required for a given FGD water monitoring study, commercially available (i.e. off the shelf) sample bottles may not meet the acceptance criteria both for frequency of blank testing and for the concentration at which the bottle is certified "clean". Field blanks (collected on site) are used in place of trip blanks (shipped to the site and back to the laboratory). Trip blanks are not required by any clean metals or Hg guidance or method.

Table 3-4
Clean Metals And Mercury Field QC Samples

Field QC Sample	Minimum Frequency	Acceptance Criteria
Trace Metals[1]		
Bottle Blank	Representative set of bottles	< RL or < 1/5 of level in associated sample, whichever is greater
Sampler Blank	Each type of sampling equipment used	< RL or < 1/5 of level in associated sample, whichever is greater
Field Blank	One with each set of samples collected from the same site at the same time, to a maximum of 10 samples	< RL or < 1/5 of level in associated sample, whichever is greater
Field Duplicate	One for every 10 samples that are collected at a given site	Relative Percent Difference should be < 20%
Field Replicate	Not specified	Not specified
Low-Level Mercury[1]		
Bottle Blank	At least 5% of the bottles from a given lot	< RL or < 1/5 of level in associated sample, whichever is greater
Sampler Blank	Each type of sampling equipment used	< RL or < 1/5 of level in associated sample, whichever is greater
Field Blank	One with each set of samples collected from the same site at the same time, to a maximum of 10 samples	< RL or < 1/5 of level in associated sample, whichever is greater
Field Duplicate	One for every 10 samples that are collected at a given site	Relative Percent Difference should be < 20%
Field Replicate	Not specified	Not specified

1. Information based on EPA Method 1669, EPA Method 1638 and EPA 1631E.

Field blanks are the QC foundation for all clean sampling procedures. EPA clean sampling guidance is clear on the field blank requirement: at least one field blank must be collected for each set of samples collected at a given site (SP) at the same time, to a maximum of 10 samples. Without an associated field blank, or if the associated field blank does not meet the acceptance criteria, the clean metals or Hg "results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes." Field duplicates are required to be collected at a frequency of 10% but have only recommended (i.e. not a required) acceptance criteria.

Specific considerations that apply to field QC requirements for clean metals and mercury sampling are summarized below:

- **Reporting Blank Data:** EPA guidance requires that equipment and field blank data be reported down to the method detection limit (MDL) for the appropriate method/element combination. This reporting allows evaluation of potential contamination bias for samples where element concentrations are very near the reporting limit (RL or ML). See also item 5.
- **Bottle Blanks:** Pre-cleaned bottles should be filled with blank water acidified to pH<2 and allowed to stand for a minimum of 24 hours. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned.
- **Sampler Blanks:** These equipment blanks are generated in the laboratory or equipment cleaning facility by processing blank water through a representative number of each pre-cleaned sampling device (e.g. tubing set, filter, dipper, splitter, etc.) using the same procedures that are to be used in the field. If any device shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected devices re-cleaned.
- **Field Blanks:** Collected prior to collecting any field samples at a given site (SP). The field blank must be collected using the same equipment and same procedures as those used to collect field samples. The field blank must be representative of the same field sampling conditions existing during collection of the field samples.
- **Field Blank Acceptance Criteria:** The field blank acceptance criteria of "< RL or < 1/5 of level in associated sample whichever is greater" must not be interpreted as allowing field blanks detected between the MDL and RL to be automatically considered acceptable. For example, if Hg is detected in the field blank at a level of 0.45 ng/L (i.e. just below the ML of 0.5 ng/L) then any sample associated with that field blank which exhibits a Hg concentration of less than 2.25 ng/L (i.e. less than 5 times the level detected in the field blank) may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.
- **Field Duplicate:** Two separate samples collected sequentially at a given site (SP) during the same sampling event.
- **Field Replicates:** Although not specified in EPA guidance, field replication represents an additional approach to collecting two samples at a SP during a single sampling event. For example two aliquots from the same larger volume 24 hour composite bottle would be considered field replicates instead of true field duplicates which would require two separate 24 hour composite pumping systems.

Conventional Sampling Field QC

Two conventional analytical methods (EPA 200.7 and 200.8) commonly used for the analysis of FGD waters have no field quality control (QC) sample requirements. EPA Method 200.7 (ICP-AES) is usually not sensitive enough to justify the use of equipment or field blanks but field duplicates should be considered to evaluate sampling variability. EPA Method 200.8 (ICP-MS) can achieve very low MQLs. If study objectives require low MQLs for one or more metals, then the use of clean sampling field QC as described in Table 3-4 should definitely be used. The frequency of field QC could be adjusted (relaxed) based on study requirements as a cost savings measure.

4

ANALYTICAL METHODS FOR NON-MERCURY METALS IN FGD WASTEWATER

FGD water is an extremely challenging matrix for trace metals analysis. First, the FGD water matrices are highly variable both between power plants as well as over time at the same facility. This means that developing or optimizing metals methods even at a single facility is not straightforward. The large variety of FGD system designs and treatment processes means that an analytical procedure that works well for one site's samples may not work for another's. The high level of variability in trace metal concentrations make it difficult to design an analysis scheme (i.e., dilutions, matrix spikes) that will be applicable from one batch of samples to another. Second, as shown in Section 2, metals of interest for environmental monitoring (e.g., selenium) can be present at concentrations hundreds or thousands of times lower than major elements. Total dissolved solids (TDS) levels can approach 50,000 ppm (seawater is 35,000 ppm) and can have unique distributions of elements (e.g., B, Ca, Fe, K, Mg, Na, S) that can produce unexpected and unusual analytical interferences. For these reasons, routine implementation of standard EPA methods will fail to produce accurate trace metals measurements for many FGD waters.

In most cases, laboratories will need to perform method evaluation/development and optimization on a site-specific water to achieve the consistent data quality required for compliance monitoring, and to a lesser extent process monitoring. Analysis of FGD waters for mercury has special requirements; although mercury can be measured by the methods discussed in this section, it is most often analyzed by specialized methods. Analytical methods for mercury are discussed in Section 5.

The difficulty in obtaining accurate metals data for FGD water is illustrated by a recent sampling and analysis effort completed by the EPA at four power plants [3-6]. Sequentially collected, duplicate samples were analyzed by two different analytical methods (EPA Methods 200.7 and 200.8). Significantly different concentrations (i.e. 2-3 fold or more difference) were observed for some elements. For example, FGD WWTP effluent arsenic and selenium concentrations exhibited up to 10-fold differences. As a result, it was impossible to determine a reasonable consensus concentration value.

FGD sample characteristics that are particularly problematic from an analytical perspective include high TDS and extremely high concentrations of several elements that impact both optical and mass spectra. The implementation of existing "standard" EPA, multi-element, plasma methods (EPA 200.7 & 200.8) in most laboratories is not robust enough to accommodate the challenging FGD sample matrices without additional method development/optimization. The EPA methods were validated primarily in low TDS waters such as publicly owned treatment works (POTW) effluents and drinking waters and were not optimized for higher TDS samples. Section 1.3 of both plasma methods have specific recommendations "to reduce potential interferences, dissolved solids should not exceed 2,000 ppm (w/v)." Simple dilution of high TDS samples can reduce but not completely eliminate potential interferences. Dilution also results in significantly elevated method detection and reporting limits (i.e., loss of sensitivity) leading to an increase in the number of non-detects and highly variable results. For example, in a recent split sample study, FGD WWTP effluent samples were analyzed by one laboratory using EPA Method 1638 at a 100 fold dilution; 36% of the measurements for the 11 elements analyzed were below the detection limit. For the same samples analyzed by EPA Method 200.7, the situation was even more pronounced, with 46% of the measurements for 26 elements below detection limits [3-6].

The situation facing FGD water analysts is analogous to that faced by chemical oceanographers in the 1970's, trying to make accurate trace metals measurements in seawater. Even though seawater is an incredibly consistent matrix with high TDS, direct analysis by plasma methods has generally proven to be ineffective. This fact is well documented in the oceanographic literature. Trace element marine chemists had to develop and optimize specialized methods (e.g., preconcentration ICP-MS; see EPA Method 1640 [16]) to perform consistently accurate trace metals measurements in seawater. FGD water metals analysis will have to undergo a similar methods development/optimization to overcome the existing analytical uncertainties. The highly variable nature of FGD waters, along with novel interferences caused by the unusual elemental distributions, will complicate the optimization process.

The optimization of analytical methods for FGD water analyses is currently hampered by the lack of a matrix-matched, certified reference material (CRM) such as those used by chemical oceanographers. A CRM is a well-characterized material that has been analyzed by multiple, highly accurate, analytical methods to derive a certified, consensus concentration of one or more analytes. Without a CRM, the only way to evaluate the accuracy of a method is through the use of multiple confirming analyses using independent analytical methods, a cumbersome and time-consuming process. The availability of one or more FGD water CRMs would assist the process of method development/optimization for both plasma related and other analytical methods.

The intent of this section is to provide guidance in selecting methods for trace metals analysis of FGD waters, and to review the current state-of-the-art in applying and optimizing methods for analysis of FGD waters. The focus is on EPA methods that are commercially available and are known to be applicable to the FGD water matrix. Both total recoverable and dissolved metals measurements in FGD waters are addressed. Sampling and analysis for metal speciation (e.g., Se^{6+}) is not addressed in this report. Speciation analyses have unique sampling and analysis requirements specific to each element, and this topic will be addressed in future EPRI research.

Analytical Methods for Metals in FGD Waters

EPA has published numerous methods for analysis of metals in ambient water and waters. In general, methods intended for analysis of metals in industrial wastes or solids (e.g., those in SW-846) are not applicable to FGD waters and should not be used, even for process monitoring. Methods used to satisfy NPDES permit monitoring requirements must be approved by the authorizing agency, and are generally limited to EPA methods published in 40 CFR, Part 136.

The EPA Office of Water has developed two series of methods for water analysis: the 200 Series and the 1600 Series [17]. The former are conventional methods intended for application to waste streams with relatively high levels of contaminants. The latter are intended for analysis of trace levels of analytes in relatively clean matrices, such as ambient waters. Despite this fact, the 1600 methods have advantages for analysis of FGD water.

Two conventional methods are often used for FGD water metals analysis: EPA Method 200.7-- Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES) and EPA Method 200.8-- Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) [18,19]. The 1600 series methods that have been applied to FGD waters include EPA Method 1638-- ICP-MS and EPA Method 1632-- Hydride Generation Quartz Furnace Atomic Absorption Spectrometry (for arsenic and selenium only) [13, 20].

The primary difference between the 200 series and 1600 series methods is that the latter contain enhanced laboratory QC and contamination control practices that allow accurate quantification at extremely low concentrations. For routine process monitoring studies that can accommodate higher MQLs, the series 200 methods can usually provide data that are usable to meet the less stringent data quality objectives often associated with non-compliance monitoring studies. Method 200.7 lacks sufficient sensitivity to quantify many target elements in FGD water; for these elements, data quality would benefit little from the use of clean analytical QC procedures. However, Method 200.8 can achieve low MQLs and, depending on the objectives of the study, the laboratory can be requested to implement clean analytical procedures even though they are not called for in the method. For example, if only higher MQLs are needed for a process study using EPA 200.8 then the conventional method QC should be sufficient. However, if lower MQLs are required then the enhanced contamination control procedures described in method 1638 should be used for 200.8 analyses.

In evaluating the performance of a method and the capabilities of a particular laboratory, it is important to understand the terminology used for detection and quantitation. The minimum quantification limit (MQL) is a general term for the lowest concentration at which an element can be accurately measured with a specified level of confidence. The MQL is usually used as the lowest calibration point for an analytical method. EPA establishes nationwide limits for promulgated methods used for compliance monitoring under 40 CFR, Part 136: these are the method detection limit (MDL) and minimum level (ML). Each laboratory performing these methods must determine their own MDL and ML based on at least seven replicate analyses, following statistical procedures established by EPA in Part 136, Appendix B. However, the laboratory may also cite a reporting limit (RL) in their lab reports, which is the concentration in a sample that is considered accurate by that laboratory. The RL of an undiluted sample of a clean water matrix should not be higher than the ML, but will be adjusted to account for the dilution of each sample.

In FGD water monitoring studies, it is very unlikely that laboratories will be able to achieve as low a ML as they can with clean water. The laboratory should be requested to determine a matrix specific MDL/MQL in a matrix such as seawater or FGD water known to have very low concentrations of the elements of interest. The MDL study should be performed by spiking replicate samples of this matrix with concentrations of the target analytes at concentrations close to the expected MQL. An MDL study performed with high concentration spikes will not produce an accurate quantitation limit.

Another difference between the 200 series and 1600 series methods is that the former require only a single matrix spike (MS), because they are typically applied to samples where the native concentrations are well above the MQL so that laboratory duplicates can be used to determine analytical precision. Clean methods add a matrix spike duplicate (MSD) so that analytical precision can be determined even if the element of interest is not detected in the unspiked sample. If low MQLs are required to meet study objectives, the addition of a MSD to Methods

200.7 and 200.8 should be considered. The use of more than one method blank could also be beneficial when trying to achieve accurate low detection limit data. This same logic applies to the tiered use of clean sample collection methods (see Table 3-2) when using conventional analytical methods for low detection limit analyses.

In order to use a method for NPDES compliance monitoring, the method must be approved by the EPA by publication in 40CFR, Part 136. Methods 200.7 and 200.8 are approved methods. EPA Method 1638 is not approved under Part 136, and therefore cannot formally be used for compliance monitoring. However, it is acceptable to use Method 200.8, modified to add the clean procedures and performance requirements of Method 1638, as long as the Method 200.8 performance requirements are met. There is no approved equivalent to EPA Method 1632; however, use of this method has been accepted in some cases by state permitting authorities. Facilities should determine from their permitting agency which methods are acceptable for a particular regulatory program. Recent updates in EPA guidance (Method Update Rule new CWA section 136.6 see references [8] and [21]) provide dischargers much more flexibility in the use of non-approved analytical methods (such as EPA 1638 and ICP-DRC-MS) for NPDES compliance monitoring.

Laboratories have developed modifications to the EPA methods that show promise in overcoming some of the interferences from the FGD water matrix and increasing the method sensitivity. These include the use of an ICP-MS (Methods 200.8 or 1638) equipped with a collision/reaction cell (CRC) or dynamic reaction cell (DRC), and substitution of an atomic fluorescence spectrometer (AFS) for the AAS specified in Method 1632. The MUR [8] added section 136.6 to Part 136 to help users of modified Part 136 methods satisfy clients, accreditors, and regulatory authorities who prefer the clarity and authority of a CWA regulation. The intent of the new section 136.6 is to codify a longstanding performance-based philosophy in the CWA program. It builds on the flexibility specified in section 9.2 of EPA's 1600-series chemical methods (e.g. see method 1638). The EPA wants users to be able to timely modify Part 136 approved methods to overcome matrix problems, automate methods, or otherwise improve the efficiency or accuracy of a compliance analysis without unnecessary delays associated with obtaining formal approval for an Alternate Test Procedure (ATP).

In general, only changes to the determinative step (e.g., the detector), the quality control, or significant chemistry of the method, are outside the scope of 40 CFR Part 136.6. Also an analyst may not modify any sample preservation and/or holding time requirements of an approved method. The method flexibility provided by section 136.6 means that modified methods can be used for NPDES compliance monitoring as long as the method performance specifications of the parent method are satisfied. Similarly, ICP-DRC-MS and ICP-CRC-MS modifications of EPA 200.8 can be used for compliance monitoring, provided that an analyst documents that the method performance specifications of EPA 200.8 ICP/MS are met [21]. Such modifications that improve the performance of CWA methods are allowed by the new section 136.6 without any formal EPA review.

Table 4-1 compares features of the analytical methods that will be covered in this section, using Se as an example. More detailed descriptions of these methods are provided later in this section. Se detection and reporting limits are listed for both ideal (i.e. dilute acid matrix) and typical FGD waters. MDL/RL information for other metals is given in later method-specific sections.

Clean Analytical Methods for Metals in FGD Waters

Clean analytical procedures go hand in hand with clean sampling protocols as a means to obtain accurate measurements at very low trace metal concentrations. It is useless to do one without the other, as carefully collected field samples can easily be compromised (contaminated) in the laboratory if appropriate clean analytical procedures are not used. Contamination control for clean analysis shares similarities with clean sampling and incorporates the following general principles:

- Use only carefully pre-cleaned analytical equipment and ultra-pure analytical acids and reagents.
- Make sure the analytical system, including the sample introduction system, is clean and delivering the lowest blank levels achievable. Avoid analyzing unknown, potentially high concentration samples on a clean instrument set up for low detection level analyses.
- Perform as much of the sample preparation and analysis as possible under clean room or otherwise carefully controlled laboratory conditions.
- Use method and other procedural blanks to document the level of contamination in all preparation and analysis procedures.
- Specific considerations that apply to the methods described in Table 4-1 are summarized below:
- EPA Methods 200.7 and 200.8 are approved for Clean Water Act (CWA) use effective 4-12-2007 [15]. Method 1638 has gone through multi-laboratory method validation but is has not been promulgated. Although use of Method 1638 has been allowed by some permitting agencies, an alternative is to use a modified Method 200.8, adding the clean procedures and enhanced quality control from Method 1638.
- EPA 200.8 and 1638 Modified for DRC or ICP-CRC-MS. No draft method has been published by the EPA for either the DRC or CRC modifications of ICP-MS. Current implementations are considered modifications of direct aspiration ICP-MS method 200.8 and draft method 1638. Modified collision cell ICP-MS methods have received EPA performance based approved for CWA use under the new Section 136.6 as discussed above [21].
- The HGAFS method described here is a modification of draft EPA Method 1632, modified for flow-injection selenium analysis by HGAFS. The method modification may be considered an allowable performance-based modification under Section 136.6 as discussed above [21], but this needs to be verified by the permitting agency.
- Methods are identified as clean or standard. Clean methods (e.g. Method 1638) are designed to support trace metals analysis requirements at low ambient water quality criteria concentrations. Clean methods require the enhanced field QC (i.e. field blanks) and laboratory contamination control procedures needed to make accurate measurements at the lowest possible MDL/MQLs achievable by the method. Standard methods (e.g. Method 200.8) do not include the enhanced QC and contamination control requirements, but these requirements can be specified in the laboratory's contract and should be used with Method 200.8 for low MQL applications.
- Instrument detection limits (IDL), method detection limits (MDLs) and reporting limits (IRL) are based on the analysis of a low concentration, ideal, dilute acid sample matrix, according to the EPA MDL guidance, and will vary from laboratory to laboratory.

- For ICP-MS, samples must be diluted to achieve an analytical TDS concentration of ~ 2,000 mg/L to avoid severe physical transport interferences. For ICP-AES a lower dilution factor of 2 should be achievable with an optimized method including a TDS- tolerant sample introduction system.

Clean analytical methods incorporate enhanced QC requirements to evaluate the accuracy, precision and lack of contamination of the analyses. Table 4-2 summarizes the enhanced QC requirements incorporated into all EPA clean analytical methods.

Table 4-1
Comparison of Analytical Methods for Selenium in A Typical Treated FGD Water[1]

Analytical Parameter	**EPA 200.7 ICP- AES**	**EPA 200.8/ EPA 1638 ICP-MS**	**EPA 200.8/ EPA 1638 ICP-DRC-MS**	**EPA 200.8/ EPA1638 ICP-CRC-MS**	**EPA 1632 mod. HGAFS**
Method description	Inductively Coupled Plasma-Atomic Emission Spectroscopy	Direct aspiration ICP-MS	ICP-MS modified for Dynamic Reaction Cell	ICP-MS modified for collision/reaction cell	Hydride generation atomic absorption (HGAA) modified for atomic fluorescence and flow injection
Method status	Approved for CWA	Approved for CWA[1]	Approved for CWA[1]	Approved for CWA	Not approved for CWA
Method type	Standard	Standard / Clean	Standard / Clean	Standard / Clean	Clean
Selenium undiluted IDL (µg/L)	15	0.45	0.2	0.21	0.05
Selenium undiluted IRL (µg/L)	50	1	1	1	0.2
Typical analytical dilution factor	2	10	10	10	2
Selenium MDL in a “typical” FGD water (µg/L) [2]	30	4.5	2	2.1	0.1
Selenium RL in a “typical” FGD water (µg/L) [2]	100	10	10	10	0.4
Method advantages	Can accommodate higher sample TDS allowing lower analytical dilutions. Sample not introduced into spectrometer, avoiding instrument contamination.	Can be very sensitive and generally unaffected by Se species present in the FGD sample	Can be very sensitive and generally unaffected by Se species present in the FGD sample. Can minimize (control) many polyatomic isobaric interferences	Can be very sensitive and generally unaffected by Se species present in the FGD sample. Can minimize (control) many polyatomic isobaric interferences	Very sensitive and can accommodate higher sample TDS allowing lower analytical dilutions

Table 4-1 (continued)
Comparison of Analytical Methods for Selenium in a Typical Treated FGD Water

Analytical Parameter	EPA 200.7 ICP- AES	EPA 200.8/ EPA 1638 ICP-MS	EPA 200.8/EPA 1638 ICP-DRC-MS	EPA 200.8/ EPA1638 ICP-CRC-MS	EPA 1632 mod. HGAFS
Method disadvantages	Lower sensitivity and needs a sample introduction system optimized for higher TDS to minimize analytical dilutions.	Sample introduced into mass spectrometer – high-concentration samples can contaminate detector. Must dilute higher TDS samples lowering sensitivity. Many lower mass polyatomic isobaric interferences are possible in complex FGD matrices	Must dilute higher TDS samples and in DRC mode signal strength (count rate) significantly reduced. New interferences created by DRC reactions are possible.	Must dilute higher TDS samples and in CRC mode signal strength (count rate) significantly reduced. New interferences created by CRC reactions are possible.	Can only measure hydride forming species. Hydride forming potential is not known for all Se species present in FGD waters. With incomplete digestion can underestimate the total Se concentration present in the FGD sample.

[1] Method 1638 is not approved for NPDES permit compliance monitoring, although it has been allowed in some cases. A modification of Method 200.8 that includes the clean procedures and performance specifications of Method 1638 is allowable.

[2] Calculated from the IDL (determined in dilute acid solution) by assuming the dilution factor shown, for a FGD water having the following composition: TSS 20 mg dry weight per liter, TDS 20,000 mg dry weight per liter, chloride 7,000 mg/L, sulfate 1,900 mg/L, calcium 2,500 mg/L, magnesium 1,300 mg/L, sodium 500 mg/L. DL, MDL, and RL are determined in each analytical laboratory.

IDL – instrument detection limit; MDL – method detection limit; RL – reporting limit; TDS – total dissolved solids; TSS – total suspended solids.

Table 4-2
Clean Analytical Method Quality Control Samples.[1]

QC Parameter	Purpose	Frequency
Method analytical control QC		
Calibration	Instrument setup for quantitative determinations	Once during analytical run
Initial Calibration Verification	Verify calibration	Once during analytical run
Initial Calibration Blank	Verify cleanliness and lack of carryover in analytical system	Once during analytical run
Continuing Calibration Verification	Verify calibration	Every 10 samples and after last sample
Continuing Calibration Blank	Verify cleanliness and lack of carryover in analytical system	Every 10 samples or three per analytical batch immediately following each continuing calibration verification standard
Quality Control Sample	Independent calibration verification	One per analytical run or one per analytical batch
Certified Reference Material	Independent calibration verification in matrix matched sample	Minimum of one per analytical run or analytical batch
Reagent Blanks	Verify cleanliness of analytical reagents	As needed per reagent lot and re-verify monthly
Sample specific QC		
Method Blank	Verify cleanliness of sample digestion	Minimum of one and up to three per analytical batch
Procedural Blank	Verify cleanliness of sample processing procedure	Minimum of one per unique procedure
Method Duplicate	Check of method precision within a given matrix	Every 10 samples
Laboratory Fortified Blank	Check of method accuracy in ideal dilute acid sample matrix	Minimum of one per analytical run
Matrix Spike / MS Duplicate (Batch specific and specific for each matrix[2])	Check of method accuracy and precision within a given matrix	Minimum of two MS/MSD per analytical batch
Matrix Spike / MS Duplicate (Discharge or matrix specific)	Check of method accuracy and precision within a given matrix	Perform MS/MSD on each unique sample matrix at frequency of 10%

1. Compilation of QC sample requirements from EPA clean metals and Hg methods including methods 1631E and 1638. All QC sample requirements may not apply to each clean analytical method. Specific acceptance criteria are listed in Appendix B.
2. For example, FGD scrubber influent and effluent samples constituent two different matrices and would each require an MS/MSD sample pair.

Specific considerations and definitions that apply to the clean metals QC samples described in Table 4-2 are summarized below:

- **The analytical batch**, used to define the frequency of many QC samples, is usually defined by the EPA as a set of up to 20 samples processed and analyzed as a group.
- **A quality control sample (QCS)** is an analytical standard prepared from a different, independent lot from that used to prepare the calibration standards.
- **CRM:** A CRM is recommended but optional in EPA clean methods. There are currently no CRMs available for FGD Water.
- **Reagent blank**: Each reagent used in the processing or analysis of clean samples must be checked for acceptably low concentrations of the elements of interest and periodically re-checked.
- **Procedural blanks:** This type of blank is used to verify the lack of sample contamination associated with any special sample processing. An example would be a filtration blank taken when field samples are filtered in the laboratory.
- **Matrix spike/ MS duplicate (MS/MSD):** These are duplicate samples of a study matrix (e.g., untreated FGD water) to which the laboratory adds a "spike" of the target analyte. The percent recovery of the spike provides valuable information on the performance of the method for that matrix. The MS/MSD requirement in EPA clean analytical methods states that "the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge". For batch specific QC, this requirement means that two MS/MSDs must be performed for each analytical batch of up to 20 samples. However, the EPA clean methods also include a discharge-specific requirement which means that an MS/MSD must be performed on each unique sample matrix (e.g. surface water, industrial discharge, waste water treatment plant influent, etc.) at a frequency of 10%. The only exception to the discharge specific MS/MSD requirement is POTW effluent, which is considered a sufficiently similar sample matrix to only require batch-specific QC.

The MS/MSD frequency requirement is misunderstood and implemented incorrectly by most analytical laboratories. Because FGD waters are so variable, and to be fully compliant with EPA clean method guidance, an MS/MSD should be performed at a frequency of 10% on each FGD water collected from a different sampling point. Because of the analytical uncertainties and challenges associated with FGD water metals analyses, this level of QC, while stringent, is prudent and justified. For a research study where the objective is a thorough understanding of the metals concentrations of FGD water, it may even be desirable to analyze a MS/MSD for every sample collected. It should be emphasized, however, that MS/MSDs are not a panacea for assessing data accuracy. Depending the analytical method being used and FGD water matrix involved, MS/MSDs may meet acceptance criteria and the associated concentration data still be inaccurate. For example, with an uncontrolled polyatomic isobaric interference in ICP-MS analyses, the MS and MSD are simply added on top of the interference and will likely give no clear indication that the element concentration in the unspiked sample is an overestimation of the true concentration present in the sample.

Analytical Method Selection for Metals in FGD Waters

Based on past experience with this challenging sample matrix, controlling analytical artifacts and interferences to achieve accurate data are a greater issue than detection limits for many elements. The importance of understanding the presence and concentrations of specific interferants in the FGD water of interest cannot be over emphasized. The presence of halogens (e.g. bromine and iodine), noble metals (e.g. silver, gold, palladium), complexing organics (e.g. measured as total organic carbon or dissolved organic carbon), and strong redox species (e.g. sulfur dioxide, sulfur, thiols, etc.) can wreak havoc with low level methods for Se and other metals. The lack of an analytical method with sufficient sensitivity to quantify metals in FGD water will likely not be the limiting factor for the large majority of FGD waters.

The most appropriate analytical method for the analysis of a specific element in FGD waters will depend on several factors. First, it is necessary to identify the concentrations (either a range or a minimum) of interest for each target metal. For compliance monitoring, the concentrations of interest will be the permitted compliance limits with whatever safety factor the permittee decides is prudent to avoid false positives. For an engineering study, they may be the target concentration in the treated effluent or a level that will allow calculation of a meaningful mass balance. Once these concentrations are identified, the most important determinant is how low an MDL/RL is needed to provide data that will achieve the data quality objectives (DQOs) or data usability requirements for that project. For example, for compliance monitoring it is recommended that the RL of the analytical method be at least 10 times lower than the compliance limit.

Having determined minimum MDL/MQLs of interest, the next logical step in deciding how to proceed with analyses is to determine the approximate range of elemental concentrations in the specific FGD water of interest. If time and budget permits, this can be accomplished by collecting a few exploratory samples prior to the main sampling event, or by asking the laboratory to pre-screen the samples. An effective approach is to first analyze the samples with a less sensitive method, then perform the final analyses with a more sensitive method, if necessary to achieve the desired MDL/RLs. The benefit of this approach is that it minimizes the number of dilutions that must be run on the more sensitive instrument to identify the optimum dilution. Pre-screening also avoids problems with contaminating the ICP-MS with a highly concentrated sample.

Considering this general approach, most metals would be initially measured by EPA 200.7, a multi-element method that has matured over the past several decades to the point where its detection limits will accommodate the data needs of most FGD engineering monitoring projects. Method 200.7 is also more "robust" than the ICP-MS based methods listed in Table 4-1 in that it can analyze complex, high-TDS samples usually with little dilution of the sample. This situation is in large measure due to the fact that 200.7 is an optical emission method and the sample matrix never enters the detector, as is the case with ICP-MS. Method 200.7 has been shown to have significant interferences for some elements in the FGD water matrix, and a thorough understanding of the specific interferences at each optical wavelength is needed to obtain accurate results.

Selecting an instrumental method with higher sensitivity than Method 200.7 will ultimately involve compromise. The multi-element capability of direct ICP-MS (EPA Methods 200.8 and 1638) allows for a more efficient generation of data, to the extent that they may be selected even when other analytical approaches (e.g., combining pre-analysis separations with several instrumental runs for individual elements) may provide superior results. ICP-DRC-MS and ICP-CRC-MS can reduce or eliminate many polyatomic (molecular ion) interferences, which is not possible with the unmodified, direct aspiration ICP-MS methods. This improved interference control usually comes at the expense of reducing the method sensitivity and the number of elements that can be accurately analyzed using the same DRC or CRC instrument setup.

The HGAFS method offers single element, low-detection limit capability for hydride forming elements (i.e. Se and As) that is minimally affected by the elevated TDS levels in FGD waters. Caution should be used when applying HGAFS to FGD waters that may contain Se species other than selenite and selenate. The hydride-forming potential of the many selenium-containing species observed in these waters has not been determined. Experience to date has shown that using special digestion procedures such as microwave or uv photo-oxidation minimizes the potential for underestimating Se concentrations in FGD waters due to the presence of un-oxidized organic (non-hydride forming) selenium species.

The method selection and optimizing process is hampered by the lack of a FGD water CRM. A possible substitute is to use available seawater certified reference materials that can be spiked with the elements of interest to levels more characteristic of a given FGD water matrix. Seawater CRMs are not ideal for this purpose because they lack many of the potentially interfering organics and other components found in FGD waters. Based on data usability needs, the use of carefully split samples and confirming analyses by one or more independent analytical methods and laboratories is probably the best currently available approach.

Additional information on each of the analytical methods discussed in this section is provided below. Another useful source of information on analytical methods is the archives of the plasmachem list server operated by the University of Syracuse [22]. This list server provides a forum for a wide ranging discussion of analytical chemistry issues. The discussions (threads) are archived and many provide useful information that is very relevant to the analysis of metals in FGD waters.

Digestion of FGD Waters for Metals Analysis

Table 4-3 provides a summary of digestion procedures useful for FGD water metals analysis. The digestion procedures are compatible with all analytical methods discussed in this report (see Table 4-1) except that the Method 1632 digestion requires a special HGAFS preparation digestion performed on an aliquot of sample digested by one of the other digestion methods listed.

In refining and optimizing analytical methods for FGD water analyses, the digestion procedures used are an important consideration. For example, it appears that some semivolatile elements (e.g., selenium) may be lost during open vessel digestions. Therefore, an open vessel digestion is not recommended if selenium is being measured.

The use of hydrochloric acid is required in most EPA digestion methods [25] but the acid acts as an interferant in direct aspiration ICP-MS analysis of Se, As and other elements. This interference can be overcome by use of DRC or CRC, but many trace metals labs still prefer to omit HCl from these digestions. Experience to date with FGD waters suggests that omitting hydrochloric acid from the digestion of FGD waters does not appear to substantially affect data accuracy.

The complete destruction (oxidation) of organic matter can be important for the analysis of Se by HGAFS and perhaps other methods. Differences in digestion methods applied to the same FGD water matrix can result in substantial differences in the metal concentrations observed. This situation has been observed in inter-laboratory and inter-method (i.e. 200.7 vs. 200.8) comparisons from FGD water split sample studies.

Table 4-3
Comparison of Digestion Procedures for FGD Waters

Digestion Method	**EPA 200.2**	**EPA 200.2**	**EPA 200.2 modified**	**EPA 200.2 modified**	**EPA 3015A**	**EPA 3051B**	**EPA 1638**	**EPA 1632 modified**
Method description	Open beaker	Open beaker	Vented closed lid PP tube	Vented closed lid PP tube	Closed microwave assisted bomb	Closed microwave assisted bomb	Closed in original bottle	Closed PP tube
Matrix	Water	Solids	Water	Solids	Water	Solids	Water	Water
Open/closed	Open	Open	Open (vented)	Open (vented)	Closed	Closed	Closed	Closed
Amount of sample	100 ml	1 g	50 ml	0.5 g	45 ml	≤0.5 g	125 ml	32 ml
HNO_3 / HCl (ml)	1 / 0.5	2 / 2	1 / 0.5	1 / 2.5	5 / 0 or 4/1	10 / 0 or 9 / 3	1.9 / 0 or 1.25 / 0.62	0 / 16
Percent volume evaporated	80 %	10%	5 %	10%	None	None	None	None
Temperature (°C)	85 – 95	85 – 95	95	95	170	175	85	85
Heating time (min)	150	180	180	360	30	10	180	150
Pressure (psi)	NA	NA	NA	NA	100-190	74-190	≤ ~ 10	≤ ~ 10
Digestion dilution factor	0.5 – 1	100	1	100	1.11	Variable	1.015	1.5

PP = polypropylene NA = not applicable

With the specific concern about volatilization loss of Se and possibly other metals during open vessel digestion, closed vessel digestion procedures should be used initially. Digestion losses can be evaluated by analyzing raw (unpreserved) FGD waters and comparing the data to digested samples. A microwave bomb provides the most aggressive closed vessel digestion and is preferred for any samples to be analyzed by HGAFS. For FGD water samples with TSS < 1%, a diluted strong acid leach procedure could be used. This approach involves diluting the elevated TSS FGD water sample prior to the digestion procedure and results in more complete extraction (dissolution) of the suspended solids. If very low RLs are needed, additional digestion procedures (e.g. ultraviolet photo-oxidation) and preconcentration ICP-MS (EPA 1640) may be beneficial to improving sensitivity. Experience to date suggests that preconcentration procedures are effective for quantifying elements in treated FGD waters that are present at very low levels. EPRI has not tested these alternative digestion procedures in FGD waters.

Digestion of FGD Water Solids

Both of EPA's plasma methods (EPA 200.7 and 200.8) require that aqueous slurries with a TSS > 1% "should be extracted as a solid" sample. This type of sample is known as biphasic, as it contains both aqueous and solid phases. Most FGD slurries and some untreated FGD water samples have TSS > 1%. The approach recommended here for biphasic samples is to separate the sample into separate solid and liquid fractions, which are analyzed individually using digestion techniques and analytical methods optimized for that phase. The metals concentration in the original FGD slurry sample is then "reconstructed" using concentration and gravimetric data from the two phases. Digestion methods for the solids phase are listed in Table 4-3. A procedure for separating biphasic samples using centrifugation is provided in Appendix A and has proven to be very effective for use with untreated FGD waters. The biphasic approach recommended here differs from the approach described in EPA 200.7 where the slurry is evaporated to a low volume and extracted (digested) as a solid. The biphasic approach recommended here, although more labor intensive, has the advantage of using a different extraction (digestion) procedure optimized for each phase.

Analytical Methods for Trace Metals in FGD Waters

This section describes the methods that are commonly applied to FGD waters, discusses the pros and cons of each method, and suggests measures that should be used to overcome contamination, interferences, and other problems.

ICP-AES (EPA Method 200.7)

EPA Method 200.7, "Trace Elements in Water, Solids and Biosolids by Inductively Coupled Plasma – Atomic Emission Spectrometry", measures the emission spectra of metals introduced into an argon plasma, at wavelengths that are specific for each element. The metals are introduced into the plasma by nebulizing an aerosol of the acid-digested sample. There are two types of plasma instruments – those in which the plasma is in line with the detector (axial configuration) and those in which the plasma is at right angles to the detector (radial configuration). The axial configuration provides generally lower MQLs (i.e. greater sensitivity) but suffers from more potential interferences especially easily ionizable element (EIE) effects (i.e. signal suppression or enhancement). EIE effects are more difficult to control in the axial configuration compared to the radial configuration. A schematic of these two instrument types is shown in Figure 4-1.

Method 200.7 has been in use for decades (first promulgated in 1979) and it has become a widely used method and the de facto standard for metals analysis in waters. As this method has become more familiar to analysts, regulators, and consultants, and as it has been applied to ever more diverse sample types, even more confidence has been placed in the robustness and reliability of the method. For most kinds of water samples this faith is well placed, but for FGD waters, the 200.7 method alone is insufficient to guarantee accurate, comparable inter-laboratory analyses even in split sample studies.

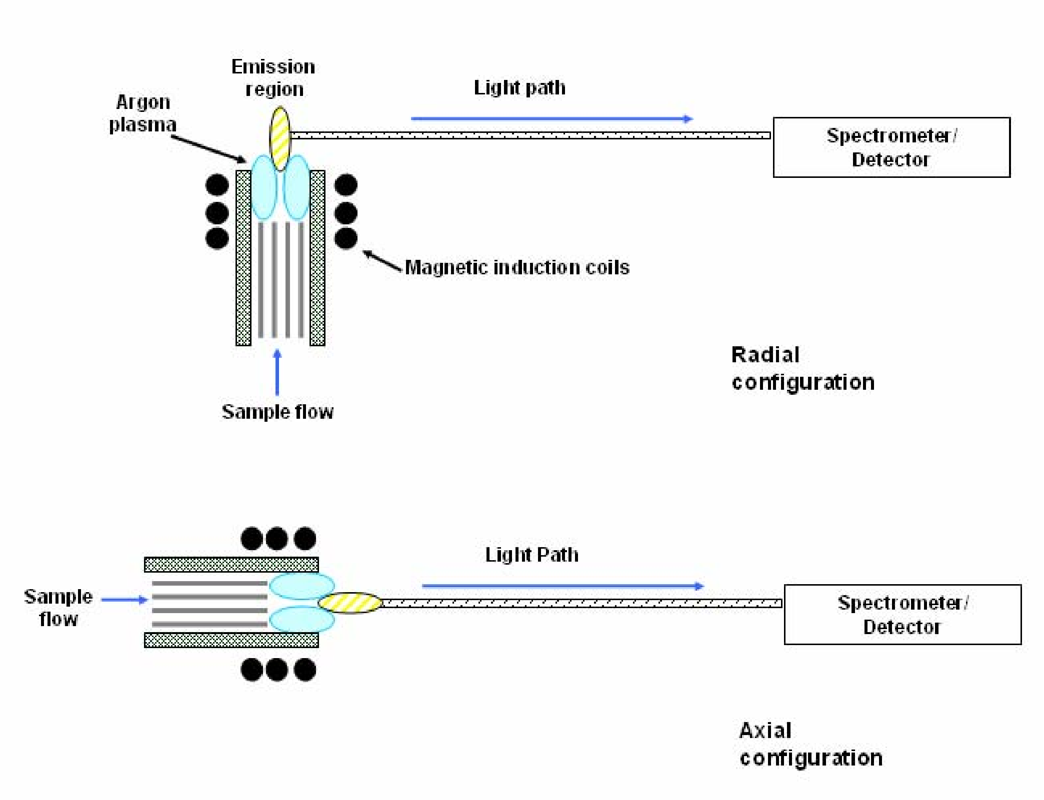


Figure 4-1
ICP-AES Analytical Systems

As frequently stated above, FGD samples are challenging due to the very high levels of dissolved solids present. Method 200.7 includes a recommendation to run samples only at a TDS of < 2,000 ppm. However, in practice much higher TDS samples can be run undiluted while still achieving acceptable data accuracy and quality. To minimize the analytical dilution, the use of less sensitive lines may be needed for certain higher concentration elements such as calcium to allow inter-element corrections to still be made at lower dilutions.

In high-TSS matrices, such as many untreated FGD waters, there are several challenges facing the analyst that are not present in routine waters or even seawater. These added interferences can vary greatly depending on the configuration of the equipment used for analysis. For example, an axially-viewed plasma instrument will suffer more easily ionized elemental (EIE) interferences than one viewed in the radial position, regardless of how closely the method is followed or the skill of the analyst, and there are no reliable mathematical corrections for these interferences. Some brands of axial ICPs incorporate design features that minimize these effects to one degree or another, and some analysts are better trained to recognize and address these issues than others. This is just one example of the potential for measurement variability by virtue of differences in hardware. For most routine work, these differences are not noticeable or will have little demonstrable impact; however, challenging samples will always magnify these effects and may contribute to poor interlaboratory precision on split samples.

Another potential problem with ICP-AES is the software used to correct for known interferences. Most labs installing a new ICP will set up a routine in the manufacturer's software that establishes procedures for element quantitation. Parameters that are set include where to look for peaks of interest, where to look near that peak to establish the peak baseline (background), as well as other parameters for calibration, interference corrections and so forth. Once established, these settings are seldom revisited, especially in large volume commercial laboratories. The routine parameters may not be appropriate or sufficient for the interferences found in a FGD water matrix.

The best opportunity for obtaining accurate and comparable results from any given laboratory on challenging samples such as FGD waters lies in a more careful approach, where the instrument is configured to the sample matrix before analysis and the resulting data are evaluated in greater detail for unexpected problems. Since FGD samples vary greatly from plant to plant, as well as over time if the source of raw materials changes, the following is a recommendation for a standardized approach to using method 200.7 for FGD water analyses.

- First, the sample should be prepared in an acid matrix that matches the standards used for analysis. The best approach uses Method 3015A with nitric and HCl under pressure, but for the initial setup and screening, a Method 200.2 type digestion is acceptable as long as the acid matrix is approximately the same.
- The ICP should be optimized for performance. A series of scans of the spectra around the lines of interest should be collected. The scans should include sufficient calibration standards and the calibration blank for reference, aliquots of individual elements used for inter-element corrections, and the sample itself. These scans should be used to evaluate which wavelengths are best suited to analyze the sample, and to optimize the off-peak point used to establish the baseline for each wavelength.
- Multiple wavelengths should be employed wherever possible for each element. In the case of major elements they can be used to extend the analytical range, and for trace components they can be used to identify potential problems and to verify the accuracy of inter-element corrections . MDL studies done by the laboratory to support any method modifications should include all wavelengths being monitored.
- If the lab is accustomed to running only the interference check standard A (ICSA) and ICSAB when verifying inter-element corrections, they would be well served to run a series of individual elemental standards at some point in their analysis. A recommended standard mixture is: 500 ppm each of Al, Ca, Fe, Mg; 50 ppm each of Co, Cr, Cu, Mn, Mo, Ni, Ti, V; 500 ppm or more of Si; 100 ppm Zr, and 50 ppm Ce. The standard mixture should also include any other elements suspected to be present in the sample (based on the prescreening analysis) at sufficiently high concentrations to interfere with one or more spectral line of interest.
- Another important consideration is that one is not able to correct for element "A" on "B" if "A" cannot be measured because it exceeded the range of the detector, or if there is no result for some other reason. This problem can be anticipated by careful review of the preliminary prescreening scan, where evidence of self-absorption or blooming or other common problems are usually obvious. For Method 200.7, these conditions can result in either an underestimation or overestimation of the true element concentration.
- It is also advisable to plan to run these kinds of samples diluted 10x or 100x at the beginning of the analytical run, followed by undiluted aliquots later in the run. To minimize carry-over

effects, the analyst can employ rinse aids and long rinse times, but it is impractical to expect the signal to return to zero for elements that are approaching saturation in solution, and unreasonable to consider detection limits relevant at such levels.

Table 4-4 lists instrument detection/reporting limits (IDL/IRL) in a dilute acid matrix and typical MDL/MQLs in FGD water for elements by Method 200.7. Table 4-5 gives a recommended multiple analytical wavelength setup for analysis of FGD waters. Method 200.7 QC requirements are summarized in Appendix Table B-1. Depending on the ICP-AES instrument being used, all wavelengths listed may not be available in all analytical laboratories. For those wavelengths listed here that are not specifically listed in EPA Method 200.7, special arrangements may have to be made with the ICP-AES laboratory to add them. Such special requests may incur additional costs.

Table 4-4
Comparison of EPA 200.7 IDL/IRL and Typical MDL/RL in FGD Waters

Element	IDL (μg/L)	IRL (μg/L)	FGD MDL (μg/L)[1]	FGD MQL (μg/L)[1]
Silver[2]	3.20	10	12.8	40
Aluminum	16	51	64	204
Arsenic	11	36	44	144
Boron	5.7	18	22.8	72
Barium[3]	0.74	2.3	2.96	9.2
Beryllium	0.089	0.28	0.36	1.12
Calcium	12	39	48	156
Cadmium	0.56	1.8	2.24	7.2
Cobalt	1.7	5.5	6.8	22
Chromium	1.7	5.5	6.8	22
Copper	4.7	15	18.8	60
Iron	12	38	48	152
Magnesium	6.5	21	26	84
Manganese	1.6	4.9	6.4	19.6
Molybdenum	13	41	52	164
Sodium	230	740	920	2960
Nickel	1.6	5.1	6.4	20.4
Lead	10	32	40	128
Antimony	14	43	56	172
Selenium	14	44	56	176
Tin	6.2	20	24.8	80
Titanium	0.66	2.1	2.64	8.4
Thallium	8.6	27	34.4	108
Vanadium	12	39	48	156
Zinc	4.6	15	18.4	60

1. Estimated MDL/MQLs for a “typical” treated FGD water with the following characteristics: TSS 20 mg dry weight per liter, TDS 20,000 mg dry weight per liter, chloride 7,000 mg/L, sulfate 1,900 mg/L, calcium 2,500 mg/L, magnesium 1,300 mg/L, sodium 500 mg/L. MDL/MQLs were estimated based on an analytical dilution factor and an additional factor of 2 to accommodate other analytical factors associated with the challenging FGD sample matrix.

2. Known interference of chloride in matrix.

3. Known interference of sulfate in matrix causing loss of soluble barium as barium sulfate.

Table 4-5
Recommendations for EPA 200.7 Analytical Conditions for FGD Water Analyses

Element	Primary Wavelength (nm) (1)	Secondary Wavelengths (nm) (1)	Potential Interferences
Silver	328.068	338.289	Mo, Cr, Mn, Fe, V
Aluminum	394.401	167.078, 308.215	Ca
Arsenic	189.042	193.759	Cr, Mo, Fe, V
Boron	249.772	249.677	Fe, Mo
Barium	455.403	233.527, 493.409	
Beryllium	313.107	313.042	Ti, Cr, V
Calcium	183.801	396.847, 422.673, 315.887	
Cadmium	214.440	228.802, 226.502	V, Mo, Ti, Al, Fe
Cobalt	228.616	237.862	Ti, Cr, Ni
Chromium	205.560	284.325	Al, Mo, Ni, Fe, Si
Copper	324.752	219.958	Mo, Fe, Ti
Iron	259.939	238.204, 244.451	
Magnesium	279.077	285.212	Cr, Mn, Fe
Manganese	257.610	293.305	Al
Molybdenum	202.031	203.844	Al, Fe
Sodium	330.237	588.995	
Nickel	231.604	221.648	Co, Fe, Al, Si
Lead	220.353		Al, Ni, Co, Cr, Ti
Antimony	206.836		Cr, Mo, Ni, Ti, Co, Fe
Selenium	196.090		Fe, Co, Ni, Mo, Ti
Tin	189.991		Ti, V
Titanium	334.940	368.519	Cr
Thallium	190.801	190.864	Ti, V, Co, Ni, Mo
Vanadium	292.402	290.882	Mo, Ti, Cr
Zinc	206.191	213.857	Cr, Mo, Fe, Si (2nd= Ni, Cu, Fe)

1. Wavelengths specifically listed in EPA Method 200.7 are underlined except for cerium (413.765), lithium (670.784), mercury (194.227), phosphorus (214.914), potassium (766.491), silica (251.611) and strontium (421.552)) that are not included in the table. EPA Method 200.7 allows other wavelengths to be used as needed.

ICP-MS (EPA Methods 200.8/1638)

The EPA Office of Water promulgated two methods using ICP- Mass Spectrometry for analysis of trace metals: EPA Method 200.8, “Determination Of Trace Elements In Waters And Wastes By Inductively Coupled Plasma - Mass Spectrometry, revision 5.4” [19], and EPA Method 1638, “Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry. [13]” The latter method is intended to be used to measure very low levels of contaminants in relatively clean surface waters and WWTP effluents, while the former method is applicable to both clean and contaminated waters.

These two methods share their “front end” (sample introduction system) with its optical emission cousin (EPA 200.7), but differ in detection method. A schematic of two modes of ICP-MS operation is shown in Figure 4-2: standard mode and collision or dynamic reaction cell (DRC) mode. The principles and use of collision and DRC mode ICP-MS systems are discussed below.

In ICP-MS, aqueous samples are passed through a nebulizer to produce a fine aerosol that is passed through an injector into an argon plasma. Temperature and energy levels are high enough within the plasma that several processes occur. Solvent (water) is removed, molecular bonds are broken, and electrons are removed, forming an ionized species. The extent of ionization depends upon the effective plasma temperature, an element’s first ionization potential, and the presence and concentrations of other elements that may promote charge transfer. Some of the atomized/ionized sample is drawn into a mass spectrometer/mass filter in which charged particles are separated by a quadrupole magnet based on their mass:charge (m:z) ratios.

By careful adjustment of electrical fields, target analyte m:z ratios are selected. Ions that pass through the mass filter are directed to a detector that counts particle arrival. Using the mass spectrometer as a mass-specific detector, elemental concentrations in unknown samples can be characterized by comparing their m:z signal intensities, measured in counts per second, with those of external calibration standards having known concentrations. Instrumental drift and subtle but important physical and chemical differences between standards and samples can to a large extent be overcome by also utilizing internal standards that are uniformly added to all calibration, QC, and “unknown” samples. However, the ICP-MS instrumental method is subject to a wide range of interferences that are not solved by either the use of internal standards or by the method’s impressive sensitivity. Although it is tempting to rely on ICP-MS to produce results at lower and lower concentrations, its interferences ultimately will determine whether this method is superior to approaches (e.g. ICP-AES) that have higher detection limits.

ICP-MS interferences can be separated into two categories, physical/chemical and spectral. Physical and chemical interferences in FGD water samples are associated most commonly with high TDS. High TDS may affect sample viscosity, and thereby the production of the aerosol droplets that are available for introduction to the plasma. Because the FGD process results in precipitation of solids, several elements are present at or above solubility levels. Any solvent loss will result in even further supersaturation and precipitation of solids within the sample introduction system.

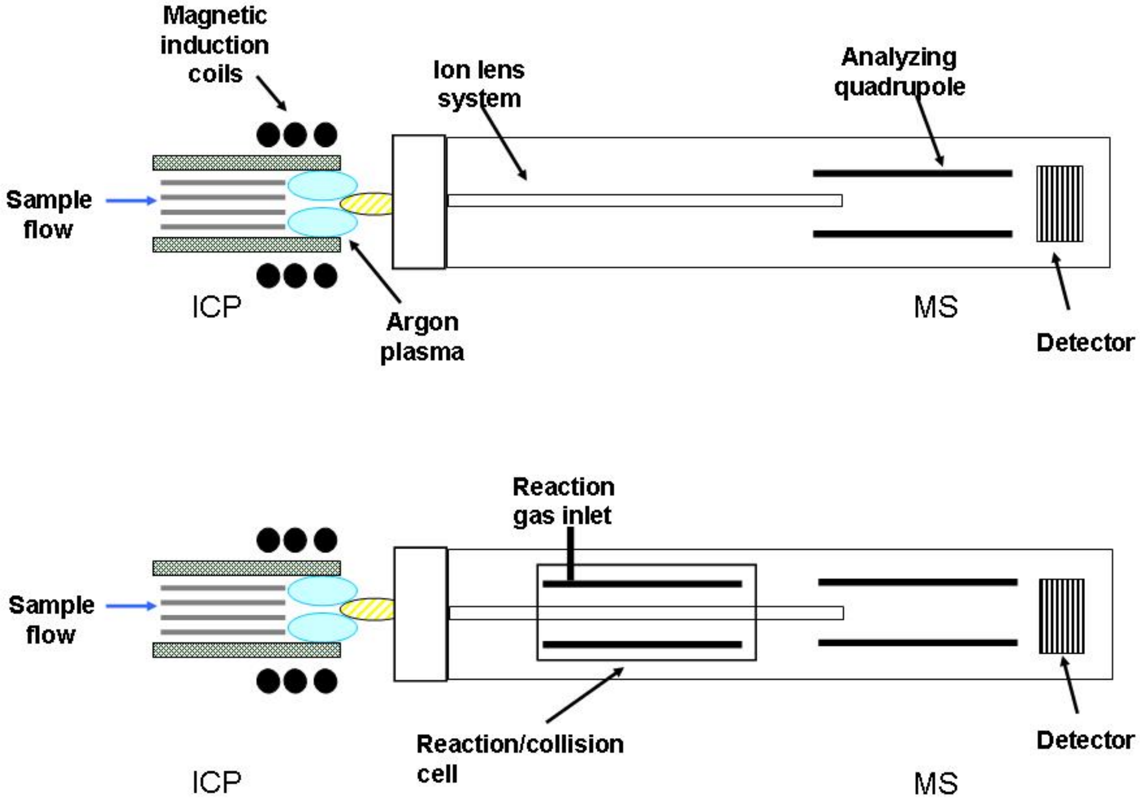


Figure 4-2
Standard Mode and Dynamic Reaction Cell or Collision Cell ICP-MS

A general rule of thumb for ICP-MS analysis is that samples should have no more than 0.2% or 2,000 ppm TDS. When samples having higher TDS are processed, instrument performance is adversely affected as solids accumulate on sampler and injector cones and on ion lenses within the spectrometer. This deposition results in accelerated instrument drift and carry-over of potentially interfering species from one sample to another. The TDS limitation is an important consideration for method selection because the large majority of FGD waters have TDS levels in excess of 1-2%. In one study, the average TDS level in FGD water was 2.8% (range 1.6 to 4.9%). TDS is not effectively removed by FGD WWTPs; thus, this issue will impact both influent and effluent samples.

The simplest approach to solving common physical and high TDS interferences is to dilute the samples so that TDS limits are not exceeded and physical effects are minimized. However, this solution has the unfortunate result of elevating detection limits, possibly to the extent that project required MDL/RL targets cannot be achieved. ICP-MS may theoretically have the sensitivity necessary to provide quantifiable measurement of low concentration elements in FGD samples but dilutions necessary to overcome TDS and physical interference problems may elevate MDLs to the extent that mostly "non-detects" result.

some sacrifice in instrument sensitivity and precision, since the optimal measurement of “ideal” samples is to measure a stable signal that has reached its maximum intensity. This disadvantage may be offset by the ability to work at lower dilution factors than would otherwise be necessary and by a reduced tendency to adversely affect instrument performance (because much less high-TDS sample is introduced when in flow injection mode). In order for the flow injection approach to benefit FGD sample analysis, the ICP-MS instrument must be coupled to a flow-injection system and must have sufficient software flexibility to allow this method of sample processing.

Another approach to dealing with physical matrix effects is to “matrix match” calibration standards so that their bulk chemistry and behavior resemble those of the samples. This approach is most effective when sample composition is generally well characterized (e.g., serum or urine). In the case of FGD samples, the inherent variability in the bulk chemistry (see Section 2) makes this approach unworkable. Other approaches for dealing with high TDS and physical matrix interferences rely upon separating the element from the bulk sample and will be discussed at greater length in the context of dealing with spectral interferences.

Mass spectrometers measure not the simple mass of an element, but the ratio of mass (m) to ionic charge (z): this quantity is termed the mass:charge ratio (m:z). Spectral interferences result from the fact that isotopic and molecular ions are sometimes too close in mass for the instrument to separate them from one another. From the perspective of the instrument, the interfering ions fall within the same m:z “window” as the target element. When this happens, the instrument accumulates counts both from the target element and the interfering species, resulting in an overestimate of the element’s true concentration. Spectral interferences can result from overlap of ions from nearby (mass-wise) elements and from doubly-charged ions having twice the mass of the target isotope. However, the most common and most challenging spectral interferences result from formation of molecular ions having the same m:z ratio (given the resolution of the spectrometer) as the isotope of the target element. Some common interferences for metals measured by ICP-MS are listed in Table 4-6.

Isotopic overlap can frequently be corrected by abundance-based correction equations and doubly charged species can be diminished by adjustment of plasma conditions, but molecular ions are less predictable and less easily corrected by either equations or instrument adjustment.

Furthermore, unlike physical or high-TDS interferences, spectral interferences cannot be eliminated by sample dilution. Both element and interferant counts are decreased by dilution, so that the interferant still represents the same proportion of counts at the target element’s m:z ratio when diluted. When the observed concentrations are multiplied by the dilution factor, the magnitude of the interferant returns to its original undiluted level. Thus, diluting ICP-MS samples does not eliminate or greatly change overestimates resulting from spectral interferences.

Table 4-6
Recommended ICP-MS Analytical Masses and Interferences for FGD Water

Element	Mass (1)	Interferences /Notes
Aluminum	$\underline{27}$	$_{12}C_{15}N_{+}$, $_{13}C_{14}N_{+}$, $_{14}N_{2}$ spread, $_{1}H_{12}C_{14}N_{+}$
Antimony	121, $\underline{123}$	$_{94}Zr_{16}O_{2}$
Arsenic	$\underline{75}$	$_{40}Ar_{35}Cl_{+}$, $_{59}Co_{16}O_{+}$, $_{36}Ar_{38}Ar_{1}H_{+}$, $_{38}Ar_{37}Cl_{+}$, $_{36}Ar_{39}K$, $_{43}Ca_{16}O_{2}$, $_{23}Na_{12}C_{40}Ar$, $_{12}C_{31}P_{16}O_{2+}$
Barium	135, $\underline{137}$	
Beryllium	$\underline{9}$	
Cadmium	106, 108, $\underline{111}$, 114	$_{40}Ca_{2}$, $_{16}O_{2}$, $_{40}Ar_{216}O_{2}$, $_{96}Ru_{16}O_{+}$, $_{98}Mo_{16}O_{+}$, $_{98}Ru_{16}O_{+}$
Chromium	$\underline{52}$, 53	$_{35}Cl_{16}O_{1}H_{+}$, $_{40}Ar_{12}C_{+}$, $_{36}Ar_{16}O_{+}$, $_{37}Cl_{15}N_{+}$ $_{34}S_{18}O_{+}$, $_{36}S_{16}O_{+}$, $_{38}Ar_{14}N_{+}$, $_{36}Ar_{15}N_{1}H_{+}$, $_{35}Cl_{17}O_{+}$
Cobalt	$\underline{59}$	$_{43}Ca_{16}O_{+}$, $_{42}Ca_{16}O_{1}H_{+}$, $_{24}Mg_{35}Cl_{+}$, $_{36}Ar_{23}Na_{+}$, $_{40}Ar_{18}O_{1}H_{+}$,$_{40}Ar_{19}F_{+}$
Copper	63, 65	$_{49}Ti_{16}O_{+}$, $_{32}S_{16}O_{21}H_{+}$, $_{40}Ar_{25}Mg_{+}$, $_{40}Ca_{16}O_{1}H_{+}$, $_{36}Ar_{14}N_{21}H_{+}$, $_{32}S_{33}S_{+}$, $_{32}S_{16}O_{17}O_{+}$, $_{33}S_{16}O_{2}$ $_{+}$, $_{12}C_{16}O_{37}Cl_{+}$, $_{12}C_{18}O_{35}Cl_{+}$, $_{31}P_{16}O_{18}O_{+}$
Lead	$\underline{206}$, $\underline{207}$, $\underline{208}$	$_{90}Pt_{16}O_{+}$, $_{191}Ir_{16}O_{+}$, $_{92}Pt_{16}O_{+}$
Manganese	$\underline{55}$	$_{40}Ar_{14}N_{1}H_{+}$, $_{39}K_{16}O_{+}$, $_{37}Cl_{18}O_{+}$, $_{40}Ar_{15}N_{+}$, $_{38}Ar_{17}O_{+}$, $_{36}Ar_{18}O_{1}H_{+}$, $_{38}Ar_{16}O_{1}H_{+}$, $_{37}Cl_{17}O_{1}H_{+}$, $_{23}Na_{32}S_{+}$, $_{36}Ar_{19}F_{+}$
Molybdenum	95, 97, $\underline{98}$	$_{81}Br_{17}O_{+}$, $_{41}K_{2}O_{+}$
Nickel	$\underline{60}$, 62	$_{44}Ca_{16}O_{+}$, $_{23}Na_{37}Cl_{+}$, $_{43}Ca_{16}O_{1}H_{+}$
Selenium	77, $\underline{82}$	$_{12}C_{35}Cl_{2+}$, $_{34}S_{16}O_{3+}$, $_{40}Ar_{21}H_{2+}$, $_{40}Ar_{37}Cl_{+}$, $_{36}Ar_{40}Ar_{1}H_{+}$, $_{38}Ar_{21}H_{+}$, $_{12}C_{19}F_{14}N_{16}O_{2+}$, HBr+
Silver	$\underline{107}$, 109	$_{91}Zr_{16}O_{+}$, $_{92}Zr_{16}O_{1}H_{+}$
Thallium	203, $\underline{205}$	$_{187}Re_{16}O_{+}$, $_{186}W_{16}O_{1}H_{+}$
Thorium	$\underline{232}$	
Uranium	$\underline{238}$	
Vanadium	$\underline{51}$	
Zinc	$\underline{66}$, 67, 68	$_{50}Ti_{16}O_{+}$, $_{34}S_{16}O_{2+}$, $_{33}S_{16}O_{21}H_{+}$, $_{32}S_{16}O_{18}O_{+}$, $_{2}S_{17}O_{2+}$, $_{33}S_{16}O_{17}O_{+}$, $_{32}S_{34}S_{+}$, $_{33}S_{2+}$
Krypton	83	Used to correct Se when Argon contains Kr
Ruthenium	99	Used to correct Mo
Palladium	105	Used to correct Cd when Pd present
Tin	118	Used to correct In Internal Standard for isobaric overlap

1. Preferred masses are underlined.

Similarly, the “standard addition” approach that is frequently useful in compensating for interferences in some other instrumental methods does not solve spectral interference problems in ICP-MS. Standard additions may compensate for certain matrix effects that impact the slope of the calibration curve but it does not eliminate the basic problem of interfering species having the same m:z ratio as the element.

High-resolution mass spectrometers can separate m:z ratios that are very close to one another, thus avoiding interferences from species with the same nominal ratio. However, instruments possessing this resolution are so costly, both in terms of purchase and operation, that they are found in very few environmental laboratories. Furthermore, they are less accommodating of high to moderate TDS samples than are the more common quadrupole “low resolution” MS instruments.

Because quadrupole ICP-MS instruments cannot overcome spectral interferences through resolution, other approaches have been developed to achieve the goal of generating reliable data. The most simple is to utilize a different isotope of the target element that is free of the interference. While some elements have only a single stable isotope (e.g., Mn and As), others have several potentially available. For alternate isotopes to be useful, their abundance should be sufficiently high to allow detection limits that satisfy FGD project objectives and must not suffer from their own spectral interferences. While alternate isotopes do sometimes provide a solution to molecular ion interferences, there are unfortunately few cases where interference-free, high abundance isotopes are available to solve complex spectral overlap problems.

A general approach that has been used to solve complex matrix/low element concentration problems in a range of samples and instrumental methods is to separate the element from the problem matrix. This can be done in “real time” by taking advantage of the chemistry and behavior of several elements. Examples of this approach are the cold vapor analysis of Hg and the hydride generation analysis of As, Se, and Sb.

When an element’s chemistry does not lend itself to simple, chemical separation from the bulk sample then alternate separation procedures can be employed. Approaches that have been attempted include solvent extraction, ion exchange, and coprecipitation (as Fe or Ga oxyhydroxides, metal-APDC complexes, or reductive precipitation). Each of these procedures may require one or more pretreatment steps, and it is rare that a single separation approach will successfully recover all target elements. However, when the target element list is limited to just a few elements, separation techniques have the dual advantage of separating element from interferants and increasing element concentrations so that previously undetectable elements may be quantified.

Recognizing Interferences in ICP-MS

Part of the extended learning curve in ICP-MS analysis of challenging samples is to recognize when interferences occur. Several indicators of interferences include:

- Method blanks are low but concentrations in known samples (e.g., reference materials) are much greater than expected. The low method blank eliminates contamination as the source of the anomalous concentration.
- The element of interest has multiple isotopes and their observed concentrations vary wildly.

- Concentrations do not agree with those obtained by other sensitive methods or by other laboratories (allowing for normal interlaboratory variation).
- Internal standard counts vary excessively indicating the presence of an internal standard element in the FGD water sample (see also Table B-2).

Lacking a CRM for FGD water, it is not straightforward to determine which is the “right” or at least “closest to the right” answer. Except in cases where correction equations might inadvertently overcorrect (underestimate) metals levels due to matrix specific interferences in FGD waters, two generalizations can be made:

1. ICP-MS interferences generally lead to a positive bias, i.e., they result in an overestimate of the true concentration. Interferences are particularly evident at low to mid mass regions.
2. The high concentrations of major cations and anions in FGD samples almost guarantees that interferences will impact direct analysis of “raw” FGD samples using EPA Method 200.8/1638 unless procedures for pre-analysis separation or run time compensation of molecular ion interferences are developed (i.e., DRC or CRC).

Given the multitude of interferences to which direct aspiration ICP-MS is susceptible and the variability and the complexity of FGD waters, is there any way to insure that direct aspiration ICP-MS results are accurate? Not by this technique alone, due to the high variability in concentrations of interfering elements, even within a single FGD water source. Even if all QC samples (e.g., MS/MSD) satisfy criteria, this is not a guarantee that the FGD results are accurate. The matrix spikes may be affected by the interference as well as the native sample.

For some elements, it may be possible to recognize and correct for interferences by comparing the results for multiple isotopes of the same element. EPRI used this approach to quantify total Se in FGD waters [7]. For elements that do not have multiple masses, or have no masses free from interferences, it may be necessary to perform additional, confirming analyses with alternative methods on a one-time basis to examine potential sources of error.

Analyzing impacted samples in DRC or CRC mode, using a gas such as ammonia ($NH_{3)}$ to transfer charge or dissociate the interferant, will remove some interferences and provide a “better”, more accurate estimate of Se concentrations. These techniques are discussed at length below. Developing a well-characterized FGD water reference material and performing confirming analyses on select samples by other sensitive methods (e.g., graphite furnace AAS and hydride generation AFS) will provide additional tools for confirming the accuracy of ICP-MS data for critical, challenging elements such as Se.

EPA 200.8/1638 Method Parameters

Table 4-6 lists recommended masses for each element for analysis of FGD waters. Table 4-7 lists typical MDL/RLs for elements by Method 200.8/1638 in an ideal dilute acid matrix and estimated MDL/RLs in typical FGD waters. Appendix Table B-2 provides typical internal standard elements used for method 200.8/1638. Appendix Table B-3 summarizes the analytical QC requirements in method 200.8/1638. Appendix Table B-4 summarizes initial operating conditions for both normal and DRC modes.

Table 4-7
Comparison of EPA Methods 200.8/1638 IDL/IRL and MDL/RL in FGD Waters[1]

Element	**IDL (µg/L)**	**MDL (µg/L) 200.8**[2]	**MDL µg/L) 1638**	**FGD MDL (µg/L)**[3]	**FGD MQL (µg/L)**[3,4]
Silver	0.004		0.029	0.4	1.2
Aluminum	0.02	1.7		85	255
Arsenic	0.02	0.4		20	60
Barium	0.03	0.04		2	6
Beryllium	0.02	0.02		1	3
Cadmium	0.02	0.03	0.025	1.5	4.5
Cobalt	0.002	0.004		0.2	0.6
Chromium	0.04	0.08		4	12
Copper	0.004	0.02	0.087	1	3
Mercury	0.2			20	60
Manganese	0.007	0.02		1	3
Molybdenum	0.005	0.01		0.5	1.5
Nickel	0.07	0.06	0.33	3	9
Lead	0.015	0.05	0.015	2.5	7.5
Antimony	0.008	0.04	0.0097	2	6
Selenium	1.3	2.1	0.45	105	315
Thallium	0.014	0.02	0.0079	1	3
Vanadium	0.006	0.9		45	135
Zinc	0.07	0.1	0.014	5	15

1. Estimated MDL/MQLs for a "typical" treated FGD water with the following characteristics: TSS 20 mg dry weight per liter, TDS 20,000 mg dry weight per liter, chloride 7,000 mg/L, sulfate 1,900 mg/L, calcium 2,500 mg/L, magnesium 1,300 mg/L, sodium 500 mg/L.
2. Where a 200.8 MDL was unavailable, 2x the IDL was used.
3. Assumes a dilution factor of 10 to achieve target TDS of < ,2000 ppm and a matrix effect that reduces the sensitivity 5 fold relative to an ideal matrix.
4. Assumes FGD MQL = 3 x FGD MDL.

EPA Methods 200.8/1638 Modified For DRC

Because quadrupole ICP-MS instruments cannot overcome spectral interferences through resolution, other approaches have been developed to obtain accurate data. Chemical ionization is used to separate the element from interferants within the instrument itself. This approach relies upon collisions of interfering molecular ions and target element ions with either inert or reactive gases. Depending upon the instrument manufacturer, the ionization reaction occurs within the cone interface region or within a "collision cell" or "dynamic reaction cell (DRC)" incorporated within the mass spectrometer. DRC is the proprietary version of a chemical ionization mass spectrometer offered by the Perkin Elmer Corporation. See Figure 4-2 for a simplified schematic of a ICP-DRC-MS instrument. The same general rule of thumb applies to ICP- DRC- MS analysis in that samples analyzed should have no more than 0.2% or 2,000 ppm TDS.

In theory, the problem of element and interferant molecular ions sharing the same m:z is solved by chemical ionization by one of several mechanisms:

1. Transferring charge from the interferant to the cell gas; this results in a neutrally charged interferant (which will not be detected) and a positively charged cell gas (which presumably is not at the same m:z as the element and so will not be a new interferant),
2. Dissociating the interferant through reaction with the cell gas, producing new uncharged and charged species that (hopefully) do not overlap with the target element's isotope, and
3. Forming a new charged species through a reaction between the element and the cell gas, moving the "new" element to a m:z that (again hopefully) is not shared by any interfering species.

Several cell gases have been employed with varying degrees of success in an attempt to eliminate or at least diminish spectral interferences. These gases include argon, helium, ammonia, hydrogen, methane, and oxygen. In most cases, the approach has been to eliminate the interferant, either through charge transfer or through reaction with the cell gas.

Collision and reaction cells compensate for the limited spectral resolution of quadrupole-based spectrometers, but at the cost of much greater analytical complexity. There is no single cell gas that solves interferences for all elements. In fact, depending upon sample composition, a cell gas that works in one sample may not work in another. A high level of expertise and appropriate equipment is required to successfully perform this method. As a result, at present this method is primarily available through specialty, trace metal analysis laboratories.

Table 4-1 listed an expected MDL/RL for Se by DRC-ICP-MS. The same masses used for normal mode ICP-MS are used for DRC Se analysis (see Table 4-6). ICP-DRC-MS uses the same QC as that for normal mode ICP-MS (Appendix Table B-3). Appendix Table B-4 suggests operating conditions for normal mode ICP-MS as well as ICP-DRC-MS analyses for Se and some additional metals.

Example of DRC Application: Selenium in FGD Water

For FGD water, standard mode ICP-MS (EPA Methods 200.8/1638) typically results in an overestimation of the true selenium concentration due to uncontrolled molecular ion interferences. These isobaric interferences come from the formation of polyatomic ions involving calcium, sulfur, chloride, bromine, argon and oxygen (see Table 4-6). Many of these elements are typically in high concentration in FGD water or in the plasma, and the overestimation of the selenium concentration can be 10-20 fold or more above the true selenium level present in the sample. The use of ICP-DRC-MS, employing ammonia or methane as the reaction cell gas, has proven to be generally effective in controlling the interferences affecting selenium in FGD waters [7]. This situation has been verified using confirming analyses by independent analytical methods that do not suffer from the same interferences.

Example of DRC Application: Arsenic in FGD Water

Recent arsenic data from a FGD water split sample study conducted by the author illustrates the potential complexity of ICP-DRC-MS method optimization and interference correction. Arsenic is monoisotopic, having only one isotope at mass 75. A common spectral interference results from formation of $^{40}Ar^{35}Cl^+$ within the plasma. This interferant can be removed by utilizing one of several cell gases (e.g., ammonia, methane, or argon), eliminating the problem in many samples. However, in FGD samples the presence of high concentrations of Ca and Cl causes formation of CaCl. The common cell gases do not breakdown this species and so they are not effective in separating the element (As) from the interferant. An alternate approach does accomplish the goal: use of O_2 as the cell gas forms AsO having a m:z ratio of 91, effectively moving the target element away from the original interferant.

One problem is solved, but is the As measurement now interference-free? Apparently not. In comparing inter-laboratory data for the same split FGD water sample, it became apparent that the ICP-DRC-MS data were affected by an unforeseen interferant. Examination of the abundance of elemental isotopes shows that ^{91}Zr could be a potential interferant at this m:z. ICP-AES scans demonstrated sufficiently high concentrations of Zr in FGD samples containing solids for this element to be considered a potential source for the anomalously high As concentration reported for the sample by ICP-DRC-MS. The result is that in this specific FGD water matrix with elevated zirconium levels, the ICP-DRC-MS method could not accurately measure arsenic in this sample. An alternate analytical method such as HGAFS will have to be evaluated in an effort to accurately measure arsenic in this FGD matrix.

EPA Methods 200.8/1638 Modified for CRC

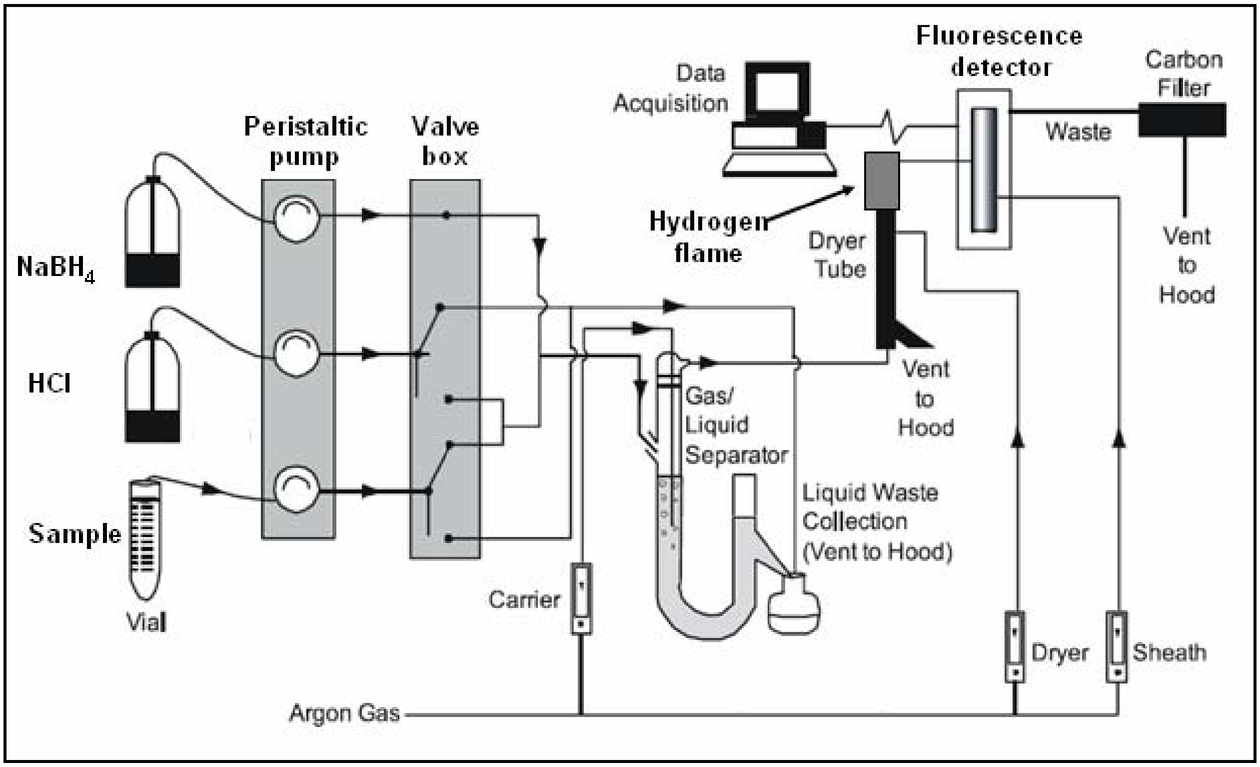
Collision cell ICP-MS operates on the same principle as ICP-DRC-MS (see Figure 4-2). CRC typically uses higher flow rates of a reaction gas (typically hydrogen or helium) to remove polyatomic isobaric interferences. For example, ICP-CRC-MS analysis of selenium uses a cell gas (hydrogen) flow rate of 3.5 ml per minute compared to < 1 ml per minute for a DRC instrument. ICP-CRC-MS requires the same < 0.2% TDS in the sample analyzed as do standard mode and ICP-DRC-MS instruments. Consequently, most FGD water samples have to diluted 10- fold or more prior to ICP-CRC-MS analysis.

Selenium has been successfully analyzed in FGD waters with ICP-CRC-MS, using hydrogen as the cell gas. Selected operational parameters include: plasma RF power of 1500 W, cell gas flow 3.5 ml per minute, plasma gas flow 15 liters per minute, and carrier gas flow 1.15 liters per minute. Typically, selenium mass 78 is used for quantitation, with indium as the internal standard. Blank count rates are low (~ 20 counts) and a 1 ppb selenium standard produces approximately 1000 counts. Other elements, including As, Cd, Cu, Cr, Ni, Pb and Zn have been analyzed in FGD waters using ICP-CRC-MS with helium as the cell gas and at a dilution factor of 10 or more from the original FGD water matrix.

Table 4-1 gives expected MDL/RLs for Se by ICP-CRC-MS. The same masses used for normal and DRC mode ICP-MS are used for CRC Se analysis (see Table 4-6). ICP-CRC-MS uses the same QC as that for normal mode ICP-MS (Appendix Table B-3).

Hydride Generation Atomic Fluorescence Spectroscopy (HGAFS)

HGAFS is potentially a very useful analytical method for the analysis of Se and As at very low levels in high TDS FGD waters. The method described here is patterned after EPA Method 1632, but is modified for flow-injection analysis for Se using a PSA Analytical Millenium atomic fluorescence analyzer. Figure 4-3 shows a schematic of an HGAFS analytical system.



Source: Modified from EPA Method 245.7

Figure 4-3
Schematic of an HGAFS Analytical System

The method can accommodate high TDS sample matrices because a volatile Se-hydride is formed which is purged from the sample matrix in a gas-liquid separator. The enhanced sensitivity of the method compared to the original Method 1632 arises from the use of an AFS detector rather than an AAS. The combination of the robustness to TDS and high sensitivity gives the HGAFS method the capability of measuring Se in even the most challenging FGD water matrices at sub-ppb levels. The method suffers from few positive interferences because the analyte (as a gaseous hydride) is removed from the original sample matrix for analysis.

However, in applying this method to FGD water analyses there are two primary concerns that must be addressed by the analyst:

1. All organo-selenium compounds in the sample must be oxidized to inorganic selenium, and
2. All inorganic selenium in the sample must be reduced to Se(IV) in order to form the volatile hydride used in the analysis.

If these two conditions are not satisfied then the HGAFS will underestimate the true total Se concentration in the FGD water sample. Preliminary methods development conducted by Albion Environmental for selected FGD waters have shown that a microwave assisted closed bomb digestion and uv photo-oxidation digestion (see Table 4-3) are sufficiently aggressive to oxidize organo-selenium species in FGD waters to inorganic Se. The second heated preparatory digestion (see also Table 4-3) is adequate to reduce all selenium in the microwave digestate to Se (IV). Confirming analysis studies have shown that HGAFS Se data are comparable with method 200.7 and ICP-DRC-MS Se data on the same sample. However, EPRI research in other laboratories has found numerous unknown Se compounds in FGD water samples [7]. At this time it is unknown whether these species will form hydrides under the method conditions. It would therefore be prudent to be cautious when using this method for FGD water analysis and perform initial confirming analysis studies using other methods.

The HGAFS method is able to achieve substantially lower RLs in high TDS matrices than any other of the analytical methods discussed in this report. For this reason, HGAFS has the potential of being the method of choice for Se and As analysis in high TDS FGD waters where sample specific RLs of < 1-2 ppb are required. Only one element can be analyzed by HGAFS at a time and each element (e.g. Se or arsenic) require a separate and different preparatory digestion prior to analysis. This makes HGAFS inherently more labor intensive and limits its use to those FGD waters with elevated TDS where very low MQLs are required. Monitoring selenium in bioreactor effluents associated with FGD WWTPs is a good example of such a monitoring application for which HGAFS appears uniquely well suited.

Table 4-1 lists the Se MDL/RL achievable in typical FGD waters. The QC used for the HGAFS method is patterned after that used for ICP-MS methods (see Appendix Table B-3).

Recommendations for the Analysis of Non-Mercury Metals in FGD Waters

In such a variable and complex matrix as FGD waters, making general recommendations is challenging. However, the following principles should be followed when evaluating or designing a metals analysis plan for FGD waters:

- For aqueous samples, a nitric acid only closed vessel type digestion should be adequate. For challenging, high TSS samples (e.g. biphasic supernatants) and for samples to be analyzed by HGAF, a more aggressive digestion procedure (e.g. microwave bomb, uv photo-oxidation) should be used.
- A heated block, open vessel, strong acid leach digestion should be adequate for slurry and dry biphasic solids samples. Be aware that not all trace metals associated with the solids will be measured using this leach digestion. A total digestion using hydrofluoric acid would be needed to determine the total metals concentrations present in the solids.
- For FGD waters with TSS > 1%, biphasic separation (after preservation) using centrifugation should be used (see Appendix A).

- Do not over-dilute samples. Dilutions for analysis should be sample (matrix) specific based on undiluted TDS levels with a target of 0.2% TDS in the final analytical dilution.
- Sequence samples to minimize carryover (memory) effects. Start with samples having the lowest solids (e.g. FGD effluent and ash pond effluent), lowest metal concentrations, and lowest TDS levels. Then progress in order of samples with increasing metals and solids concentration. Run high solids samples (FGD influent and ash pond influent) last.
- Increase the length of inter-sample rinses and adjust the strength of rinse solutions (i.e., minimum of 1% nitric acid) based on the level of "carryover" observed for "sticky" elements such as B, Mo, Sb.
- Perform matrix spike/MS duplicate analyses on each unique FGD water matrix at a frequency of 10%. Use element specific spiking levels between 1-5 times the unspiked sample concentration along with acceptance criteria of 75-125 percent recovery and a relative percent difference of < 20%.
- Use DRC or ICP-CRC-MS for selenium and arsenic analyses but also for chromium, nickel, vanadium and zinc determinations. Normal mode ICP-MS can generally be used for other elements. Where possible monitor multiple masses (e.g. for selenium masses 77, 78, 82) to look for interferences.
- When measuring low (< 5-10 ppb) Se in high TDS samples, use HGAF analyses in combination with microwave or uv photo-oxidation digestions.
- Perform confirming analysis on each unique FGD water matrix using a second independent method to confirm data accuracy.
- Use standard reference materials as an independent confirmation of data accuracy and analytical control.
- Method blank corrections may be needed to improve ICP-MS data accuracy at low ppb concentrations. Always evaluate the final data using both blank corrected and uncorrected paired data points.

5

ANALYTICAL METHODS FOR MERCURY IN FGD WATER

Analysis of mercury (Hg) in FGD waters has unique challenges due to the extremely low regulatory action levels in effect in some regions. For example, industries in the Great Lakes Region are required to meet a discharge criterion of 1.3 ng/liter (parts per trillion). As shown in Table 3-1, EPA Region 6 is proposing to require a MQL of 0.5 ng/liter. A multi-laboratory validation study conducted by EPRI in1998 determined that EPA's clean method for trace level Hg, 1631E, could quantify Hg at 0.5 ng/liter with acceptable precision and accuracy in reagent water, but not in a lake water [24].To achieve even close to the required level of sensitivity, clean sampling and analysis techniques will be required. This conclusion is reinforced by recent EPA guidance [Hanlon memo] which states [25]:

> … "in the light of existing regulatory requirements for NPDES permitting, only the most sensitive methods such as Methods 1631E and 245.7 are appropriate in most instances for use in deciding whether to set a permit limitation for mercury and for sampling and analysis of mercury pursuant to the monitoring requirements within a permit."

Two EPA Office of Water approved, low-level, Hg methods (EPA 1631E and 245.7) will be described in this report. Table 5-1 compares the general features of the two methods.

Table 5-1
Comparison of EPA Low-Level Mercury Methods 1631E and 245.7

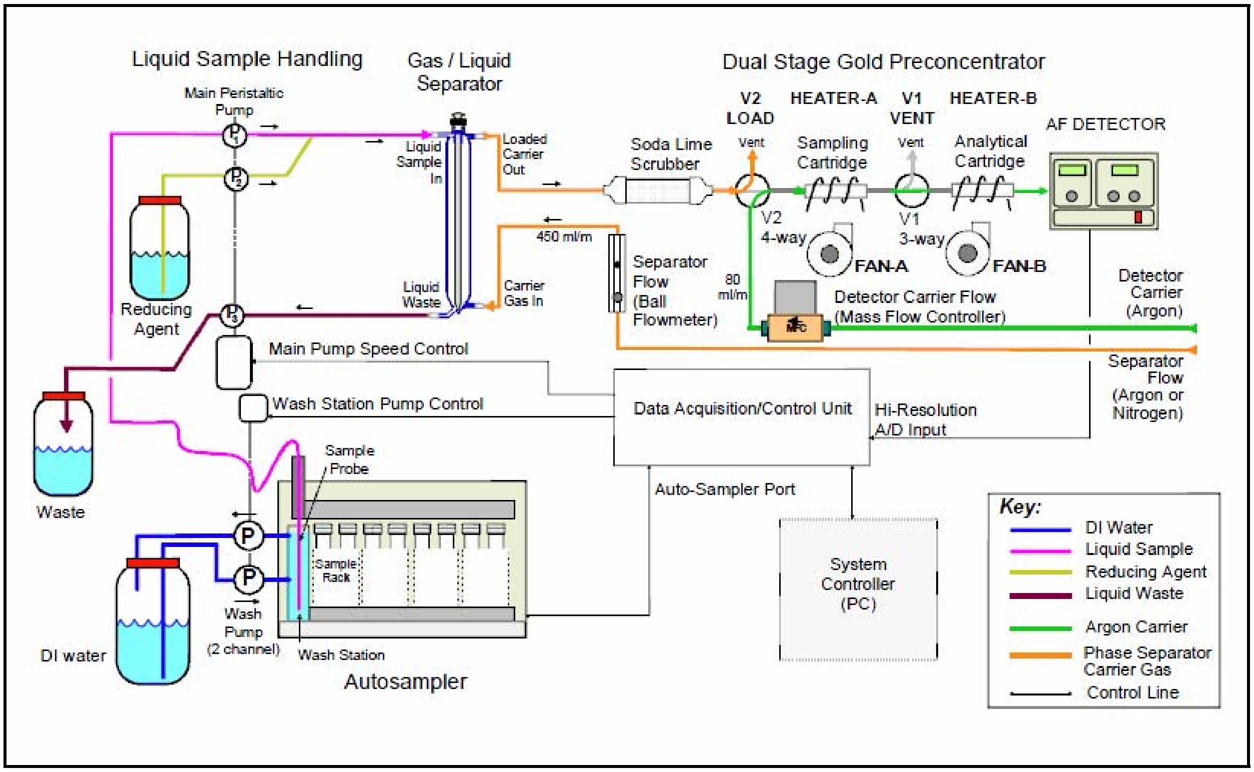
Method Characteristic	Method 1631E	Method 245.7
Preservation	BrCl	12N HCl
Digestion	BrCl / $SnCl_2$ /NH_2OH•HCl	KBr /$KBrO_3$ /$SnCl_2$ /NH_2OH•HCl
Separation	1. Vapor Separation 2. Gold Trap	1. Vapor Separation 2. Dryer Tube (Nafion)
Detection	CVAFS	CVAFS
MDL / ML	0.2 / 0.5 ng/L	1.8 / 5.0 ng/L
Instrument Range	0.5 – 100 ng/L	5 – 100 ng/L

If the Hg data are intended for process monitoring, engineering design, or other non-compliance purposes, it may be possible to use less sensitive methods or dispense with some of the rigorous quality control requirements. Higher detection limit Hg methods (i.e. EPA 245 and EPA 7473) are also discussed briefly in this section. However, it is expected that for most data uses, the more sensitive methods will be required.

EPA Method 1631E

EPA Method 1631E, approved for CWA use in November 2002, is the most widely used clean Hg analytical method. The method involves oxidation of all mercury in the sample to the ionic Hg(II) form, followed by reduction to elemental mercury, Hg(0). The mercury vapor is purged from the aqueous sample by bubbling gas through the sample using either a manual bubbler or a flow-injection, gas liquid separator. The Hg(0) is collected on a gold trap by amalgamation, thermally desorbed onto a second gold trap and then desorbed into a AFS detector. Figure 5-1 shows a schematic of the flow-injection implementation of the method.

An important difference between Method 1631E and Method 245.7 is that 1631E uses gold amalgamation, which has two benefits: it reduces potential matrix interferences caused by differences in the kinetics of Hg vapor release from varying sample matrices, and it preconcentrates Hg on the gold traps, thus giving lower detection limits.



Source: U.S. EPA Method 1631E

Figure 5-1
EPA Method 1631 Cold Vapor Atomic Fluorescence Mercury Analytical System

Preservation And Digestion of FGD Waters for EPA Method 1631E

The 1631E preservation requirements are summarized in Table 3-3. It is prudent to leave minimal headspace in the samples to minimize any bias from Hg volatilizing out of the aqueous phase after collection. The preservation status of each sample should be verified prior to further processing or analysis. Over time, the pH of BrCl-preserved/digested FGD water samples may increase. Prior to analysis, the sample should be confirmed to have pH < 2 or an acceptable starch strip test, indicating the presence of excess halogens.

At a minimum, a heated (~ 65 deg. C for 6 hours) BrCl digestion in the original bottle is needed for complete digestion. For more difficult FGD water matrices, especially those with elevated levels of TSS or dissolved organics, more complete mercury recovery may be obtained by using a microwave-assisted (EPA 3051A) digestion [26, 33, 34], 1631E Appendix A [29], or EPA 245-style digestion [28]. Heated BrCl digestions have proven to be sufficient for accurate Hg measurements in most FGD waters, including some slurry samples. Using a 245-style digestion is recommended for FGD water samples with TSS levels > 1% or for separated solids from biphasic samples. If there is suspicion of incomplete digestion, a comparison of closed microwave bomb versus closed original bottle BrCl digestion can be run on splits of the sample.

Analysis of Mercury In FGD Waters Using EPA Method 1631E

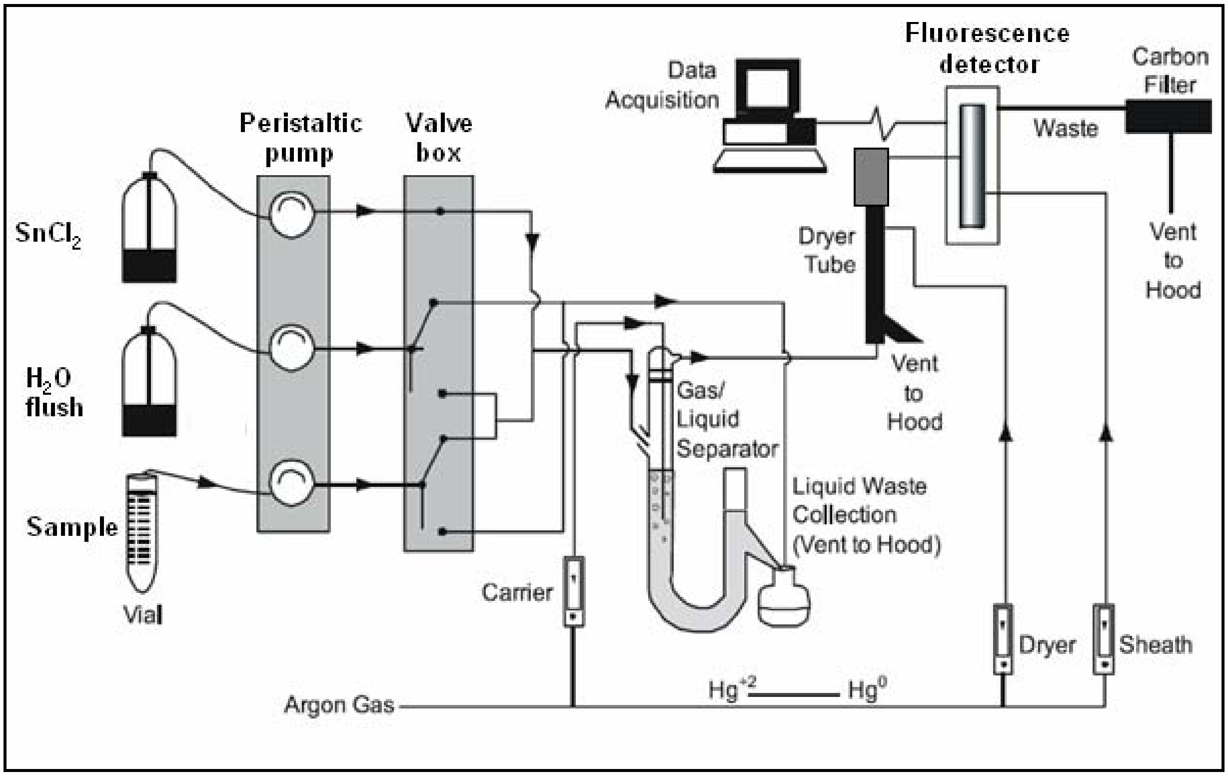
Analysis of Hg in FGD waters can be performed as specified in the method [12]. To obtain the lowest detection limits, it is important for the laboratory to maintain a clean analytical system with low method blanks. Clean blanks are facilitated by not analyzing undiluted higher Hg concentration samples (e.g. > 50 to 100 nanograms per liter) and by thoroughly cleaning the instrument if higher level samples are inadvertently analyzed. Contamination of samples or reagents with stannous chloride must be avoided to minimize the loss of Hg vapor from samples prior to actual analysis.

Method 1631E is largely free from interferences from other elements in the sample. The only interferants of concern are gold and iodine. The iodine interference can be overcome by increasing the pH of the Hg vapor stripping process. There is no way to control interference from gold contamination of the sample. These interferants should be directly measured initially in the FGD waters of interest to evaluate the level of possible concern.

The MDL and RL for EPA 1631E are shown in Table 5-1. Because of the sensitivity of the method, non-detects rarely occur for FGD waters. Appendix Table B-5 shows the QC requirements for Method 1631E. Appendix Table B-6 gives a suggested analytical batch run sequence for the method.

EPA Method 245.7

EPA Method 245.7 [30] was approved for CWA use in April 2007 as part of the omnibus Method Update Rule [8]. A schematic for the Method 245.7 analysis is shown in Figure 5-2. Most flow-injection EPA 1631E capable instruments can be easily modified or adapted to perform method 245.7 analyses by bypassing the gold traps and adding a drying tube (Nafion) to remove water vapor coming from the gas liquid separator.



Source: U.S. EPA Method 245.7

Figure 5-2
EPA Method 245.7 Cold Vapor Atomic Fluorescence Mercury Analytical System

With a reporting limit of 0.005 ppb Hg, the same clean sampling and analysis procedures must be used for Method 245.7 samples as for Method 1631E samples. Method 245.7 is not as sensitive, and is less resistant to interferences than Method 1631E, largely because of the lack of gold trap amalgamation. The lower sensitivity may not be an issue for many applications involving FGD waters. However, the lower resistance to interferences is a concern. An EPA multi-laboratory validation study [31] demonstrated that method 245.7 gave consistently low recoveries with marine waters and with industrial waters, the sample matrices in the study that were most similar to FGD waters. For this reason when considering the use of Method 245.7 for a particular FGD water, the potential for interferences (i.e. low recovery) should be confirmed initially by analyzing splits with Method 1631E, to confirm that acceptable data can be obtained with this method 245.7.

Preservation and Digestion of FGD Waters for 245.7 Analyses

The EPA 245.7 preservation and digestion requirements are summarized in Tables 3-3 and 5-1. Unlike Method 1631E, the preservation and digestion procedures are separate in Method 245.7. Pre-tested, low-mercury, concentrated hydrochloric acid is used to preserve the samples within 48 hours of collection. The method specifies a holding time of 28 days after preservation. For FGD waters, the preservation status of 245.7 samples must be monitored to insure proper preservation prior to further processing or analysis. Over time, the pH of acid-preserved FGD water samples may increase. Prior to analysis, the preserved sample should be confirmed to have pH < 2. The separate digestion procedures involve the addition of separate solutions of potassium bromate ($KBrO_3$) and potassium bromide (KBr) at least 24 hours prior to analysis. Although not described in the method, digested 245.7 samples should at a minimum be heated (~ 65 deg. C for 6 hours) in the original bottle to facilitate complete digestion. An excess of $KBr/KBrO_3$ should be confirmed either visually (presence of a yellow color) or with starch iodide indicating paper, using a separate sample aliquot, prior to sample processing or direct analysis to ensure the sample has been properly preserved and digested.

To reduce possible interferences in more difficult FGD water matrices, especially those with elevated levels of TSS or dissolved organics, microwave assisted (EPA 3051A), or EPA 245 style digestions should be evaluated. If there is suspicion of incomplete digestion, a comparison of closed microwave bomb versus closed microwave bomb versus closed original bottle digestions can be run on splits of the same sample to compare digestion efficacies. Using a 245 style digestion is recommended for FGD water samples with TSS levels > 1% or for separated solids from biphasic samples.

Analysis of Mercury in FGD Waters Using EPA Method 245.7

Many of the same caveats discussed under method 1631E (e.g. maintaining a clean analytical system, avoiding stannous chloride contamination of samples, etc.) also apply to method 245.7. An important consideration specific to Method 245.7 is to ensure that the permeation dryer (Nafion) is clean and operating properly.

The EPA 245.7 validation study showed that Hg spike recoveries in marine waters and complex industrial waters were consistently low, frequently < 60 % [33]. The primary reason for this finding is the direct (real time), flow-injection design of the method (i.e., no gold trap amalgamation). The low recoveries result from a combination of two factors:

1. The sample matrix can inhibit volatilization (slowing the kinetics) in the gas/liquid separator, thus imposing signal suppression in comparison to the calibration standards run in a dilute $KBrO_3/KBr$ solution;
2. Air, oxygen or organics not removed by the Nafion (Perma-Pure) permeation dryer cause quenching of the fluorescence signal.

If Hg levels are sufficiently high in a sample, dilution to better matrix match the sample to the calibration standards may improve recovery. The purge and trap methodology (gas phase gold amalgamation) employed with method 1631E helps minimize the kinetics inhibiting and quenching type interferences compared to direct purge and flow-injection approach employed in Method 245.7. It is not clear if adding a gold trap to the 245.7 analytical process would constitute a sufficiently major change to invalidate the method as approved. If the evaluation of Method 245.7 for a given FGD water suggests that low recovery may be a concern, moving to Method 1631E is more prudent then trying to add a gold trap to a 245.7 instrument.

The only way to demonstrate low Hg recovery is to perform a matrix spike/ MS duplicate analysis on each FGD water sample matrix in question. All other method QC may be acceptable (e.g. calibration curve, method blanks, continuing calibration verification, unspiked duplicates reproducible, etc.) but the matrix-specific interference can still produce low recovery. However, one must also be aware that depending on the form of the Hg in the FGD water of interest the matrix spike/ MS duplicate may not always reveal a matrix specific interference. This situation is because the inorganic Hg in the MS/MS spiking solution may behave differently than other Hg species that could be present in the FGD water. This is an under appreciated nuance of the use of MS/MSD for both metals and Hg and is best addressed by taking steps to insure complete digestion of the sample to remove (oxidize) as many organic species of the elements of interest.

EPA Methods 245 and 7473

Typically, it is desirable to select an analytical method with a reporting limit at least ten times below the lowest expected concentration of the analyte of interest. For many FGD water applications, the low reporting limits provided by clean Hg methods (1631E and 245.7) may be needed to meet study objectives including minimizing the possibility of false positives. However, where low reporting limits are not needed, the use of conventional Hg methods can be considered. EPA Method 245, cold vapor atomic fluorescence (CVAA), has a reporting limit of ≤ 0.2 µg/l in aqueous samples [28]. This method can also be used for solid samples (e.g. biphasic separations) with a typical reporting limit of 20 to 30 µg/kg dry weight. As discussed previously, the Method 245 heated digestion procedure is sufficiently aggressive to accommodate all FGD water matrices including slurry samples (< 1 % TSS) and biphasic solids. Most implementations of Method 245 involve the use of gas/liquid separators. Consequently matrix specific interferences should also be evaluated for the FGD water matrices of interest as described for Method 245.7.

For the analysis of Hg in solids, the use of a direct Hg analyzer according to Method 7473 can be considered. In this method, a dry sample is combusted in a high temperature furnace and volatilized Hg is analyzed by CVAA [32]. Reporting limits in the 1-5 µg/kg dry weight range are achievable. Drying and homogenizing (grinding) the solids prior to analysis provides the most straightforward analytical procedure. To avoid Hg loss, freeze-drying is the preferred method for drying solids.

Recommendations for the Analysis of Mercury in FGD Waters

The following recommendations are made concerning the analysis of Hg in FGD waters:

- Regardless of the analytical method being considered, the method should be evaluated on the specific FGD waters of interest to insure accurate and acceptable Hg data are obtained. The evaluation should include matrix specific MS/MSD analyses, certified reference materials (if available) and confirming analyses using a different analytical method or digestion procedure.
- EPA Method 1631E with a heated bromine monochloride (BrCl) digestion has proven to be a robust method for the analysis of Hg in many different FGD waters with TSS levels < 0.5 to 1%. Clean sampling and analysis procedures should be used to avoid contamination and minimize the occurrence of false positives.
- For any FGD water matrix where incomplete 1631E digestion could be a concern (e.g. high TSS slurry samples, highly colored organic rich samples, etc.), confirming analyses should be performed using the more aggressive digestion procedure of Method 245. Albion Environmental has found that this procedure produces more complete recovery from complex matrices.
- Method 245.7 is not recommended for Hg analyses in FGD waters due to the tendency of the method to underestimate Hg levels in complex sample matrices. If Method 245.7 is used, it

should be evaluated for each specific FGD water matrix using the approach described in the first bullet, and an initial comparison with Method 1631E analyses should be performed for each water type.

- For FGD waters with TSS > 1%, biphasic separation using centrifugation should be used (after preservation). In this approach, the liquid (supernatant) and solids phases are analyzed as separate samples and the Hg concentration in the original whole sample is reconstructed from the Hg levels in the two separate phases. An example procedure is provided in Appendix A.
- Where sub-ppb Hg reporting limits are not needed, conventional Hg methods such as Method 245 (liquids and solids) and Method 7473 (solids) should be considered. Do not overly relax clean sampling and analysis procedures when collecting and analyzing conventional Hg samples.

6

SELECTION OF SAMPLING EQUIPMENT AND ANALYTICAL LABORATORIES

With the increased need for clean sampling due to more stringent discharge criteria, and the analytical uncertainties and difficulties associated with FGD waters, there are a limited number of commercial laboratories with the necessary equipment and experience to support state-of-the-art FGD water monitoring studies. Many high-volume, commercial laboratories used for NPDES compliance monitoring lack the required expertise and specialized equipment. As additional FGD systems are installed, the number of qualified laboratories is expected to increase; however, at present very few have the expertise and experience with FGD water. The purpose of this section is to outline factors to consider in equipping a clean sampling effort and writing a laboratory Request for Proposal (RFP).

Clean sampling equipment and analytical laboratories should be selected with full awareness of the level of data accuracy and quality needed for a specific FGD study, the “cost” of incorrectly reporting both regulatory and non-regulatory data, and the ability of the laboratory to provide data reports and an electronic data deliverable (EDD) in the format required for the project. Inaccurate results can either underestimate or overestimate the true value, and each error has its consequences. Overestimating regulated metals can lead to false positive violations of discharge limits, resulting in possible fines, adverse publicity, and costly engineering solutions for problems that don’t really exist. In contrast, underestimates may lead to a lack of appreciation for the effectiveness of the FGD scrubbing system and potential environmental impacts on a receiving water. The additional cost of purchasing clean sampling equipment and using a laboratory with sufficient experience in clean methods may be less expensive in the long run compared to the consequences of reporting inaccurate data.

The first step in the selection process is to identify the data quality objectives for the study and select the methods to be used, as outlined in Section 3. In the interest of controlling costs, and for internal monitoring studies where the DQOs can be relaxed while still meeting study objectives, some of the recommendations can be considered optional. Particular attention should be given to the strengths and weakness of the methods and issues relevant to a specific study. For example, if high levels of potential interferants of concern (e.g. Br, I, Au, Zr, etc.) are present in your FGD waters at significant levels (i.e. varies by element but generally • 100 ppm). Some of the issues to be decided are as follows:

- Are the samples required to meet NPDES objectives or are they for an engineering study?
- Are there liquid samples, solid samples, biphasic samples?
- What type of samples need to be collected (i.e. composite, grabs, splits, etc.)?
- How many separate sampling events will be needed to meet study objectives?
- What type and number of sampling points will be used and how easily accessible are they?
- What clean sampling tier is needed? As discussed earlier, this should be the least restrictive tier that will limit sample contamination to a level acceptable for all target metals. However,

it is advisable to start with a cleaner sampling method and loosen the requirements after acceptable blanks are obtained in initial testing.

- Will dissolved metals measurements be needed that will require filtration within 15 minutes to meet the new EPA requirement for trace metals?
- What trace metals and other elemental data are needed and at what MDL/MQLs to meet study objectives?
- What digestion method is needed for adequate recovery from the matrix (i.e. microwave, open vessel, etc.)?
- What analytical method is most appropriate?
- Are there any specialized QA/QC requirements?
- What supporting data are needed (e.g. TSS, TDS, flows, etc.)?
- What is the turn-around time (TAT) required? To control costs, do not request any faster TATs than are required to meet study objectives.
- Are there any specialized data reporting needs (e.g., electronic data deliverables, detailed QC information and data that would allow for an independent data validation)?

Selecting a Clean Equipment Supplier or Field Sampling Contractor

If clean sampling equipment or contracted sampling services will be required, the best success will come from using a supplier with specific experience in certifying and providing clean sampling equipment and conducting clean sampling for industrial monitoring studies. Rather than trying to write detailed equipment specifications at the outset, it can be expedient to provide experienced suppliers with a general sampling plan and ask them to fill in specifics along with a cost estimate. In reviewing the supplier's proposal, consider the following factors:

- Is the supplier familiar with EPA clean metals and Hg guidance as indicated by the proposed plan? Specifically, does the plan include all equipment blanks, field blanks and field duplicates at the correct frequencies as required by EPA guidance?
- Does the scope include collection of field blanks at each sampling point until it is clear that the sampling personnel and procedures are consistently producing acceptable field blanks. As the field blank frequency is decreased, the number of associated field samples that could be invalidated (significantly biased by sampling contamination) by a single field blank failure increases.
- Does the plan include the necessary specialized supporting equipment such as pre-cleaned tubing sets, sampling tap adapters, etc., that may be required to perform clean sampling at less accessible sampling points?
- Does the supplier do all equipment cleaning in-house or does he/she use outside suppliers (e.g. for sample containers)? Make sure the supplier will provide the equipment blank data required by EPA guidance. What will the cost be for the equipment blank certification? Be sure the equipment blank data will be reported down to the MQLs needed for the study. If the supplier uses outside suppliers, the equipment blank data provided by the manufacturer may not be low enough to meet study needs.
- Does the supplier propose glass bottles for clean Hg sampling? Glass is a cheaper alternative to the Teflon containers specified in methods 1631E and 245.7. Does the supplier provide specific return shipping materials for glass bottles to avoid breakage?

- Current EPA guidance recommends laboratory preservation of samples and requires no icing for both metals and Hg samples as contamination control measures. Is the supplier aware of this updated guidance?

Other considerations for planning a clean sampling study for FGD waters are as follows:

- In many cases, local plant personnel will be used to collect study samples. Ask prospective equipment suppliers for clean sampling instructions that can be used to train and guide plant personnel.
- To control costs, use the tiered approach to clean sampling as summarized in Table 3-2.
- Ask prospective suppliers what is the frequency of field blank failures they experience when local plant personnel collect samples using their equipment and instructions.
- What previous experience does the prospective supplier have with projects of similar size and scope? Has the supplier provided equipment for use by State or Federal EPA projects?
- The lowest-cost supplier may not be the best choice. A higher cost supplier that can consistently provide high quality, pre-cleaned equipment may in the end be cheaper because of fewer field blank failures and invalidated data points or need for re-sampling.
- Expedited shipping costs can significantly increase overall project costs. If the project can be planned with sufficient lead time in ordering equipment, the cost savings by using only ground shipping can be substantial.

Selecting a Clean Trace Metals Analytical Laboratory

Ideally, an analytical laboratory should have experience in providing clean analytical services for FGD water. If a laboratory has analyzed other complex industrial matrices but not FGD water, it is strongly recommended that the facility provide familiarization samples to the laboratory before collecting any study samples. It would also be advisable to split the first set of samples with a laboratory that does have FGD water experience. The familiarization sample will be used to optimize the sample preparation and instrument conditions for the facility's water.

Currently, few laboratories have chemists with experience in the clean methods that give the best performance for FGD waters. Based on recent experience in FGD monitoring studies, the laboratories selected should provide, at a minimum, the following equipment and capabilities:

- Experienced in the use of EPA Methods 200.8 or 1638, modified for the use of dynamic reaction cell (DRC) or collision cell (CRC) ICP-MS for non-mercury trace metals in FGD water.
- Specific experience in optimizing ICP-DRC-MS or collision cell ICP-MS to reduce interferences for arsenic and selenium. This optimization requires a high level of professional skill to select an appropriate reaction gas, tune the instrument conditions, and evaluate the impact of the reaction gas on multiple interferences. DRC or CRC should always be used for As and Se analysis. EPRI is currently evaluating application of these techniques to other metals.
- Experienced in the use of method 200.7 for FGD waters for prescreening FGD samples, or for confirming selected elements by an independent analytical method. If 200.7 is used as the primary method (i.e., for higher-concentration metals), the ICP-AES instrument should

support multiple wavelengths per element, and the laboratory staff should have expertise in optimizing the instrument conditions for nonstandard wavelengths.

- Experienced in the use of Method 1631E for Hg analysis in more challenging FGD matrices.
- Clean room for processing samples and analytical laboratories specially configured for low-level analyses.
- Capable of performing biphasic separations by centrifugation
- Capable of hydride generation atomic fluorescence analyses, if low detection limit selenium or arsenic is to be measured in higher-TDS FGD waters for confirming analyses or final data generation.

EPRI's experience has been that laboratories that specialize in trace element analysis may not be able to supply all of the analytical requirements of a typical FGD monitoring project. For example, a specialized trace metal laboratory may not perform conventional metals and surrogate parameters methods, or it may be more cost-effective to have these analyses done at a routine commercial laboratory. If samples are sent to multiple laboratories, it is recommended that the samplers collect true replicate splits using the procedures discussed in Section 3. This will reduce between-sample variability from the temporal and spatial hetereogeneity of FGD waters.

Writing specifications for a laboratory Request for Proposal (RFP) can be laborious and time consuming. However, well developed analytical specifications can help insure usable data that meet study objectives at a moderate cost. A RFP for FGD water analysis should:

- Describe the waters to be sampled, including the approximate concentrations of TSS, TDS, and target and interfering elements.
- Request lists of equipment to be used (including instrument model), number of samples analyzed for similar matrices
- Request qualifications of laboratory and key personnel who will actually be materially involved in the project. Some indications of expertise include participation in conferences or publication in peer-reviewed journals, involvement in method-development projects, and participation in low-level inter-calibration exercises (e.g. U.S. Geological Survey's Standard Reference Sample Program) as well as higher level National Environmental Laboratory Accreditation Conference-type water pollution studies.
- Specify the type of sample digestion to be used for aqueous, slurry and biphasic solids matrices. For aqueous samples, a nitric acid only closed vessel type digestion should be adequate. Depending on how challenging your FGD waters are, you may also want to compare more aggressive digestion procedures (e.g. microwave bomb or open heated block) on selected samples to evaluate their effect (if any) on metals data obtained. However, many laboratories do not have this equipment or are not experienced in its use. A heated block, open vessel, strong acid leach digestion should be adequate for slurry and dry biphasic solids samples.
- Request a list of any modifications to the promulgated methods needed for the project
- Specify that the laboratory not over-dilute samples. Plasma methods only require dilution to achieve 0.2% TDS. Dilutions for analysis should be sample (matrix) specific based on TDS levels.
- Assess how a laboratory plans to sequence FGD water samples. The RFP should include a request that the laboratory propose their approach to properly sequencing the samples to

minimize carryover or memory effects. FGD water samples with the lowest solids (such as FGD effluent and ash pond effluent), lowest metal concentrations, and lowest TDS levels should be run first. Then sequence samples in terms of increasing concentrations and solids levels prior to running the high solids samples (FGD influent and ash pond influent). Labs should also modify the length of inter-sample rinses and adjust the strength of rinse solutions (i.e., minimum of 1% nitric acid) to moderate the impact of "carryover" on sample results.

- Specify MS/MSD frequency and acceptance criteria. EPA clean methods require that both batch and matrix specific MS/MSD be performed. Due to the variable nature of FGD waters, it may be necessary, at least initially, to analyze a MS/MSD pair for each SP. Laboratories vary in how many MS/MSDs will be included in the cost of sample analysis, so this cost must be factored in to the laboratory's proposal.
- Consider using confirming analyses with independent methods (see Section 4) to insure accurate data are obtained for elements (e.g. selenium) and sample matrices (e.g. FGD effluent) of special engineering or regulatory interest. This approach will increase cost but only has to be performed on a smaller subset of samples to confirm data accuracy.
- For elements of special interest, consider having the laboratory monitor and report data for multiple masses (e.g. for selenium masses 77, 78, 82) or wavelengths (e.g. copper 324.752 and 219.958 nm). This approach can help reveal potential interferences without adding substantial additional per sample cost. To control costs request that a laboratory optimize on a single mass and just report data for other masses that are obtained under the single set of analytical conditions.
- Use a standard reference material as an independent confirmation of data accuracy and analytical control. There is no FGD water CRM currently available; however, the laboratory should at a minimum analyze and report results for an aqueous CRM such as a seawater or river water.
- When working at low concentrations, method blank corrections may be needed to improve data accuracy. Require the laboratory to report final data both with and without blank corrections, as required by EPA clean metals guidance.

Specific data acceptance criteria and specific clear communications with the laboratory are essential for successful trace metals analysis of FGD waters. Because of the high variability of the FGD matrix, it may be difficult for laboratories to gauge in advance the appropriate matrix spikes and dilutions without prescreening analysis. Often, multiple dilutions and extensive optimization of instrument conditions will be needed to meet method acceptance criteria. The RFP should clearly spell out expectations for prescreening or reanalysis of samples, and those expectations need to be explicitly reflected in the price quote provided by the laboratory.

7

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A

BIPHASIC SEPARATION OF ELEVATED TSS SAMPLES

The following centrifugation procedure has been used successfully to separate liquid and solid phases in high-TSS FGD waters. The procedure has the advantage of being done in closed centrifuge tubes to minimize the chance of contaminating especially the liquid phase. Acid preserved slurry samples are used instead of unpreserved samples, to minimize loss of metals to adsorption onto sample container walls.

1. Depending on the objectives of the study, clean sample handling procedures should be used to process the samples during this separation process.

2. The parent slurry sample is first preserved to a pH < 2 using ultrapure nitric acid and allowed to equilibrate for 24 hours prior to further processing. Before starting the biphasic separation procedure, the pH of the sample should be confirmed to be < 2 or more nitric acid should be added, and the sample allowed to equilibrate for another 24 hours. This procedure should be repeated as needed until a stable pH < 2 is achieved. A preservation blank matching the treatment of the slurry sample should be prepared at the same time.

3. The preserved parent slurry sample is shaken vigorously to insure that all particulate matter is in suspension and not adhering to bottle walls. Adsorption is a definite concern because loss of particulates to the walls can lead to errors in TSS measurements. Tared, acid pre-cleaned, capped, 50-ml centrifuge tubes are used. The number of 50 ml centrifuge tubes used will depend on the volume of sample that needs to be processed.

4. A "multipour" approach is used for sub-aliquoting. The preserved, parent slurry sample is shaken thoroughly and approximately 10 ml is poured into the first centrifuge tube. The sample is shaken again, and a ~ 10 ml aliquot is poured into the second centrifuge tube. This procedure is repeated sequentially until each 50 ml centrifuge tube contains approximately 50 ml achieved in ~ 10 ml increments. The filled centrifuge tubes are re-weighed and the volume of the sample in each tube is determined gravimetrically using the sample specific gravity.

5. Each filled centrifuge tube is centrifuged at approximately 1,200 g for 30 minutes. Care should be taken after centrifuging not to agitate the tubes and stir up any pelleted solid material.

6. The supernatant is carefully decanted into a single tared pre-cleaned bottle. The bottle is re-weighed, and the total supernatant volume is determined gravimetrically using the sample specific gravity. Re-check that the pH of the supernatant is < 2 and that the supernatant is ready for further processing and digestion using an appropriate aqueous sample digestion procedure.

7. The solid material is typically well compacted by centrifugation so that little particulate matter is included in the supernatant during the decanting step. The liquid-free centrifuge tubes are re-weighed and then covered with plastic wrap, frozen and freeze dried.

8. After freeze-drying, the solids are transferred to a single container to provide a single, pooled solids sample. If needed, the composited, freeze-dried solids sample is ground to a fine, homogeneous powder using a mortar and pestle prior to taking sub-aliquots for digestion using an appropriate solids digestion procedure.

9. At every step in the procedure weights are taken to evaluate the variability in the procedure and to determine an average acid preserved TSS value to be used in the reconstruction calculations. Table A-1 gives an example of the weight data from a slurry sample processed using this centrifuged biphasic separation.

10. The digested supernatant and solids sub-samples are analyzed for the elements of interest. The total “aqueous” concentration (Ct) in the original whole slurry sample is reconstructed using the following equation:

$$Ct= Cs*(TSS/1,000,000) + C_L$$

where:	Ct	Total reconstructed aqueous metal concentration in micrograms per liter (parts per billion, ppb)
	Cs	Solids metal concentration in micrograms per kilogram dry weight (ppb)
	TSS	Total acid preserved suspended solids concentration in milligrams dry weight per liter (ppm)
	C_L	Liquid (supernatant) metal concentration in micrograms per liter (ppb)

Table A-1
Example of Biphasic Centrifugation Separation Data for a ~ 500 ml FGD Water Sample

Sample ID	**C-Tube Tare Weight (g)**	**Weight C-Tube + Sample (g)**	**Weight of Liquid Sample (g)**	**Aliquot Volume Liquid Sample (ml)**	**C-Tube Wt. after Decant Wet Solids (g)**	**Weight Wet Solids (g)**	**C-Tube Wt. after Freeze-Dry Solids (g)**	**Weight Freeze-Dried Solids (g)**	**Acid-Preserved TSS mg dw/L**
ALIQUOT-1	13.868	65.109	51.241	49.13	15.286	1.418	14.762	0.894	18197
ALIQUOT-2	13.745	63.843	50.098	48.03	15.151	1.406	14.675	0.930	19362
ALIQUOT-3	13.774	66.556	52.782	50.61	15.345	1.571	14.759	0.985	19464
ALIQUOT-4	13.695	65.087	51.392	49.27	15.24	1.545	14.637	0.942	19118
ALIQUOT-5	13.713	65.105	51.392	49.27	15.238	1.525	14.643	0.930	18874
ALIQUOT-6	13.748	65.978	52.230	50.08	15.308	1.560	14.723	0.975	19470
ALIQUOT-7	13.859	65.549	51.690	49.56	15.372	1.513	14.817	0.958	19331
ALIQUOT-8	13.658	65.699	52.041	49.90	15.154	1.496	14.608	0.950	19040
ALIQUOT-9	13.844	65.697	51.853	49.72	15.354	1.510	14.809	0.965	19411
ALIQUOT-10	13.622	65.606	51.984	49.84	15.075	1.453	14.554	0.932	18700
								Mean TSS (n=10) ->	**19,100**
								Std Dev TSS (n=10) ->	**410**

B

SUMMARY OF VARIOUS REQUIREMENTS FOR ANALYTICAL METHODS

Table B-1
EPA Method 200.7 Quality Control (QC) Tests and Acceptance Criteria

Parameter	Description	Minimum Frequency	Acceptance Criteria
Method Detection Limit (MDL)	Seven aliquots of a solution containing concentrations at 2-3 times the expected instrument detection limit	Initial demonstration, or anytime operating procedures or conditions are changed; annually at a minimum	MDLs with sufficient sensitivity for reporting requirements
Calibration	Calibration across the LDR from ML to the determined upper-end of the LDR	Once per analytical day and when CCV fails	Instrument performance check (IPC) solution ± 5% R after calibration
Internal Standards	Allows for the correction of instrument drift and physical interferences, allowed by Section 11.5	Every sample analyzed	Not specified, use 60 – 125 %R, relative to calibration blank as a starting point
Inter-Element Corrections	Evaluates spectral interferences by the periodic analysis of the SIC solution	No minimum is specified, only periodically	A 10% change requires evaluation
Instrument Performance Check (IPC)	Initial and continuing evaluation of percent recovery in a standard solution	Immediately following calibration, then every 10 samples	± 5% R following calibration, ±10% R there after
Calibration Blanks	Establishes baseline for quantitative measurements	One with calibration sequence, then with every IPC	Less than IDL
Laboratory Reagent Blank (LRB)	Verifies the preparative reagents used to analyze samples are free of contamination.	One for each batch of 20 samples	Less than 10% of the analyte in an associated sample, or less than 2.2 times the MDL

Table B-1 (Continued)
EPA Method 200.7 Quality Control (QC) Tests and Acceptance Criteria

Parameter	Description	Minimum Frequency	Acceptance Criteria
Laboratory Fortified Matrix (LFM)	Evaluates method performance on a specific sample matrix. Spike samples at the sample level as the LFB	Not less than 10% from a given sampling site or discharge	± 30% R
Laboratory Fortified Blank (LFB)	Evaluates percent recovery of a standard solution to verify accuracy	One for each batch of 20 samples	± 15% R
Quality Control Sample (QCS)	Provides an independent verification of system performance. The sample analyzed must be in the calibration range and from a different source than the calibration standards	After initial demonstration, quarterly, or as required	% R ± 5% of CV

Table B-2
EPA Methods 200.8/1638 Recommended Internal Standard Masses and Limitations

Element	Mass	Notes
Lithium	6	Note 1
Scandium	45	Polyatomic ion interference
Yttrium	89	Note 1,2
Rhodium	103	
Indium	115	Isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	Note 1

1. May be present in environmental samples.

2. In some instruments Yttrium may form measurable amounts of YO+ (105 amu) and YOH+ (106 amu). In these cases, care should be taken in the use of the cadmium elemental correction equation.

Table B-3
EPA Method 200.8 Quality Control (QC) Tests and Acceptance Criteria

Parameter	**Description**	**Minimum Frequency**	**Acceptance Criteria**
Method Detection Limit (MDL)	Follow 40 CFR 136, Appendix B	Initial demonstration, or anytime operating procedures or conditions are changed	Less than or equal to the MDL specific in Table 1 of the Method document
Calibration	Calibration across the LDR from ML to the determined upper-end of the LDR	Once per analytical day and when CCV fails	Blank and at least three standards with RSD < 20% (1)
Internal Standards	Allows for the correction of instrument drift and physical interferences	Every sample analyzed	60 – 125 %R, relative to calibration blank
Correction Equations	Compensates for atomic ion spectral overlap, not for molecular ions	Every sample analyzed	NA
Initial Precision and Recovery (IPR) (2)	Evaluation of percent recovery and relative standard deviation of a solution that is 2-3 times the ML to determine if analytical system is in control	Initial demonstration of 4 replicates	See Table 2 in the Method document
Initial Calibration Verification (ICV) (3)	Evaluation of percent recovery of mid-point calibration standard to determine system performance	Immediately following system calibration	See Table 2 in the Method document
Continuing Calibration Verification (CCV) (3)	Evaluation of percent recovery of mid-point calibration standard to determine system performance	Every 10 samples and after last sample	See Table 2 in the Method document
Method Blanks (4)	Verifies the preparative reagents used to analyze samples are free of contamination.	One for each group of 10 or fewer samples	Less than MDL specified in Table 1 of the Method document

Table B-3 (continued)
EPA Method 200.8 quality control (QC) tests and acceptance criteria

Parameter	Description	Minimum Frequency	Acceptance Criteria
Method Duplicates (5)	Evaluates inter-sample precision	One for each group of 10 samples, may be obtained from MS/MSD pair	RPD < 20%
Matrix Spike / Matrix Spike Duplicate (MS/MSD) (6)	Evaluates method performance on a specific sample matrix. Spike samples at the compliance limit, 1-5x sample background or 1-5x the ML, whichever is greater	Not less than 10% from a given sampling site or discharge	See Table 2 in the Method document
Ongoing Precision and Recovery (OPR) (7)	Evaluation of percent recovery and relative standard deviation of a solution that is 2-3 times the ML to determine if analytical system is in control	One for each group of 10 or fewer samples	See Table 2 in the Method document
Quality Control Sample (QCS)	Provides an independent verification of system performance. The sample analyzed must be in the calibration range and from a different source than the calibration standards	After initial demonstration, quarterly, or as required	% R ± 10% of CV

1. EPA Method 200.8 requires at least one blank and one data point.

2. Initial Precision and Recovery is determined by the analysis of a QCS sample in EPA Method 200.8

3. Section 9.3.4 of EPA Method 200.8 calls for the re-analysis of the calibration blank and standards immediately following the calibration sequence and every 10 samples there on.

4. EPA Method 200.8 requires a laboratory reagent blank (LRB) with every batch of 20 samples. If 10% of the analyte from an associated sample is detected in the LRB or if the LRB is 2.2 times the MDL, fresh aliquots of the samples and another LRB must be re-prepared and reanalyzed.

5. Method duplicates are not mentioned in EPA Method 200.8.

6. EPA Method 200.8 refers to this analytical parameter as a Laboratory Fortified Matrix (LFM) and call for a spiking level similar to the LFB (see Note 7), percent recovery allowed ± 30% from background.

7. EPA Method 200.8 refers to this analytical parameter as a Laboratory Fortified Blank (LFB) and should be analyzed with each group of 20 samples. The spike should be 40-100 µg/L for all elements (except Se at 200-500 µg/L), percent recovery allowed ± 15%.

Table B-4
EPA Methods 200.8/1638 Initial Operating Conditions

Condition	Setting	Notes
Nebulizer Gas Flow	0.95 LPM	
Aux Gas Flow	1.6 LPM	
Plasma Gas Flow	16 LPM	
Lens Voltage	8	
Auto-Lens	On	
ICP RF Power	1500	
Analog Stage Voltage	-1725	
Pulse Stage Voltage	1100	
Quadrupole Rod Offset Std	0	
Cell Rod Offset Std	-10	
Discriminator Threshold	70	
Cell Path Voltage Std	-20	
Axial Field Voltage	400	
Rpa	0	
RPq	0.25	Std Mode
RPq	0.75	DRC Mode, Ammonia Cell Gas
RPq	0.25	DRC Mode, Oxygen Cell Gas
Cell Gas A	0.5	Using Ammonia (elements other than Fe)
Cell Gas A	1	Using Ammonia (Fe Only)
Cell Gas A	0.8	Using Oxygen (As Only)

Rpq – repelling potential quadrapole

Table B-5
EPA Method 1631E Quality Control (QC) Tests and Acceptance Criteria

Parameter	Description	Minimum Frequency	Acceptance Criteria
Method Detection Limit (MDL)	Follow 40 CFR 136, Appendix B	Initial demonstration, or anytime operating procedures or conditions are changed.	0.2 ng/L or one-third of regulatory compliance limit, whichever is greater
Initial Precision and Recovery (IPR)	Evaluation of percent recovery and relative standard deviation of a 5.0 ng/L solution to determine if analytical system is in control.	Initial demonstration of 4 replicates	Average % R= 79-121 RSD = 21%
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	Evaluates method performance on a specific sample matrix. Spike samples at the compliance limit, 1-5x sample background or 1-5x the ML, whichever is greater.	Not less than 10% from a given sampling site or discharge.	Average % R = 71-125 RPD = 24%
Bubbler Blanks	Verifies the analytical system is free of contamination and in control.	One after each OPR and at least 3 per batch of 20 samples.	Each blank should be < 50 pg, the average of three blanks should < 25 pg, with a standard deviation < 10 pg
System Blanks	Verifies the analytical system is free of contamination and in control in a flow-injection system.	Three during calibration and at least 3 per batch of 20 samples.	Each blank should be < 0.5 ng/L, the average of three blanks should be < 0.5 ng/l with a standard deviation <0.1 ng/L
Reagent Blanks	Verifies the preparative reagents used to analyze samples are free of contamination.	When each new batch is prepared.	The amount of Hg in 0.5% (v/v) BrCl and 0.2% (v/v) hydroxylamine hydrochloride must be <20 pg (0.2 ng/L)
Ongoing Precision and Recovery (OPR)	Continuous evaluation of percent recovery of a 5.0 ng/L solution to verify acceptable system performance.	Prior to and after each analytical batch or sequence.	Recovery = 77 – 123 %
Quality Control Sample (QCS)	Provides an independent verification of system performance. The sample analyzed must be in the calibration range and from a different source than the calibration standards.	One per analytical batch.	According to manufacturer / supplier specifications.

Table B-6
EPA Method 1631E Suggested Analytical Batch Sequence

1. Clean[1]
2. System Blank -1
3. System Blank -2
4. System Blank -3
5. Standard – 1[2]
6. Standard – 2[2]
7. Standard – 3[2]
8. Standard –41[2]
9. Standard – 5[2]
10. COB
11. OPR-1[3]
12. CCB-1
13. Sample # 1[4]
14. Sample # 2
15. Sample # 3
16. Sample # 4
17. Sample # 5
18. Sample # 6
19. Sample # 7
20. CCB-2
21. Sample # 8
22. Sample # 9
23. Sample # 10
24. Sample # 11
25. Sample # 12
26. Sample # 13
27. Sample # 14
28. CCB-3
29. Sample # 15
30. Sample # 16
31. Sample # 17
32. Sample # 18
33. Sample # 19
34. Sample # 20
35. OPR-2
36. CCB-4
37. Sample # 21

1. After the instrument is initially turned on, two cleaning sequence are performed which involves heating the gold trap while purging the inert carrier gas through the analytical system.
2. A minimum of five non-zero calibration standards are analyzed from 0.5 ng/L to 100 ng/L
3. The following sequence repeats as necessary until all samples have been analyzed, or re-calibration is required.
4. The necessary QA/QC samples are analyzed as individual samples within this sequence as appropriate (i.e. QCS standard, reagent blanks, etc.).

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