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from Container No. 5B 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 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in Sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per Section 8.3.1, 100 ml from Container No. 7 per Section 8.3.2, and 100 ml from Container No. 8A per Section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per Section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in Section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in Section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per Section 11.1.1 and/or Section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per Section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP–MS Analysis. Follow the respective quality control descriptions in Section 8 of Methods 6010 and 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix 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 matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP–MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in Section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i), 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.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP–MS or AAS analysis as described in Sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in Section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the H_2SO_4/$KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in Section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29–2. 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 ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i).

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.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–3 to determine which techniques and procedures to apply for each target metal. Use Table 29–3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to Section 10.3 and follow the quality control procedures specified in Section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using NOTE NO. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F 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. 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 the 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 Method 7470 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 HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 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 in-stack detection limit given in Table 29–1, 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 this section: (*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.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Analytical detection limit, μg/ml.

B = Liquid volume of digested sample prior to aliquotting for analysis, ml.

C = Stack sample gas volume, dsm^3.

C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, μg/ml.

C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (μg/ml).

C_s = Concentration of a metal in the stack gas, mg/dscm.

D = In-stack detection limit, $\mu g/m^3$.

F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see Section 8.3.4.)

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 1A is diluted to 10 ml to place it in the calibration range, $F_d = 5$).

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

Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, μg.

$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, μg.

Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, μg.

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), μg.

Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, μg.

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

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

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

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

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

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

M_t = Total mass of that metal collected in the sampling train, μg; (substitute Hg_t for M_t for the H_g calculation).

Q_{bh2} = Quantity of Hg, μg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis . NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$Q_{bh3(A,B,C)}$ = Quantity of Hg, μg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis* (see NOTES in Sections 12.7.1 and 12.7.2 describing the quantity ''Q'' and calculate similarly).

Q_{fh} = Quantity of Hg, μg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis*. NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate

and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see Section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml. NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in Section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to Section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml. NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in Section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in Sections 12.7.1 and 12.7.2, describing the quantity ''V'' and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3}$ mg/µg.

12.2 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 12.3 of Method 5.

12.3 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 Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29–4 using the conditions described in Section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \qquad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \qquad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–2 through 29–4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-3}$$

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

$$M_t = \left(M_{fh} - M_{fhb}\right) + \left(M_{bh} - M_{bhb}\right) \qquad \text{Eq. 29-4}$$

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 in.^{2} of the sample filter), use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. The lesser of (a) M_{fhb}, or (b) 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, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. The lesser of (a) M_{bhb}, or (b) 5 percent of M_{bh}.

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount ofHg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–5:

$$Hg_{fh} = \frac{Q_{fh}}{V_{flB}}\left(V_{soln,1}\right) \qquad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–6: