SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 501.1

DETERMINATION OF TOTAL NON-METHANE ORGANIC VAPORS FROM ORGANIC LIQUID LOADING AND STORAGE

OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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TABLE OF CONTENTS

Section

METHOD 501.1

DETERMINATION OF TOTAL NON-METHANE ORGANIC VAPORS FROM ORGANIC LIQUID LOADING AND STORAGE

Section 1 of 4

1. Overview

1.1 Principle

1.1.1 Organic Liquid Loading

Organic emissions are collected using Method 25.1 sampling equipment or equivalent (cold traps are not used); and analyzed for carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), total non-methane hydrocarbon (TNMHC), oxygen (O_2), average TNMHC molecular weight, and carbon number. Exhaust flow is measured using Method 2.1, 2.2 or equivalent, as appropriate. The volume of organic liquid transferred is obtained from company meters or records. The emissions are reported as lb/1000 gallons transferred.

1.1.2 Organic Liquid Storage

Organics are collected at both inlet and outlet simultaneously, using Method 25.1 sampling equipment or equivalent (use of cold traps is optional) and analyzed for CO_2, CO, CH_4, TNMHC, and O_2. Mass flow at both inlet and outlet are either measured using an approved method or calculated using an appropriate balance method. For vapor recovery systems an oxygen balance generally can be used. For vapor incineration systems a carbon balance usually is the best choice. The results are reported as percent control efficiency.

1.1.3 Special Considerations

When multiple outlets are present manifolding or simultaneous sampling usually is required.

When vapor holders are part of the vapor collection system, testing can only be concluded when the vapor holder bladder returns to the same position it had when testing started, or there must be some accurate method for determining the change in volume. (This may be extremely difficult or impossible to do.)

1.2 Applicability

This method most often is used to measure organic emissions encountered during bulk gasoline transfer to fixed roof storage tanks or trailer trucks.

1.3 Interferences

The presence of liquid or vapor leaks in the delivery or vapor control system precludes the use of this method, unless the leaks can be accurately quantified (may be difficult or impossible).

METHOD 501.1

DETERMINING OF NON-METHANE ORGANIC VAPORS FROM ORGANIC LIQUID LOADING AND STORAGE

Section 2 of 4

2. Field Procedures

2.1 Sampling Apparatus

Schematics of possible sampling configurations are shown in Figures 501.1-1 thru 501.1-6.

2.1.1 Sampling Tray

The sampling trays used in this method are those described and shown in Method 25.1, with the following modifications:

a. Cold traps are used only when speciation is not required. (Traps cannot be used with chlorinated hydrocarbon vapors.)

b. Sample tank volume may be larger than 8 liters if conditions warrant.

2.1.2 Flow Measurement

Method 2.1 (Pitot traverse), Method 2.2 (positive displacement meters), and other alternative methods (orifice plates, computational methods, etc.) described in Chapter X are utilized, when appropriate.

2.1.3 Piping

Flexible and/or rigid piping can be used to connect the vapor recovery system exhaust(s) to a positive displacement meter or other acceptable flow measuring device. The piping also can be used as a flow straightener and/or as a heat exchanger, as needed. Piping also should be connected to the meter outlet to divert the vapor away from the work area and to ensure the integrity of the gas sample (collected at or near the meter).

2.2 Pretest Procedures

Using a combustible gas detector, inspect the organic loading rack and/or storage tanks, the vapor holding tank and the vapor collection and control system (especially pressure relief valves) for liquid and vapor leaks. If any leaks are found, they must be repaired or quantified before sampling starts.

Assemble and leak test the sampling apparatus as outlined in Method 25.1.

2.3 Sampling

Conduct the test for a minimum of 6 hours or 75,000 gallons throughput. Make sure that the testing interval includes peak loading hours. If this is not feasible due to operating conditions, this requirement may be waived with the approval of the Executive Officer.

When testing a vapor control unit that cycles on and off, start the test when the unit starts.

Record the following, as applicable:

a. Initial positive displacement meter reading(s).

b. Vapor holding tank diaphragm height.

c. Barometric pressure.

d. Initial product meter readings for all the loading arms vented to the Vapor Control System (VCS). If the terminal has a bulk transfer line to fixed roof tanks, record the initial readings from the bulk product transfer line meter.

e. The times when the VCS processing cycle begins and the duration of each cycle.

f. The positive displacement meter reading at 15 minute intervals during the VCS processing cycle. If flow rate meters (orifice or Pitot tube, etc.) are used, record the rate every 5 minutes and when rates change by more than 10 percent.

g. The vacuum gauge reading(s) of the sample tanks(s) at 15 minute intervals during the VCS processing cycle.

h. The vapor temperature at the positive displacement meter at 15 minute intervals during VCS processing.

i. The meter readings when the meter stops or reverses. If flow reverses, take two meter readings, one when the reversal starts and one when the flow is in the right direction. If the optional check valve system is used, flow reversals at the meter should not occur.

Periodically check the loading rack, vapor holding tank, and the VCS for liquid and gaseous leaks.

The test ends for systems having a vapor holding tank when the vapor holding tank diaphragm height is at the same level as when the test started. For all other systems the test should end at a convenient time when testing requirements have been met.

2.4 Post-Test Procedures

Leak check and disassemble the Total Combustion Analysis (TCA) sampling apparatus as described in Section 2.8 and 2.9 of Method 25.1.

Record the following:

a. The final positive displacement meter reading.

b. The final vacuum gauge reading(s) on the sample tanks.

c. The final readings of the product meters for the loading arms at the loading racks and bulk transfer lines to fixed roof storage tanks.

Record all data in a form shown in Figure 501.1-7.

METHOD 501.1

DETERMINATION OF TOTAL NON-METHANE ORGANIC VAPORS FROM ORGANIC LIQUID LOADING AND STORAGE

Section 3 of 4

3. Laboratory Procedures

3.1 Apparatus

3.1.1. Sampling Apparatus (see Section 2.1.1)

3.1.2 Sample Recovery

a. Manometer capable of reading to 1 mm Hg in the 0 to 900 mm range.

b. Pressurizing system capable of pressurizing required sampling tanks to 900 mm Hg.

3.1.3 Sample Analysis

For CO, CO_2, CH_4, TNMHC. Refer to Method 25.1, Section 3.1.3.

3.1.4 Sample Analysis - Speciation

a. Chromatograph

A Perkin Elmer Sigma 3B GC equivalent equipped with a flame ionization detector. The chromatographic column oven must be temperature programmable from -40°C to + 200°C at a rate of 8°C increase per minute.

b. Sample Injection

A Carle, sixport, gas sampling valve with a 5 cc sample loop.

c. Syringe

100 ml, gas tight.

d. Chromatographic Column

H-P, 10 percent SF-96 on 60/80 GC-Q (15 ft x 1/8 in. ss).

e. Integrator

To sum the area under the chromatographic peaks over time.

3.1.5 Sample Analysis - Oxygen

a. Chromatograph

A chromatograph capable of maintaining approximately 80°C oven temperature and equipped with a thermal conductivity detector.

b. Chromatographic Column

Type 316 stainless steel, 4 feet in length, 1/4 inch OD and 0.28 inch wall thickness, packed with Linde Type 5A, 42 to 60 mesh molecular sieve.

c. Syringe

100 ml, gas tight.

d. Sample Injection

A sixport gas sampling valve with a 1 cc sample loop.

e. Chart Recorder

For measuring peak height.

3.2 Reagents

3.2.1 Sample Collection Train Preparation

Compressed nitrogen, 99.9 percent pure, with less than 1 ppm total hydrocarbon (THC).

3.2.2 Sample Recovery

Compressed nitrogen (see Section 3.2.1).

3.2.3 Sample Analysis

For CO, CO_2, CH_4, TNMHC. Refer to Method 25.1, Section 3.2.3.

3.2.4 Sample Analysis Reagents for Speciation

a. Carrier Gas

N_2 - 99.9 percent pure, flow 30 ml/min.

b. FID Gases

Air - Breathing grade, flow 300 ml/min.

H_2 - 99.9 percent pure, flow 30 ml/min.

c. Sub-ambient Oven Operation

Liquid N_2 for oven cooling.

d. Standard

C_1-C_6 paraffinic hydrocarbon standard, nominally 100 ppm each compound. Scott II analyzed gases, can mix 220, accuracy of analysis ± 2 percent, Scott Environmental Technology.

3.2.5 Sample Analysis Reagents for Oxygen

a. Calibration Gas

Ambient air.

b. Carrier Gas

Argon (99.99 percent purity).

3.3 Pretest Preparation

Before testing, assemble the required equipment and reagents to check readiness. It is important that analytical, recovery, and sampling equipment are all leak-free to produce reliable results.

Flow controllers must be flushed with clean air or nitrogen between tests.

Evacuate and fill sample tanks with nitrogen at least ten times to flush residual hydrocarbon from the tanks. Tanks should be filled with nitrogen and tested for hydrocarbons by TCA/NDIR before final evacuation.

Clean probes by flushing with air at 80 cc/min while flaming with a Bunsen burner.

Note: All tank and flow controller assemblies shall be marked and used for vapor recovery samples only. Segregation of tanks and flow controller assemblies is done to minimize the risk of contamination of low ppm outlet samples (Method 25.1).

3.4 Sample Collection Apparatus Preparation

Assemble according to Figure 501.1-6.

3.5 Leak Check

Sample should be leak checked according to the procedure in Section 2.

3.6 Sample Recovery

Allow the sampling tanks to equilibrate to room temperature. Using a manometer, measure and record the individual pressure of each tank to the nearest 1 mm Hg. Pressurize with 99.9 percent nitrogen until a pressure between 860-910 mm Hg is reached. Shut off the pressure, wait until the reading stabilizes, record the reading, and seal the container until ready for analysis.

Purge the pressurizing system with nitrogen to avoid contaminating the next sample.

3.7 Sample Analysis - CO, CO_2, CH_4, TNMHC O_2

3.7.1 TCA/NDIR

Refer to Method 25.1, Section 3.6.1. Vapor recovery samples may or may not have CO_2 present, but usually contain high concentrations of C_2 compounds which elute near CO_2. A second injection is needed to determine if the first peak obtained after placing the room temperature water on the Porapak column is CO_2.

3.7.2 Speciation

To calibrate the instrument, a standard must be injected. Use a 100 ml gas tight syringe to flush the sample loop in the load mode with standard gas. Turn the sampling valve to the inject mode to transfer the loop contents to the column inlet. Program the column oven temperature to hold for 2 minutes at -40°C and to increase temperature by 8°C/min. to 175°C. Total run time is approximately 27 minutes. Record the area and retention time of the peaks on the integrator/recorder (see Figure 501.1-8).

Obtain an aliquot of sample in the 100 ml, gas tight syringe and load it into the sample loop. Turn the valve to the inject mode so the column carrier gas will flush the loop contents to the column. The gas chromatograph operating conditions must be identical for standard and sample runs. The column and the oven temperature program separate the eluting hydrocarbons into distinct bands by boiling point. These peaks form discernible groups around the straight chain hydrocarbon peaks. Integrate these groups of peaks and assign the retention time of the co-eluting straight chain hydrocarbon to the sum of the areas (see Figure 501.1-8).

3.7.3 Oxygen

Set the instrument response to oxygen as close to maximum as possible (about 90 percent) with ambient air. Obtain an aliquot of the sample in a 100 ml gas tight syringe and flush it through the sample loop. Inject the sample into the column and allow it to elute. If the sample contains high amounts of hydrocarbons, it will be necessary to increase the analysis time to allow for the elution of these compounds, otherwise "ghost" peaks may appear after the next injection. Run the sample in duplicate.

Run ambient air in duplicate before and after each set, or every ten samples, whichever is first. Duplicate determinations must agree within 5 percent.

3.8 Calibrations

3.8.1 TCA/NDIR

Refer to Method 25.1, Section 3.8.

3.8.2 Speciation Calibrations

First, run the standards through the GC. Retention times and areas of duplicate runs must agree within ± 5 percent. If a more accurate determination of branched chain and aromatic hydrocarbon retention times is deemed necessary, these classes of compounds should be run as qualitative standards to more accurately bracket the groups of hydrocarbon peaks to be summed. The sample may need to be diluted to bring it into the standard range of 100 ppm each straight chain hydrocarbon. The dilution is accomplished by serial syringe dilution. The duplicate sample runs must agree within ± 5 percent.

Calibrate the normal chain hydrocarbon values of the standard against NBS-standard propane.

3.8.3 Oxygen Calibrations

Use dry room air for oxygen calibration and assume it to be 20.958 percent.

Using dry room air, set the response of the instrument close to maximum (about 90 percent). Calibrate the instrument at the beginning and end of each set, or every ten samples, whichever is first. Response to the standard must be within 5 percent of average.

3.9 Calculations

3.9.1 TCA/NDIR

(Refer to Method 25.1, Section 3.7).

3.9.2 Speciation

Concentrations of gaseous effluent components present in the sample are represented by areas beneath the corresponding peaks. Choose the groups of peaks to be summed by the integrator by the retention time limits set in the standardization process (see Section 3.8.2). Assign these groupings the carbon number of the co-eluting straight chain hydrocarbon.

Alternatively, each peak of the chromatogram can be identified and its area summed with all other peaks of the same carbon number content.

Sum the TNMHC by assigned carbon number. Divide the sums by the TNMHC to give a percent of each carbon number present. These percentages should total 100. Multiply each carbon number by its percent present in the sample. This gives a weighted percent hydrocarbon present in the sample. Calculate the average carbon number, the sum of the weighted percent hydrocarbons divided by 100, as follows:

$$C_{avg} = \frac{\sum_{n=2}^{6} C_n \times P_n}{100}$$

where:

C_{avg} = Average carbon number

C_n = Carbon number

P_n = Area percent of C_n

$$= \frac{A_n}{\sum_{n=2}^{6} A_n} \times 100 \text{ percent}$$

A_n = Area of C_n

The Average Molecular Weight is found from the Average Carbon Number as follows:

Average Molecular Weight =

$(12 \times C_{avg}) + (2 \times C_{avg}) + 2$ =

$(14\ C_{avg.} + 2)$

3.9.3 Oxygen

Calculate percent oxygen by relative peak heights and correct for sample pressurization as follows:

$$\text{Percent } O_2 = \frac{h_{spl}}{h_{std}} \times 20.95 \text{ percent}$$

$$\times \frac{P_f}{P_i}$$

where:

Percent O_2 = Percent of Oxygen (V/V)

h_{spl} = Average peak height of the sample

h_{std} = Average peak height of the standard

P_f = Final pressure, in mm (in.) Hg, after pressurization with N_2

P_i = Pressure of the sample as received mm (in.) Hg

METHOD 501.1

DETERMINATION OF TOTAL NON-METHANE ORGANIC VAPORS FROM ORGANIC LIQUID LOADING AND STORAGE

Section 4 of 4

4. Engineering Calculations and Reporting

4.1 Calculations

The corrected volume of vapors vented from the Vapor Control System (VCS) outlet.

$$V = V_o \frac{(P_{bar})(520)}{(29.92)(T_o)}$$

where:

V = Corrected meter volume, scf

V_o = Uncorrected meter volume, ft^3

P_{bar} = Barometric pressure

T_o = Average vapor temperature at meter, ^{o}R

520 = Standard temperature, ^{o}R

29.92 = Standard pressure, in. Hg

The mass of total non-methane hydrocarbon emitted from the VRS outlet:

$$M = \frac{(C_o)(MW)(V)}{(1{,}000{,}000)(CN)(379)}$$

where:

M = Mass of TNMHC emitted from the VCS, lb

C_o = Average TNMHC concentration at the VRS outlets, as carbon dioxide (CO_2) in parts per million (ppm)

MW = Average weight of the NHMC at the VRS outlet, lb/lb mole

V = Corrected meter volume, scf

CN = Average TNMHC carbon number at VCS outlet

379 = Molar constant, scf/lb mole at 60^oF

The VCS outlet emission factor:

$$E = \frac{(M)(1000)}{G}$$

where:

E = TNMHC emissions per thousand gallons of product loaded, lb/1000 gal

M = Average TNMHC emitted from VCS, lb

1000 = Gallon Factor

G = Volume of product loaded during the test, gal

4.2 Reporting

Report results as lb/1000 gallons transferred per organic liquid loading operation and as percent control efficiency for organic liquid storage.

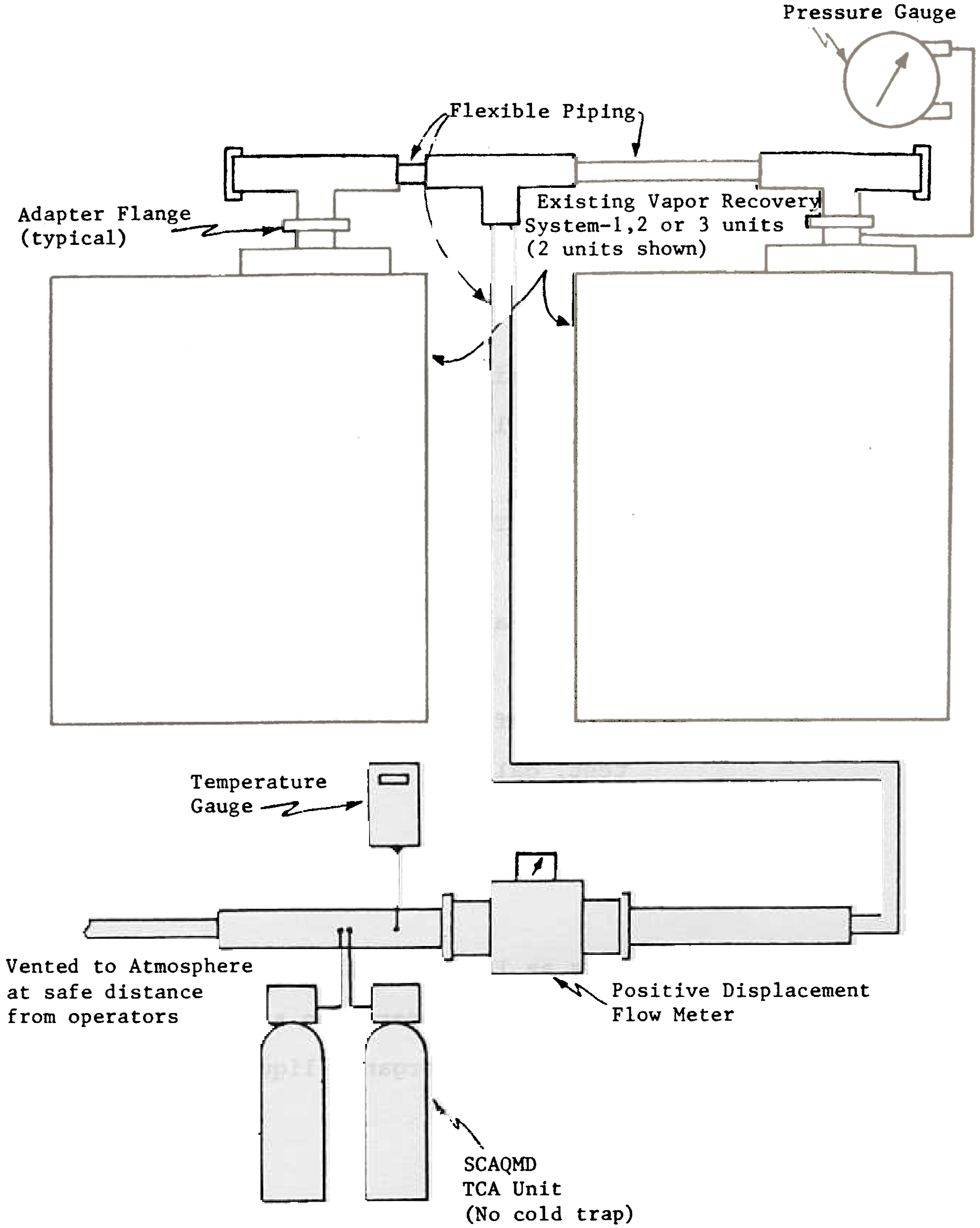


Figure 501.1-1A

Vapor Recovery Sampling Setup

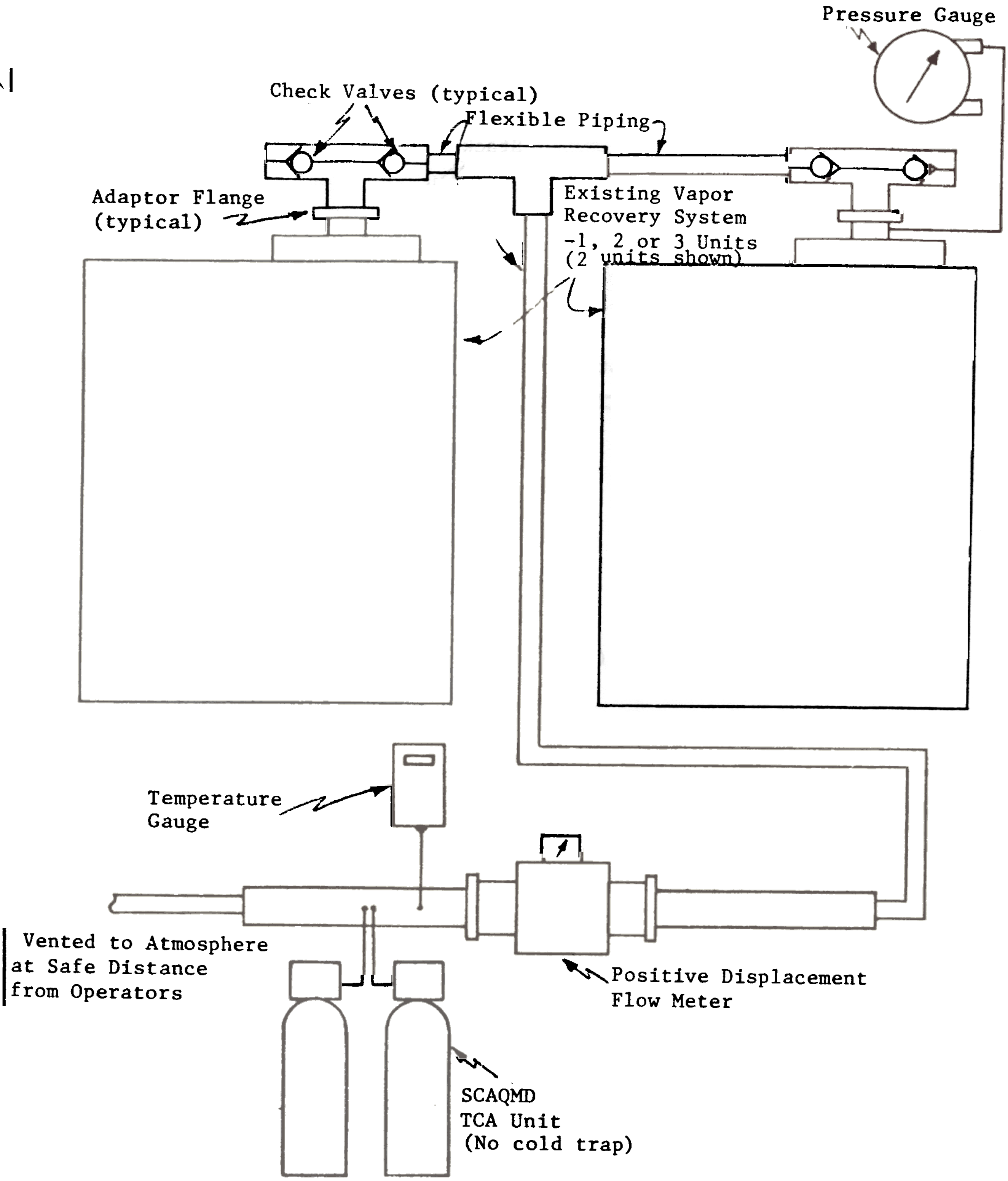


Figure 501.1-1B

Vapor Recovery Sampling Setup. (Alternative to Setup Shown in Figure 501.1-1A)

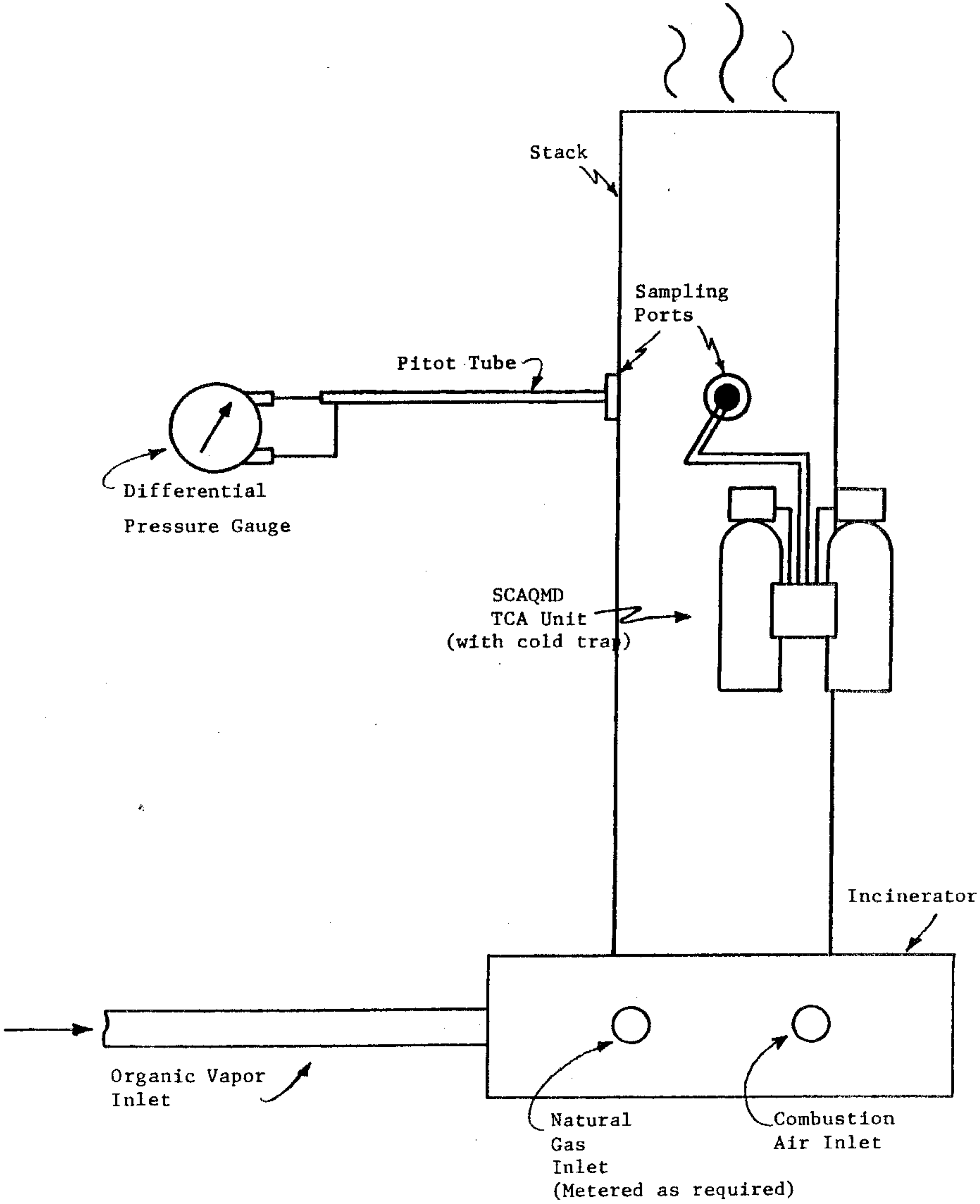


Figure 501.1-2

Sampling Setup at an Organic Vapor Incinerator to Measure Outlet

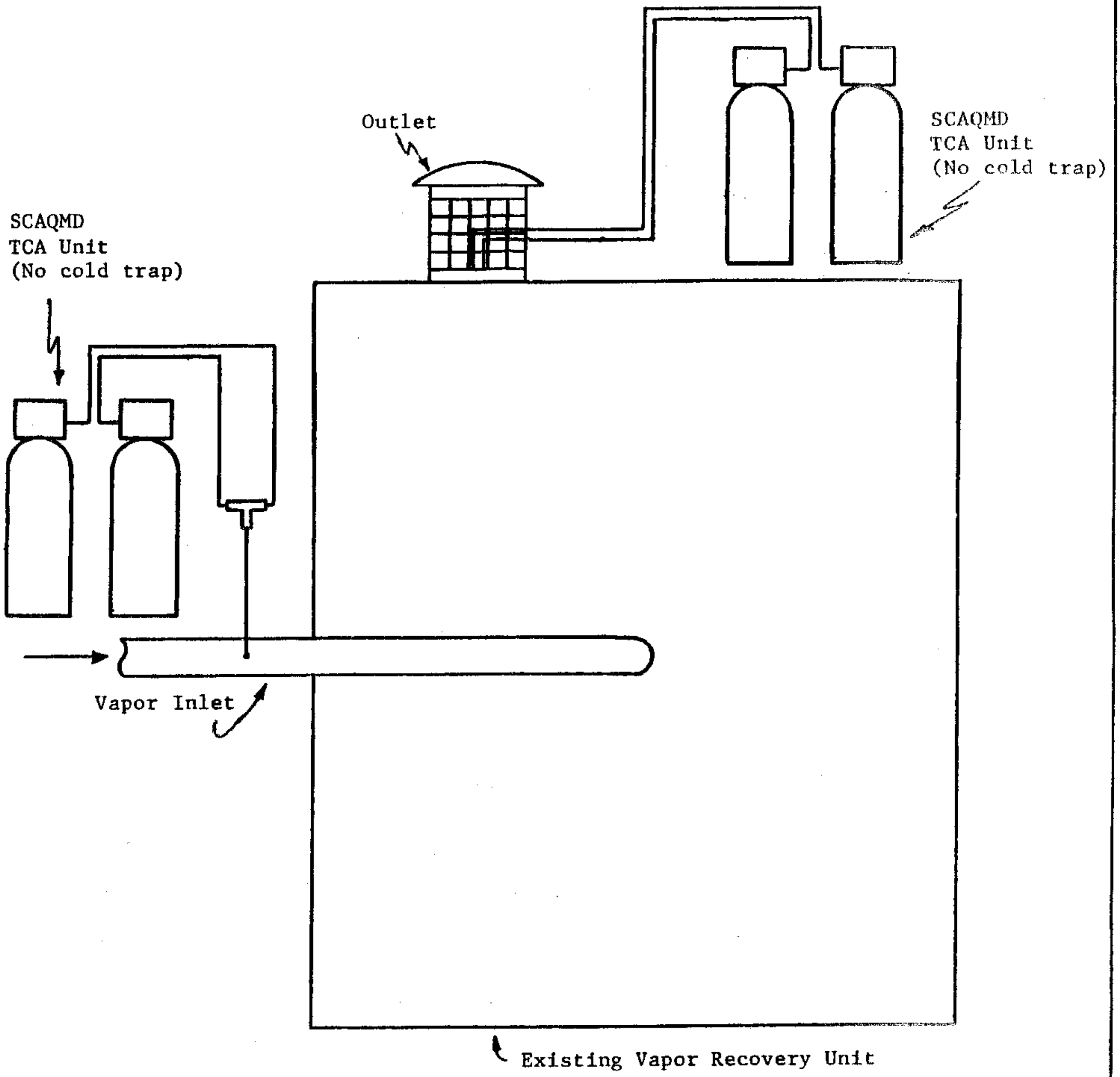


Figure 501.1-3

Sampling Setup at a Vapor Recovery Unit for Efficiency Measurements

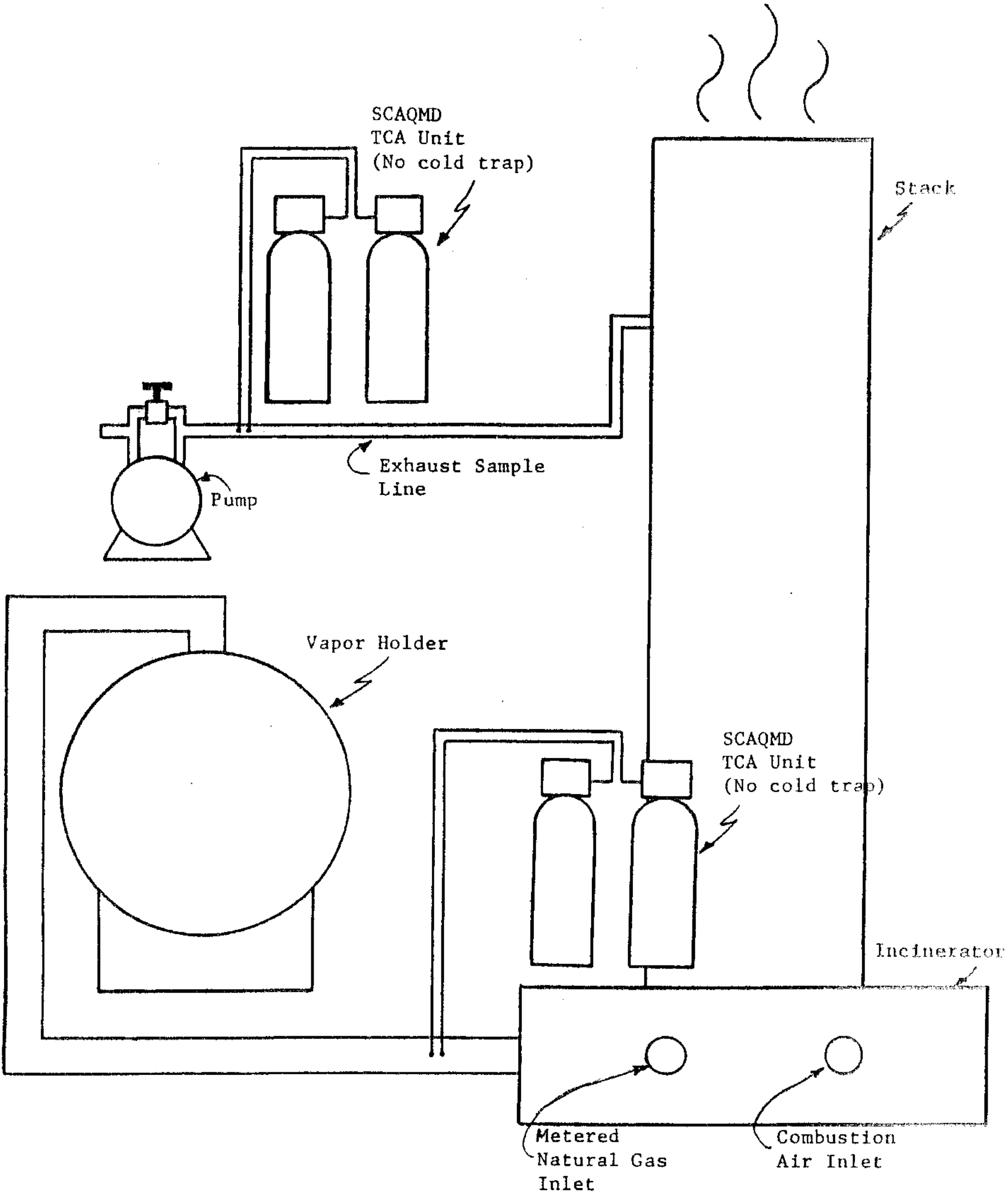


Figure 501.1-4

Sampling Setup at an Organic Vapor Incinerator with Inlet from Vapor Holder for Efficiency Measurements

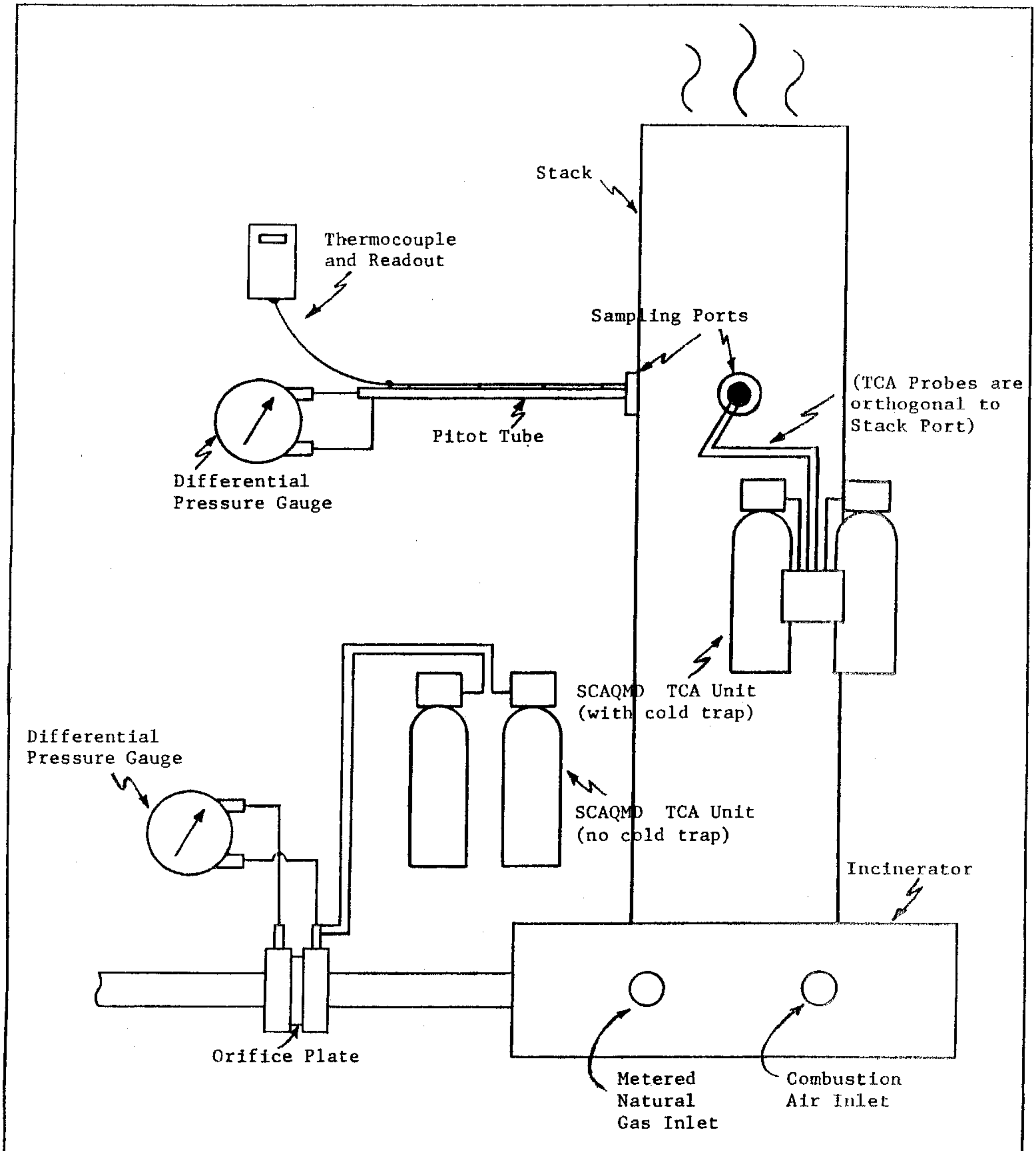


Figure 501.1-5

Sampling Setup at an Organic Vapor Incinerator to Measure Inlet and Outlet

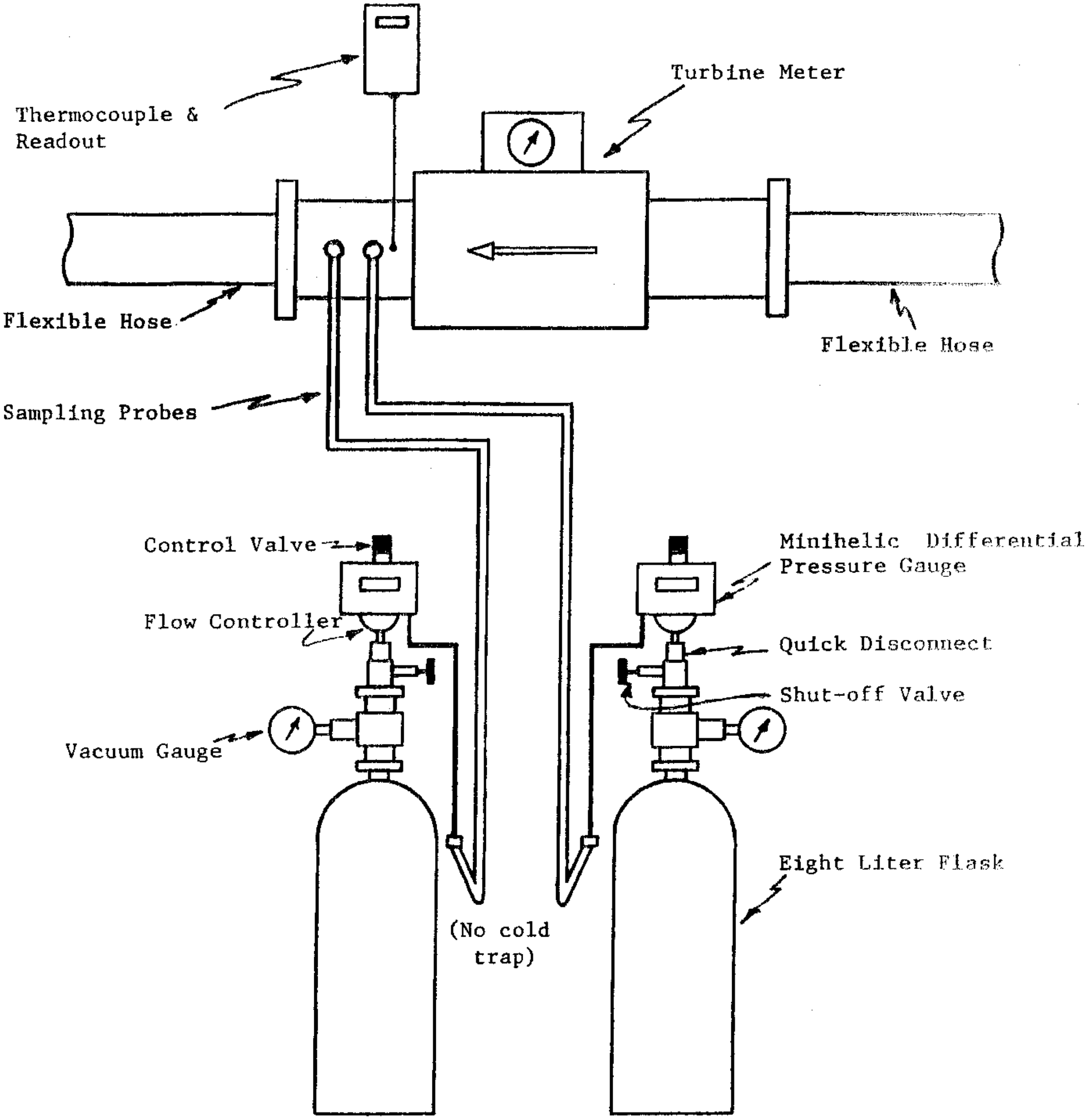


Figure 501.1-6
Detail of SCAQMD TCA Units and Turbine Meter Connections

VAPOR RECOVERY UNIT TEST DATA SHEET

Test No.______ Date______

Company____

Sampling Location____________________________________

Test Performed by____________________________________

Test Observed by_____________________________________

Leak Check: Post Test______________ Pretest____________

Vapor Sphere Tank Level: Initial__________ Final__________

Bar Pressure:

Time (min)	Meter Reading (ft^3)	TCA Tray Vacuum (in. Hg)		Vapor Temperature (^{o}F)	Comments
		Tank #	Tank #		

Calibration Data

Tested by____________

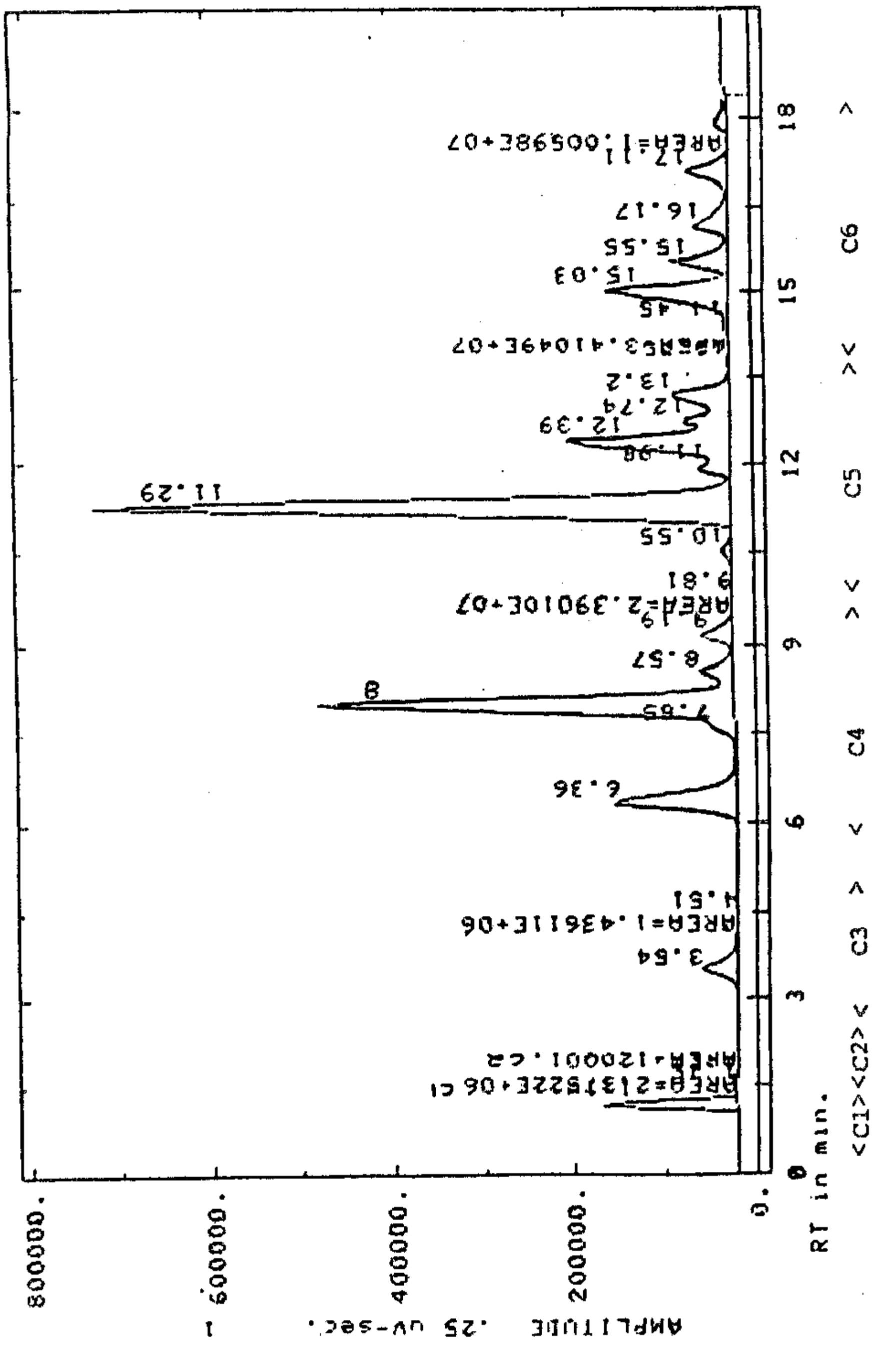
Potentiometer No:_____________ Calibration Date____________

Thermocouple No:______________ Calibration Date____________

Meter (Singer) No:____________ Calibration Date____________

Figure 501.1-7

Vapor Recovery Test Data Sheet



MANUAL PEAK INTEGRATION

Figure 501.1-8