State of California
Air Resources Board

Method 12

Determination of Inorganic Lead Emissions from Stationary Sources

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Method 12 - Determination of Inorganic Lead Emissions from Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method applies to the determination of inorganic lead (Pb) emissions from specified stationary sources only.

1.2 Principle. Particulate and gaseous Pb emissions are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

2. RANGE, SENSITIVITY, PRECISION, AND INTERFERENCES

2.1 Range. For a minimum analytical accuracy of ±10 percent, the lower limit of the range is 100 µg. The upper limit can be considerably extended by dilution.

2.2 Analytical Sensitivity. Typical sensitivities for a 1-percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 µg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 Precision. The within-laboratory precision, as measured by the coefficient of variation ranges from 0.2 to 9.5 percent relative to a run-mean concentration. These values were based on tests conducted at a gray iron foundry, a lead storage battery manufacturing plant, a secondary lead smelter, and a lead recovery furnace of an alkyl lead manufacturing plant. The concentrations encountered during these tests ranged from 0.61 to 123.3 mg Pb/m^3.

2.4 Interferences. Sample matrix effects may interfere with the analysis for Pb by flame atomic absorption. If this interference is suspected, the analyst may confirm the presence of these matrix effects and frequently eliminate by using the Method of Standard Additions.

High concentrations of copper may interfere with the analysis of Pb at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

3. APPARATUS

3.1 Sampling Train. A schematic of the sampling train is shown in Figure 12-1; it is similar to the Method 5 train. The sampling train consists of the following components:

3.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer, and Gas Density

Determination Equipment. Same as Method 5, Sections 2.1.1 to 2.1.6 and 2.1.8 to 2.1.10, respectively.

3.1.2 Impingers. Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip. Place a thermometer, capable of measuring temperature to within 1 ^{o}C (2 ^{o}F) at the outlet of the fourth impinger for monitoring purposes.

3.2 Sample Recovery. The following items are needed:

3.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.6, and 2.2.7, respectively.

3.2.2 Wash Bottles. Glass (2).

3.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for 0.1 N nitric acid (HNO_3) impinger and probe solutions and washes, 1000-ml. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to chemical attack by 0.1 N HNO_3 (Narrow mouth glass bottles have been found to be less prone to leakage.)

3.2.4 Graduated Cylinder and/or Balance. To measure condensed water to within 2 ml or 1 g. Use a graduated cylinder that has a minimum capacity of 500 ml, and subdivisions no greater than 5 ml. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less.)

3.2.5 Funnel. Glass, to aid in sample recovery.

3.3 Analysis. The following equipment is needed:

3.3.1 Atomic Absorption Spectrophotometer. With lead hollow cathode lamp and burner for air/acetylene flame.

3.3.2 Hot Plate.

3.3.3 Erlenmeyer Flasks. 125-ml, 24/40 Ts.

3.3.4 Membrane Filters. Millipore SCWPO 4700, or equivalent.

3.3.5 Filtration Apparatus. Millipore vacuum filtration unit, or equivalent, for use with the above membrane filter.

3.3.6 Volumetric Flasks. 100-ml, 250-ml, and 1000-ml.

4. REAGENTS

4.1 Sampling.
Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. The reagents used in sampling are as follows:

4.1.1 Filter. Gelman Spectro Grade, Reeve Angel 934 AH, MSA 1106 BH, all with lot assay for Pb, or other high-purity glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. Conduct the filter efficiency test using ASTM Standard Method D 2986-71 or use test data from the supplier's quality control program.

4.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 3.1.2, 3.1.4, and 3.1.5, respectively.

4.1.3 Water. Deionized distilled, to conform to ASTM Specification D 1193-77, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

4.1.4 Nitric Acid, 0.1 N. Dilute 6.5 ml of concentrated HNO_3 to 1 liter with water. (It may be desirable to run blanks before field use to eliminate a high blank on test samples.)

4.2 Pretest Preparation. 6 N HNO_3 is needed. Dilute 390 ml of concentrated HNO_3 to 1 liter with water.

4.3 Sample Recovery. 0.1 N HNO_3 (Same as in Section 4.1.4 above).

4.4 Analysis. The following reagents are needed for analysis (use ACS reagent grade chemicals, or equivalent, unless otherwise specified):

4.4.1 Water. Same as in Section 4.1.3.

4.4.2 Nitric Acid, Concentrated.

4.4.3 Nitric Acid, 50 Percent (v/v). Dilute 500 ml of concentrated HNO_3 to 1 liter with water.

4.4.4 Stock Lead Standard Solution, 1000 µg Pb/ml. Dissolve 0.1598 g of lead nitrate [$Pb(NO_3)_2$] in about 60 ml water, add 2 ml concentrated HNO_3, and dilute to 100 ml with water.

4.4.5 Working Lead Standards. Pipet 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the stock lead standard solution (Section 4.4.4) into 250-ml volumetric flasks. Add 5 ml of concentrated HNO_3 to each flask, and dilute to volume with water. These working standards contain 0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 µg Pb/ml, respectively. Prepare, as needed, additional standards at other concentrations in a similar manner.

4.4.6 Air. Suitable quality for atomic absorption analysis.

4.4.7 Acetylene. Suitable quality for atomic absorption analysis.

4.4.8 Hydrogen Peroxide, 3 Percent (v/v). Dilute 10 ml of 30 percent H_2O_2 to 100 ml with water.

5. PROCEDURE

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

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

5.1.2 Preliminary Determinations. Follow the same general procedure given in Method 5, Section 4.1.2.

5.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 ml of 0.1 N HNO_3 in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Set up the train as shown in Figure 12-1.

5.1.4 Leak-Check Procedures. Follow the general leak-check procedures given in Method 5, Sections 4.1.4.1 to 4.1.4.3.

5.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the glassware inlet where the probe was fastened, and cap the inlet. Remove the umbilical cord from the last impinger, and cap the impinger. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to a cleanup area, which is clean and protected from the wind so that the chances of contaminating or losing the sample are minimized.

Inspect the train before and during disassembly, and note any abnormal conditions. Treat the samples as follows:

5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder, and place it in its identified petri dish container. If it is necessary to fold the filter, do so such that the sample-exposed side is inside the fold. Carefully transfer to the petri dish any visible sample matter and/or filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush or a sharp-edged blade. Seal the container.

5.2.2 Container No. 2 (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover sample matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO_3 and placing the wash into a glass sample storage container. Measure and record (to the nearest 2 ml) the total amount of 0.1 N HNO_3 used for each rinse. Perform the 0.1 N HNO_3 rinses as follows:

Carefully remove the probe nozzle, and rinse the inside surfaces with 0.1 N HNO_3 from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO_3 rinse shows no visible particles, then make a final rinse of the inside surface.

Brush and rinse with 0.1 N HNO_3 the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with 0.1 N HNO_3. While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO_3, tilt the probe, and squirt 0.1 N HNO_3 into its upper end. Let the 0.1 N HNO_3 drain from the lower end into the sample container. The tester may use a glass funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, squirt 0.1 N HNO_3 into the upper end of the probe as the probe brush is being pushed with a twisting action through the probe; hold the sample container underneath the lower end of the probe, and catch any 0.1 N HNO_3 and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO_3 and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the brush with 0.1 N HNO_3, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

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

After insuring that all joints are wiped clean of silicone grease, brush and rinse with

0.1 N HNO_3 the inside of the front half of the filter holder. Brush and rinse each surface three times or more, if needed, to remove visible sample matter. Make a final rinse of the brush and filter holder. After all 0.1 N HNO_3 washings and sample matter are collected in the sample container, tighten the lid on the sample container so that the fluid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

5.2.3 Container No. 3 (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to the 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. It is not necessary to remove the small amount of particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow procedure for Container No. 3 under Section 5.4 (Analysis).

5.2.4 Container No. 4 (Impingers). Due to the large quantity of liquid involved, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease, and cap the joints.

2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

3. Transfer the contents of the impingers to a 500-ml graduated cylinder. Remove the outlet ball joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within 2 ml. Alternatively, determine the weight of the liquid to within 0.5 g. Record in the log the volume or weight of the liquid present, along with a notation of any color or film observed in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).

4. Transfer the contents to Container No. 4.

5. NOTE: In steps 5 and 6 below, measure and record the total amount of 0.1 N HNO_3 used for rinsing. Pour approximately 30 ml of 0.1 N HNO_3 into each of the first three impingers and agitate the impingers. Drain the 0.1 N HNO_3 through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N HNO_3; transfer this rinse into Container No. 4. (Do not rinse or brush the glass- fritted filter support.) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly.

5.2.5 Blanks. Save 200 ml of the 0.1 N HNO_3 used for sampling and cleanup as a blank. Take the solution directly from the bottle being used and place into a glass sample container labeled "0.1 N HNO_3 blank."

5.3 Sample Preparation.

5.3.1 Container No. 1 (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-ml Erlenmeyer flask. Rinse the petri dish with 10 ml of 50 percent HNO_3 to insure a quantitative transfer, and add to the flask. NOTE: If the total volume required in Section 5.3.3 is expected to exceed 80 ml, use a 250-ml flask in place of the 125-ml flask.

5.3.2 Containers No. 2 and No. 4 (Probe and Impingers). Check the liquid level in Containers No. 2 and No. 4, and confirm as to whether leakage occurred during transport; note observation on the analysis sheet. If a noticeable amount of leakage had occurred, either void the sample or take steps, subject to the approval of the Executive Officer, to adjust the final results. Combine the contents of Containers No. 2 and No. 4, and take to dryness on a hot plate.

5.3.3 Sample Extraction for Lead. Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Then transfer the residue from Containers No. 2 and No. 4 to the 125-ml Erlenmeyer flask that contains the filter using rubber policeman and 10 ml of 50 percent HNO_3 for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO_3, whichever is larger.

Place the Erlenmeyer flask on a hot plate, and heat with periodic stirring for 30 minutes at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO_3. Add 10 ml of 3 percent H_2O_2, and continue heating for 10 minutes. Add 50 ml of hot (80°C) water, and heat for 20 minutes. Remove the flask from the hot plate, and allow to cool. Filter the sample through a Millipore membrane filter, or equivalent, and transfer the filtrate to a 250-ml volumetric flask. Dilute to volume with water.

5.3.4 Filter Blank. Determine a filter blank using two filters from each lot of filters used in the sampling train. Cut each filter into strips, and place each filter in a separate 125-ml Erlenmeyer flask. Add 15 ml of 50 percent HNO_3, and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot water. Filter and dilute to a total volume of 100 ml using water.

5.3.5 HNO_3 Blank, 0.1 N. Take the entire 200 ml of 0.1 N HNO_3 to dryness on a steam bath, add 15 ml of 50 percent HNO_3, and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot water. Dilute to a total volume of 100 ml using water.

5.4 Analysis.

5.4.1 Lead Determination. Calibrate the spectrophotometer as described in

Section 6.2, and determine the absorbance for each source sample, the filter blank, and 0.1 N HNO_3 blank. Analyze each sample three times in this manner. Make appropriate dilutions, as required, to bring all sample Pb concentrations into the linear absorbance range of the spectrophotometer.

If the Pb concentration of a sample is at the low end of the calibration curve and high accuracy is required, the sample can be taken to dryness on a hot plate and the residue dissolved in the appropriate volume of water to bring it into the optimum range of the calibration curve.

5.4.2 Check for Matrix Effects on the Lead Results.

Since the analysis for Pb by atomic absorption is sensitive to the chemical composition and to the physical properties (viscosity, pH) of the sample (matrix effects), the analyst shall check at least one sample from each source using the Method of Additions as follows: Add or spike an equal volume of standard solution to an aliquot of the sample solution, then measure the absorbance of the resulting solution and the absorbance of an aliquot of unspiked sample.

Next, calculate the Pb concentration Cs in µg/ml of the sample solution by using the following equation:

$$C_s = C_a \frac{A_s}{A_t - A_s} \qquad \text{Eq. 12-1}$$

Where:
C_a = Pb concentration of the standard solution, µg/ml.

A_s = Absorbance of the sample solution.

A_t = Absorbance of the spiked sample solution.

Volume corrections will not be required if the solutions as analyzed have been made to the same final volume. Therefore, Cs and Ca represent Pb concentration before dilutions.

Method of Additions procedures approved by the United States Environmental Protection Agency may also be used. In any event, if the results of the Method of Additions procedure used on the single source sample do not agree to within 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Additions procedure.

5.4.3 Container No. 3 (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

6. CALIBRATION

Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the probe nozzle, pitot tube, metering system, probe heater, temperature gauges, and barometer according to Method 5, Sections 5.1, 5.2, 5.3, 5.4, 5.5, and 5.7, respectively. Conduct the leak-check of the metering system according to Method 5, Section 5.6.

6.2 Spectrophotometer. Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement ($\pm$3 percent) is obtained between two consecutive readings. Plot the absorbance (y-axis) versus concentration in µg Pb/ml (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than $\pm$0.003 absorbance units, check for incorrectly prepared standards and for curvature in the calibration curve.

To determine stability of the calibration curve, run a blank and a standard after every five samples, and recalibrate, as necessary.

7. CALCULATIONS

7.1 Dry Gas Volume. Using the data from this test, calculate Vm(std), the total volume of dry gas metered corrected to standard conditions (20 ^{o}C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{w(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

7.2 Volume of Water Vapor and Moisture Content. Using data obtained in this test and Equation 5-2 and 5-3 of Method 5, calculate the volume of water vapor Vw(std) and the moisture content Bws of the stack gas.

7.3 Total Lead in Source Sample. For each source sample, correct the average absorbance for the contribution of the filter blank and the 0.1 N HNO_3 blank. Use the calibration curve and this corrected absorbance to determine the µg Pb concentration in the sample aspirated into the spectrophotometer. Calculate the total Pb content C^{o}_{Pb} (in µg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

7.4 Lead Concentration. Calculate the stack gas Pb concentration CPb in mg/dscm as follows:

$$C_{Pb} = K \frac{C_{Pb}}{V_{m(std)}} \qquad \text{Eq. 12-2}$$

Where:

K = 0.001 mg/µg for metric units.

= 2.205 x 10^{-9} lb/µg for English units.

7.5 Isokinetic Variation and Acceptable Results. Same as in Method 5, Sections 6.11 and 6.12, respectively. To calculate v_s, the average stack gas velocity, use Equation 2-9 of Method 2 and the data from this field test.

8. ALTERNATIVE TEST METHODS FOR INORGANIC LEAD

8.1 Simultaneous Determination of Particulate and Lead Emissions. The tester may use Method 5 to simultaneously determine Pb provided that the tester (1) uses acetone to remove particulate from the probe and inside of the filter holder as specified by Method 5, (2) uses 0.1 N HNO_3 in the impingers, (3) uses a glass fiber filter with a low Pb background, and (4) treats and analyzes the entire train contents, including the impingers, for Pb as described in Section 5 of this method.

8.2 Filter Location. The tester may use a filter between the third and fourth impingers provided that the filter is included in the analysis for Pb.

8.3 In-Stack Filter. The tester may use an in-stack filter provided that the tester (1) uses a glass-lined probe and at least two impingers, each containing 100 ml of 0.1 N HNO_3 after the in-stack filter and (2) recovers and analyzes the probe and impinger contents for Pb. Recover sample from the nozzle with acetone if a particulate analysis is to be made.

8.4 Alternative Analytical Instrumentation. Inductively coupled plasma - atomic emission spectrometry (ICP - AES) may be used in lieu of atomic absorption spectrometry (AA) for analysis of lead if the following conditions are met:

8.4.1 Sample collection, sample preparation and analytical preparation procedures are as defined in this test method except as necessary for the ICP-AES application;

8.4.2 Quality Assurance/Quality Control (QA/QC) procedures specified in this test method are adhered to; and

8.4.3 The limit of quantitation (defined as 10 times the standard deviation of the blank value, where the standard deviation of the blank value is determined from the analysis of seven blanks) for the ICP-AES is demonstrated and the sample concentrations reported are at least two times the limit of quantitation.

8.5 Alternative Methodology. ARB Method 436, ADetermination of Multiple Metals Emissions from Stationary Sources@, may be used instead of ARB Method 12.

9. BIBLIOGRAPHY

1. EPA Method 12, Determination of Inorganic Lead Emissions from Stationary Sources, CFR40, Part 60, Appendix A

2. ARB Method 5, Determination of Particulate Matter Emissions from Stationary Sources

3. ARB Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

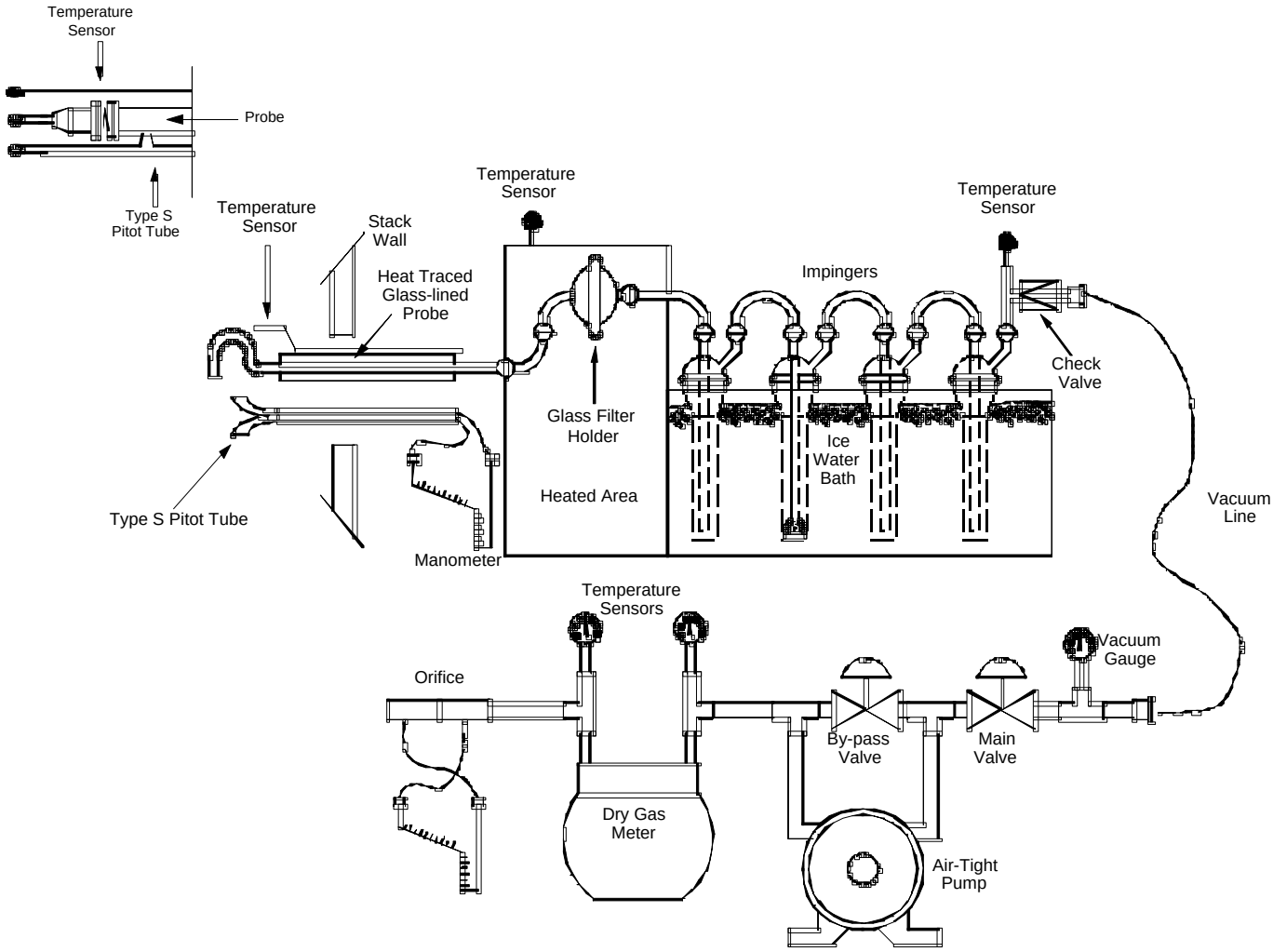

Figure 12-1. Inorganic Lead Sampling Train