

METHOD 0061

DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of hexavalent chromium (Cr^{+6}) emissions from hazardous waste incinerators, municipal waste incinerators, municipal waste combustors, and sewage sludge incinerators. With the approval of the Administrator, this method may also be used to measure total chromium. The sampling train, constructed of Teflon components, has only been evaluated at temperatures of less than 300°F. Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.

1.2 Range: If employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in solution). With sample dilution, there is no upper limit. Follow your manufacturer's specific instructions on employing the preconcentration procedure for these analyses.

2.0 SUMMARY OF METHOD

2.1 For incinerators and combustors, the Cr^{+6} emissions are collected isokinetically from the source: To eliminate the possibility of Cr^{+6} reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for Cr^{+6} by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the Cr^{+6} as chromate ($\text{CrO}_4^{=}$) from other diphenylcarbazide reactions that occur in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system may also be used in conjunction with the IC/PCR.

3.0 INTERFERENCES

3.1 Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6} . A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences.

3.2 The chromatographic separation of Cr^{+6} using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause interference.

3.3 Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be obtained by increasing the injection volume of the samples to ten times the size of the sample loop.

4.0 APPARATUS

4.1 Sampling Train: Schematics of the recirculatory sampling trains employed in this method are shown in Figures 1 and 2. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon, and are to be cleaned as per Section 6.0. The metering system is identical to that specified by Method 5; the sampling train consists of the following components:

4.1.1 Probe Nozzle: Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be $\leq 30^\circ$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. 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 sample 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 Section 7.1.1.

4.1.2 Teflon Aspirator or Pump/Sprayer Assembly (see Figures 1 and 2): Teflon aspirator capable of recirculating absorbing reagent at 50 mL/min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator. A Teflon union-T is connected behind the nozzle to provide the absorbing reagent/sample gas mix; a peristaltic pump is used to recirculate the absorbing reagent at a flow rate of at least 50 mL/min. Teflon fittings, Teflon ferrules, and Teflon nuts are used to connect a glass or Teflon nozzle, recirculation line, and sample line to the Teflon aspirator or union-T. Tygon, C-flex or other suitable inert tubing for use with peristaltic pump.

4.1.3 Teflon Sample Line: Teflon, 3/8" ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.

4.1.4 Teflon Recirculation Line: Teflon, 1/4" O.D. and 1/8" I.D., of suitable length to connect first impinger to aspirator (or T-union).

4.1.5 Teflon Impingers: Four Teflon impingers; Teflon tubes and fittings, such as made by Savillex*, can be used to construct impingers 2" diameter by 12" long, with vacuum-tight 3/8" O.D. Teflon compression fittings. Alternatively, standard glass impingers that have been Teflon-lined, with Teflon stems and U-tubes, may be used. Inlet fittings on impinger top to be bored through to accept 3/8" O.D. tubing as impinger stem. The second and third 3/8" OD Teflon stem has a 1/4" OD Teflon tube, 2" long, inserted at its impinger stem should extend to 2" from impinger bottom, high enough in the impinger reagent to prevent air from entering recirculating line; the second and third impinger stems should extend to 1/2" from impinger bottom. The first impinger should include a 1/4" O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger to trap solution carried over from the previous impingers.

NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

4.1.6 Glass Impinger: Silica gel impinger, Vacuum-tight impingers, capable of containing 400 g. of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (1/2" ID at tip of stem).

4.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

4.1.8 Metering System, Barometer, and Gas Density Determinations Equipment: Same as Method 0010.

4.2 Sample Recovery: Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinse thoroughly with reagent water before use.

4.2.1 Nitrogen Purge Line: Inert tubing and fittings capable of delivering 0 to 1 scf/min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder (see Figure 3).

4.2.2 Wash Bottles: Two polyethylene wash bottles, for reagent water-nitric rinse solution.

4.2.3 Sample Storage Containers: Polyethylene, with leak-free screw cap, 500-mL or 1000-mL.

4.2.4 1000-mL Graduated Cylinder and Balance.

4.2.5 Plastic Storage Containers: Air tight containers to store silica gel.

4.2.6 Funnel and Rubber Policeman: To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.

4.3 Sample Preparation for Analysis: Sample preparation prior to analysis includes purging the sample train immediately following the sample run, and filtering the recovered sample to remove particulate matter immediately following recovery.

4.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders: Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in Section 5.1.3 and rinse between use with 0.1 M HNO₃ and reagent water.

4.3.2 Filtration Apparatus: Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

4.4 Ion Chromatograph: Refer to Section 4.0 of Method 7199 for instrument and equipment specifications.

4.4.1 Preconcentrator: System in-line with the ion chromatograph.

OR

4.5 Sample preconcentration system: A high performance ion chromatograph (HPIC) non-metallic column with acceptable anion retention characteristics and sample loading rates as described in the analytical method.

5.0 REAGENTS

5.1 All inorganic reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for Cr^{+6} to assure that contamination is below the analytical detection limit for direct injection or, if selected, preconcentration. If total chromium is also to be determined, the reagents should also be checked by the analytical technique selected to assure that contamination is below the analytical detection limit.

5.2 Sampling.

5.2.1 Reagent water: Reagent water shall be interferences free. All references to water in the method refer to reagent water unless otherwise specified. A definition of reagent water can be found in Chapter One.

5.2.2 Potassium Hydroxide, 0.1 M: Add 5.6 gm of KOH(s) to approximately 900 mL of reagent water and let dissolve. Dilute to 1000 mL with reagent water. A brief unpublished EPA study showed sources of 2N KOH with concentrations of hexavalent chromium ranging from 1.02 ppb to 7.86 ppb. If the lowest detection limit is needed for a given project, an effort should be made to obtain KOH with the minimum possible contamination. Initial attempts to develop an acceptable purification procedure have been unsuccessful.

NOTE: At sources with high concentrations of acids and/or SO_2 , the concentration of KOH should be increased to 0.5 M to insure that the pH of the solution is above 8.5 after sampling.

5.2.3 Silica Gel and Crushed Ice: Same as Method 5.

5.3 Sample Recovery: The reagents used in sample recovery are as follows:

5.3.1 Water: Same as Section 5.2.1.

5.3.2 Nitric Acid, 0.1 M: Add 6.3 mL of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 mL of reagent water. Dilute to 1000 mL with reagent water, and mix well.

5.3.3 pH Indicator Strip: pH indicator capable of determining pH of solution between the pH range of 7 and 12, at 0.5 pH intervals.

5.4 Sample Preparation

5.4.1 Reagent water: Same as Section 5.2.1.

5.4.2 Nitric Acid, 0.1 M: Same as Section 5.3.2.

5.4.3 Filters: Acetate membrane, or equivalent, filters with 0.45 micrometer or smaller pore size to remove insoluble material.

5.5 Analysis

5.5.1 Refer to Section 5.0 of Method 7199 for instruction on preparation of analytical reagents.

5.6 Performance Audit Sample: A performance audit sample should be analyzed in conjunction with the samples. The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Section 6.0 of Method 7199 for the proper procedures when collecting, preserving, and handling samples.

6.2 If sample preconcentration is used, dropwise addition of the ammonium sulfate/ammonium hydroxide buffer may not be appropriate, since the added sulfate may lead to premature overloading of the column.

6.3 A holding time of 14 days is appropriate for samples collected by Method 0061, even though Method 7199 has a 24 hr. hold for other samples. The Method 0061 samples are already stabilized in an alkaline solution, as opposed to many samples from other media which may be submitted for analysis in an unstable condition. An optional method of demonstrating stability is to field spike some of the sample matrix with known amounts of Cr⁺⁶ and determine recovery.

7.0 PROCEDURE

CAUTION: Wear Safety Glasses At All Times During This Test Method.

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

7.1.1 Sample Train Calibration: Calibrate the sample train components according to the indicated sections of Method 5: Probe Nozzle; Pitot Tube; Metering System; Temperature Gauges; Leak-Check of the Metering System; and Barometer.

7.1.2 Pretest Preparation: All components shall be maintained and calibrated according to the procedures described in APTD-0576, unless otherwise specified herein. Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with reagent water. All the components and container should then be soaked overnight, or a minimum of 4 hours, in a 10 % (v/v) nitric acid solution, then rinsed three times with reagent water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

7.1.3 Preliminary Determinations: Same as Method 5, Section 4.

7.1.4 Preparation of Sampling Train: Measure 300 mL of 0.1 M KOH into a graduated cylinder (or tare-weighed precleaned polyethylene container). Place approximately 140 mL of the 0.1 M KOH reagent in the first Teflon impinger. Split the rest of the 0.1 M KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a preweighed 200-to 400-g portion of indicating silica gel in the final glass impinger. (For sampling periods in excess of two hours, or for high moisture sites, 400-g of silica gel is recommended). Retain reagent blanks of the 0.1 M KOH equal to the volumes used with the field samples.

7.1.5 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.

7.1.6 Sampling Train Operation: Follow the procedures given in Method 5, Section 4.1.5. If the sampling train should be iced down with water and ice to insure heat transfer with the Teflon impingers.

NOTE: If the gas to be sampled is above 200°F, it may be necessary to wrap three or four feet of the Teflon sample and recirculating lines inside the ice bath to keep the recirculated reagent cool enough so it does not turn to steam.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5. At the end of the sampling run, determine the pH of the reagent in the first impinger using a pH indicator strip. The pH of the solution shall be greater than 8.5. If the pH is not above 8.5, discard the solution. Prepare a clean sampling train as described above using 0.5 M KOH instead of 0.1 M KOH, as noted in Section 5.2.2. For use of the train at relatively high acid sources, it may be necessary to employ extra caustic, stronger caustic, shorter sampling times, and closer monitoring of pH. See the references for suggestions. Leak-check and operate the sampling train as described above. Repeat the sampling run.

7.1.7 Calculation of Percent Isokinetic: Same as Method 5, Section 4.

7.2 Post-test Nitrogen Purge. The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state. The purge is effective in the removal of SO₂ from the impinger contents. Attach the nitrogen purge line to the input of the impinger train. Check to insure the output of the impinger train is open, and that the recirculating line is capped off. Open the nitrogen gas flow slowly and adjust the delivery rate to 10 L/min. Check the recirculating line to insure that the pressure is not forcing the impinger reagent out through this line. Continue the purge under these conditions for one-half hour periodically checking the flow rate.

7.3 Sample Recovery: Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run. The probe assembly may be disconnected from the sample train prior to sample purging. The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sample train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a clean up 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.

7.3.1 Container No. 1 (Impingers 1 through 3): Disconnect the first impinger from the second impinger and disconnect the recirculation line from the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighted precleaned polyethylene sample container and measure the volume of the liquid to within 1 mL or 1 gm. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. If necessary, transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With reagent water, rinse four times the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting tubing, and combine the rinses with the impinger solution in the sample container.

7.3.2 Container No. 2 (HNO₃ rinse optional for total chromium): With 0.1 M HNO₃, rinse three times the entire train assembly, from the nozzle to the fourth impinger, and combine the rinses into a separate precleaned polyethylene sample container for possible total chromium analysis. Repeat the rinse procedure a final time with reagent water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.3 Container No. 3 (Silica Gel): Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.

7.3.4 Container No. 4 (0.1 M KOH Blank): Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.5 Container No. 5 (Reagent Water Blank): Once during each field test, place a volume of reagent water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.6 Container No. 6 (0.1 M HNO₃ Blank): Once during each field test if total chromium is to be determined, place a volume of 0.1 M HNO₃ reagent equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.4 Sample Preparation: For determination of Cr^{+6} , the sample should be filtered immediately following recovery to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process (see Figure 4). Filter the entire impinger sample through a 0.45 micrometer acetate filter (or equivalent), and collect the filtrate in a 1000-mL graduated cylinder. Rinse the sample container with reagent water three separate times and pass these rinses through the filter, and add the rinses to the sample filtrate. Rinse the Teflon reservoir with reagent water three separate times and pass these rinses through the filter, and add the rinses to the sample. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container. Label the container clearly to identify its contents. Rinse the Teflon reservoir once with 0.1 M HNO_3 and once with reagent water and discard these rinses. If total chromium is to be determined, quantitatively recover the filter and residue and place them in a vial. (The acetate filter may be digested with 5 mL of 70% nitric acid; this digestion solution may then be diluted with reagent water for total chromium analysis by inductively coupled plasma atomic emission or graphite furnace atomic absorption spectrometric methods.)

NOTE: If the source has a large amount of particulate in the effluent stream, testing teams may wish to filter the sample twice, once through a 2-5 micrometer filter, then through the 0.45 micrometer filter.

7.4.1 Container No. 2 (HNO_3 rinse, optional for total chromium): This sample shall be analyzed in accordance with the selected procedure for total chromium analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.

7.4.2 Container 3 (Silica Gel): Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

7.5 Sample Analysis: The Cr^{+6} content of the sample filtrate is determined by ion chromatography coupled with a post column reactor (IC/PCR). Method 7199 should be used for this analysis. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR. Prior to preconcentration and/or analysis, all field samples will be filtered through a 0.45 μm filter. This filtration should be conducted just prior to sample injection/analysis.

7.5.1 Preconcentration: The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent, followed by removal of the analyte from the absorbent.

Refer to Section 7.0 of Method 7199 for the proper sample analysis protocol.

7.6 Calculations

7.6.1 Dry Gas Volume: Using the data from the test, calculate $V_{m(\text{std})}$, the dry gas sample volume at standard conditions as outlined in Method 5.

7.6.2 Volume of Water Vapor and Moisture Content: Using the data from the test, calculate $V_{w(\text{std})}$ and B_{ws} , the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.

7.6.3 Stack Gas Velocity: Using the data from the test and Equations 2-9 of Method 2, calculate the average stack gas velocity.

7.6.4 Total $\mu\text{g Cr}^{+6}$ Per Sample. Calculate as described below:

$$m = (S-B) \times V_{\text{is}} \times d$$

Where:

m = Mass of Cr^{+6} in the sample, μg ,
S = Concentration of Sample, $\mu\text{g Cr}^{+6}/\text{mL}$,
B = Concentration of blank, $\mu\text{g Cr}^{+6}/\text{mL}$,
 V_{is} = Volume of sample after filtration, mL, and,
d = Dilution factor (1 if not diluted).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate quality control procedures.

9.0 METHOD PERFORMANCE

9.1 Sensitivity: A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution). Follow instrument manufacturers instructions for sample preconcentration.

9.2 Precision: The precision of the IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 ug/dscm of total chromium is 25% and 9% for Cr^{+6} and total chromium, respectively; for hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6} it is 20%.

9.3 Refer to Section 9.0 of Method 7199 for additional analytical method performance information.

10.0 REFERENCES

1. Carver, Anna C.; Laboratory and Field Evaluation of the Methodology for Determining Hexavalent Chromium Emissions from Stationary Sources. EPA No. 600/3-92/052, February 1992.
2. Steinsberger, S.C., DeWees, W.G., Bell, A.C., Finken, R.A., Knoll, J.E., Midget, M.R. "Development and Validation of the US EPA Hexavalent Chromium Source Emissions Measurement Method," *Fuel Processing Technology* 39 ,pp.265-276 (1994).
3. Steinsberger, S.C., Carver, A.C., DeWees, W.G., Knoll, J.E., Butler, F.E., Midget, M.R. "Sampling and Analytical Methods for Measurement of Low Levels of Hexavalent Chromium from Stationary Sources," *Proceedings of the 1989 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Air & Waste Management Association, Pittsburgh, PA, 1989, pp.308-313.

4. Knoll, J.E., Midget, M.R., Carver, A.C., Steinsberger, S.C., DeWees, W.G. "Development of a Source Test Method for Hexavalent Chromium," *Proceedings of the 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Air & Waste Management Association, Pittsburgh, PA, 1990, pp.579-585.
5. Rom, J.J., "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment" *APTD-0576*, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1972.
6. US EPA Method 5, *Code of Federal Regulations, Title 40, Part 60, Appendix A*, U.S. Government Printing Office, Washington, DC, 1993.

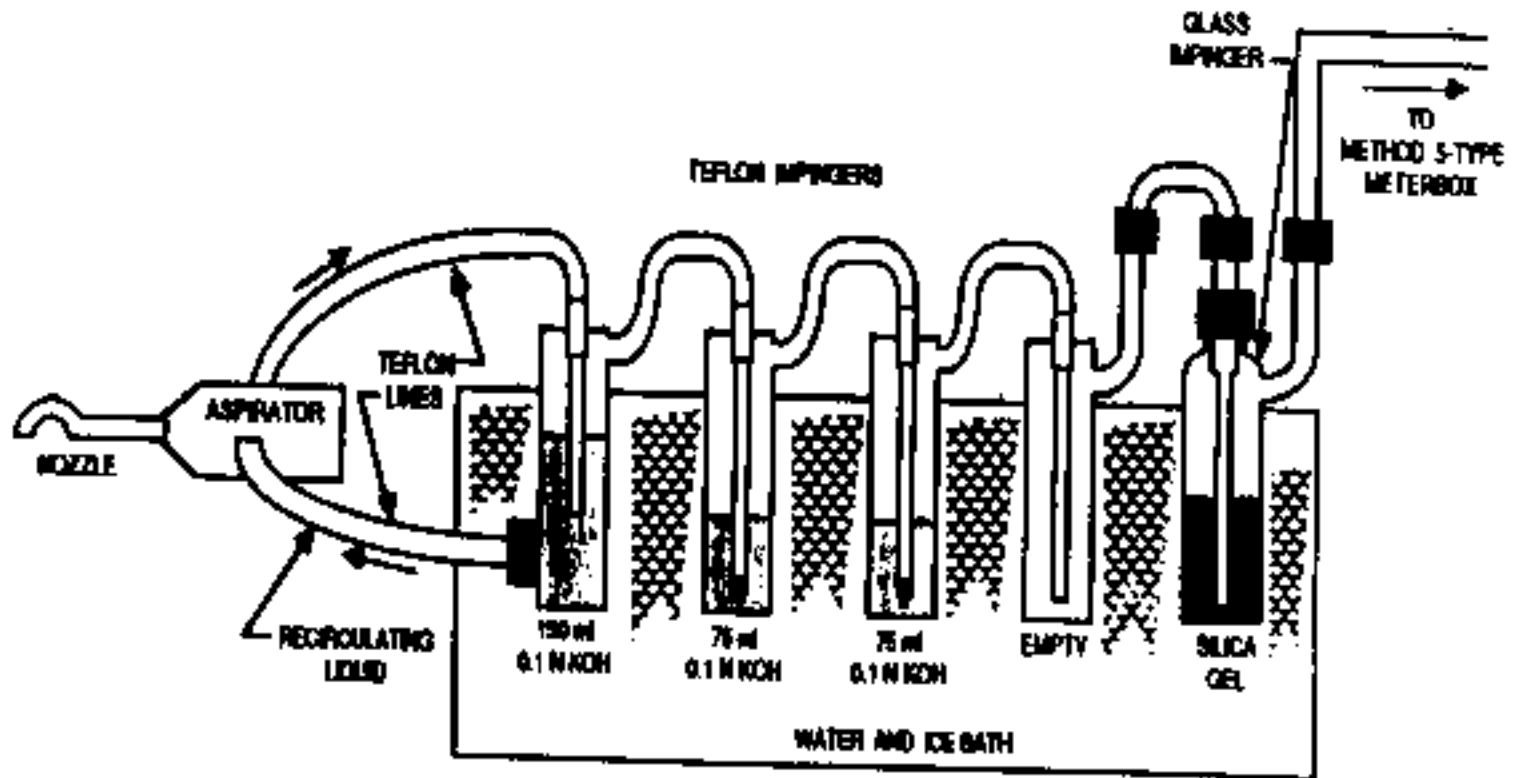


FIGURE 1. TEFLON IMPINGERS - SCHEMATIC OF RECIRCULATORY IMPINGER TRAIN WITH ASPIRATOR ASSEMBLY.

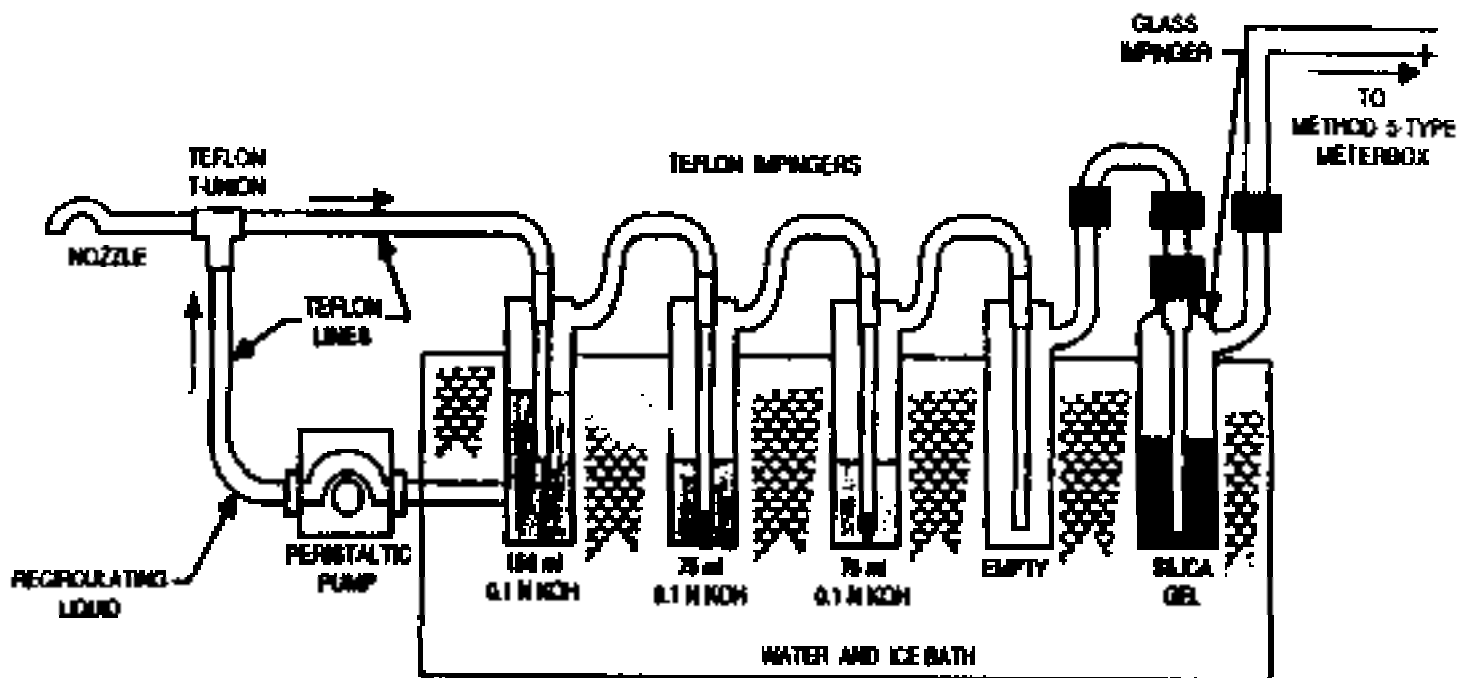


FIGURE 2. TEFLON IMPINGERS - SCHEMATIC OF RECIRCULATORY IMPINGER TRAIN WITH PUMP/SPRAYER ASSEMBLY.

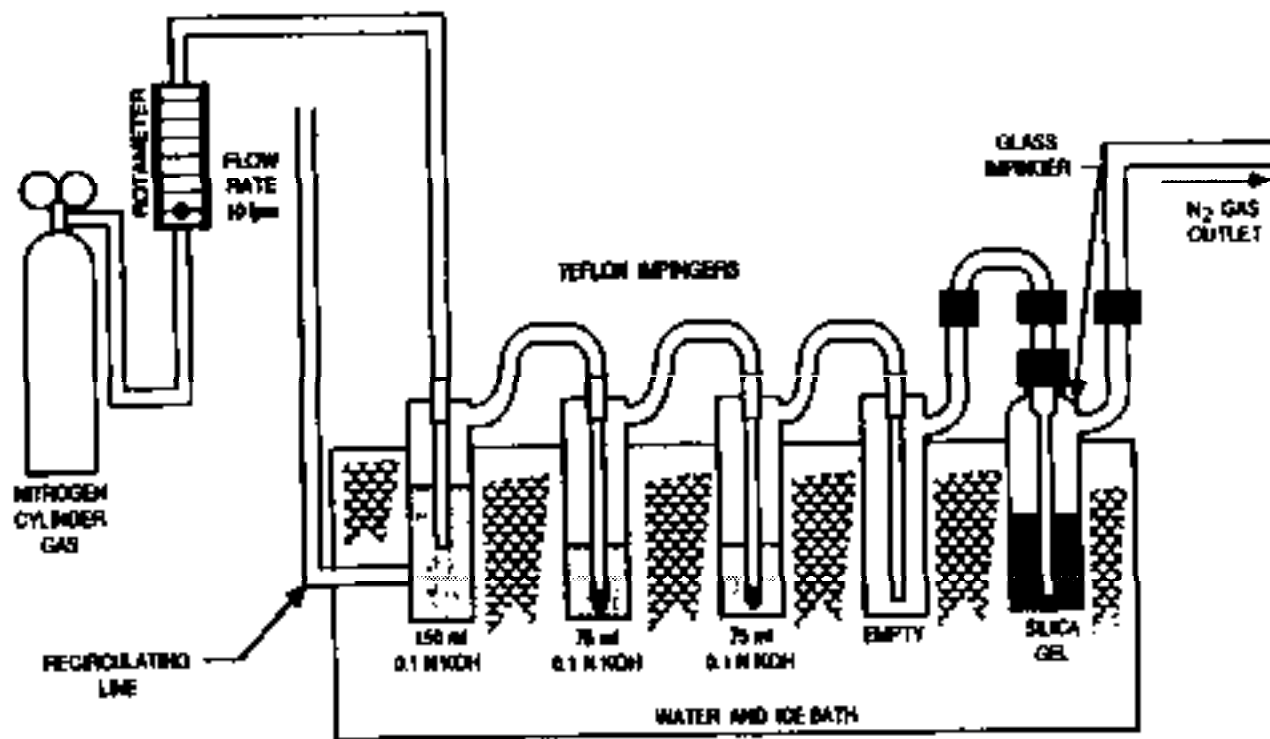


FIGURE 3. TEFLON IMPINGERS - SCHEMATIC OF POST TEST NITROGEN PURGE SYSTEM

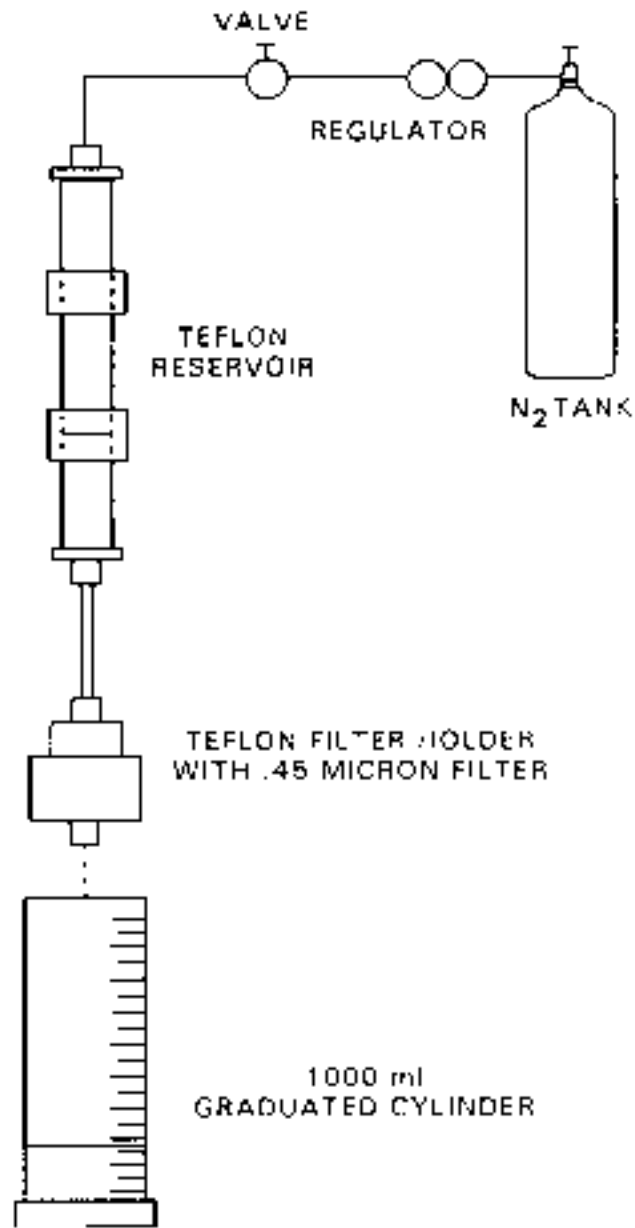
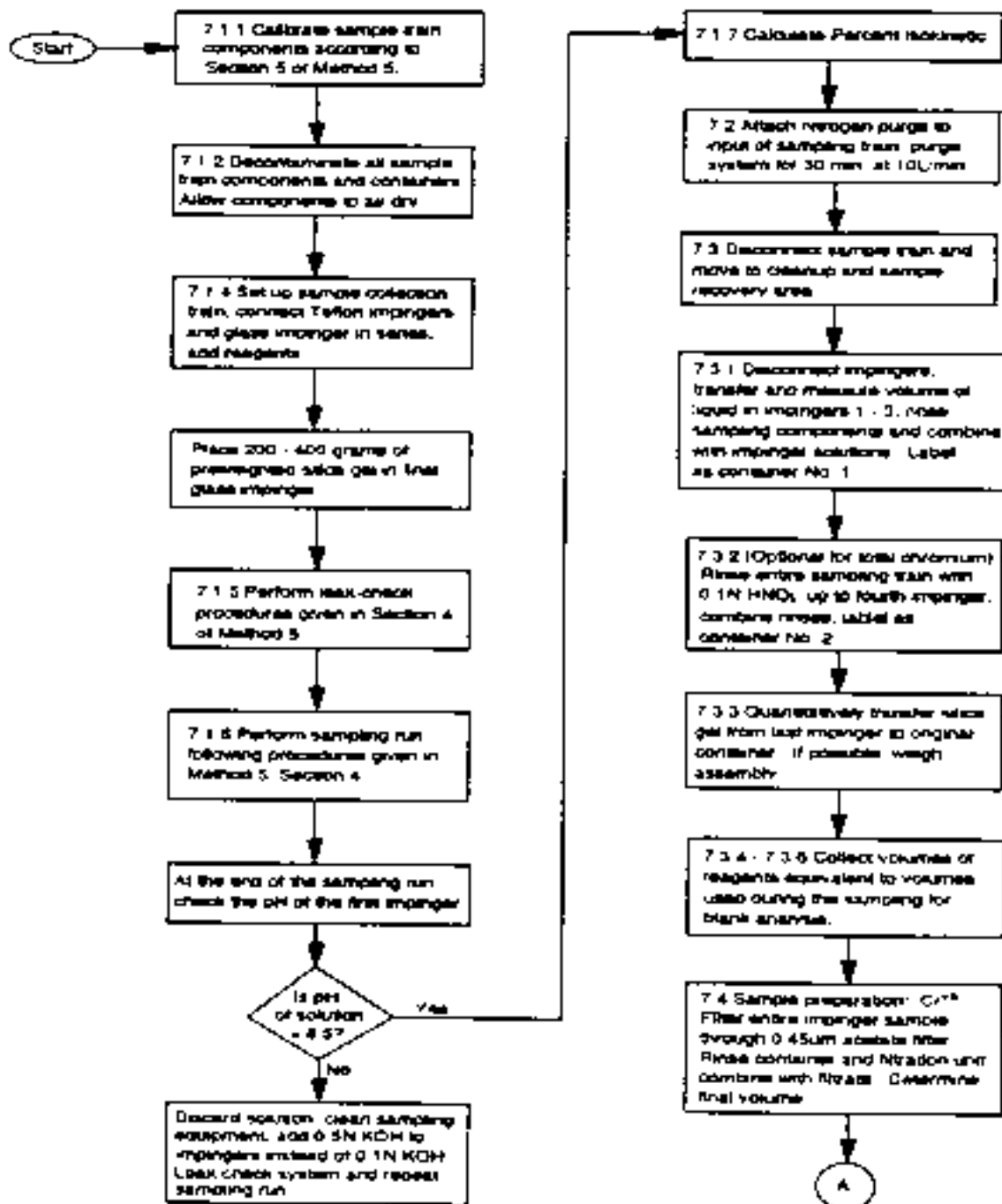


FIGURE 4. SCHEMATIC OF THE METHOD 0040 SAMPLING TRAIN

METHOD 0061
DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS
FROM STATIONARY SOURCES



METHOD 0061
DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS
FROM STATIONARY SOURCES (Cont.)

