

California Environmental Protection Agency



Method 436

Determination of Multiple Metals
Emissions from Stationary Sources

Adopted: July 28, 1997

Method 436

Determination of Multiple Metals Emissions from Stationary Sources

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Method 436

DETERMINATION OF MULTIPLE METALS EMISSIONS FROM STATIONARY SOURCES

1 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), vanadium (Vn) and zinc (Zn) stack emissions from stationary sources. This method is not suitable for the determination of hexavalent chromium or particulate matter emissions.

Any modification of this method shall be subject to approval by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in two impingers (analyzed for all metals), and acidic potassium permanganate solution in two impingers (analyzed only for Hg).

Sampling train components are recovered into separate front and back half fractions and acid digested using conventional Parr^R Bomb or microwave digestion techniques to dissolve inorganics and to remove organic constituents that may create analytical interferences. The analytical sensitivity achieved for a given sample will depend upon the sample matrix, types and concentrations of other chemical compounds in the sample matrix, as well as the original sample mass and instrument sensitivity.

After digestion, portions of the probe, filter and nitric acid/hydrogen peroxide digestion solutions are combined into a single front half composite and analyzed for Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, P, Pb, Sb, Se, Tl, V and Zn by inductively coupled plasma atomic emission spectroscopy (ICPAES), inductively coupled plasma mass spectrometry (ICPMS) or direct aspiration atomic absorption spectroscopy (DAAAS). The acidic potassium permanganate impinger digestion solution, the HCl rinse solution and an aliquot from the front half composite sample are analyzed for mercury (Hg) by cold vapor atomic absorption spectroscopy (CVAAS).

Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, cobalt, lead, selenium and thallium, if these elements require greater analytical sensitivity than can be obtained by ICPAES. Additionally, if desired, the tester may use DAAAS for analysis of

all metals if the resulting reporting limits meet the goal of the testing program. Similarly, inductively coupled plasma mass spectroscopy (ICPMS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, P, Pb, Mn, Ni, Tl and Zn.

The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance (QA) measures, as necessary, including actual sample matrix effects checks. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition shall be used to establish the quality of the data. The QA requirements of this method are detailed in Section 9.

1.3 DEFINITIONS

1.3.1 End User

For the purposes of this method, the regulating agency or its authorized representative shall be considered the end user if a determination of metals emissions from a stationary source is required as part of a regulatory process. Otherwise the end user shall be the party who defrays the cost of performing this method. The pre-test protocol must identify the end user.

1.3.2 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). The tester shall ultimately be responsible for performance of this method whether directly or indirectly through co-ordination of the efforts of the sampling and analytical groups.

1.3.3 Source Target Concentration

This is the target concentration for each emitted metal of interest specified by the end user of the test results. The target concentration shall be expressed in units of target metal mass per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/m^3 or $\mu\text{g}/\text{m}^3$).

1.3.4 Method Detection Limit

The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is based on the precision of detection of the analyte concentration near the instrument detection limit.

1.3.5 Reporting Limit

The reporting limit (RL) is a limit for each metal at or below which data must not be reported. It is based on the minimum analyte mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision established by the MDL determination.

2 RANGE, PRECISION, METHOD DETECTION LIMIT, REPORTING LIMIT AND INTERFERENCES

2.1 ANALYTICAL RANGE

For the analyses described in this methodology and for similar analyses the ICPAES response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter ($\mu\text{g/ml}$) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 $\mu\text{g/ml}$ of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 $\mu\text{g/ml}$ of cadmium should be diluted to that level before analysis.

2.2 METHOD PRECISION

The precision (relative standard deviation) for each metal detected in an EPA method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.3 METHOD DETECTION LIMIT (MDL)

Method detection limits for the target metals using the various analytical techniques referenced in this method are estimated in Table 1. The MDLs shown in Table 1 assume complete digestion and a final sample volume of 300 mL. For example, if the sample fraction volume is reduced from 300 mL to 30 mL, the MDL for that fraction is improved by a factor of ten. Actual MDLs are sample dependent and will vary based on the final sample volume, the sample matrix and the skill of the analyst.

ICPAES method detection limits for the sample solutions (based on SW-846, Method 6010-A) are approximately as follows: Sb (32 ng/mL), As (53 ng/mL), Ba (2 ng/mL), Be (0.3 ng/mL), Cd (4 ng/mL), Cr (7 ng/mL), Co (7 ng/mL), Cu (6 ng/mL), Pb (42 ng/mL), Mn (2 ng/mL), Ni (15 ng/mL), P (75 ng/mL), Se (75 ng/mL), Ag (7 ng/mL), Tl (40 ng/mL), and Zn (2 ng/mL). ICPMS method detection limits shown in Table 1 are estimated MDL's and generally are lower by a factor of ten or more. The actual sample method detection limits are sample dependent and may vary due to the sample matrix.

The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000-A series) are approximately as follows: Sb (200 ng/mL), As (2 ng/mL), Ba (100 ng/mL), Be (5 ng/mL), Cd (5 ng/mL), Cr (50 ng/mL), Co (50 ng/mL), Cu (20 ng/mL), Pb (100 ng/mL), Mn (10 ng/mL), Ni (40 ng/mL), Se (2 ng/mL), Ag (10 ng/mL), Tl (100 ng/mL), and Zn (5 ng/mL).

The detection limit for Hg by CVAAS (on the resultant volume of the digestion of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/mL, depending upon the type of CVAAS analytical instrument used.

The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/mL), As (1 ng/mL), Be (0.2 ng/mL), Cd (0.1 ng/mL), Cr (1 ng/mL), Co (1 ng/mL), Pb (1 ng/mL), Se (2 ng/mL), and Tl (1 ng/mL).

2.4 REPORTING LIMIT (RL)

The tester shall calculate the reporting limits (RLs) for the target metals. This value will be 5 times the MDL determined for the pre-test blank contamination checks or 5 times the field blank sample results if no pre-test analyses are performed. If the field blank analytical results yield unacceptable RLs, then the field reagent blanks may be analyzed to calculate RLs.

The RL is a required parameter for pre-test minimum sample volume and minimum sample time determination. Therefore, when no pre-test contamination checks are performed, the minimum RL for each target metal shall be estimated as 5 times the MDL shown in Table 1 or 5 times the MDL estimated by the laboratory performing sample analysis.

Note: If reagent blanks are not analyzed prior to testing, the RLs are calculated as 5 times the MDL or detection level, whichever is greater, determined for the field blank sample train. If the field blank detection levels yield unacceptable RLs, then the RLs may be established by analysis of the field reagent blank samples.

2.5 INTERFERENCES

2.5.1 ICP

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Background and overlap corrections may be used to adjust for spectral interferences. Refer to EPA SW-846, Method 6010-A and Method 6020 for details on potential interferences for this method.

2.5.2 GFAAS

The chemical, physical and spectral interferences associated with GFAAS are described in EPA SW-846, Method 7000-A, Section 3.2. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

2.5.3 DAAAS

The chemical, physical and spectral interferences associated with DAAAS are described in EPA SW-846, Method 7000-A, Section 3.1.

2.5.4 CVAAS

The chemical, physical and spectral interferences associated with CVAAS are described in EPA SW-846, Method 7470-A, Section 3.0.

3 RECOMMENDED PRE-TEST PREPARATION

The procedures presented in Section 3.1 through Section 3.5 are recommended procedures only. They are intended to help the tester maximize method performance by providing algorithms for estimating sample volume and times based upon predetermined analytical and process parameters. Failure to perform these procedures should not, by itself, constitute a fatal error when evaluating or auditing Method 436 test results. However, their omission could result in unacceptable test results.

3.1 RESPONSIBILITIES OF THE END USER AND TESTER

3.1.1 The End User

Before testing may begin, the end user of the test results shall specify the source target metals concentrations to be determined by this method using the guidelines of Section 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (Section 3.2) have been met.

3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall coordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

The tester shall obtain all relevant data that are required for pre-test calculations of sampling parameters. The tester shall develop and write a pre-test protocol before performing this method to help ensure satisfactory results.

The tester shall be responsible for ensuring that all sampling and analytical reporting requirements are met.

3.2 PRE-TEST PROTOCOL

The pre-test protocol should include the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

- (1) source target concentration of each emitted metal of interest (3.2.1),
- (2) preliminary analytical data (3.3) for each target metal, and
- (3) planned sampling parameters (3.5).

The protocol should demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. In addition, the pre-test protocol should include information on equipment, logistics, personnel and other resources necessary for an efficient and coordinated test.

At a minimum, the pre-test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be approved by the end user of the results and the tester.

The tester should not proceed with the performance of the remainder of this method unless the pre-test protocol is approved by the tester and the end user.

3.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

3.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

3.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

3.2.1.3 Interests of the End User, the Tester and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user must then provide applicable emissions results if they are available from previous tests of the facility to be tested. Otherwise, an estimate of metals emissions from the source must be obtained from the results of tests performed at similar sources. This target concentration is necessary for the calculation of the target sampling parameters required by Section 3.5.

3.3 PRELIMINARY ANALYTICAL DATA

3.3.1 Results of Blank Contamination Checks

Ideally, the tester should obtain from the analyst the results of pre-test metals contamination checks performed on the filter and reagent batches to be used for sample collection. The analytical report must satisfy the reporting requirements of Section 11.

In some instances, logistical and/or practical considerations may preclude obtaining preliminary contamination checks. In these cases, the tester shall use the analytical results for the field blank sample or the field reagent blank samples to calculate the RL. However, the tester must be aware that calculating the RL in this manner may yield an unacceptable RL resulting in unsatisfactory test data.

3.4 EXPECTED RANGE IN TARGET CONCENTRATIONS

The tester shall calculate the mass or concentration of each target metal expected in the sample that will be submitted for analysis (Section 1.3.3).

Metal analytes in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration metal could contain levels of other metals that exceed the upper limit of the method.

In some cases the solution is two analyses - first with undiluted composite, and then again after appropriate dilution of the composite. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained.

3.5 SAMPLING RUNS, TIME, AND VOLUME

3.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

3.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable target metal mass for quantitation. It must be based on a) the reporting limit (1.3.5), b) the source target concentration (3.2.1), and c) sampling limitations. Use Equation 436-1 to calculate the target MSV for each target metal analyte.

$$\text{MSV (dscm)} = \text{RL} \times \frac{1}{\text{STC}} \quad \text{Eq. 436-1}$$

Where:

MSV = Minimum sample volume, dscm
RL = The reporting limit, ng/sample (Section 1.3.5)
STC = The source target concentration, ng/dscm (Section 3.2.1)

3.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected volumetric sampling rate. Use Equation 436-2 to calculate the minimum sampling time required to collect the minimum sample volume calculated in section 3.5.2. The tester should

use an average volumetric sampling rate (VSR) appropriate for the source to be tested. If the sampling rate (VSR) cannot be achieved in the field (Section 5.1.7), the sampling time shall be revised in Equation 436-2 to achieve the target MSV. The sampling time must be such that the emissions test is conducted during representative operating conditions of the source.

$$\text{MST (hours)} = \frac{\text{MSV}}{\text{VSR}} \times \frac{1}{60} \quad \text{Eq.} \quad 436-2$$

Where:

MST = Minimum sampling time, hours
VSR = Expected average volumetric sampling rate, dscmm
60 = Factor to convert minutes to hours

The end user must decide whether the MSTs are all practically feasible. Based on this decision, the tester must use either Section 3.5.4 (a) or 3.5.4 (b) to calculate a planned sample volume (PSV).

3.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the RL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either (a) or (b). If the end user has decided that the MSTs are practically feasible, the tester must calculate the PSV according to Section 3.5.4 (a) and Equation 436-3.

- (a) Calculate the PSV using the largest of the target MSV values calculated in Section 3.5.2 and the largest value for F that will give a practical sample volume. Use this PSV to calculate the planned sampling time (Section 3.5.5) and Equation 436-5.

- (b) If the MSTs are not all practical, the tester and the end user must agree on a maximum practical sampling time (Section 3.5.5). This value must then be used for the PST in Equation 436-4 to calculate the PSV. The PST will be less than the MST and the PSV will be less than the MSV. Therefore, the primary reporting objective of the test cannot be achieved for all of the target metals. If the primary reporting objective cannot be achieved for all of the target metals, it must be discussed in the protocol and the alternative reporting objective (section 3.5.6) must be approved by the end user of the results.

$$\text{PSV(dscm)} = \text{MSV} \times \text{F} \quad \text{Eq. 436-3}$$

$$\text{PSV(dscm)} = \text{PST} \times \text{VSR} \quad \text{Eq. 436 - 4}$$

Where:

- PST = Planned sampling time from Section 2.5.5 (b)
 MSV = Minimum sample volume, dscm
 F = A safety factor (≥ 1) that allows for deviation from ideal sampling and analytical conditions

The amount that is actually collected will be determined by practical sampling limitations, the intended use of the data and the level of uncertainty that the end user can tolerate in the measurement of the target concentrations.

3.5.5 Planned Sampling Time (PST)

Two options are available depending on whether the primary objective can be achieved for all of the target metals.

- (a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target metals and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field, the sampling time must be recalculated using the actual VSR and the target PSV in equation 436-5.
- (b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$\text{PST} = \frac{\text{PSV}}{\text{VSR}} \times \frac{1}{60} \quad \text{Eq. 436 - 5}$$

$$\text{F} = \frac{\text{PST}}{\text{MST}} \quad \text{Eq. 436 - 6}$$

Where:

PST	=	Planned sampling time, hours
PSV	=	Planned sample volume, dscm
VSR	=	Expected average volumetric sampling rate, dscmm
60	=	Factor to convert minutes to hours

3.5.6 Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for the source for each target metal. The SRL shall be calculated using Equation 436-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$\text{SRL} = \frac{\text{RL}}{\text{PSV}} \quad \text{Eq. 436 - 7}$$

Where:

SRL	=	Preliminary estimate of source reporting limit, ng/dscm
RL	=	Reporting limit, ng/sample
PSV	=	Planned sample volume, dscm

4 APPARATUS

The sampling and recovery apparatus, reagents and analytical equipment necessary for satisfactory performance of this method are described in this section.

The identification and quantitation of target metals in stationary source emissions tests are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Section 9 are used to monitor the performance of the sampling method, identify problems, and take corrective action.

4.1 SAMPLING TRAIN

The following sampling apparatus is required. The tester may use alternative apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 1. It is similar to the ARB Method 5 Train. The train consists of a nozzle, heated probe, heated filter, a series of five or six impingers emersed in an ice bath and a silica gel impinger or cartridge. A cyclone or similar device in the heated filter box may be used for sampling environments with high particulate matter concentrations.

The optional first impinger is initially dry and strongly recommended for sources with high moisture content. Its purpose is to prevent dilution of impinger reagent contained in the second and third impingers by serving as a moisture trap.

4.1.1 Probe Nozzle

Same as ARB Method 5, Sections 2.1.1 and 2.1.2, constructed of quartz or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° or less and the taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in ARB Method 5, Section 5.1.

4.1.2 Probe

The probe should be lined or made of quartz, borosilicate glass, or Teflon with a heating system capable of maintaining an exit gas temperature during sampling of 120±14°C (248±25°F), or other such temperature as approved by the Executive Officer. For high temperature applications (≥260°C, 500°F) a non-heated probe liner or a single glass tube consisting of a combined probe and nozzle may be used.

4.1.3 Preseparator

A cyclone, high capacity impactor or other device may be used if necessary to remove the majority of particles before the gas stream is filtered. This catch must be used for any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other materials may be used subject to approval by the Executive Officer.

4.1.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon filter support or other non-metallic, non-contaminating support and glass to glass seal or Teflon gasket. Glass filter supports may be used where stack gas temperatures exceed 260°C (500°F). Other holder and gasket materials may be used subject to approval by the Executive Officer.

The filter holder shall be contained in a heated enclosure capable of maintaining a temperature of 120±14°C (248±25°F) around the filter holder during sampling. A temperature gage capable of measuring temperature to within 3°C (5.4°F) shall be installed so the temperature around the filter holder can be monitored and regulated during sampling.

4.1.5 Sample Transfer Line

For sample train configurations where the first impinger is not directly connected to the filter holder, a sample transfer line must be used. The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings capable of forming vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6 Impinger Train

The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The impinger train shall consist of five or six

impingers, depending on whether or not a moisture knockout impinger is used. Impingers are connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings and immersed in an ice bath. The first impinger is optional and is recommended as a water knockout trap for use during test conditions where high stack gas moisture content might result in considerable dilution of the impinger solutions.

The impingers to be used in the metals train are described as follows. When the first impinger is used as a water knockout, it shall be of the Greenburg-Smith design modified to have either a short or long stem, appropriately sized for the expected moisture catch and installed empty. The second impinger shall be of the Greenburg-Smith design modified to have a long stem as described for the first impinger in ARB Method 5, Section 2.1.7 and contain 100 mL of 5% $\text{HNO}_3/10\% \text{H}_2\text{O}_2$ solution (Section 4.3.1). The third impinger (or the impinger used as the second $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be of the Greenburg-Smith design with the standard tip as described for the second impinger in ARB Method 5, Paragraph 2.1.7 and contain 100 mL of 5% $\text{HNO}_3/10\% \text{H}_2\text{O}_2$ solution (Section 4.3.1).

The fourth impinger shall be installed empty and shall be of the Greenburg-Smith design modified to have a short stem. The function of the fourth impinger is to prevent commingling of the solution in the second and third impingers with the solution in the fifth and sixth impingers. The fifth and sixth impingers shall be of the Greenburg-Smith design modified to have a long stem and shall each contain 100 mL of acidic potassium permanganate (4% $\text{KMnO}_4/10\% \text{H}_2\text{SO}_4$) solution (Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

In summary, the optional first impinger is empty, the second and third shall each contain 100 mL of a nitric acid/hydrogen peroxide solution (5% $\text{HNO}_3/10\% \text{H}_2\text{O}_2$, Section 4.3.1), the fourth shall be empty, the fifth and sixth shall each contain 100 mL of acidic potassium permanganate solution (4% $\text{KMnO}_4/10\% \text{H}_2\text{SO}_4$, Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out (first) impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

4.1.7 Silica Gel Cartridge

A silica gel cartridge or impinger shall be placed at the exit of the sixth (last) impinger. The silica gel may be contained in an impinger in the ice bath or an external cartridge if desired. The cartridge or impinger shall contain 200 to 300 grams of silica gel or equivalent desiccant for use in determining stack gas moisture and to prevent damage to the metering system.

4.1.8 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube

occurs as part of an assembly, the configuration must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free configurations are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.9 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.10 Metering System

Vacuum gage, leak-free pump, thermometers accurate to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 1. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.11 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft.) elevation increase or vice versa for elevation decrease.

4.1.12 Gas Density Determination Equipment

Temperature sensor and pressure gage, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred and alternative configurations of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.13 Teflon Tape

For capping openings and sealing connections on the sampling train. Teflon or other non-contaminating caps, sleeves or seals may also be used.

4.2 SAMPLING MATERIALS AND REAGENTS

A reagents used in performance of this test method shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, unless otherwise approved by the Executive Officer.

4.2.1 Filters

Filters shall contain less than 1.3 $\mu\text{g}/\text{in}^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks should be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders such as the Pallflex 2500QAT-UP shall be used. However, if glass fiber filters which meet these requirements become available, they may be used. The

filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles.

4.2.2 Water

Deionized, distilled. Water conforming to ASTM Specification D1193-77, Type II (incorporated by reference) is recommended. If necessary, analyze the water for all target metals prior to field use (see Sections 7.1 through 7.3). All target metal concentrations shall be less than 1 ng/mL.

4.2.3 Nitric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide

Thirty Percent (V/V).

4.2.6 Potassium Permanganate

4.2.7 Sulfuric Acid

Concentrated.

4.2.8 Silica Gel and Crushed Ice

Same as ARB Method 5, Sections 3.1.2 and 3.1.4 respectively.

4.3 SAMPLING REAGENT PREPARATION

4.3.1 Nitric Acid (HNO₃)/Hydrogen Peroxide (H₂O₂) Absorbing Solution, 5 Percent HNO₃/10 Percent H₂O₂

Add carefully with stirring 50 mL of concentrated HNO₃ to a 1000-mL volumetric flask or graduated cylinder containing approximately 500 mL of water, and then add 333 mL of 30 percent H₂O₂. Dilute to volume with water. Mix well. The reagent shall contain less than 2 ng/mL of each target metal.

4.3.2 10 Percent H₂SO₄ (V/V)

Mix carefully, with stirring, 100 mL of concentrated H₂SO₄ into 800 mL of water, and add water with stirring to make a volume of 1 L: this solution is 10 percent H₂SO₄ (V/V).

4.3.3 Acidic Potassium Permanganate (KMnO₄) Absorbing Solution, 4 Percent KMnO₄ (W/V), 10 Percent H₂SO₄ (V/V)

Prepare fresh daily. Dissolve, with stirring, 40 g of KMnO₄ in sufficient 10 percent H₂SO₄ to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/mL of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of KMnO₄ with H₂SO₄, there could be pressure buildup in the solution storage bottle. Therefore, these bottles shall not be fully filled and shall be vented to relieve excess pressure and reduce explosion potential. Venting should be performed in a manner that will not allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.3.4 Nitric Acid (HNO₃), 0.1 N

Carefully add, with stirring, 6.3 mL of concentrated HNO₃ (70 percent) to a graduated cylinder containing approximately 900 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of each target metal.

4.3.5 Hydrochloric Acid (HCl), 8 N

Carefully add, with stirring, 690 mL of concentrated HCl to a graduated cylinder containing 250 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of Hg.

4.4 GLASSWARE CLEANING REAGENTS

4.4.1 Nitric Acid, Concentrated

Fisher ACS grade or equivalent.

4.4.2 Water

As specified in Section 4.2.2.

4.4.3 Nitric Acid, 10 Percent (V/V)

Carefully add, with stirring, 500 mL of concentrated HNO₃ to a graduated cylinder containing approximately 4000 mL of water. Dilute to 5000 mL with water. Mix well. This reagent shall contain less than 2 ng/mL of each target metal.

4.5 SAMPLE DIGESTION AND ANALYSIS REAGENTS

Target metals standards, except Hg, may also be made from solid chemicals as described in EPA Methods 6010-A or 7470-A (SW-846). Refer to Citations 1, 3 or 4 of the Bibliography for additional information on Hg standards. The 1000 µg/mL Hg stock solution standard may be made according to Section 6.2.5 of ARB Method 101A.

- 4.5.1 Hydrochloric Acid, Concentrated
- 4.5.2 Hydrofluoric Acid, Concentrated
- 4.5.3 Nitric Acid, Concentrated
Baker Instra-analyzed or equivalent.
- 4.5.4 Nitric Acid, 50 Percent (V/V)
Carefully, with stirring, add 125 mL of concentrated HNO₃ to 100 mL of water. Dilute to 250 mL with water. Mix well. Reagent shall contain less than 2 ng/mL of each target metal.
- 4.5.5 Nitric Acid, 5 Percent (V/V)
Carefully, with stirring, add 50 mL of concentrated HNO₃ to 800 mL of water. Dilute to 1000 mL with water. Reagent shall contain less than 2 ng/mL of each target metal.
- 4.5.6 Water
As specified in Section 4.1.2.
- 4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution
See EPA SW 846, Method 7470-A for preparation.
- 4.5.8 Stannous Chloride
See EPA SW 846, Method 7470-A for preparation.
- 4.5.9 Potassium Permanganate, 5 Percent (W/V)
See EPA SW 846, Method 7470-A for preparation.
- 4.5.10 Sulfuric Acid, Concentrated
- 4.5.11 Potassium Persulfate, 5 Percent (W/V)
See EPA SW 846, Method 7470-A for preparation.
- 4.5.12 Nickel Nitrate, Ni(NO₃)₂·6H₂O
- 4.5.13 Lanthanum Oxide, La₂O₃
- 4.5.14 Al Standard (AAS Grade), 1000 ug/mL
- 4.5.15 Ag Standard (AAS Grade), 1000 ug/mL

- 4.5.16 As Standard (AAS Grade), 1000 ug/mL
- 4.5.17 Ba Standard (AAS Grade), 1000 ug/mL
- 4.5.18 Be Standard (AAS Grade), 1000 ug/mL
- 4.5.19 Cd Standard (AAS Grade), 1000 ug/mL
- 4.5.20 Co Standard (AAS Grade), 1000 ug/mL
- 4.5.21 Cr Standard (AAS Grade), 1000 ug/mL
- 4.5.22 Cu Standard (AAS Grade), 1000 ug/mL
- 4.5.23 Fe Standard (AAS Grade), 1000 ug/mL
- 4.5.24 Hg Standard (AAS Grade), 1000 ug/mL
- 4.5.25 Mn Standard (AAS Grade), 1000 ug/mL
- 4.5.26 Ni Standard (AAS Grade), 1000 ug/mL
- 4.5.27 P Standard (AAS Grade), 1000 ug/mL
- 4.5.28 Pb Standard (AAS Grade), 1000 ug/mL
- 4.5.29 Sb Standard (AAS Grade), 1000 ug/mL
- 4.5.30 Se Standard (AAS Grade), 1000 ug/mL
- 4.5.31 Tl Standard (AAS Grade), 1000 ug/mL
- 4.5.32 V Standard (AAS Grade), 1000 ug/mL
- 4.5.33 Zn Standard (AAS Grade), 1000 ug/mL
- 4.5.34 Mercury Standards and Quality Control Samples

Prepare fresh weekly a 10 µg/mL intermediate mercury standard by adding 5 mL of 1000 µg/mL mercury stock solution (see EPA SW-846 Method 7470-A, Section 5.9 for preparation) to a 500 mL volumetric flask; dilute to 500 mL by first adding 20 mL of 15 percent HNO₃ and then adding water to the 500 mL volume. Prepare a 200 ng/mL working mercury standard solution fresh daily: add 5 mL of the 10 µg/mL intermediate standard to a 250 mL volumetric flask and dilute to 250 mL with 5 mL of 5 percent (w/v) KMnO₄ (Section 4.5.9), 5 mL of 15 percent HNO₃, and then water.

Use at least five separate aliquots of the working mercury standard solution and a blank to prepare the standard curve in the linear range of the instrument. These aliquots and blank shall

contain 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/mL standard and diluting until in the calibration range.

4.5.35 ICP Standards and Quality Control Samples

Calibration standards for ICP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICP ANALYSIS	
Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Co, Cu, Fe,
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/mL solutions with 5 percent nitric acid. Use a minimum of one standard and a blank to form each calibration curve. Also prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve. Suggested standard levels are 25 µg/mL for Al, Cr and Pb, 15 µg/mL for Fe, and 10 µg/mL for the remaining elements. Standards containing less than 1 µg/mL of metal should be prepared daily. Standards containing greater than 1 µg/mL of metal are typically stable for a minimum of 1 to 2 weeks. For ICPMS, follow Method 6020 in SW-846.

4.5.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Cobalt, Lead, Selenium, and Thallium

Prepare a 10 µg/mL standard by adding 1 mL of 1000 µg/mL standard to a 100 mL volumetric flask. Dilute to 100 mL with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/mL standard by adding 1 mL of the 10 µg/mL standard to a 100 mL volumetric flask and dilute to 100 mL with the appropriate matrix solution. Prepare other standards by dilution of the 100 ng/mL standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/mL. Prepare quality control samples by making a separate 10 µg/mL standard and diluting until it is in the range of the samples. Standards containing less than 1 µg/mL of metal should be prepared daily. Standards containing greater than 1 µg/mL of metal are typically stable for a minimum of 1 to 2 weeks.

4.5.37 Matrix Modifiers

4.5.37.1 Nickel Nitrate, 1 Percent (V/V)

Dissolve 4.956 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in approximately 50 mL of water in a 100 mL volumetric flask. Dilute to 100 mL with water.

4.5.37.2 Nickel Nitrate, One tenth (0.1) Percent (V/V)

Dilute 10 mL of 1 percent nickel nitrate solution (Section 4.5.37.1) to 100 mL with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

4.5.37.3 Lanthanum

Carefully dissolve 0.5864 g of La_2O_3 in 10 mL of concentrated HNO_3 and dilute the solution by adding it with stirring to approximately 50 mL of water and then dilute to 100 mL with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

4.5.38 Whatman 40 and 541 Filter Papers (or equivalent)

For filtration of digested samples.

4.6 SAMPLE RECOVERY APPARATUS

Same as ARB Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman. and Glass Funnel), respectively, with the following exceptions and additions:

4.6.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs

For quantitative recovery of materials collected in the front half of the sampling train.

4.6.2 Sample Storage Containers

Glass bottles (see the precaution in Section 4.3.3 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 500 mL and 1000 mL, shall be used for storage of acidified KMnO_4 containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

4.6.3 Graduated Cylinder

Glass or equivalent.

- 4.6.4 Funnel
Glass or equivalent.
- 4.6.5 Labels
For identification of samples.
- 4.6.6 Polypropylene Tweezers and/or Plastic Gloves
For recovery of the filter from the sampling train filter holder.
- 4.7 SAMPLE PREPARATION AND ANALYTICAL EQUIPMENT
- 4.7.1 Volumetric Flasks, 100 mL, 250 mL, and 1000 mL
For preparation of standards and sample dilution.
- 4.7.2 Graduated Cylinders
For preparation of reagents.
- 4.7.3 Parr^R Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent)
For sample digestion.
- 4.7.4 Beakers and Watchglasses
250 mL beakers for sample digestion with watchglasses to cover the tops.
- 4.7.5 Ring Stands and Clamps
For securing equipment such as filtration apparatus.
- 4.7.6 Filter Funnels
For holding filter paper.
- 4.7.7 Whatman 541 Filter Paper (or equivalent)
For filtration of digested samples.
- 4.7.8 Disposable Pasteur Pipets and Bulbs
- 4.7.9 Volumetric Pipets
- 4.7.10 Analytical Balance
Accurate to within 0.1 mg.

4.7.11 Microwave or Conventional Oven

For heating samples at fixed power levels or temperatures.

4.7.12 Hot Plates

4.7.13 Atomic Absorption Spectrometer (AAS)

Equipped with a background corrector.

4.7.13.1 Graphite Furnace Attachment

With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA SW846, Methods 7041 (antimony), 7060-A (arsenic), 7131-A (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium). Pyrolytically-treated graphite platforms and tubes are recommended.

4.7.13.2 Cold Vapor Mercury Attachment

With a mercury hollow cathode lamp or electrodeless discharge lamp. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as EPA SW846, Method 7470-A. See **Note No. 2:** Section 7.3 for other acceptable approaches for analysis of Hg in Which analytical detection limits of 0.02 µg Hg/mL were obtained.

4.7.14 Inductively Coupled Plasma Spectrometer

With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010-A.

5 SAMPLE COLLECTION AND RECOVERY PROCEDURES

The complexity of this method is such that, to obtain reliable results, tester and analyst must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment; analytical calculations; reporting and the specific procedural descriptions throughout this method.

5.1 SAMPLING

5.1.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

5.1.2 Sample Train and Sample Recovery Apparatus Preparation

Follow the same general procedure given in ARB Method 5, Section 4.1.1, except that the filter need not be desiccated or weighed. First rinse all sampling train glassware (including filter support), funnels, flasks, beakers and sample storage containers (if previously used) with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water,

followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water and allow to air dry. Glassware may be dried in oven if desired. Cover all glassware openings where contamination can occur with a non-contaminating material (**do not use aluminum foil**) until the sampling train is assembled for sampling.

5.1.3 Preliminary Determinations

Same as ARB Method 5, Section 4.1.2.

5.1.4 Sample Train Assembly

Assemble the sampling train as shown in Figure 1. Follow the same general procedures given in ARB Method 5, Section 4.1.3 except place 100 mL of $\text{HNO}_3/\text{H}_2\text{O}_2$ solution (Section 4.3.1) in each of the second and third impingers as shown in Figure 1. Place 100 mL of the acidic KMnO_4 absorbing solution (Section 4.3.3) in each of the fifth and sixth impingers as shown in Figure 1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger or cartridge. Alternatively, the silica gel may be weighed directly in the impinger or cartridge just prior to train assembly. It is recommended that each impinger also be weighed just prior to train assembly to allow weight difference determinations for moisture calculations. Use the sampling train set-up and recovery sheet shown in Figure 5 or similar data form to record set-up parameters.

5.1.5 Sample Train Configuration Options

Several options are available to the tester based on the source specific sampling requirements and conditions.

5.1.5.1 Elimination of First Impinger

The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 100 mL.

5.1.5.2 Mercury Determination

The tester shall include an empty fourth impinger between the two $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers and the two impingers containing acidic potassium permanganate solution for all test runs for which mercury is to be determined. Use the procedure described in Section 7.1.1 of ARB Method 101A, if necessary, to maintain the desired color in the last permanganate impinger. Mercury emissions can be measured, alternatively, in a separate train using ARB Method 101A.

Precaution: Take extreme care to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent acidic hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.5.3 Preseparator

Subject to the approval of the Executive Officer, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or

when water droplets are present in the stack gas.

5.1.5.4 Teflon Tape

Teflon tape or seals or other non-contaminating material should be used if necessary to ensure leak-free sampling train connections. The use of silicone grease is prohibited.

5.1.6 Leak-Check Procedures

Follow the leak-check procedures given in ARB Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.7 Sampling Train Operation

Follow the procedures given in ARB Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of ARB Method 5.

Note: When sampling for Hg, the tester must take steps to maintain the desired color of the acidified permanganate solution in the last impinger, such as described in Section 7.1.1 of ARB Method 101A. Alternatively, the tester may replace the last impinger, as necessary, with an impinger containing 100 mL of fresh acidified permanganate solution to prevent discoloration. If additional permanganate solution is used during a sample run, it must be combined with the original permanganate solution during sample recovery.

5.1.8 Field Blank Train

There shall be at least one field blank train for each series of three tests or fewer. For sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three tests or fewer.

Prepare and configure the blank train in a manner identical to the actual sampling trains. The field blank train shall be taken through all of the steps from preparation through leak check without actual sampling. Upon completion of the leak check, the entrance and exit of the blank train shall be sealed with non-contaminating material.

Recover the field blank train in the same manner as described for stack samples in Section 5.2. Follow all subsequent sections for digestion, analysis and data reporting.

5.1.9 Calculation of Percent Isokinetic

Same as ARB Method 5, Section 4.1.6.

5.2 SAMPLE RECOVERY

Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. Record all post-test sample recovery parameters on the set-up and recovery sheet shown in

Figure 5 or a similar data sheet.

Allow the probe to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, with the undesired result of drawing liquid from the impingers into the filter or commingling of the impinger contents.

The tester may opt to disassemble the sampling train into components before moving the sampling train from the sampling area to the cleanup site. If so, remove the probe or probe-filter assembly from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends, then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

The sample is recovered and treated according to the schematic shown in Figure 2. Assure that all items necessary for recovery of the sample do not contaminate the sample. Do not use any metal-containing tools or materials when recovering the train.

Note: Some gloves may contain dust which is high in zinc and may contaminate samples.

5.2.1 Container No. 1 (Filter)

Carefully remove the filter from the filter holder and place it in its labeled petri dish container. Use acid-washed polypropylene or Teflon coated tweezers or clean, single-use surgical gloves rinsed with water to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering the filter. Seal the labeled petri dish.

5.2.2 Container No. 2 (Probe and Filter Holder Front Half Rinses)

Quantitatively recover material deposited in the nozzle, probe liner and front half of the filter holder by thoroughly rinsing and brushing with a measured volume of 0.1 N nitric acid and place the wash into a labeled sample storage container. Perform the rinses as described in ARB Method 5, Section 4.2 using 0.1 N nitric acid in place of acetone. It is recommended that two

people recover the probe to minimize sample losses. Brush until the 0.1 N nitric acid rinse shows no visible particles, after which make a final rinse of the inside surface with 0.1 N nitric acid. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the volume of the combined rinse and concentrated nitric acid used for pH adjustment (when applicable) to the nearest 2 mL. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water and discard these rinses.

5.2.3 Container No. 3 (Impingers 1 through 3, Contents and Rinses)

Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container.

Wipe off the outside of each impinger to remove excess water and other material. Record the weight of each impinger or measure the liquid in the first three impingers volumetrically to within 0.5 mL using a graduated cylinder and record the volume of liquid. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with a measured volume of 0.1 N nitric acid. Repeat this rinsing, then inspect the impingers for any abnormal conditions. Rinse each piece of glassware used to connect the impingers twice with a measured volume of 0.1 N HNO₃; transfer this rinse into a labeled Container No. 3. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the total rinse volume and concentrated nitric acid used for pH adjustment (when applicable). Combine the rinses and impinger solutions, measure and record the final weight or final volume of Container 3. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.4 Container No. 4 (Impinger 4 - Middle knock-out)

Wipe off the outside of the impinger to remove excess water and other material. Record the weight of the fourth (previously empty) impinger or measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Quantitatively rinse the impinger with a measured volume of 0.1 N HNO₃. Add the rinse and impinger catch to a labeled Container No. 4. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the total rinse volume and concentrated nitric acid used for pH adjustment (when applicable). Seal the container and mark the fluid level. Record the final weight of the container or record the final volume of its contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 5 & 6)

Wipe off the outside of each impinger to remove excess water and other material. Record the

weights of both permanganate impingers (fifth and sixth) or measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas.

Combine the contents of impingers 5 and 6 into a labeled glass storage bottle identified as container 5. Using measured volumes of fresh KMnO_4 , rinse impingers 5 and 6 and their connecting glassware a minimum of three times and pour the rinses into container 5. Similarly, using measured volumes of water, rinse impingers 5 and 6 and their connecting glassware a minimum of three times and pour the rinses into container 5, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

Do NOT rinse with 8 N HCl if no visible deposits remain after rinsing with the fresh KMnO_4 .

5.2.6 Container No. 6 (HCl Rinse)

Examine impingers 5 and 6 for sample residue. If residue is observed, rinse these impingers with 25 mL of 8 N HCl. First, place 200 mL of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 mL of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 mL of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Properly seal and label container No. 6.

5.2.7 Container No. 7 (Silica Gel)

Observe the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. If a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g. Alternatively, transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.

5.2.8 Container No. 8 (0.1 N Nitric Acid Field Reagent Blank)

At least once during each field test, place 100 mL of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in

Figure 6.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Field Reagent Blank)

At least once during each field test, place 200 mL of 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Field Reagent Blank)

At least once during each field test place 100 mL of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Field Reagent Blank)

Collect only if HCl rinse described in Section 5.2.6 was conducted. At least once during each field test, place carefully and with stirring, 25 mL of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into 200 mL water in a labeled container for use in the back half field reagent blank for mercury and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.12 Container No. 12 (Filter Blank)

Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish and make the appropriate entries in the reagent blank field data sheet shown in Figure 6. Store and transport on wet ice together with the sample filters. This will be used as the field reagent blank.

5.3 SAMPLE STORAGE

5.3.1 Filters

All filters shall be stored in their labelled petri dish away from possible contamination sources. Source filters should be separated from field and reagent blank filters to prevent cross contamination.

5.3.2 Liquid Samples

All liquid samples shall be stored in their respective labelled sample jars away from possible contamination sources. Source samples should be separated from field and reagent blank samples to prevent cross contamination. The tester should also consider separating the acidified KMnO_4 samples due to their volatile nature.

6 ANALYTICAL PREPARATION

6.1 FIELD SAMPLES AND REAGENT BLANKS

Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If leakage has occurred, either void the sample or use methods, subject to the approval of the Executive Officer, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3. Record the data necessary to process, digest and prepare the sample containers for analysis using the data sheets supplied in Figure 7 through Figure 11.

6.1.1 Container No. 1 (Filter)

Divide the filter with its filter catch into portions weighing approximately 0.5 g each. Place the filter pieces into the analyst's choice of either individual microwave pressure relief vessels or Parr^R Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12 to 15 minutes of total heating time at 600 watts in intervals as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). For conventional heating, heat the Parr^R Bombs at 140°C (285 °F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.2, below.

- Notes:**
1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Sufficient heating is evidenced by sorbent reflux within the vessel.
 2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

6.1.2 Container No. 2 (Probe Rinse)

Rinse the sample into a beaker with water and cover the beaker with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Digest the sample in microwave vessels or Parr^R Bombs by carefully adding 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid and then continuing to follow the procedures described in Section 6.1.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 6.1.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 150 mL (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 mL. Quantitatively remove a 15 mL aliquot (or 10% of the Fraction 1 volume) and label as Fraction 1B. Label the remaining 135 mL portion (or 90% of the Fraction 1 volume) as Fraction 1A. Analytical Fraction 1A is analyzed using ICP or AAS for all metals except Hg.

Analytical Fraction 1B is analyzed using CVAAS for front half Hg.

6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 3 as Fraction 2A.

Rinse the sample into a beaker with water and cover with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Then follow either of the digestion procedures described in Sections 6.1.3.1 and 6.1.3.2 below.

Fraction 2A is combined with Fraction 1A to form Analytical Fraction A and analyzed using ICP or AAS for all metals except Hg. Fraction 2B is combined with Fraction 1B to form Analytical Fraction B and analyzed using CVAAS to determine front half mercury.

6.1.3.1 Conventional Digestion Procedure

Add 30 mL of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 mL of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 mL of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

6.1.3.2 Microwave Digestion Procedure

Add 10 mL of 50 percent nitric acid and heat for 6 minutes total heating time in alternating intervals of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 6.1.1. Allow the sample to cool. Add 10 mL of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 mL of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

6.1.4 Container No. 4 (Impinger 4)

Measure and record the volume of impinger 4 to within 0.5 mL and place in Container No. 4. Label the contents of container No. 4 as Analytical Fraction C. Analytical Fraction C will be separately analyzed for Hg using CVAAS.

6.1.5 Container Nos. 5 and 6 (Impingers 5, 6 and HCl Rinse, If Necessary)

To remove any brown MnO_2 precipitate from the contents of Container No. 5, filter its contents through Whatman 40 filter paper into a 500 mL volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 mL filtrate from Container No. 5 to be Analytical Fraction D. Analyze Analytical Fraction D for Hg within 48 hours of the filtration step.

Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2 , add 25 mL of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

Filter the contents of Container No. 6 through a Whatman 40 filter into a 500-mL volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5 through a Whatman 40 filter into the same 500-mL volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-mL dilute HCl solution as Analytical Fraction E. Analyze Analytical Fractions C, D and E according to the procedures in Section 7.3.

6.1.6 Container No. 7 (Silica Gel)

Weigh the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g using a balance (this step may be conducted in the field).

6.1.7 Field Reagent Blanks

The field reagent blank samples in Container Numbers 8 through 12 produced previously in Sections 5.2.8 through 5.2.12, respectively, are used to correct sample values when authorized by the Executive Officer. These field reagent blanks shall be processed, digested, and analyzed as shown in Figure 4 and described as follows. Digest and process Container No. 12 contents per Section 5.3.1. Combine Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.3. Combine the diluted digestates from Containers 8, 9 and 12. Use aliquots as Fractions A and B Blanks. Container No. 10 and Container No. 11 contents are Fraction C Blank and Fraction E Blank respectively. Analyze Fraction C and E Blanks (if applicable) per Section 7.3.

7 SAMPLE ANALYSIS

For each sampling train, four to five individual samples are generated for analysis. Three to four of these samples are specific to mercury, the remaining sample is specific to all other target metals. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.

Fractions A and B consist of the digested samples for the train from the probe rinse through impinger 3. Fraction A is for ICPAES, ICPMS or AAS analysis as described in Sections 7.1 and/or 7.2. Fraction B is for determination of front half mercury as described in Section 7.3. Fraction C consists of the impinger contents and rinses from impinger 4 (middle knockout impinger). Fraction D consists of the impinger

contents and rinses from permanganate Impingers 5 and 6. These samples are analyzed for mercury as described in Section 7.3.

Depending on the test, there may be a separate sample from an HCl rinse of impingers 5 and 6 combined with the digested MnO₂ precipitate from Fraction D. This sample should be analyzed for mercury and included in the total back half mercury catch. The total back half mercury catch is determined from the sum of Fraction C, Fraction D and Fraction E. Report the analytical results on the Laboratory Analytical Results data sheet shown in Figure 12.

7.1 ICPAES AND ICPMS ANALYSIS

Analyze analytical fraction A by ICPAES using Method 6010-A or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICP, and set up an analysis program as described in Method 6010-A or Method 200.7. Follow the quality control procedures described in Section 9.4.1. Recommended wavelengths for analysis are as follows:

<u>Element</u>	<u>Wavelength (nm)</u>
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Cobalt	228.616
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorous	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICPMS analysis by following Method 6020 in SW-846.

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

7.2 AAS by Direct Aspiration and/or Graphite Furnace

Analysis of metals in Fraction A using graphite furnace or direct aspiration AAS is often a preferred option. Use Table 2 to determine which techniques and methods should be applied for each target

metal. Table 2 also lists possible interferences and ways to minimize these interferences. Calibrate the instrument according to Section 8.3 and follow the quality control procedures specified in Section 9.4.2.

7.3 Cold Vapor AAS Mercury Analysis

Analyze analytical fractions B, C, D (if applicable) and E (if applicable) separately for Hg using CVAAS following the method outlined in EPA SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 245.1 and 245.2, or, optionally using **NOTE No. 2** at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470-A, Section 4.5.34 of this method or similar to Method 245.1 and 245.2 using 300-mL BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 mL to 10 mL. Dilute the aliquot to 100 mL with water. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 mL aliquot is suggested for the first dilution to 100 mL (see **NOTE No. 1** at end of this Section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-mL BOD bottle, and add enough water to make a total volume of 100 mL. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of SW-846 Method 7470-A or Method 303F. (See **NOTE No. 2** at the end of this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-mL aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO₃ (1.5 mL concentrated HNO₃ per liter aqueous solution) so that when a 1- to 10-mL aliquot of the "0.15 HNO₃ percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE No. 1: When Hg levels in the sample fractions are below the RLs given in Table 1, select a 10 mL aliquot for digestion and analysis as described.

NOTE No. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in Section 4.5.7 (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

8 CALIBRATION

Maintain a laboratory log of all calibrations.

8.1 Sampling Train Calibration

Calibrate the sampling train components according to the indicated sections of ARB Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

8.2 Inductively Coupled Plasma Spectrometer Calibration

Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. Check the instrument calibration once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed. Perform ICPMS calibration by following Method 6020 in SW-846.

8.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses

Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

9 QUALITY CONTROL

9.1 PRE-TEST DETERMINATIONS (RECOMMENDED)

Determine the linear range and minimum detectable and quantifiable limits of the analytical instrument selected for the respective target metals. Determine the reporting limit, minimum sample volume, planned sample volume and planned sample time according to Section 3 of this method.

9.2 FIELD REAGENT BLANKS (IF ANALYZED)

Follow the steps in Figure 4 of this method.

9.2.1 Filter, Front and Back Half

Combine one filter from the same lot as those used for sample collection (Container No. 12) with the reduced digestate from container 8. Combine 15 mL of this sample with a 15 mL aliquot from Container No. 9 and analyze for Hg. Combine the remainder of this sample with digested portion of Container No. 9 and analyze for multimetals.

9.2.2 Potassium Permanganate and Hydrochloric Acid

Analyze the contents of Container No. 10 and Container No. 11 (if applicable) for Hg.

9.2.3 Reagent Water Check

Analyze a minimum of triplicates of the water described in Section 4.2.2 for concentrations of target metals. All target metal concentrations shall be less than 1 ng/mL.

9.3 SAMPLING

9.3.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

9.3.2 Blank Train

At least one blank train per field test shall be prepared, leak-checked and recovered in the field. The blank train shall be labelled and analyzed as if it were a sample train. The blank train results are used primarily for determining reporting limits (RL's) and as a check for on-site contamination. They also provide information regarding the magnitude of source emissions relative to background.

9.3.3 Dedicated Impingers

Impingers should be coded for easy identification. Impingers used for potassium permanganate should not be used as nitric acid impingers for other tests to avoid contamination.

9.4 SAMPLE HANDLING

9.4.1 Storage and Holding Times

Adjust the pH of all liquid samples in acid solutions to pH 2 or lower during sample recovery. It is recommended that pH paper be used to verify pH 2 or lower condition. All liquid samples should be stored in a secure location immediately after sample train recovery. Analyze appropriate sample fractions for mercury within 28 days of sample date. Analyze Fraction A for target metals other than mercury within sixty days of sampling date.

9.5 ANALYTICAL QC

Analytical QA/QC requirements for ICP and AA analysis are summarized in Figure 13.

9.5.1 ICPAES and ICPMS Analysis

Follow the respective quality control descriptions in Section 8 of Methods 6010-A and 6020 of SW-846. For the purposes of a three run test series, these requirements have been modified as follows: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 20% of average or repeat all analysis). All reagent blank values shall be reported with sample values to allow project

engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese, Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc

Analyze all samples in duplicate. Perform a matrix spike on one sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. Analyze a quality control sample to check the accuracy of the calibration standards. The results must be within 20 percent or the calibration repeated. All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.3 Cold Vapor AAS Analysis for Mercury

Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (within 15% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Method 245.1 and 245.2. Fraction B blank, fraction C blank and fraction E blank (if applicable) values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

10 CALCULATIONS

10.1 DRY GAS VOLUME

Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of ARB Method 5.

10.2 VOLUME OF WATER VAPOR AND MOISTURE CONTENT

Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of ARB Method 5.

10.3 STACK GAS VELOCITY

Using the data from this test and Equation 2-9 of ARB Method 2, calculate the average stack gas velocity.

10.4 METALS (Except Hg) IN SOURCE SAMPLE

10.4.1 Total Metals (except Hg); Analytical Fraction A

Calculate separately the amount of each metal collected in Analytical Fraction A of the sampling train using the following equation:

$$M_A = C_{a1} F_d V_{\text{soln},1} \quad \text{Eq. 436-8}$$

where:

M_A = Total mass of each metal (except Hg) collected in the front half of the sampling train (Analytical Fraction A), μg .

C_{a1} = Concentration of metal in Analytical Fraction A as read from the standard curve, $\mu\text{g/mL}$.

F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1} . For example, if a 2 mL aliquot of Analytical Fraction A is diluted to 10 mL to place it in the calibration range, $F_d = 5$).

$V_{\text{soln},1}$ = Total volume of digested front half sample solution (sum of Analytical Fractions 1A and 2A), mL.

10.4.2 Total Metals (Fraction A), Method Blank Corrected (except Hg)

In cases when the Executive Officer allows correction of analytical results for method (laboratory) blank metals concentrations, calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_A - M_{ab}) \quad \text{Eq. 436-9}$$

where:

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, μg .

M_{ab} = Blank correction value for mass of metal detected in the Fraction A method (laboratory) blank, μg .

10.5 Hg IN SOURCE SAMPLE

10.5.1 Front-Half Hg; Analytical Fraction B

Calculate the amount of Hg collected in the filter and probe rinse combined with impingers 1 through 3 to form Analytical Fraction B of the sampling train by using Equation 436-10:

$$Hg_{fh} = \frac{Q_B}{V_B} (V_{soln,B}) \quad \text{Eq. 436-10}$$

where:

Hg_{fh} = Total mass of Hg collected in Analytical Fraction B (filter, probe rinse and first three impingers of the sampling train), μg .

Q_B = Quantity of Hg, μg , TOTAL in the ALIQUOT of Analytical Fraction B analyzed. **NOTE:** For example, if a 10 mL aliquot of Analytical Fraction B is digested, but only 1 mL is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 mL aliquot for Q_B .

$V_{soln,B}$ = Total volume of Analytical Fraction B, mL.

V_B = Volume of aliquot of Analytical Fraction B analyzed, mL. **Note:** For example, if the 10 mL aliquot of Analytical Fraction B mentioned above was first diluted to 50 mL with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 mL of that 50-mL was digested according to Section 7.3 and analyzed, V_B would be 0.2 mL (10 mL/50 mL).

10.5.2 Back Half Hg; Analytical Fractions C, D and E

10.5.2.1 Calculate the amount of Hg collected in Analytical Fraction C (middle knockout impinger 4), Analytical Fraction D (impingers 5 and 6) and Analytical Fraction E (HCl rinse) by using Equation 436-11:

$$Hg_{C,D,E} = \frac{Q_{C,D,E}}{V_{C,D,E}} (V_{soln,C,D,E}) \quad \text{Eq. 436-11}$$

where:

$Hg_{C,D,E}$ = Total mass of Hg collected in Analytical Fraction C, D or E μg .

$Q_{C,D,E}$ = Quantity of Hg, μg , TOTAL in the ALIQUOT of Analytical Fraction C, D or E analyzed. **NOTE:** For example, if a 10 mL aliquot of Analytical Fraction C is digested, but only 5 mL is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 5 mL aliquot for Q_C .

$V_{\text{soln},C,D,E}$ = Total volume of Analytical Fraction C, D or E, mL.

$V_{C,D,E}$ = Volume of Analytical Fraction C, D or E analyzed, mL. **Note:** For example, if the 10 mL aliquot of Analytical Fraction C mentioned above was first diluted to 100 mL with 0.15 percent HNO_3 as described in Section 7.3 to bring it into the proper analytical range, and then 5 mL of that 100mL was digested and analyzed, V_C would be 0.1 mL (10 mL/100 mL).

10.5.2.2 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 436-13:

$$\text{Hg}_{\text{bh}} = \text{Hg}_C + \text{Hg}_D + \text{Hg}_E \quad \text{Eq. 436-12}$$

where:

Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg .

10.5.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 436-14:

Note: Blank corrections may only be applied with the approval of the Executive Officer or his or her authorized representative.

$$\text{Hg}_t = (\text{Hg}_{\text{fh}} - \text{Hg}_{\text{fhb}}) + (\text{Hg}_{\text{bh}} - \text{Hg}_{\text{bbh}}) \quad \text{Eq. 436-13}$$

where:

Hg_t = Total mass of Hg collected in the sampling train, μg .

Hg_{fhb} = Blank correction value (if applicable) for mass of Hg detected in front half method blank, μg .

Hg_{bbh} = Blank correction value (if applicable) for mass of Hg detected in back-half method blank, μg .

Note: If the total of the measured blank values ($\text{Hg}_{\text{fhb}} + \text{Hg}_{\text{bbh}}$) is in the range of 0.0 to 0.6 μg ,

then use the total to correct the sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 0.6 μg , use the greater of I. or II:

- I. 0.6 μg .
- II. the lesser of (a) ($Hg_{fhh} + Hg_{bhh}$), or (b) 5 percent of the sample value ($Hg_{fh} + Hg_{bh}$).

10.6 INDIVIDUAL METAL CONCENTRATIONS IN STACK GAS

Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 436-15:

$$C_s = \frac{M_t}{V_{m(std)}} \quad \text{Eq. 436-14}$$

where:

- C_s = Concentration of a metal in the stack gas, $\mu g/dscm$.
- M_t = Total mass of that metal collected in the sampling train, μg ; (substitute Hg_t for M_t for the Hg calculation).
- $V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

10.7 ISOKINETIC VARIATION AND ACCEPTABLE RESULTS

Same as Method 5, Sections 6.11 and 6.12, respectively.

11 REPORTING REQUIREMENTS

At a minimum, any test report must include all of the calculations described in Section 10 and all of the sampling and laboratory data resulting from Section 5. Example forms for documenting field testing and laboratory work are provided as Figures 5 through 12. The quality assurance data required by Section 9 must be reported in detail (see Figure 13). This test report shall be maintained by the tester for the period of time required by the appropriate Air Pollution Control District (APCD) or Air Quality Management District (AQMD). For all tests required or requested by the local APCD/AQMD, ARB, U.S. EPA or other government agency, these records shall be made available to the Executive Officer upon request.

12 ALTERNATIVE TEST METHODS

Alternative test methods may be used provided that they are equivalent to Method 436 and approved in writing by the Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

13 BIBLIOGRAPHY

EPA Methods 6010-A (1992), 6020 (1994), 7000-A (1992), 7041 (1986), 7060-A (1994), 7131-A (1994), 7421 (1986), 7470-A (1994), 7740 (1986), and 7841 (1986), Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1986. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

ARB Methods 1 through 5, California Code of Regulations, Title 17, Part III, Chapter 1, Subchapter 8, Article 2.

ARB Method 101A, California Code of Regulations, Title 17, Part III, Chapter 1, Subchapter 8, Article 2.

EPA Method 29, Code of Federal Regulations, Title 40, Part 60, Appendix B, April 25, 1996.

TABLE 1

**MINIMUM DETECTION AND REPORTING LIMITS (ug/sample)
USING ICP, GFAAS, DAAAS AND CVAAS
ASSUMING INSTRUMENT DETECTION LIMITS PUBLISHED IN EPA SW-846***

ANALYTICAL METHOD	ICPAES		ICPMS		GFAAS		DAAAS		CVAAS	
	MDL	RL	MDL	RL	MDL	RL	MDL	RL	MDL	RL
METAL										
Aluminum (Al)			0.17	0.85					--	--
Antimony (Sb)	9.6	48	0.05	0.25	0.9	4.5	60.	300.	--	--
Arsenic (As)	16	80.	0.62	3.1	0.3	1.5	0.6	3	--	--
Barium (Ba)	0.6	3	0.02	0.10	--	--	30.0	150.	--	--
Beryllium (Be)	0.09	0.45	0.02	0.10	0.06	0.3	1.5	7.5	--	--
Cadmium (Cd)	1.2	6	0.003	0.02	0.03	0.15	1.5	7.5	--	--
Cobalt (Co)	2.1	10.5	0.002	0.01	0.3	1.5	15	75	--	--
Chromium (Cr)	2.1	10.5	0.43	0.22	0.3	1.5	15	75	--	--
Copper (Cu)	1.8	9	0.02	0.10	--	--	6.0	30.	--	--
Lead (Pb)	12.6	63	0.003	0.02	0.3	1.5	30.0	150.	--	--
Manganese (Mn)	0.6	3	0.008	0.04			3.0	15	--	--
Mercury (Hg)	--	--	--	--	--	--	--	--	0.06 [@]	0.3 [@]

Table 1 (CON'T)

Nickel (Ni)	4.5	22.5	0.02	0.10	--	--	12	60.	--	--
Phosphorous (P)	22.5	112.5	2.9	14.7			--	--	--	--
Selenium (Se)	22.5	112.5	1.27	6.40	0.6	3	0.6	3	--	--
Silver (Ag)	2.1	10.5	0.02	0.10	--		3.0	15	--	--
Thallium (Tl)	12	60.	0.26	1.3	0.3	1.5	30.0	150.	--	--
Vanadium (V)			1.4	7.0					--	--
Zinc (Zn)	0.6	3	0.05	0.3	--	--	1.5	7.5	--	--

* assumes volume of sample from total train = 300 mL prior to aliquot for analysis

@ assumes instrument detection limit of 0.2 ng Hg/mL

MDL - Minimum detection limit

RL - Reporting limit = MDL x 5

TABLE 2

**APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE
FOR AAS ANALYSIS**

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Sb	Aspiration	7040	217.6	100 mg/mL Pb, Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample and standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
AS	Furnace	7060-A	193.7	Arsenic volatilization	Spiked samples & add nickel nitrate solution to digestates prior to analyses. Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al	Add 0.1% fluoride Use method of standard additions
Cd	Aspiration	7130	228.8	Absorption & Light scattering	Background correction is required
Cd	Furnace	7131-A	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7191	357.9	Alkali metal Absorption & scatter	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	Add calcium nitrate for a known constant effect and to eliminate effect of phosphate

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Cu	Aspiration	7210	324.7	Absorption & light scattering	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care should be taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorous acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co & Cr Non linear response	Background correction required Matrix matching or a nitrous-oxide/acety flame Sample dilution or use 352.4 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples & reference materials & add nickel nitrate to minimize volatilization. Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorption & light scattering AgCl insoluble Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample & standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatilization by spiked samples or standard audit Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Strontium removes Cu and phosphate Care should be taken to avoid contamination

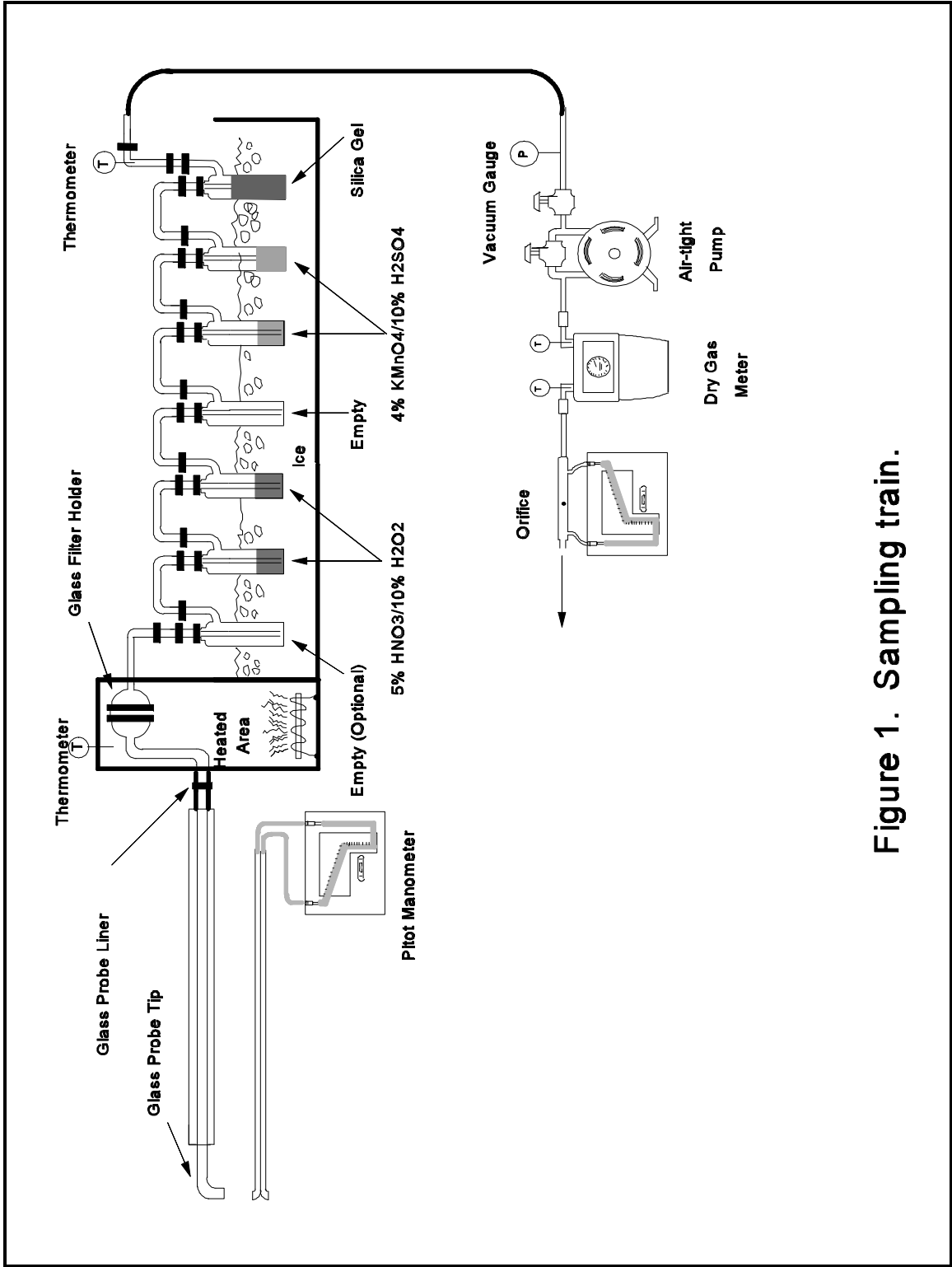
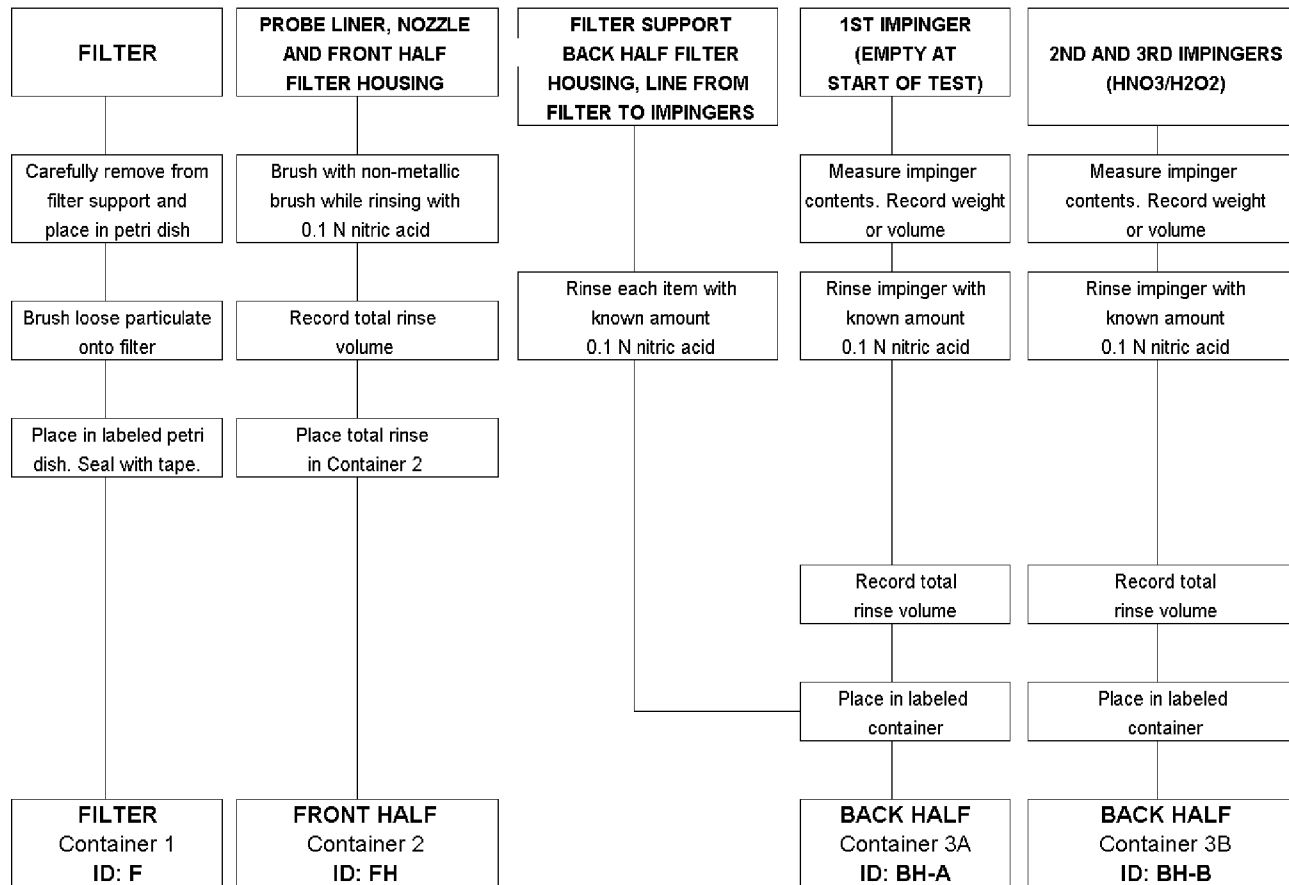


Figure 1. Sampling train.

FIGURE 2
SAMPLE TRAIN RECOVERY



NOTE: Containers 3A and 3B may be combined if desired. Alternatively, more containers may be required.

FIGURE 2 (cont'd)

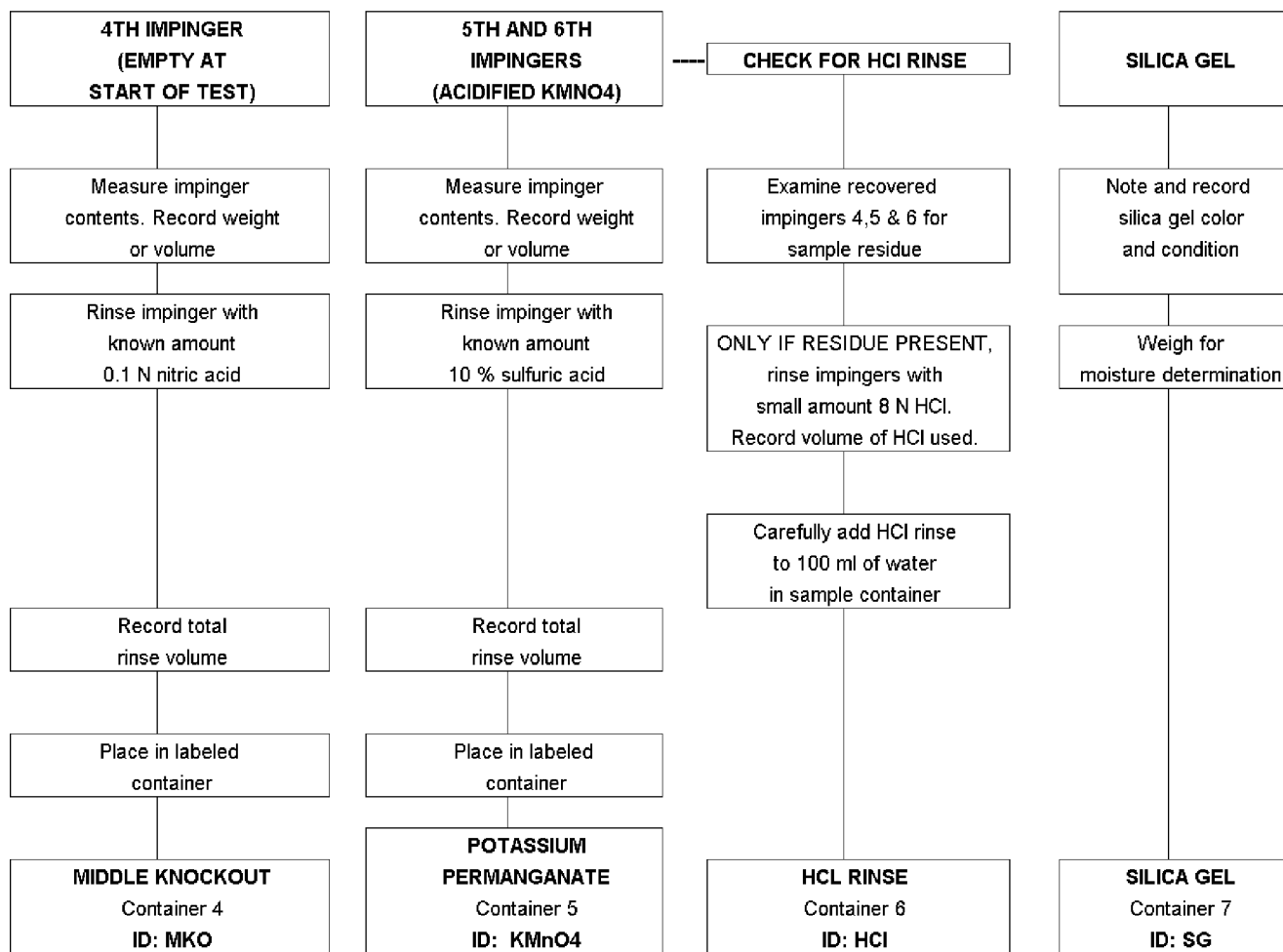


FIGURE 3

Method 436 Sample Analysis Scheme
Sample and Field Blank Preparation and Analysis Flowchart

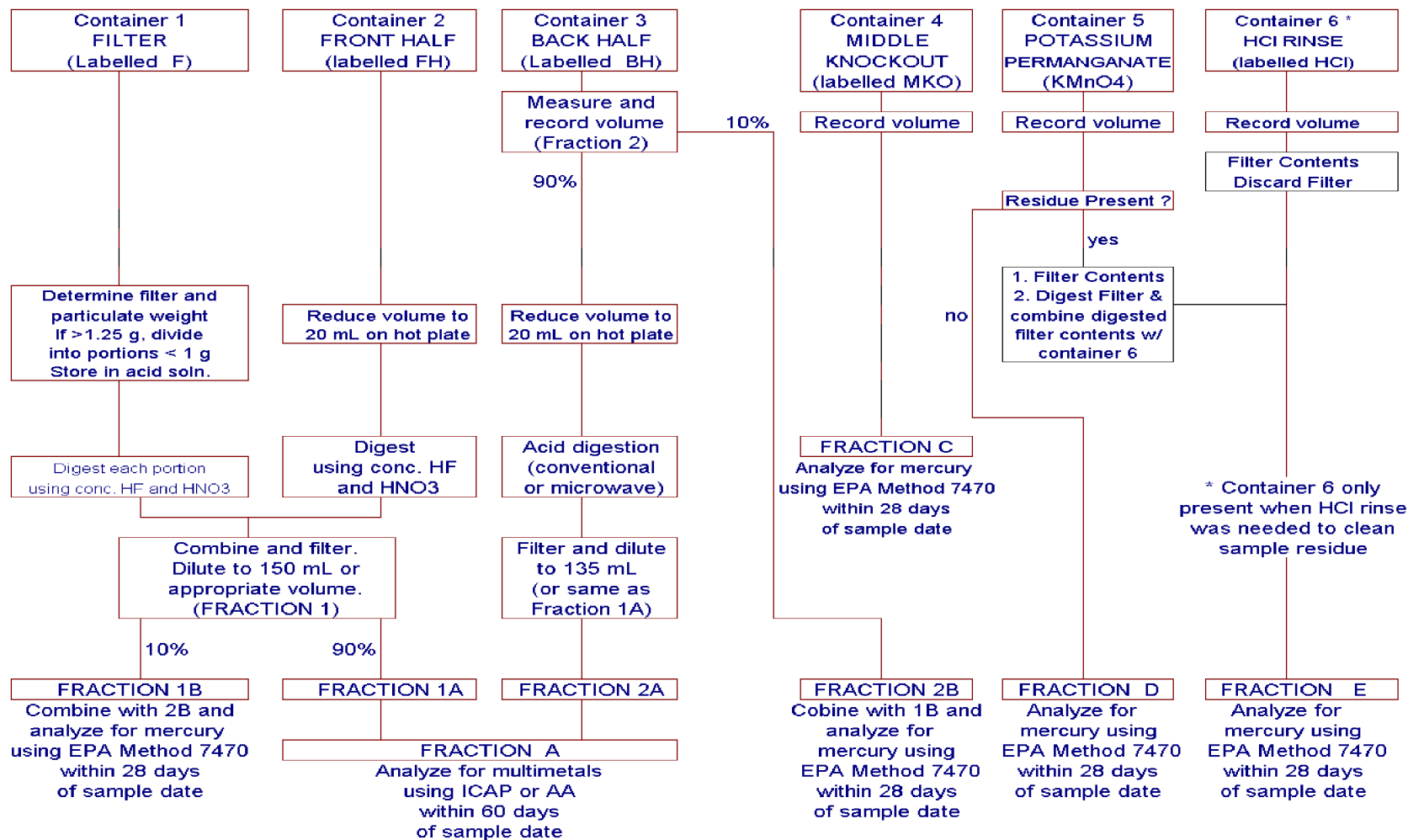


FIGURE 4

METHOD 436 REAGENT BLANK ANALYSIS SCHEME
 FIELD REAGENT BLANK SAMPLE PREPARATION AND ANALYSIS FLOWCHART

