

(Adopted January 21, 2000)

**RULE 1189. EMISSIONS FROM HYDROGEN PLANT PROCESS VENTS**

(a) Purpose and Applicability

The purpose of this rule is to reduce emissions of volatile organic compounds (VOCs) from hydrogen plant process vents. The rule applies to all hydrogen plants that produce any hydrogen for use in petroleum refining operations.

(b) Definitions

For the purpose of this rule, the following definitions shall apply:

- (1) EXISTING HYDROGEN PLANT is a hydrogen plant that is not a new or reconstructed hydrogen plant.
- (2) HYDROGEN PLANT is a facility that produces hydrogen with steam hydrocarbon reforming, partial oxidation of hydrocarbons, or other processes. Hydrogen plants include steam reforming or hydrogen generation reactors, shift conversion reactors, gas purification or separation units, condensate deaerators or degassifiers, steam generators, direct or indirect contact cooling systems, and their associated systems including the units used to recover carbon dioxide from the vent gas. Hydrogen plants do not include refinery process units, such as catalytic reforming and isomerization units, where hydrogen is produced as a byproduct, provided that all gaseous streams are vented to closed systems except for safety relief devices.
- (3) NEW OR RECONSTRUCTED HYDROGEN PLANT is a hydrogen plant for which a permit to construct is issued or, if construction has not begun, an extension to the permit to construct is granted on or after January 21, 2000. A hydrogen plant shall be considered as "reconstructed" if the fixed capital cost of the alteration exceeds 50 percent of the fixed capital cost that would be required to construct a comparable new plant.
- (4) PETROLEUM REFINING is a process by which gasoline, kerosene, distillate fuel oils, residual fuel oils, or lubricants are produced, through fractionation or straight distillation of crude oil, redistillation of unfinished petroleum derivatives, cracking or other processes, as defined in the Standard Industrial Classification Manual as Industry No. 2911, Petroleum Refining.

- (5) PROCESS VENT is an opening where a gas stream is continuously or periodically discharged during normal operation of a hydrogen plant. Process vents include openings where gas streams are discharged directly to the atmosphere, or are discharged to the atmosphere after being routed to a control device or a product recovery device. Process vents do not include any exhaust stack from a process heater or furnace to which a hydrogen plant vent stream may be directed, provided that the vent stream is introduced into a location where the vent stream will be exposed to a minimum temperature of 1,400 degrees F for at least one second, and that the combustion device has been issued a valid permit by the Executive Officer in accordance with all District rules applicable to the device.
  - (6) THIRD-PARTY FACILITY is a carbon dioxide recovery facility owned and operated by a person (or persons under common control) other than the operator of the hydrogen plant.
- (c) Requirements for Existing Hydrogen Plants
- (1) On or before July 1, 2000, the operator of an existing hydrogen plant shall conduct initial source testing in accordance with the test methods listed in subdivision (f) to determine the emission rate of the plant and submit a complete test report to the Executive Officer. Notwithstanding the above, the initial source testing and reporting for an existing hydrogen plant that has been placed out of operation for more than one year as of January 21, 2000, shall be conducted within six months of startup of the plant.
  - (2) On or after July 1, 2001, an operator shall not operate any existing hydrogen plant, unless the plant complies with one of the following:
    - (A) The total VOC emissions from all process vents of the plant combined are less than 2.5 pounds of VOC per million standard cubic feet of hydrogen produced as determined by test methods listed in subdivision (f); or
    - (B) The total VOC content in the process condensate is reduced by at least 80 percent from the baseline levels determined by the initial source testing pursuant to paragraph (c) (1). The total VOC content in the process condensate shall be determined in ppm VOC as carbon by weight using the condensate trap analysis of District Method 25.3. Representative samples of process condensate shall

be collected downstream of the cooler following the final shift reactor or at the inlet to the deareator, as appropriate; or

- (C) The low temperature shift reactor of the hydrogen plant is equipped and operating exclusively with a low-methanol generating catalyst for which the operator demonstrates compliance by submitting to the Executive Officer, prior to July 1, 2001, the following:
  - (i) A bill of sale indicating the catalyst type and manufacturer.
  - (ii) A written statement that the catalyst has been installed and is in operation.
  - (iii) Catalyst manufacturer's pilot study data or other supporting document verifying that, under the representative operating conditions of the hydrogen plant, the catalyst produces at least 80 percent less methanol over the catalyst's life cycle, when compared with the conventional catalyst supplied by the manufacturer.
- (3) On or after January 1, 2003, an operator shall not operate any existing hydrogen plant, unless the total VOC emissions from all process vents of the plant combined are less than 2.5 pounds of VOC per million standard cubic feet of hydrogen produced as determined by test methods listed in subdivision (f). Notwithstanding the above, the compliance date may be extended to July 1, 2003, provided that the operator submits a written statement to the Executive Officer no later than January 1, 2003, indicating that a retrofit control equipment is required for the hydrogen plant to comply with the emission limit of 2.5 pounds of VOC per million standard cubic feet of hydrogen produced and a complete application for Permit to Construct has been filed.
- (d) Requirements for New or Reconstructed Hydrogen Plants
  - (1) Within six months of its initial startup, the operator of a new or reconstructed hydrogen plant shall conduct an initial source testing in accordance with test methods listed in subdivision (f) and submit a complete test report to the Executive Officer.
  - (2) An operator shall not operate a new or reconstructed hydrogen plant, unless the total VOC emissions from all process vents of the hydrogen

plant combined are less than 0.5 pounds per million standard cubic feet of hydrogen produced as determined by test methods listed in subdivision (f).

(e) Monitoring, Reporting and Recordkeeping Requirements

- (1) The operator of a hydrogen plant shall conduct annual compliance testing to demonstrate compliance with paragraphs (c)(2), (c)(3), and (d)(2), as applicable. All compliance testing subsequent to the initial source testing for an existing, new or reconstructed hydrogen plant shall be conducted and test reports submitted to the Executive Officer within 12 calendar months from previous testing and reporting. Notwithstanding the above, an operator who elects to comply with subparagraph (c)(2)(C) shall conduct semiannual testing commencing no later than July 1, 2001, and submit the test reports to the Executive Officer within six calendar months from previous testing and reporting until the operator complies with the requirements of paragraph (c)(3), after which the annual compliance testing is required.
- (2) To demonstrate compliance with paragraphs (c)(2), (c)(3), and (d)(2), as applicable, the operator shall certify that the information contained in the test reports is, to the best of his or her knowledge, accurate and represents the actual operating conditions of the plant at the time of the testing. The operator shall further certify that, based on the test results, the hydrogen plant is or is not in compliance with the applicable emission limit of this rule.
- (3) In the event that a VOC-containing process stream from a hydrogen plant is delivered to a third-party facility for processing, the Executive Officer may exclude VOC emissions from process vents located at the third-party facility from the compliance demonstration required in paragraphs (c)(2), (c)(3), and (d)(2), as applicable, provided that the operator of the hydrogen plant complies with the following:
  - (A) The operator submits a written request to the Executive Officer to exclude such emissions; and
  - (B) The operator conducts source testing in accordance with the test methods listed in subdivision (f) to quantify the VOCs contained in the process stream entering the third-party facility and reports them as VOC emissions for compliance determination purposes.

- (4) The operator of a hydrogen plant shall install a metering device to measure the total flow rates of hydrogen produced. This metering device shall be maintained in good operating condition and calibrated for the range in which it operates during source tests.
  - (5) The operator of a hydrogen plant shall maintain all information required to determine the emission rate for compliance demonstration, including but not limited to the test results and operating parameters as required under Attachment A - Source Test Protocol for VOC Emissions from High Moisture Hydrogen Plant Process Vents. This information shall be maintained in a manner approved by the Executive Officer for a period of at least five years and made available to the Executive Officer upon request.
- (f) **Test Methods**
- The following test methods shall be used, as applicable, to determine compliance with this rule. All test methods referenced below shall be the most recent version issued by the respective organization. Alternative test methods may be used if they are determined to be equivalent and approved in writing by the Executive Officer, and by the California Air Resources Board and the U.S. Environmental Protection Agency.
- (1) District Source Test Protocol for VOC Emissions from High Moisture Hydrogen Plant Process Vents - Attachment A of this rule, or any equivalent revisions hereafter as approved by the Executive Officer.
  - (2) District Method 25.3 - Determination of Low Concentration Non-Methane Non-Ethane Organic Compound Emissions from Clean Fueled Combustion Sources.
  - (3) District Method 5.1 - Determination of Particulate Matter Emissions from Stationary Sources Using a Wet Impingement Train.
  - (4) EPA Method 5 - Determination of Particulate Emissions from Stationary Sources.



**Attachment A****Source Test Protocol for VOC Emissions from High Moisture  
Hydrogen Plant Process Vents****PURPOSE**

This source test protocol provides guidance for determining the VOC emission rates from hydrogen plant process vents in terms of pounds of VOCs per million standard cubic feet of hydrogen produced (lb/MMscf). It specifies general conditions under which the source tests should be conducted in order for the Executive Officer to accept the test results as evidence for compliance demonstration with applicable provisions of Rule 1189. The SCAQMD Method 25.3 is the primary reference test method upon which this test protocol relies to determine the VOC and CO<sub>2</sub> concentrations in various streams. Other standard methods such as SCAQMD Methods 1.1/2.1 and 5.1 are also used to determine flow rates and for collecting representative samples. The protocol establishes guidelines for appropriate use of these test methods on hydrogen plant process vents. Since some of the vent streams from the hydrogen plants are difficult or in some cases impossible to be tested by the reference methods, the protocol also establishes criteria under which the principles of mass balance (material balance) may be used instead.

**GENERAL REQUIREMENTS**

1. The sampling, analysis, and reporting must be conducted by an SCAQMD Laboratory Approval Program (LAP) approved laboratory for the reference test methods where LAP approval is available.
2. All of the applicable process vents from a hydrogen plant must be tested simultaneously. This includes the deaerator, CO<sub>2</sub>, and any other atmospheric process vents that may contain VOC emissions. Alternatively, the testing of the individual stacks can be conducted at different times provided that the operating conditions listed in Item No. 4 below remain constant and records of operating conditions are properly maintained.
3. Testing must be conducted under normal operating conditions. Additionally, the hydrogen production must not be less than the annual operating hourly average.
4. The following operational parameters must be recorded during sampling and reported along with the measured emissions: hydrogen production rate, gas feed rate, shift reactor catalyst type, catalyst age, shift reactor inlet temperature, shift reactor inlet and outlet CO concentrations, steam-to-carbon ratio, and other measurable operating parameters that may affect VOC emissions.
5. All test results and calculation methods, including mass balance calculations, are subject to SCAQMD approval as to their consistency with the SCAQMD published and/or

approved test methods, procedures, and protocols, as well as to the engineering and scientific principles, as applicable.

6. All measurements and process information used in calculating the emissions for compliance, particularly the hydrogen production rate, must be obtained using calibrated equipment within the range for which it is calibrated. Furthermore, the equipment must be calibrated within the calibration intervals specified by the manufacturer. The purity of the hydrogen product must also be determined using calibrated instrumentation or an SCAQMD approved analytical method so that the monitored product stream flow rate can be corrected to reflect exclusively the hydrogen production rate.

#### **DETERMINATION OF FLOW RATE**

Flow rates shall be determined by direct measurement except when direct measurement is infeasible and the Executive Officer approves an alternative mass balance approach upon request. Direct flow rate measurement shall follow the standard SCAQMD Method 1.1/2.1 Pitot tube traverse approach with sampling ports installed. Cyclonic flow checks are required as part of each test. Installation of sampling ports, when possible, is recommended for purposes of improved accuracy.

Where sample location or other constraints do not allow direct measurement of flow rates, the hydrogen plant operator shall submit a written request to the Executive Officer for approval of an alternative mass balance approach. The request shall include descriptions of the test constraints, the input to be used for calculating the flow rate and descriptions of the reliability of the input. Flow rates of CO<sub>2</sub> vents can be calculated by a carbon mass balance on the process and feed material. Mass emissions by this approach would require measurements of VOC and CO<sub>2</sub> at the CO<sub>2</sub> vents utilizing SCAQMD Method 25.3 as described in this protocol. Flow rates must be determined and carbon and hydrogen stoichiometric analyses must be performed for all feed streams that enter the process.

Flow rates for the deaerator vents can be difficult to measure either directly or by mass balance. Direct measurement is impeded by the common use of silencers at the deaerator vents causing elevated pressures at sampling ports. When practicable, a stack extension shall be employed in these cases for sampling. Mass balances cannot be applied for calculating flow rate since the primarily steam effluent condenses to an unknown extent in the process. Therefore, upon approval by the Executive Officer, an alternative mass balance approach may be used to directly calculate VOC mass emissions from deaerator vents without determining the flow rate. This approach is described in the section *Determination of Deaerator Emissions Using Mass Balance*.

#### **DETERMINATION OF GASEOUS VOC OR TOTAL VOC WHEN DROPLETS ARE NOT PRESENT**

To determine the appropriate sampling method for the VOC emissions, a determination of whether or not droplets are present at the sampling location must be made. The absence of droplets is verified by a stack temperature above the dew point of the gases at the sampling



location (higher temperature if under pressure). Alternatively, the absence of droplets can be verified by similar (within 10%) emissions as measured by both condensable methods of this protocol (Method 5.1 versus Method 25.3) as measured by previous testing.

Provided that it has been determined that droplets are not present at the sampling location, SCAQMD Method 25.3 as shown in Figure 1 must be used to measure the gaseous portion of the VOC, and/or the total VOC. For most cases, the CO<sub>2</sub> vent can be sampled by using Method 25.3 since the temperature is expected to be above the dew point at the sampling location. For the primarily steam, deaerator exhaust, Method 25.3 must be supplemented by impinger sampling if the temperature is less than 212 °F.

For the deaerator vent, the trap volume specified in Method 25.3 must be increased to accommodate the high moisture. Using the six-liter canisters specified in Method 25.3, approximately 50 ml condensing water may be present. To accommodate for an initial 10 ml water charge and 1 ml of line rinse, a trap volume of 70 - 90 ml should be employed. For the CO<sub>2</sub> vent, the trap volume specified in Method 25.3 may or may not need to be increased depending on the moisture present.

To accommodate for potentially high concentrations as compared to the 50 ppm range that Method 25.3 is intended, the calibration range of the analytical instrument can be extended and/or dilution techniques employed. This is acceptable to the applicability of Method 25.3 since the method allows its use for higher concentrations when primarily water soluble VOC are present, subject to SCAQMD approval.

In employing Method 25.3, condensation must not occur prior to the flexible Teflon connector hose as in Figure 1.

#### **DETERMINATION OF CONDENSABLE VOC WHEN DROPLETS ARE PRESENT**

When droplets are present, a sample must be collected isokinetically using SCAQMD Method 5.1 (EPA Method 5) with the filter omitted. This method is likely to be applied exclusively to the deaerator vent and only when the temperature is less than 212 °F and the mass balance approach cannot be applied. The allowable range of isokinetics can be extended to 110% or less due to difficulties in maintaining isokinetics with the high moisture causing isokinetics of much less than 100%. The condensable VOC is expected to consist primarily of water-soluble methanol. For purposes of this protocol only, it can be assumed that the minimum 30 cubic feet of required sampling volume can be satisfied by applying the wet volume collected with an added safety margin. A minimum wet volume of 60 actual cubic feet and a minimum dry volume of 1.5 dry cubic feet are therefore required. These are similar to the volumes collected in previous development work. This wet sample volume is subject to the additional requirement that the analysis yields results of greater than five times the lower detection limit. The sampling rate is, therefore, much lower than is normally seen at the meter. The nozzle is sized so that the specified sample volume is collected over an approximate 60 minute period or less if the last non-silica gel impinger becomes full during the sampling. For sampling periods of less than 60 minutes, triplicate sampling is required.

Method 5.1 has provisions for including additional or larger volume impingers for high moisture sources. For 100 cubic feet of wet sample, this equates 2000 ml or more of condensate, which is capable of filling several standard impingers. The additional impinger approach is preferred over the enlarged impinger approach due to difficulties associated with poor heat-transfer surface area. The front impingers have been observed to experience overflow difficulties due to higher gas velocities in the front section. For these reasons a precondenser is highly recommended. The recommended configuration is a precondenser followed by five empty impingers followed by the standard Method 5.1 train without a filter as shown in Figure 2.

After completion of the sampling, the sampling train must be tightly sealed and kept chilled by ice or kept at 32 °F - 45 °F until analysis and during recovery. The sampling train is weighed then recovered and mixed into two composites (back and front sections) of the impinger contents using a minimal amount of rinse water. The back section consists of the last two impingers before the silica gel. The front section consists of the remaining non-silica gel impingers and probe and line rinses. During the recovery, sample agitation must be kept at a minimum to avoid loss of the volatile components. The samples must be analyzed within 72 hours of collection. The front section and back section composites are weighed and analyzed separately for VOC by the condensate trap analysis of SCAQMD Method 25.3. The stack concentration and mass emissions are calculated as in the Calculation section.

#### **DETERMINATION OF DEAERATOR EMISSIONS USING MASS BALANCE**

The mass balance approach for calculating deaerator mass emissions must only be used when safety constraints dictate that direct measurement should not be performed. Since past experiences with the mass balance approach have yielded high variability, a minimum of eight runs are required. Each run shall consist of collecting process samples and flow rate data for all streams that enter and exit the deaerator including the steam (condensate). The samples must be collected in an inert container such as glass with Teflon lined lids with zero headspace. The samples must be kept chilled until analysis and analyzed within 72 hour of collection for ppm VOC as carbon by weight by the condensate trap analysis in SCAQMD Method 25.3. Process flow rates must be obtained using calibrated instruments. Additionally, aside from the VOC emissions rate, the deaerator vent rate must be calculated as the difference between total inlet and outlet flows for quality assurance. A negative value, a high positive value, or large deviation between runs may be an indicator of an error and may cause the Executive Officer to reject the test results.

**CALCULATION PROCEDURES**

**CO<sub>2</sub> Vent Flow Rate - Material Balance Alternative.** If the CO<sub>2</sub> vent flow rate is determined by the carbon material balance, the flow rate shall be determined by the following relationship:

$$Q_{CO_2} = Q_{Cin} - Q_{Cout} \quad \text{Equation 1}$$

Where:

$Q_{CO_2}$  = CO<sub>2</sub> vent flow rate (dscfm)

$Q_{Cin}$  = Flow rate into the unit on a carbon basis (dscfm) based on the feed rates or the average hydrogen production rate and a stoichiometric analysis of carbon and hydrogen in the process feed during testing.

$Q_{Cout}$  = Flow rate out of the unit on a carbon basis for streams containing carbon such as with the hydrogen product stream.

**Condensable VOC when Droplets are Present.** If droplets are present and the Method 5.1 sampling was employed, the concentration of condensable VOC is determined for both front and back sections of each sample using the following equation in Method 25.3 Section 4.7 with the variables redefined as follows:

$$C_w = (C_i \times V_i \times V_{id}) / (V_c \times A_c) \quad \text{Equation 2}$$

Where:

$A_c$  = Atomic weight of carbon (12.01 g/mol)

$C_w$  = gaseous concentration of TOC as ppmC in condensate trap water

$C_i$  = TOC concentration in ug/ml of condensate trap water

(Assume TOC concentration ug/g = ug/ml at 4°C)

$V_i$  = volume collected in all impingers excluding the silica gel in ml

$V_{id}$  = volume of ideal gas per mole (gram mole) at 60 °F (0.836 scf/mol)

$V_c$  = metered gas volume in dry standard cubic feet

If the back section concentration is more than 10% of the front section concentration, then the sampling must be invalidated and re-run with more cooling in the front section.

**VOC Concentration.** If droplets were present, as verified by stack temperature or previous testing, the VOC concentration (ppmC) is reported as the sum of both sections of the VOC analysis of the Method 5.1 train, and the canister portion of the Method 25.3 analysis in units of ppmC. If no droplets were present, the ppm VOC is reported as the sum of the Method 25.3 trap and canister analysis as ppmC. The following relationship is used generically for both cases for each process vent:

$$C = C_{\text{cond}} + C_{\text{gas}} \quad \text{Equation 3}$$

Where:

$C$  = VOC concentration (ppmC by volume)

$C_{\text{cond}}$  = Concentration of condensable VOC by both sections of Method 5.1 if droplets present or by Method 25.3 if no droplets present (ppmC by volume)

$C_{\text{gas}}$  = Concentration of gaseous VOC by Method 25.3 (ppmC by volume)

**VOC Mass Emissions.** Mass emissions from each stack are calculated using the concentration in Equation 3 in ppmC by volume, the dry standard volumetric flow rate from each stack, and the molecular weight and carbon number of methanol (MW = 32 lb/lb-mol, C# = 1) as follows:

$$M = F \times C \times (MW/C\#) \times Q \quad \text{Equation 4}$$

Where:

$F$  =  $1.583 \times 10^{-7}$  (Conversion factor in min-lb-mol/hr-scf-ppm)

$M$  = VOC mass emissions (lb/hr)

$C$  = VOC concentration (ppmC as volume)

$MW/C\#$  = 32 lb/lb/mol

$Q$  = Flow rate (dscfm)

**Alternative VOC Mass Emissions for Deaerator.** When the mass balance approach is used, the emissions from the deaerator vent may be calculated using process flow rates and Method 25.3 analyses of process samples using the following equation:

$$M = \sum (Q_{\text{in}} \times C_{\text{in}} \times F_{\text{mw}} / 10^6) - \sum (Q_{\text{out}} \times C_{\text{out}} \times F_{\text{mw}} / 10^6) \quad \text{Equation 5}$$

Where:

$M$  = VOC mass emissions (lb/hr)

$Q_{in}$  = Inlet Process Flow Rates (lb/hr)

$C_{in}$  = VOC concentration in inlet process streams by Method 25.3 (ppmw)

$F_{mw}$  = Molecular weight correction = (32 lb/lb-mole) / (12 lb/lb-mole) = 2.67

$Q_{out}$  = Outlet Process Flow Rates (lb/hr)

$C_{out}$  = VOC concentration in outlet process streams by Method 25.3 (ppmw)

**Total VOC Mass Emissions.** Total VOC Mass Emissions in lb/hr is calculated by summing VOC Mass Emissions from all vent stacks using the following equation:

$$T = \sum M \quad \text{Equation 6}$$

Where:

$T$  = Total VOC Mass Emissions (lb/hr)

$M$  = VOC Mass Emissions from all individual vents stacks (lb/hr)

**Total VOC Mass Emissions per Hydrogen Produced.** Total VOC Mass Emissions in units of lb/MMscf<sub>hydrogen produced</sub> is calculated by using the following equation:

$$E = (2400 \times T) / (P \times H_2) \quad \text{Equation 7}$$

Where:

$E$  = Emissions in lb/MMscf<sub>hydrogen produced</sub>

$T$  = Total VOC Mass Emissions (lb/hr)

$P$  = Purity of hydrogen product stream (%) as determined by an approved method

$H_2$  = Average hydrogen production rate during testing (MMdscfm)

## TEST REPORT REQUIREMENTS

The final Source Test Report must include the following information:

1. A summary of the Source Test results presented in units of lb/MMscf of hydrogen produced.

2. A brief process description. Indicate equipment operation during testing, the operating parameters as specified in this protocol, as well as any other information which may influence the final report.
3. A simple schematic diagram of the process, showing the sampling locations.
4. A stack schematic depicting the sampling locations with respect to the upstream and downstream distances from flow disturbances. Also include a cross-sectional diagram of the stack or duct at the sampling location, depicting the sampling points with respect to compass direction.
5. The sampling and analytical procedures. Be specific about all aspects of sampling and analysis. Include diagrams of test equipment and methods.
6. Complete raw field data, including production data indicative of the testing interval, lab analyses, and the test results (show all calculations). The lab analyses must also include the associated chromatograms or other raw data generated during both sample and standard runs.
7. Calibration data regarding all sampling and measuring equipment utilized during testing (see District Source Testing Manual, Chapter III or "Quality Assurance Handbook For Air Pollution Measurement Systems", Vol. III, US EPA-600/4-77-0276).
8. A "No Conflict of Interest Statement" pursuant to SCAQMD Rule 304.
9. The sample "Chain of Custody" containing time and dated signatures of the person of responsible charge of the sample from the point of origination to analysis.

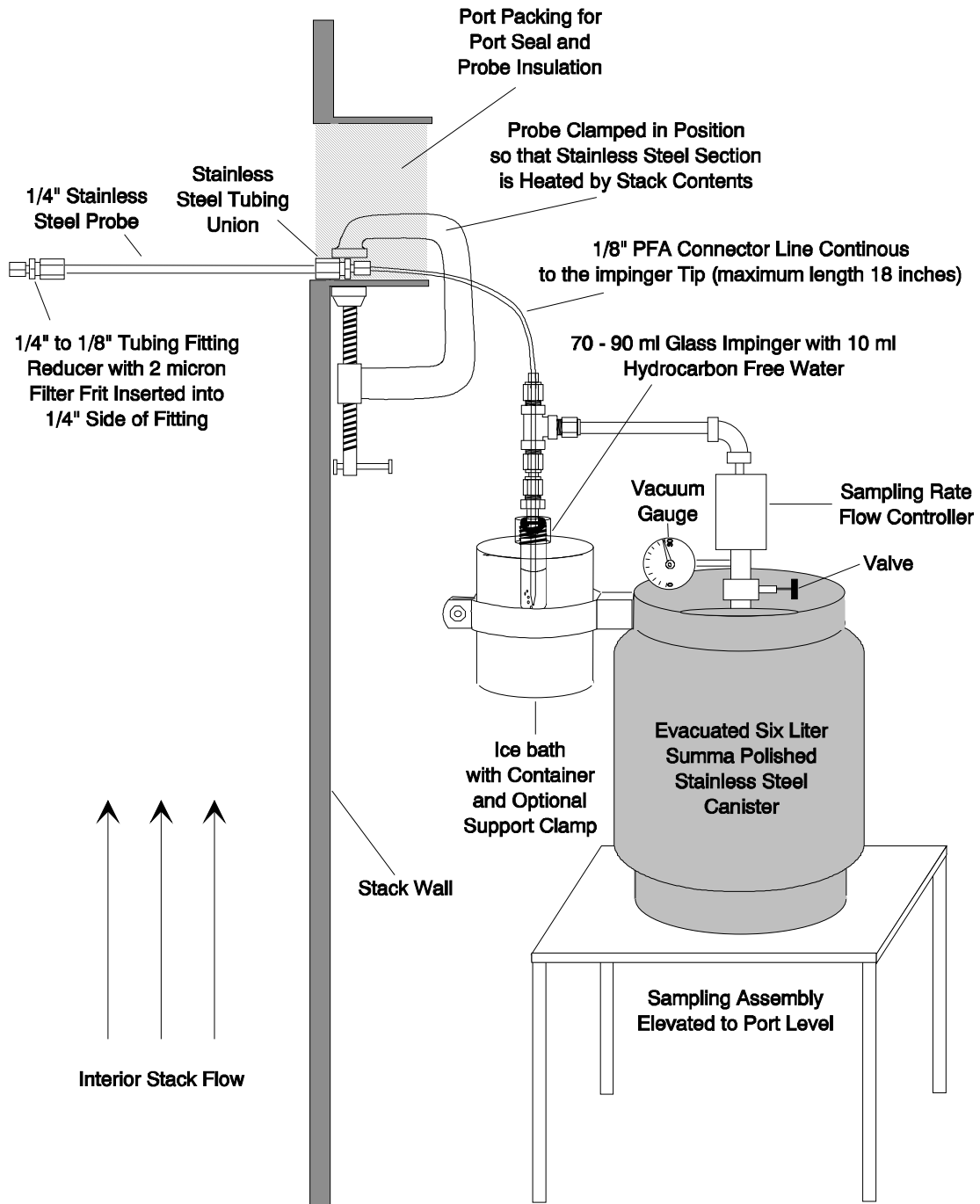


Figure 1- Sampling Equipment for Gaseous VOC or Total VOC When Droplets are not Present

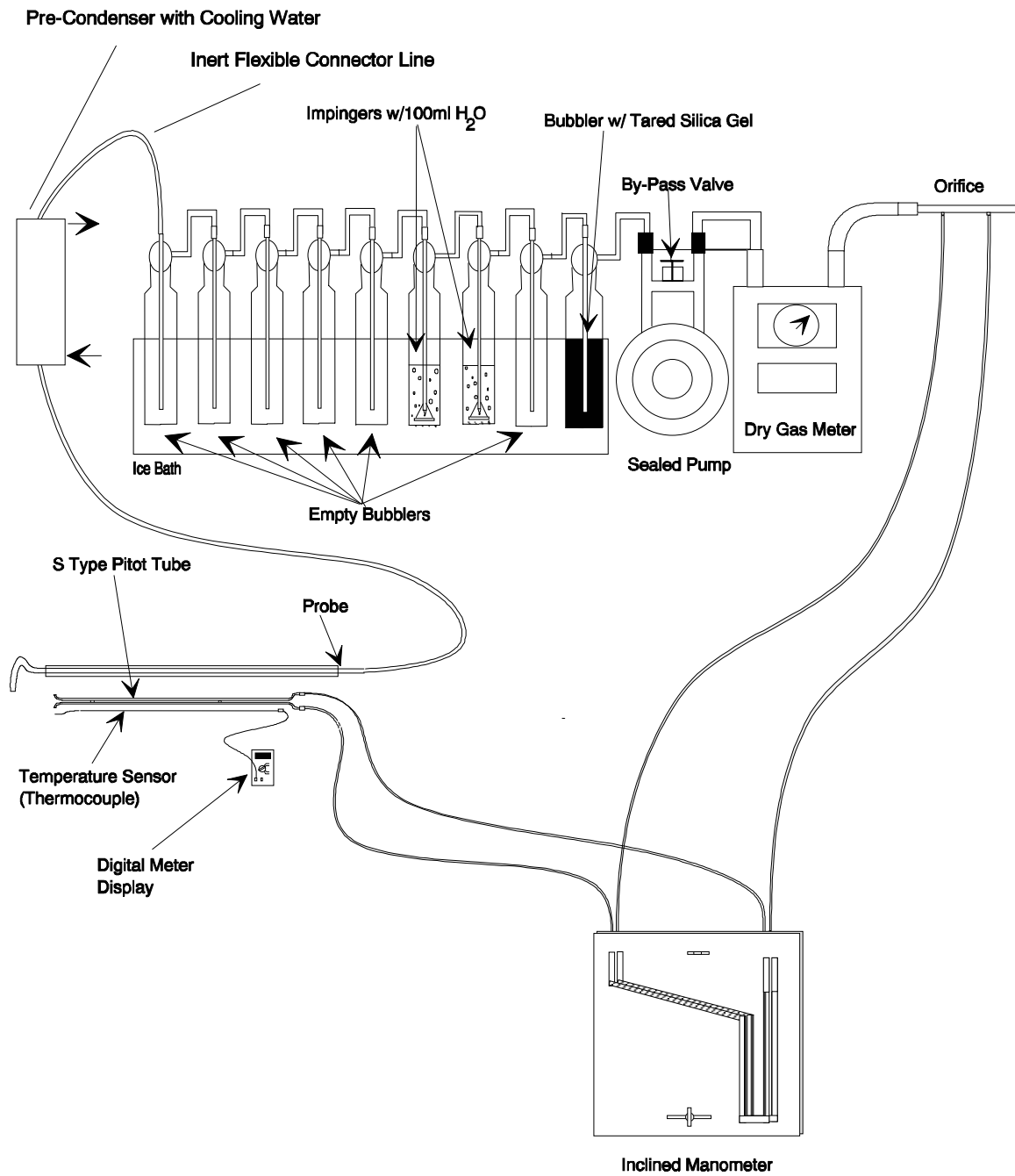


Figure 2- Sampling Equipment for Condensable VOC when Droplets are Present