METHOD 0060

DETERMINATION OF METALS IN STACK EMISSIONS

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of metals in stack emissions from hazardous waste incinerators and similar combustion processes. Using the detection limits shown, the following parameters can be determined by this method:

TABLE 1. ESTIMATED IDLS FOR METALS DETERMINED BY METHOD 0060

Analyte	ICP-AES[a] µg/L	Flame AA[b] µg/L	GFAA[c] µg/L	CVAA[d] µg/L
Antimony (Sb)	40[e]	200[e]	3[e]	
Arsenic (As)	60	2[f]	1	
Barium (Ba)	2	100		
Beryllium (Be)	0.3	5	0.2	
Cadmium (Cd)	4	5	0.1	
Total chromium (Cr)	7	50	1	
Cobalt (Co)	7	50	1	
Copper (Cu)	6	20		
Lead (Pb)	50	100	1	
Manganese (Mn)	2	10		
Mercury (Hg)				0.2
Nickel (Ni)	20	40		
Phosphorus (P)	60			
Selenium (Se)	80	2[f]	2	
Silver (Ag)	7	10		
Thallium (Tl)	40	100	1	
Zinc (Zn)	2	5		

a Estimated IDLs by ICP-AES, Method 6010.
b Estimated IDLs by direct aspiration Flame AA, Method 7000.
c Estimated IDLs by Graphite Furnace AA, Method 7000.
d Estimated IDL by Cold Vapor AA, Method 7470.
e Detection limit for Sb may be higher depending on digestion used.
f Estimated IDLs for As and Se by Hydride AA, Method 7000.

1.2 This method may also be used for the determination of particulate emissions following the additional procedures described in Section 7.1.5.2.

1.3 For the analyses described in this methodology and for similar analyses, the response for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is linear over several

orders of magnitude. Samples containing metal concentrations in the micrograms per liter (µg/L) to milligrams per liter (mg/L) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 mg/L of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 mg/L of cadmium should be diluted to that level before analysis.

1.4 The actual method detection limits are sample dependent and may vary as the sample matrix affects the limits. Method detection limits for antimony can also be dependent on the digestion method used and may be considerably higher than the estimated detection limits. Method detection limits for all analytes may differ from the estimated detection limits when hydrofluoric acid digestion is used. For more information on MDLs, refer to Chapter One.

1.5 The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced and as knowledgeable as required in source sampling, in handling and preparing (including mixing) reagents as discussed, and in using adequate safety procedures and protective equipment. The experience and knowledge should assure adequacy as described above in all of the source emission determination activities including planning of the desired detection limits.

2.0 SUMMARY

2.1 The stack sample is withdrawn isokinetically from the source. Particulate emissions are collected in the probe and on a heated filter and gaseous emissions are collected in a series of chilled impingers as shown in Figure 1 and described in Section 4.1.6. Two impingers are empty, two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide, two other impingers contain acidic potassium permanganate solution, and the last impinger contains a desiccant.

2.2 Sampling train components are recovered and digested in separate front-half and back-half fractions. Materials collected in the sampling train are acid digested to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed by using either digestion techniques of this manual, or the Method 29 (Ref. 3) procedures.

2.3 The nitric acid and hydrogen peroxide impinger solution, the hydrochloric acid rinse solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by Cold Vapor Atomic Absorption Spectrometry (CVAA). All of the sampling train catches, except for the permanganate solution, hydrochloric acid rinse solutions, and reagent water used to recover Hg, may be analyzed for target metals as presented in Table 1 by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) or Flame Atomic Absorption Spectrometry (FLAA). Similarly, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. If antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, selenium, and thallium require greater analytical sensitivity than can be obtained by ICP-AES, then Graphite Furnace Atomic Absorption Spectrometry (GFAA) is used for the analysis. Additionally, if desired, the tester may use FLAA for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program.

2.4 For convenience, aliquots of each digested sample Fraction 1A, as described in Section 7.2.3.2, plus Fraction 2A, as described in Section 7.2.4, can be combined for a single

analytical determination, proportionally with respect to the original Fractions 1A and 2A. Fraction 1A is normally diluted to 300 mL following digestion prior to analysis and the concentrated Fraction 2A is normally diluted to 150 mL following digestion and prior to analysis.

2.5 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 measures as described in Section 8.0 of this method including actual sample matrix effects checks.

3.0 INTERFERENCES

3.1 Refer to the appropriate determinative method for instructions on minimization of interferences.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train - A schematic of the sampling train is shown in Figure 1. It is similar to the Method 5 (Ref. 3) train. The sampling train consists of the following components.

4.1.1 Probe nozzle (probe tip) and borosilicate or quartz glass probe liner - Same as Method 5, except that glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

4.1.2 Pitot tube and differential pressure gauge - Same as Method 2 (Ref. 3).

4.1.3 Filters - Quartz fiber or glass fiber filters without organic binders shall be used. The filters shall contain less than 1.3 µg/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 must be analyzed for each target metal prior to emission testing. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test should be conducted in accordance with ASTM Standard Method D2986-71 (Reference 4). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described Method 5. Quartz fiber filters that meet these requirements are recommended.

4.1.4 Filter holder - Glass, same as Method 5, except that a Teflon filter support or other non-metallic, non-contaminating support must be used to replace the glass frit.

4.1.5 Filter heating system - Same as Method 5.

4.1.6 Condenser

4.1.6.1 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 condensing system should consist of three to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Teflon impingers of substantially the same shape, size and function

compared to the glass impingers and connected with leak-free non-contaminating fittings may be used: - additionally, the distance from the bottom of the gas conduit stem of the Teflon impinger assembly to the bottom of the portion of the impinger assembly which holds the aqueous acidic solutions must meet the same distance requirements as the glass impingers. The first impinger is optional and is recommended as a moisture knockout trap for use during test conditions which require such a trap. The first impinger shall be empty. The second and third impingers shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 5.8). The fourth shall be empty. The fifth and sixth impingers shall contain a known quantity of acidic potassium permanganate solution (Section 5.12), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger.

4.1.6.2 The first impinger shall be appropriately sized for a potentially large moisture catch and constructed generally as described for the first impinger in Method 5. The second impinger (or the first HNO_3/H_2O_2 impinger) shall also be as described for the first impinger in Method 5. The third impinger (or, in any case, the impinger used as the second HNO_3/H_2O_2 impinger) shall be the same as the Greenburg-Smith impinger with the standard tip described as the second impinger in Method 5. All other impingers used in the metals train are the same as the first HNO_3/H_2O_2 impinger.

4.1.6.3 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 mL. When the moisture knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.

4.1.7 Metering system, barometer, and gas density determination equipment - Same as Method 5.

4.1.8 Teflon tape - For capping openings and sealing connections, if necessary, on the sampling train.

4.2 Sample recovery. Same as Method 5, with the following exceptions and additions:

4.2.1 Non-metallic probe-liner and probe-nozzle brushes or swabs - For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes or swabs to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

4.2.2 Sample storage containers - Glass bottles, 1000 mL and 500 mL, with Teflon-lined caps which are non-reactive to oxidizing solutions, shall be used for samples and blanks containing $KMnO_4$. Polyethylene bottles may be used for other sample types.

4.2.3 Polypropylene tweezers and/or plastic gloves - For recovery of the filter from the sampling train filter holder.

4.3 Sample preparation and analysis equipment.

4.3.1 Refer to the appropriate preparation and analytical techniques for the proper apparatus and materials. Refer to Section 7.2 for a description of preparation techniques.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise use the best available grade.

5.2 Reagent Water. Refer to Chapter One for a definition of reagent water. Analyze the water for all target metals prior to field use. All target metals should be less than the MDL.

5.3 Nitric acid, concentrated - Baker Instra-analyzed or equivalent.

5.4 Nitric acid (0.1 M) - Add, with stirring, 6.3 mL of concentrated HNO_3 to a flask containing approximately 900 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 µg/L of each target metal.

5.5 Nitric acid, 10 percent (V/V). Add, with stirring, 500 mL of concentrated HNO_3 to a flask containing approximately 4000 mL of water. Dilute to 5000 mL with water. Mix well. Reagent shall contain less than 2 µg/L of each target metal.

5.6 Nitric acid, 5 percent (V/V). Add, with stirring, 50 mL of concentrated HNO_3 to 800 mL of water. Dilute to 1000 mL with water. Reagent shall contain less than 2 µg/L of each target metal.

5.7 Nitric acid, 50 percent (V/V). Add, with stirring, 125 mL of concentrated HNO_3 to a flask containing approximately 100 mL of water. Dilute to 250 mL with water. Mix well. Reagent shall contain less than 2 µg/L of each target metal.

5.8 Nitric acid (HNO_3)/hydrogen peroxide (H_2O_2) absorbing solution, 5 percent HNO_3/10 percent H_2O_2. Add carefully, with stirring, 50 mL of concentrated HNO_3 to a 1000-mL volumetric flask containing 500 mL of water. Carefully add 333 mL of 30% H_2O_2 to the flask. Dilute to volume with water. The reagent shall contain less than 2 µg/L of each target metal.

5.9 Hydrochloric acid (8M), HCl - Carefully add with stirring 690 mL of concentrated HCl to a flask containing 250 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 µg/L of Hg.

5.10 Hydrogen peroxide, 30 percent (V/V).

5.11 Potassium permanganate, 5 percent (W/V).

5.12 Acidic potassium permanganate ($KMnO_4$) absorbing solution, 4 percent $KMnO_4$ (W/V), 10 percent H_2SO_4 (V/V) - Prepare fresh daily. Carefully mix 100 mL of concentrated H_2SO_4 into 800 mL of water. Add water, with stirring, to make a volume of 1000 mL. This solution is 10% H_2SO_4

(V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into sufficient 10% H_2SO_4 to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 µg/L of Hg.

CAUTION: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the solution; a No. 70-72 hole drilled in the container cap and Teflon liner is suggested.

5.13 Sulfuric acid, concentrated.

5.14 Silica gel and crushed ice - Same as Method 5.

5.15 Hydrofluoric acid, concentrated.

5.16 Refer to the appropriate preparation and analytical technique for reagent and standard preparation procedures.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers should be trained and experienced with the test procedures.

6.1.1 Pretest preparation. Follow the same general procedure given in Method 5, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with reagent water. All glassware should then be soaked in a 10% (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with reagent water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

6.1.2 Sampling train calibration. Maintain a laboratory log of all calibrations. Calibrate the sampling train components according to the appropriate sections of Method 5: probe nozzle; pitot tube; metering system; probe heater; temperature gauges; leak-check of the metering system; and barometer.

6.1.3 Preliminary determinations. Same as Method 5.

6.1.4 Preparation of Sampling Train.

6.1.4.1 Follow the same general procedures given in Method 5, except place 100 mL of the nitric acid/hydrogen peroxide solution (Section 5.8) in each of the two HNO_3/H_2O_2 impingers (normally the second and third impingers) as shown in Figure 1. Place 100 mL of the acidic potassium permanganate absorbing solution (Section

5.12) in each of the two permanganate impingers. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

6.1.4.2 Several options are available to the tester based on the sampling conditions. The empty first impinger is not needed if the moisture to be collected in the impingers is calculated or determined to be less than 100 mL.

6.1.4.3 Retain for reagent blanks, volumes of the nitric acid/hydrogen peroxide solution and 100 mL of the acidic potassium permanganate solution. These reagent blanks should be labeled and analyzed as described in Section 7. Set up the sampling train as shown in Figure 1. If necessary to ensure leak-free sampling train connections, Teflon tape or other non-contaminating material should be used instead of silicone grease to prevent contamination.

CAUTION: Extreme care should be taken 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 manganese. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

6.1.4.4 Alternatively, mercury emissions can be measured in a separate train which measures only mercury emissions by using Method 101A (use only the version of Method 101A which incorporates the changes promulgated on April 25, 1996, in 61 FR 18278 through 18280, or later).

6.1.5 Leak-check procedures. Follow the leak-check procedures given in Method 5: pretest leak-check, leak-checks during the sample run, and post-test leak-checks.

6.1.6 Sampling train operation. Follow the procedures given in Method 5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5. When sampling for Hg, use a procedure analogous to that described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger.

6.1.7 Calculation of percent isokinetic. Same as Method 5.

7.0 PROCEDURE

7.1 Sample recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

7.1.1 The probe should be allowed 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, thus causing the undesired result of drawing liquid from the impingers into the filter.

7.1.2 Before moving the sampling train to the cleanup site, 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.

7.1.3 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.

7.1.4 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.

7.1.5 The sample is recovered and treated as follows (see schematic in Figure 2). Assure that all items necessary for recovery of the sample do not contaminate it.

7.1.5.1 Container No. 1 (filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean disposable surgical gloves rinsed with water should be used 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 this train. Seal the labeled petri dish.

NOTE: Follow the procedure in Section 7.1.5.2 only if determination of particulate emissions are desired in addition to metals emissions. If only metals emissions are to be determined, skip Section 7.1.5.2 and go to Section 7.1.5.3.

7.1.5.2 Container No. 2 (acetone rinse).

7.1.5.2.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting (fittings made of plastic such as Teflon, polypropylene, etc. are recommended to prevent contamination by metal fittings, further, if desired a single glass piece may be used, but it is not a requirement of this methodology), probe liner, and front half of the filter holder by washing these components with 100 mL of acetone and placing the wash in a glass container. The use of exactly 100 mL is necessary for the subsequent blank correction procedures. Reagent water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Adminstrator; in these cases, save a water blank and follow the Administrators directions on analysis. In these cases, save a water blank. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, after which

make a final rinse of the inside surface with acetone. Brush and rinse the sample exposed inside of the Swagelok fitting with acetone in a similar way until no visible particles remain.

7.1.5.2.2 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe. Rinse and brush three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

7.1.5.2.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.1.5.2.4 Clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

7.1.5.3 Container No. 3 (probe rinse). Keep the probe assembly clean and free from contamination as described in Section 7.1.5.2 during the 0.1M nitric acid rinse described below. Rinse the probe liner, probe nozzle, and filter, and front half of the filter holder thoroughly with 100 mL of 0.1 M nitric acid and place the wash into a sample storage container.

NOTE: The use of exactly 100 mL is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. 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 followed by acetone and discard these rinses.

7.1.5.4 Container No. 4 (Impingers 1 through 3, HNO_3/H_2O_2 impingers and moisture knockout impinger, when used, contents and rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from Impingers 1, 2, and 3 in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 mL using a graduated cylinder or weigh quantitatively to 0.5 g using **calibrated** scales. Record the volume of liquid present. 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 100 mL of 0.1 M nitric acid using the procedure as applicable and generally as described in Method 12, Section 5.2.4.

NOTE: The use of exactly 100 mL of 0.1 M nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level on outside of container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

7.1.5.5 Containers No. 5A (0.1M HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8M HCl rinse and dilution). If mercury is not being measured in this train, then Impingers 4, 5, and 6, as shown in Figure 1, are not necessary and may be eliminated.

7.1.5.5.1 Pour all the liquid, if any, from the impinger which was empty at the start of the run (normally Impinger 4) and which precedes the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 mL of 0.1M HNO_3 and place this into Container No. 5A. Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Place this $KMnO_4$ absorbing solution stack sample from the two permanganate impingers into Container No. 5B. Using 100 mL total of the fresh acidified potassium permanganate solution, rinse the permanganate impinger and connecting glass pieces a minimum of three times. Place the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers into Container No. 5B. Using 100 mL total of water, rinse the permanganate impingers and connecting glass pieces a minimum of three times, and place the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated material, if any, from the two impingers into Container No. 5B. 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 properly prepare 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 bottle. These bottles shall not be filled full and shall be vented to relieve excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner is suggested.

7.1.5.5.2 If no visible deposits remain after the above described water rinse, do not rinse with HCl. The previous rinses are designed to remove all of the

permanganate residues, but if any remain, perform the HCl cleanup in a well ventilated area or vent hood as necessary to prevent exposure to any chlorine gases which may be released by the following HCl cleanup procedure. If deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 mL of 8M HCl, and place the wash in a separate sample container labeled Container No. 5C that contains 200 mL of water. 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 8M 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 8M HCl rinse carefully with stirring into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

7.1.5.6 Container No. 6 (silica gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. 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. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5g.

7.1.5.7 Container No. 7 (acetone blank). If particulate emissions are to be determined, at least once during each field test, place 100-mL portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.

7.1.5.8 Container No. 8A (0.1 M nitric acid blank). At least once during each field test, place 300 mL of the 0.1 M nitric acid solution used in the sample recovery process into a labeled container for use in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container.

7.1.5.9 Container No. 8B (water blank). At least once during each field test, place 100 mL of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

7.1.5.10 Container No. 9 (5 percent nitric acid/10 percent hydrogen peroxide blank). At least once during each field test, place 200 mL of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

7.1.5.11 Container No. 10 (acidified potassium permanganate 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. Prepare the container as described in Section 7.2.5.5.1 note.

7.1.5.12 Container No. 11 (8M HCl blank). At least once during each field test, place 200 mL of water into a sample container. Then pour 25 mL of 8M HCl carefully with stirring into the 200 mL of water in the container. Mix well and seal the container.

7.1.5.13 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. This will be used in the front-half field reagent blank.

7.2 Sample preparation. Note the level of the liquid in each of the containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred either void the sample or use approved methods 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. 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. Acid digestion is performed by using either prescribed digestion techniques of this manual, or the Method 29 procedures.

7.2.1 Container No. 1 (filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual fluorocarbon based microwave pressure relief vessels or Parr® Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample according to Method 3051. For conventional heating, heat the Parr® Bombs in an oven at 140°C (285°F) for 6 hours following the manufacturer's recommendations for Bomb loading, assembly and disassembly, cleaning, and handling. Cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 7.2.3.

NOTE: Hydrofluoric acid (HF) has been identified as an exceptional health and contact hazard. Burns and other symptoms can be severe and may not appear immediately. The analyst should perform all operations with HF under appropriate laboratory conditions (i.e., in a fume hood suitable for HF work), should be fully informed regarding the appropriate safety data (e.g., all hazard warnings, storage and handling requirements, spill cleanup procedures, and emergency treatments for exposure), and should wear the appropriate laboratory protective equipment (e.g., goggles, face shield, lab coat, rubber apron, long rubber gloves) when preparing and handling digestates and other solutions containing HF.

7.2.2 Container No. 2 (acetone rinse). Measure the liquid in this container either volumetrically to ±1 mL or gravimetrically to ±0.5 g. Transfer the contents to an acid-cleaned tared 250-mL beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 mL concentrated nitric acid and carefully, with stirring, combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the Section 7.2.3.

7.2.3 Container No. 3 (probe rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified by careful addition, with stirring, with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and

the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Then follow one of the digestion procedures listed below.

7.2.3.1 Digest the sample using the appropriate method (Method 3010, 3015, or Parr Bomb), using the HF modification and then continuing to follow the procedures described in Section 7.2.1.

7.2.3.2 Combine with the digestate prepared in Section 7.2.1. The resultant combined sample is a Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 mL (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 mL. Quantitatively remove a 50-mL aliquot and label as Fraction 1B. Label the remaining 250 mL portion as Fraction 1A. Fraction 1A is used for ICP-AES, ICP-MS, or AA analysis for all metals except mercury. Fraction 1B is used for the determination of front-half mercury.

7.2.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove a 75-to 100-mL aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion which is normally 150 mL. Concentrated Fraction 2A is analyzed for all the metals except mercury. The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 7.4.7. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Acid digestion is performed by using either prescribed digestion techniques of this manual, or the Method 29 procedures.

7.2.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other.

7.2.5.1 Measure and record the volumes of 5A and 5B each to within 0.5 mL. Dilute Sample 5C to 500 mL with water. The Samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 7.4.

7.2.5.2 Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

7.2.6 Container No. 6 (silica gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field).

7.3 Calibration

Refer to the appropriate analytical methods for the proper calibration procedures.

7.4 Sample analysis.

7.4.1 For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICP-AES and AA analysis as described in Section 7.4.5. Fraction 1B is for determination of front-half mercury as described in Section 7.4.7.

7.4.2 The back half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICP-AES or AA analysis. Fraction 2B will be analyzed for mercury.

7.4.3 Samples 5A, 5B, and 5C are labeled Fractions 3A, 3B, and 3C, respectively. They consist of the impinger contents and rinses from the empty Impinger 4 and the permanganate Impingers 5 and 6. These samples are analyzed for mercury as described in Section 7.4.7. The total back-half mercury catch is determined from the sum of Fraction 2B and Fraction 3A, 3B, and 3C.

7.4.4 Initially, analyze all samples for iron, aluminum, and all the target metals except mercury . If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead.

NOTE: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used. Since all front-half samples will contain hydrofluoric acid, use an alumina torch.

7.4.5 ICP-AES analysis. Fraction 1A and Fraction 2A are analyzed by ICP-AES using Method 6010. Refer to Method 6010 for the proper analytical procedures.

7.4.6 AA by direct aspiration and/or graphite furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AA is desired, Table A-2 should also be consulted to determine possible interferences and techniques to use for their minimization. Refer to Vol. 1A of this manual to determine the appropriate analytical protocol.

7.4.7 Cold vapor AA mercury analysis. Fraction 1B, Fraction 2B, and Fraction 3A, 3B, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectrometry following the method outlined in Method 7470. Refer to Method 7470 for the proper analytical protocol. If no prior knowledge exists of the expected amount of mercury

in the sample, dilute a 1-mL to 10-mL aliquot of each original sample to 100 mL. Record the amount of the aliquot used for dilution to 100 mL. Digest the sample according to Method 7470. To determine the stack emission value for mercury, the amount of the aliquot of the sample used for dilution and analysis is dependent on the amount of mercury in the aliquot: the total amount of mercury in the aliquot used for analysis must be less than 1 ug, and within the range (zero to 1000 ng) of the calibration curve.

7.4.8 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. Refer to Method 6020 for the proper analytical procedure.

7.5 Calculations

7.5.1 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 Method 5.

7.5.2 Volume of water vapor and moisture content. Using the data obtained from this test, 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 Method 5.

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

7.5.4 Metals (except mercury) in source sample.

7.5.4.1 Fraction 1A, front half, metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{a1} F_d V_{soln,1} \qquad \text{Eq. } 1^1$$

where:

M_{fh} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), µg.

C_{a1} = concentration of metal in sample Fraction 1A as read from the standard curve (µg/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, when a 2 mL volume of Fraction 1A is diluted to 10 mL, F_d = 5).

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), mL.

7.5.4.2 Fraction 2A, back half, metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. } 2^1$$

[1]If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), µg.

C_{a2} = concentration of metal in sample concentrated Fraction 2A, as read from the standard curve (µg/mL).

F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A. See Section 7.2.4.

V_a = total volume of digested sample solution (concentrated Fraction 2A), mL. See Section 7.2.4.

7.5.4.3 Total train, metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \quad \text{Eq. } 3^1$$

where:

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

M_{fhb} = bank correction value for mass of metal detected in front-half field reagent blank, µg.

M_{bhb} = blank correction value for mass of metal detected in back-half field reagent blank, µg.

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to "A" µg [where "A" µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in square inches of the filter used in the emission sample], M_{fhb} may be used to correct the emission sample value (M_{fh}); if M_{fhb} exceeds "A" µg, the greater of the two following values may be used: "A" µg, or the lesser value of M_{fhb} or 5 percent of M_{fh}.

If the measured blank value for the back half (M_{bhb}) is in the range 0.0 to 1 µg, M_{bhb} may be used to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, the greater of the two following values may be used: 1 µg or the lesser value of M_{bhb}or 5 percent of M_{bh}.

7.5.5 Mercury in source sample.

7.5.5.1 Fraction 1B, front half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \left(\frac{Q_{fh}}{V_{f1B}}\right) \times V_{soln,1} \quad \text{Eq. 4}$$

[1]If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

Hg_{fh} = total mass of mercury collected in the front half of the sampling train (Fraction 1), µg.
Q_{fh} = quantity of mercury in analyzed sample, µg.
$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), mL.
V_{f1B} = volume of Fraction 1B analyzed, mL. See the following Note.

NOTE: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 mL of Fraction 1B were diluted to 100 mL to bring it into the proper analytical range, and 1 mL of the 100 mL dilution was analyzed, V_{f1B} would be 0.01.

7.5.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, back half, Hg. Calculate the amount of mercury collected in Fraction 2 using Equation 5 and Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} \times V_{soln,2} \qquad \text{Eq. 5}$$

where:

Hg_{bh2} = total mass of mercury collected in Fraction 2, µg.
Q_{bh2} = quantity of mercury in analyzed sample, µg.
$V_{soln,2}$ = total volume of Fraction 2, mL.
V_{f2B} = volume of Fraction 2B analyzed, mL (see the following note).

NOTE: V_{f2b} is the actual amount of Fraction 2B analyzed. For example, if 1 mL of Fraction 2B were diluted to 10 mL to bring it into the proper analytical range, and 5 mL of the 10-mL dilution was analyzed, V_{f2b} would be 0.5 mL. Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, 3B, and 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \times V_{soln,3(A,B,C)} \qquad \text{Eq. 6}$$

where:

$Hg_{bh3(A,B,C)}$ = total mass of mercury collected separately in Fractions A, 3B, or 3C, µg.
$Q_{bh3(A,B,C)}$ = quanty of mercury in separately analyzed samples, µg.
$V_{f3(A,B,C)}$ = volume Fraction 3A, 3B, or 3C analyzed, mL (see above and calculate similarly).
$V_{soln,3(A,B,C)}$ = total volume of Fraction 3A, 3B, or 3C, mL.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, ug.

7.5.5.3 Total train mercury catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \quad \text{Eq. 8}$$

where:

Hg_t = total mass of mercury collected in the sampling train, µg.
Hg_{fhb} = blank correction value for mass of mercury detected in front-half field reagent blank, µg.
Hg_{bhb} = blank correction value for mass of mercury detected in back-half field reagent blank, µg.

NOTE: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0 to 6 ug, then the total may be used to correct the emission sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 6 µg, the greater of the following two values may be used: 6 µg or 5 percent of the emission sample value ($Hg_{fh} + Hg_{bh}$).

7.5.6 Metal concentration of stack gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, cobalt, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4 (M_t/V_{m(std)}) \quad \text{Eq. 9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.
K_4 = 10^{-3} mg/µg.
M_t = total mass of each metal collected in the sampling train, µg; (substitute Hg_t for M_t for the mercury calculation).
$V_{m(std)}$ = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

7.5.7 Isokinetic variation and acceptable results. Same as Method 5, Sections 6.11 and 6.12, respectively.

8.0 QUALITY CONTROL

8.1 Sampling Blanks.

Field Reagent Blanks (FRBs). When analyzed, the blank samples in Container Nos. 7 through 12 shall be processed, digested, and analyzed as follows. Digest and process one of the filters from Container No. 12 contents per Section 7.2.1, 100 mL from Container No. 7 per Section 7.2.2, and 100 mL from Container No. 8 per Section 7.2.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. (If desired, the other two filters may be digested separately according to Section 7.2.1, diluted separately to 300 mL each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blank 1A and Fraction Blank 1B. The three Fraction Blank 1A values will be calculated as three values of M_{fhb} in Equation 3 of Section 7.5.4.3, then the three values shall be totalled and divided by three to become the value M_{fhb} to be used in the computation of M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hg_{fhb} in Equation 8 of Section 7.5.5.3. The analyses of the two extra filters are optional and are not a requirement of this method, but if the analyses are performed, the results must be considered as described above.) Combine 100 mL of Container No. 8A with 200 mL of the contents of Container No. 9 and digest and process the resultant volume per Section 7.2.4. This produces concentrated Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. A 100-mL portion of Container No. 8A is Fraction Blank 3A. Combine 100 mL of the contents of Container No. 10 with 33 mL of the contents of Container No. 8B. This produces Fraction Blank 3B. (Use 400 mL as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 mL of the contents of Container No. 11 to 500 mL with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 7.4.5 and/or Section 7.4.6 Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blank 3A, 3B, and 3C per Section 7.4.7. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of Fraction Blank 2A produces the back-half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B and 3 produce the back-half reagent blank correction value for mercury.

8.2 Quality Control Samples. The following quality control samples should be analyzed. All appropriate Chapter One quality control procedures should be followed.

8.2.1 ICP-AES or ICP-MS analysis. Follow the quality control shown in Chapter One and Section 8 of Method 6010 or 6020 as appropriate.

8.2.2 Direct aspiration and/or graphite furnace AA analysis for antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc. All samples should be analyzed in duplicate. Perform a post-digestion spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the post-digestion spike, analyze each sample by the method of standard additions.

8.2.3 Cold vapor AA analysis for mercury. All samples should be analyzed in duplicate. Perform a post-digestion or matrix spike on one sample from the nitric acid impinger portion (must be within 25% or samples must be analyzed by the method of standard additions).

9.0 METHOD PERFORMANCE

9.1 To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

9.2 Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table 2 for a specific test by using one or more of the following options:

- A 1-hour sampling run collects a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased and 5 m^3 are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (i.e., the method is four times more sensitive than an hour run).

- The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 mL for the front half (Fraction 1) and 150 mL for the back half (Fraction 2A). If the volume of the front half is concentrated from 300 mL to 30 mL, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back-half volume is concentrated from 150 mL to 25 mL, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. Reduction to a volume of less than 25 mL may not allow redissolving of the residue and may increase interference by other compounds.

- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase detection limits (i.e., the method would be less sensitive). The front-half and back-half samples (Fractions 1A plus 2A) can be combined proportionally prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample as described does not

allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of the mercury fraction must be considered.

- The above discussion assumes no blank correction.

9.3 Using (1) the procedures described in this method, (2) the analytical detection limits listed in Section 1, (3) a volume of 300 mL for the front half and 150 mL for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3, the corresponding in-stack method detection limits are presented in Table A-2 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where:

A = analytical detection limit, µg/mL.
B = volume of sample prior to aliquot for analysis, mL.
C = stack sample volume, dscm (dsm^3).
D = in-stack detection limit, $\mu g/m^3$.

Values in Table A-2 are calculated for the front and back half and/or the total train.

10.0 REFERENCES

1. Method 303F, Standard Methods for the Examination of Water Wastewater, available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.

2. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C.

3. EPA Methods 1 through 5, 12, and 29 Code of Federal Regulations, Title 40, Part 60, Appendix A.

4. ASTM Standard Method D2986-71, available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

TABLE 2. IN-STACK METHOD DETECTION LIMITS (µg/m^3)
FOR TRAIN FRACTIONS USING ICP-AES AND AA

Metal	Front Half Fraction 1 Probe and Filter	Back Half Fraction 2 Impingers 1-3	Back Half Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Cobalt	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18.0	9.0		27.0
Selenium	18.0 (0.5)*	9.0 (0.3)*		27.0 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

( )* Detection limit when analyzed by GFAA.
** Detection limit when analyzed by CVAA, estimated for back-half and total train.

NOTE: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

TABLE 3. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AA ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/mL Pb Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic vola-tilization Aluminum	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 High Mg & Si	Add 0.1% fluoride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips

(continued)

TABLE 3 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scattering	KCl ionization suppressant in sample & standard Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a known constant effect and to eliminate effect of phosphate
Cu	Aspiration	7210	324.7	Absorpt & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	283.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternative	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorus acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternative	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternative Fe, Co, & Cr Nonlinear response	Background correction required Matrix matching or a nitrous-oxide/acetyl flame Sample dilution or use 352.4 nm line

(continued)

TABLE 3 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Se	Furnace	7740	196.0	Volatility	Spike samples & reference materials & add nickel nitrate to minimize volatilization
				Adsorpt & scatter	Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt & scatter	Background correction is required
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex
				Viscosity	Sample & standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8		Background correction is required
				Hydrochloric acid or chloride	Verify that losses are not occurring for volatization by spiked samples or standard additions Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P	Strontium removes Cu and phosphate
				Contamination	Care should be taken to avoid contamination

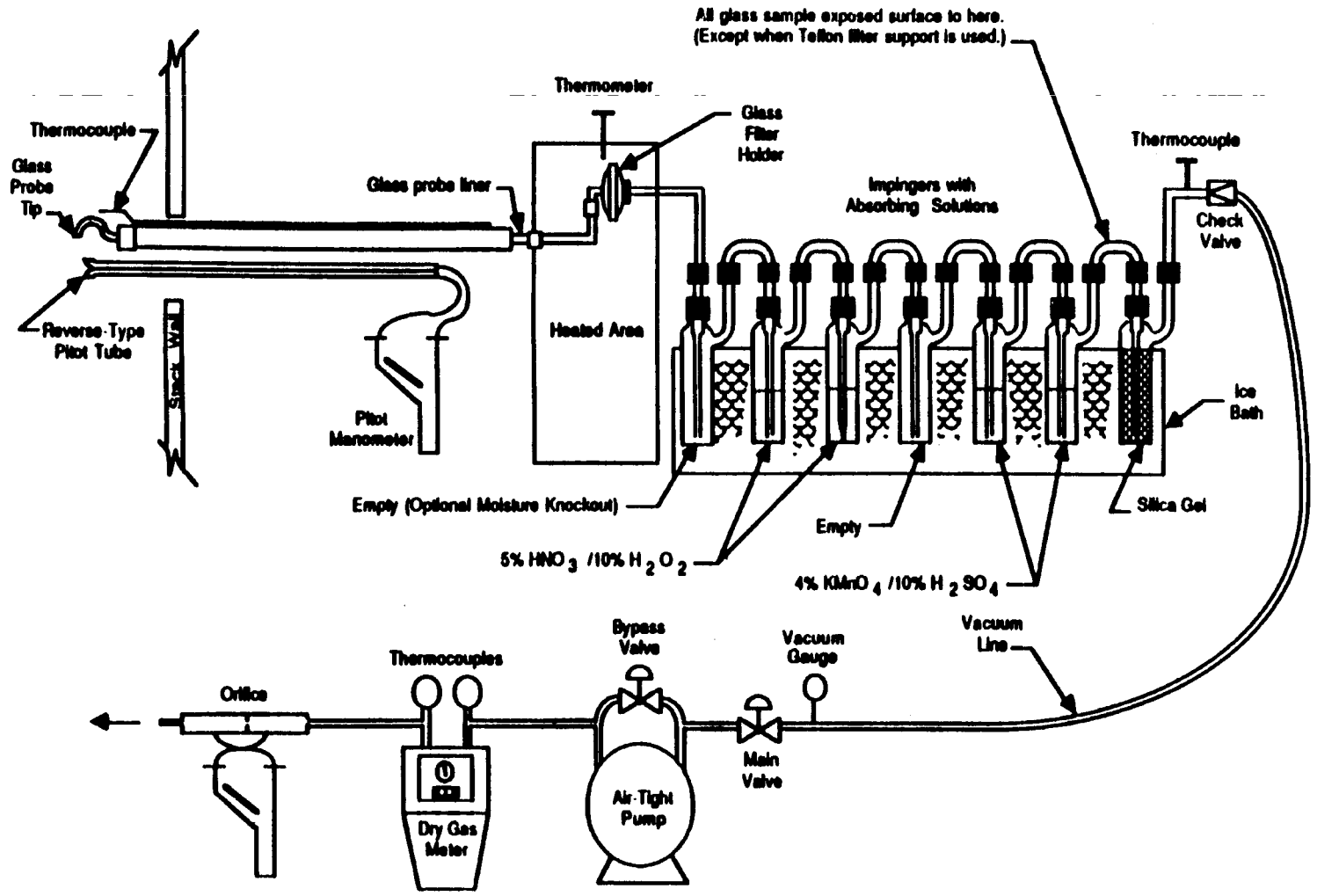
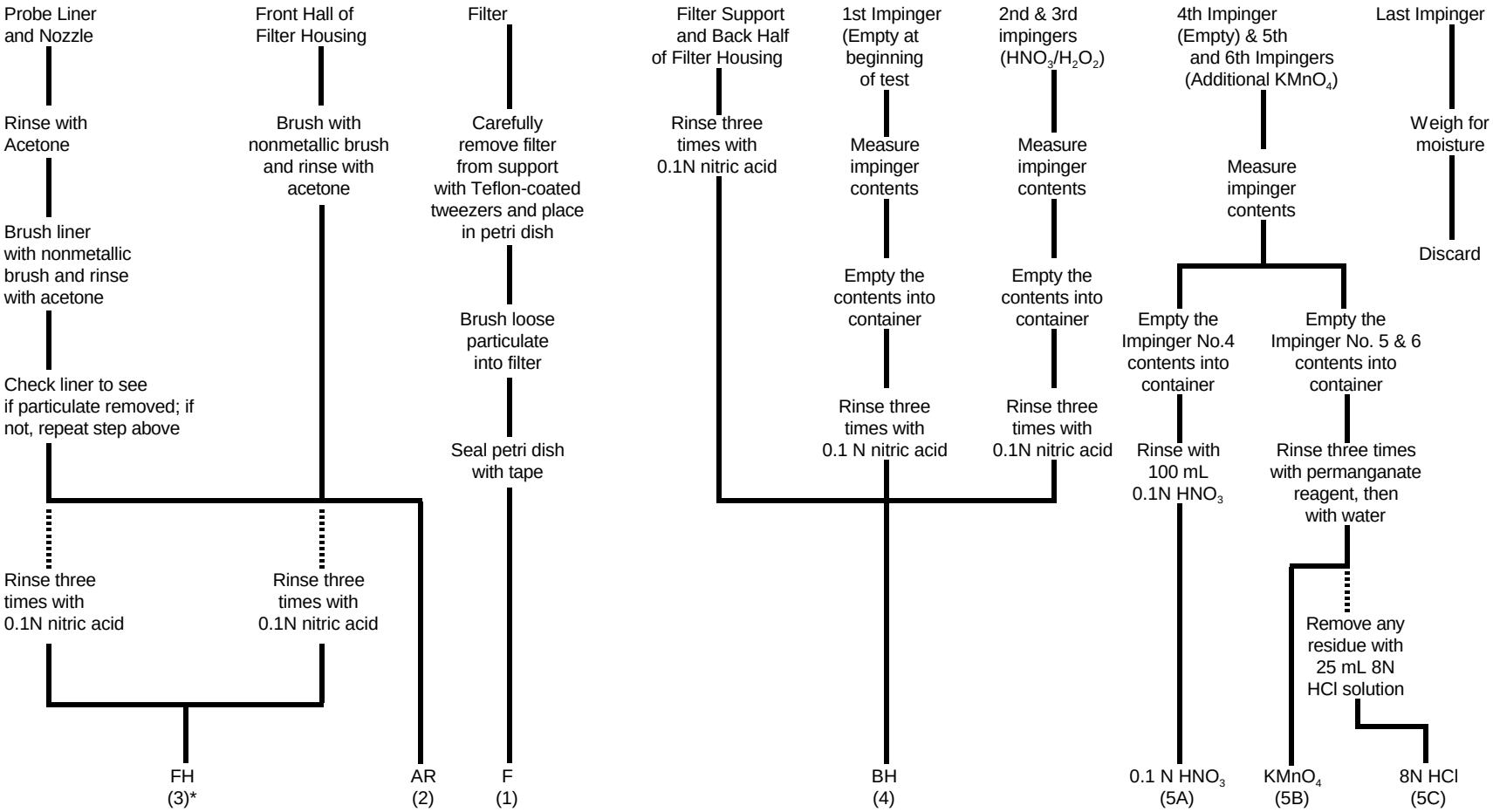


FIGURE 1. SCHEMATIC OF MULTIPLE METALS SAMPLING TRAIN CONFIGURATION



* Number in parentheses indicates container number

FIGURE 2. SAMPLE RECOVERY SCHEME

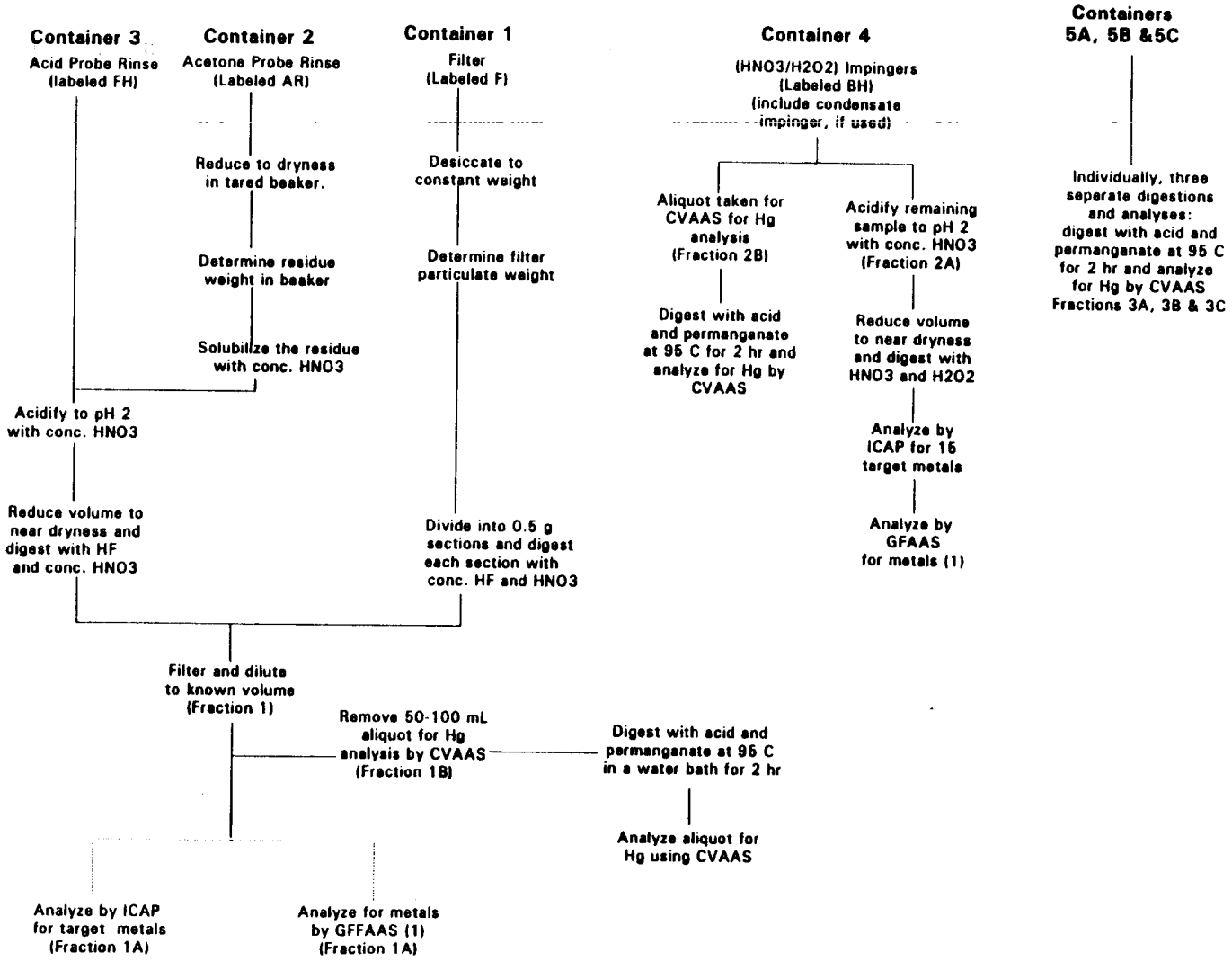
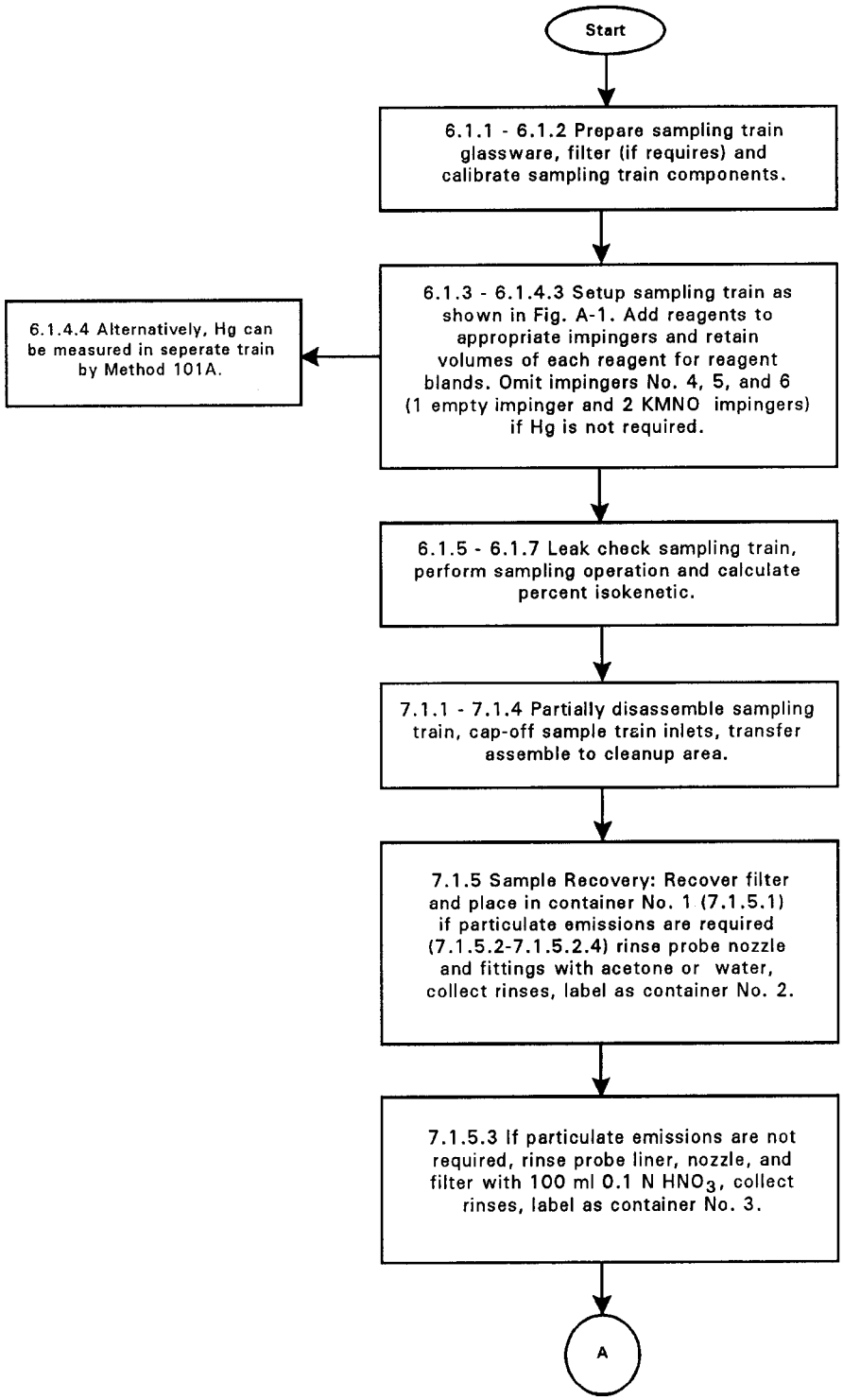
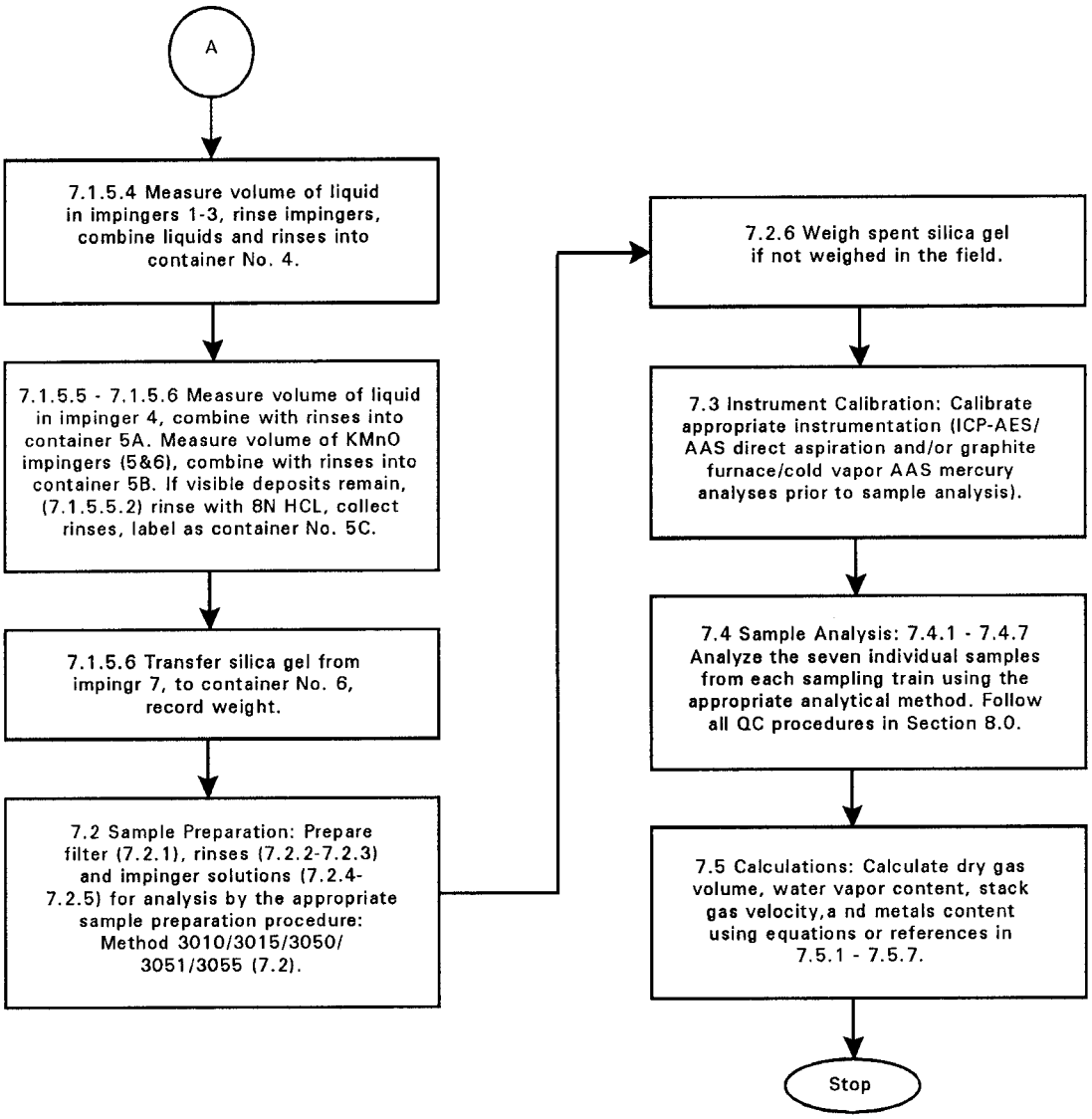


FIGURE 3. SAMPLING PREPARATION AND ANALYSIS SCHEME


Start
6.1.1 - 6.1.2 Prepare sampling train glassware, filter (if requires) and calibrate sampling train components.
6.1.3 - 6.1.4.3 Setup sampling train as shown in Fig. A-1. Add reagents to appropriate impingers and retain volumes of each reagent for reagent blands. Omit impingers No. 4, 5, and 6 (1 empty impinger and 2 KMNO impingers) if Hg is not required.
6.1.4.4 Alternatively, Hg can be measured in seperate train by Method 101A.
6.1.5 - 6.1.7 Leak check sampling train, perform sampling operation and calculate percent isokenetic.
7.1.1 - 7.1.4 Partially disassemble sampling train, cap-off sample train inlets, transfer assemble to cleanup area.
7.1.5 Sample Recovery: Recover filter and place in container No. 1 (7.1.5.1) if particulate emissions are required (7.1.5.2-7.1.5.2.4) rinse probe nozzle and fittings with acetone or water, collect rinses, label as container No. 2.
7.1.5.3 If particulate emissions are not required, rinse probe liner, nozzle, and filter with 100 ml 0.1 N HNO_3, collect rinses, label as container No. 3.
A


A
7.1.5.4 Measure volume of liquid in impingers 1-3, rinse impingers, combine liquids and rinses into container No. 4.
7.1.5.5 - 7.1.5.6 Measure volume of liquid in impinger 4, combine with rinses into container 5A. Measure volume of KMnO impingers (5&6), combine with rinses into container 5B. If visible deposits remain, (7.1.5.5.2) rinse with 8N HCL, collect rinses, label as container No. 5C.
7.1.5.6 Transfer silica gel from impingr 7, to container No. 6, record weight.
7.2 Sample Preparation: Prepare filter (7.2.1), rinses (7.2.2-7.2.3) and impinger solutions (7.2.4-7.2.5) for analysis by the appropriate sample preparation procedure: Method 3010/3015/3050/ 3051/3055 (7.2).
7.2.6 Weigh spent silica gel if not weighed in the field.
7.3 Instrument Calibration: Calibrate appropriate instrumentation (ICP-AES/ AAS direct aspiration and/or graphite furnace/cold vapor AAS mercury analyses prior to sample analysis).
7.4 Sample Analysis: 7.4.1 - 7.4.7 Analyze the seven individual samples from each sampling train using the appropriate analytical method. Follow all QC procedures in Section 8.0.
7.5 Calculations: Calculate dry gas volume, water vapor content, stack gas velocity,a nd metals content using equations or references in 7.5.1 - 7.5.7.
Stop