METHOD 25.1

DETERMINATION OF TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS AS CARBON

Section 1 of 5

1. Overview

1.1 Principle

Duplicate gas samples are withdrawn from a source at a constant rate through condensate traps immersed in dry ice followed by evacuated 8 liter (nominal) tanks (Figure 25.1-1). Heavy organic components condense as liquids and solids in the condensate traps. Lighter components pass as gases through the traps into the tanks. Volatile Organic Compounds (VOC) as Total Gaseous Non-Methane Organics (TGNMO) are determined by combining results from independent analyses of condensate in the traps and gases in the tanks. These results are used to determine a qualitative and quantitative expression of the effluent gas stream. Duplicate sampling is designed into the system to ensure precision.

After sampling is completed, carbon dioxide (CO_2) is stripped from the condensate trap and the remaining organics are oxidized to CO_2. This CO_2 is quantitatively collected in an evacuated vessel and measured by injection into the gas analysis module of the total combustion analyzer (TCA) and detected by non-dispersive infrared (NDIR) detector.

The organic content of the sample fraction collected in each tank is measured by injecting a portion into the gas analysis module of the TCA which uses a GC column to separate the non-methane organics (NMO) from carbon monoxide (CO), CO_2 and methane (CH_4) prior to combusting to CO_2. The NMO are eluted off the column as "backflush" or "foreflush".

For greater sensitivity (<25 ppm TGNMO), a gas analysis module using catalytic reduction to CH_4 and FID may be substituted for the NDIR based unit.

TGNMO as CO_2 is calculated by summing the values obtained from analysis of backflush, foreflush and trap condensate. Since all CO, CH_4, and VOC are oxidized to CO_2, to which the NDIR is specifically sensitized, no response factors to other compounds need to be determined.

1.2 Applicability

This method measures VOC as TGNMO, expressed as carbon. In particular, this method is only applicable to processes that change the composition and form of organic compounds (e.g. ovens, afterburners, and combustion processes) and processes containing organics that cannot be measured accurately by any other direct detection method. Sources where organic particulate matter may be present (e.g. spray booths or hoods venting paint coaters) either an in-stack particulate filter must be used or the sampling nozzle must be pointed downstream. Otherwise, random particles containing carbon collected from the gas stream will yield a higher response and also affect the accuracy and precision of the results.

The detection limits (as CO_2) for CO, CO_2, CH_4, and TGNMO are 25 ppm, 50 ppm, 50 ppm, and 25 ppm, respectively, when non-condensable organics are not a significant portion of the sample (i.e. insignificant foreflush and backflush). See Section 5 for lower detection limits by using an FID.

Care should be exercised in the combustion of samples containing high concentrations of chlorinated compounds to avoid non-combustion or incomplete combustion. The combustion products formed are extremely reactive and could seriously damage the oxidizer tube. The condensate traps must be eliminated from the sampling apparatus because of the corrosive products created in analysis.

This method reports only the concentration of carbon sampled and not bonded oxygen, hydrogen, chlorine, or other elements. However, this method can be used in combination with GC analysis, or knowledge of the specific VOC emitted, to obtain the carbon molecular weight ratio or other compound ratios.

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DETERMINATION OF TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS AS CARBON

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2. Field Procedures

2.1 Sampling Apparatus

The duplicate gas sampling systems consist of condensate traps, flow controllers, and sample tanks (Figure 25.1-1). Each system can be constructed from commercially available components or components fabricated in a machine shop. The following components are required for each system:

a. Probe

Seamless stainless steel tubing, 3.2 mm OD (1/8 in.) x .66 mm (0.026 in.) wall thickness.

b. Sample Flow Valve

Stainless steel control valve for starting and stopping sample flow.

c. Flow Rate Controller

An adjustable vacuum flow regulator (Variflow) or other system capable of maintaining the sample rate to within ± 10 percent of the selected minihelic _P.

d. Vacuum Gauge

Gauge for monitoring the vacuum of the sample tank during leak checks and sampling (0 to 30 in. Hg.).

e. Sample Tank

Stainless steel tank with a volume of 8 liters (nominal). Tank volumes must be calibrated to the nearest 10 ml (see Section 3.9).

f. Differential Pressure Indicator

A minihelic gauge (0 to 3 in. H_2O) or other indicator capable of measuring _P across the sample probe and a trap as a function of time and stack temperature.

g. Condensate Trap

Constructed of Type 316 stainless steel and stainless steel wool as shown in Figure 25.1-2.

2.2 Sampling Reagents

Crushed or pelletized dry ice required during sampling.

2.3 Pretest Determinations

Select a sampling location where representative gas samples can be taken and use Methods 1.1 and 2.1 to obtain the flow rate temperature. Use the TCA Sampling Interval Table (Table 25.1-1) to determine the minihelic setting on the controllers to maintain a constant flow rate over a sample time interval equal to or greater than that prescribed. Since this method is not suited to traversing, the sampling location should be where the hydrocarbon concentration is uniformly distributed.

Record identification numbers from condensate traps, controllers, and evacuated tanks. Record the vacuum readings from each evacuated tank gauge (Figure 25.1-3).

2.4 Assembly

Engage the controllers to the evacuated tanks at their quick-connect fittings. Attach the condensate traps to the flow controllers. **Important**: Keep fittings clean from dust. Use surgical gloves when touching fittings.

Do not engage a sealed condenser trap/controller combination to the quick-connect portion of the evacuated tanks because it may damage the minihelic gauge and controller.

2.5 Pretest Leak Check

A pretest leak check is required. After assembling the duplicate gas sampling systems, assure that each probe tip is tightly plugged and the clamp (Figure 25.1-4) is in the closed position to protect its minihelic gauge (flow indicator). Record the tank vacuum as indicated by the vacuum gauge and record the barometric pressure. Open the sample flow valves, wait for a minimum of 10 minutes, and recheck the indicated vacuum.

During this waiting period, leak check each minihelic by following the leak check procedure outlined in Method 2.1. If the tank vacuum gauge readings have not changed and the minihelic gauges are leak-free, the entire duplicate gas sampling system is considered acceptable. Close the sample flow valves. Before opening each clamp at each probe tip, remove the plug to avoid damaging the minihelic gauges.

If a rotometer and critical flow limiting valve are used as a flow controller system, the leak test may be run for only 2 minutes.

2.6 Sampling Operation

Attach flow nozzle to probe end of each trap. Use soft high temperature wire to secure probe ends together. Five minutes prior to sampling, put crushed dry ice in condensate trap container to within 2.5 to 5 cm of the point where each inlet tube joins its trap body. Place the probes into the stack at a preselected point with nozzle inlet facing downstream of the stack flow. Be careful not to touch either probe opening against the stack.

For stacks with a negative or positive static pressure, insert a static pressure balance tube into the stack near the sampling point and connect it to the low pressure side of each minihelic gauge (see Figure 25.1-5). For stacks with a negative static pressure, assure the sample port is sufficiently sealed to prevent air from leaking in around the probe. Record the clock time and begin sampling by opening the sample flow valves. Adjust the flow rate controller valves (on vacuum regulator) to obtain the pre-determined minihelic value. End the sampling when the sample time period has been reached or the minimum vacuum gauge reading on any tank is 5 in. Hg, whichever occurs first. Close the sample flow valves and record the final clock time and vacuum tank gauge readings. Remove probes from stack and let cool.

If sampling is interrupted due to an upset in the source being sampled, close the sample flow valves. Record vacuum gauge readings and clock time. If source resumes operation in less than 5 minutes, reopen sample flow valves and record clock time. If source takes longer than 5 minutes to resume operation, remove probes from stack and wait until source resumes operation.

2.7 Reference Point Velocity

Monitor velocity at a reference point during sampling. Take velocity readings every 10 minutes or when the velocity or temperature changes by more than 20 percent. Use the reference point readings to correct the average stack velocity obtained during the traverse.

2.8 Post Test Leak Check

A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack, remove the nozzles, plug the probe tips, and close each clamp. Open the sample flow valve and monitor the sample tank vacuum gauges for 10 minutes. The leak check is acceptable if there is no visible change in the tank vacuum gauge. If the sampling train does not pass the post leak check, invalidate the run.

2.9 Disassembly

Close the sample flow valve. Disconnect the condensate traps at the flow controller and tightly seal both ends of the condensate traps. Keep the condensate traps packed in dry ice until the samples are returned to the laboratory for analysis.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sample Collection Train Preparation

a. Probe

3.2 mm OD (1/8 in.) stainless steel tubing.

b. Sample Flow Valve

Stainless steel control valve for starting and stopping sample flow.

c. Flow Rate Controller

An adjustable vacuum flow regulator (Variflow) or other system capable of maintaining the sampling rate to within ± 10 percent of the selected minihelic ΔP.

d. Vacuum Gauge

Gauge for monitoring the vacuum of the sample tank during leak checks and sampling (0 to 30 in. Hg).

e. Sample Tank

Stainless steel tank with a volume of 8 liters (nominal). Tank volumes must be calibrated to the nearest 10 ml (see Section 3.9).

f. Differential Pressure Indicator

A minihelic gauge (0 to 3 in. H_2O) or any system that is capable of indicating the ΔP across the sample probe and trap as a function of time and stack temperature.

g. Condensate Trap

Constructed of Grade 316 stainless steel. Construction details of suitable trap are shown in Figure 25.1-2.

h. Manometer

Must be capable of measuring pressure to within 1 mm Hg in the 0-900 mm range. Manometer must be NBS traceable.

i. Vacuum Pump

Capable of producing a vacuum of <10 mm Hg. This is to evacuate the sample tanks and intermediate collection vessels (see Sections 3.3 and 3.4).

3.1.2 Sample Recovery

a. Cryogenic Freezer

Freezer must have the capacity to store all condensate samples at -80^{o}C until the sample recovery can be completed. Storage in dry ice is not recommended.

b. Heat Source

A heat source sufficient to heat the condensate trap, including probe, to a temperature where the trap turns a "dull red" color. A system using an electric muffle-type furnace, electrical clamps for internal resistance heating, and a Bunsen burner is recommended.

c. Oxidation System

A system capable of oxidizing CH_4 with an efficiency of at least 95 percent.

d. Water Trap

Any leakproof moisture trap capable of removing moisture from the gas stream.

e. NDIR Detector

A detector capable of indicating CO_2 concentration in the 0 to 1 percent range. This detector is required for monitoring the progress of combustion of the organic from the condensate trap.

f. Flow Controller

Stainless steel needle valve or mass flow controller (MFC) required to maintain the cryogenic trap recovery system at a near constant gas flow.

g. Intermediate Collection Vessel

Stainless steel or aluminum collection vessel equipped with female quick-connect and a pressure-vacuum gauge (see h. below). Tanks with nominal volumes in the 1 to 4 liter range are recommended. Tank volumes must be calibrated to the nearest 10 ml, (see Section 3.9).

h. Pressure-Vacuum Gauge

The intermediate collection vessel is fitted with a gauge capable of measuring -1 to 0.5 atm.

i. Gas Direction Valve

Valve must be capable of switching flow through the condensate trap from a low-oxygen mixture to a high-oxygen mixture during sample recovery, without loss of sample or change of flow rate.

The above components are assembled as an entire sample recovery system. See Figures 25.1-6 and 25.1-7 for assembly.

3.1.3 Sample Analysis

a. Chromatograph

Must be capable of resolving CO, CH_4, and CO_2; separating them from the higher boiling organic compounds; and have backflush capability (see Section 3.2 Reagents for column types). Chromatograph must have the capacity to select between large and small sample loops.

b. Furnace

Capable of oxidizing CH_4, CO, and organic compounds to CO_2 with at least 95 percent efficiency.

c. Non-Dispersive Infrared (NDIR) Detector

Specific for CO_2.

d. Integrator

To sum area under backflush peaks, which cannot be measured using peak height.

e. Syringe

100 ml gas-tight.

f. Dewars Flask

Size sufficient to surround the chromatographic columns.

g. Flow Controller (Optional)

A flow controller capable of maintaining constant flow to the NDIR may be necessary.

3.2 Reagents

3.2.1 Sample Collection Train Preparation

a. Compressed nitrogen, 99.9 percent pure, with THC less than 1 ppm.

3.2.2 Sample Recovery

a. Compressed Nitrogen.

See Section 3.2.1.

b. Carrier Gas

Hydrocarbon-free air. THC less than 1 ppm.

c. Combustion Gas

Zero grade oxygen. 99.6 percent pure. THC less than 1 ppm.

d. Dry Ice

3.2.3 Sample Analysis

a. Carrier Gas

See Section 3.2.2 b.

b. Chromatographic Columns

The columns used for separating the various carbon compounds are set in series as follows:

(1) The initial column is a 1/8 in. OD column approximately 7 in. long packed with 10 percent silicone W-98 oil on Chromosorb W, 80 to 100 mesh.

(2) The second column is a 1/8 in. OD x 10 ft long column packed with Porapak Q, 100 to 200 mesh.

c. Dry Ice

d. 2-Propanol

99.9 percent 2-propanol is used with dry ice pellets in the ice bath.

e. Water Baths

Water baths at 0^{o}C (ice water), 20^{o}C (nominal-ambient), and 100^{o}C (boiling water) are required.

f. Calibration Gases

CO_2 in N_2 (approximately 2000 ppm, 6000 ppm, and 1 percent); CH_4 in N_2 (approximately 2000 ppm), calibrated against an NBS certified CO_2 standard (7 percent).

g. Combustion Gas

See Section 3.2.2 c.

3.3 Pretest Preparation

Before testing, assemble the required equipment and reagents to check readiness. All analytical, recovery, and sample equipment must be leak-free to produce reliable results. Sampling flow controllers must be flushed with clean air or nitrogen between test. Sample tanks and intermediate collection tanks must be evacuated and filled with nitrogen at least four times before final evacuation in order to flush residual hydrocarbons and CO_2 from the tanks. Condensate recovery module should be in the standby mode to reduce warm-up time.

3.4 Preparation of Sample Collection Train

Evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a manometer), then leak check the sample tank by isolating it from the vacuum pump and allowing the tank to sit for at least 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

Just prior to assembly, measure the tank vacuum using a manometer. Record this vacuum at this time. With the flow shutoff valve in the closed position, assemble the sampling system as shown in Figure 25.1-1.

3.5 Sample Recovery

3.5.1 Condensate Traps

Keep traps as pairs until analysis of the traps has begun. Immediately place the trap pairs in a cryogenic freezer until sample recovery can be completed.

3.5.2 Tanks

Allow the sampling tanks to equilibrate to room temperature; then, using a manometer, measure the pressure of each sample to the nearest 1 mm Hg. After recording the initial pressure of the bulb or tank, pressurize with 99.9 percent N_2 to a pressure between 860-910 mm Hg. Shut off pressure, wait until reading is stable, record the reading, and then seal container until ready for analysis.

3.6.2 Condensate Recovery

3.5.2.1 Condensate Recovery System Warm-Up

Approximately one hour is required for warm-up from standby conditions (see Section 3.6.2.4

for standby condition). Warm-up is as follows:

Turn on the trap heating furnace and set the control for 600^{o}C. Set the control for the oxidizer furnace to the 850^{o}C setting. Cover the bottom 5 in. of the water trap with dry ice pellets, and connect the outlet of the trap to the tubing leading to the post-burn rotameter.

Confirm that the supply gases are at 80 psig. Set the carrier flow at 80 ml/min, and set 0_2 flow at 20 ml/min. Leak check the carrier connection with soap and water solution and check to see that the post burn rotameter indicates a flow approximately equal to the sum of the individual gases.

3.5.2.2 Condensate Recovery System Blank

It is necessary to run a blank to determine how much CO_2 is obtained from contaminants bleeding from the condensate module plumbing or from leakage. The blank may be important for accurate analysis of outlet traps where very little organic matter is present.

The stepwise procedure for running a blank is as follows:

Connect an evacuated collection tank to the quick-fit connection. Confirm that the CO_2 vent valve is in the vent position and open the collection tank shutoff valve. An evacuated tank should give a reading of 30 in. vacuum on the condensate module vacuum gauge.

Place the CO_2 vent valve in the collect position and mark the collection start point on the NDIR recorder chart.

Approximately 5 minutes after starting, place the gas-directing valve in the decoke mode, that is, switch the oxygen flow from the oxidizer furnace to the trap. Ten minutes after start, return the gas-directing valve to the normal burn mode. At approximately 17 minutes after start of collection, the collection tank will be at atmospheric pressure. Stop collection at this time by placing the CO_2 vent valve in the vent position. The recording chart is used to determine mode changes and the end of sample collection.

Close the shutoff valve of the collection tank and disconnect the tank from the system. Pressurize the collection tank, read the pressure using a manometer to the nearest 1 mm Hg, and record the reading.

3.5.2.3 Condensate Sample Recovery

Whenever possible, traps should be processed in the following order: blank, outlet traps, and inlet traps. This sequence minimizes the risk of contaminating low concentration outlet traps or the blank with residual traces of organic material from very high concentration inlet traps.

CO_2 trapped inside a cold trap must be removed by stripping with carrier (reversed from normal sampling flow) while the cold trap is held at dry ice temperature. If the recorder does not indicate zero CO_2 after 4 minutes of stripping, it may be assumed that all the CO_2 reading indicated by the NDIR is caused by loss of sample from the cold trap. If collection is started after 4 minutes of stripping, sample loss will be insignificant.

Place the two traps in a Dewar flask and cover the bottom 6 inches with dry ice pellets.

Remove a pair of traps from the -80^{o}C freezer and remove the heat sink clamp from a pair of cold traps. Then connect the 1/8 in. probe arm (inlet side) of the cold trap to the 1/8 in. union on the metering valve. The cold trap which is still in dry ice is now being flushed with carrier gas directly into the recovery system. Leak check the trap connections and the 1/8 in. probe arm using soap and water leak detector, and check to see that the post-burn rotameter indicated a flow rate approximately equal to the sum of the oxygen and carrier gas flow rates (100 ml/min.).

If the carrier pressure gauge reads less than 6 psig at the normal carrier flow rate of 80 cc/min., throttle the metering valve until a steady pressure reading of 5 psig is obtained. If the carrier pressure is 6 psig or greater, the metering valve may be left open. Connect an evacuated collection tank. Open the collection tank shutoff valve. The condensate module vacuum gauge should give a reading of 30 inches.

Check the NDIR trace. The trace should show a peak as residual CO_2 is flushed from the trap. When the recorder trace reaches zero, or if 4 minutes of stripping has been completed, place the CO_2 vent valve in the collect position. This allows the trap to be flushed through the oxidizer and NDIR into the intermediate collection tank.

To begin volatilizing the trap contents, remove the trap from the dry ice and cautiously place it in the tube furnace.

Connect three heater clamps to the probe arm with two negative terminals at each end and the positive terminal in the center. Use a Bunsen burner to heat any cold spots beneath the clamps if necessary. Slowly increase the variable transformer setting until the probe arm is hot enough to char paper, but not yet glowing red.

The trap contents may volatilize rapidly, cause the system pressure to rise, and the NDIR output to rise to 100 percent full scale. If the pressure rises rapidly, remove the trap from the furnace and return it to a dry ice bath if necessary to control the volatization rate. Very volatile or combustible organics may begin to explode in the trap and create a "pinging" sound. Prevent this condition, as sample loss and system contamination may occur.

When the recorder trace nears the CO_2-free baseline on the strip chart recorder after the trap has been heated to furnace temperature, the volatile component has been removed. To remove carbon residue from the trap, switch the gas-directing valve to the "decoke position," which will direct high-oxygen gas through the trap itself. Reposition the electrical probe arm heater clamps to heat the tubing that was previously under the clamps. Using a burner, flame the unheated parts of the trap and the snubber union.

When the strip chart recorder again return to the CO_2-free baseline, return the gas-directing valve to the normal-burn mode. If at any point during the recovery the collection tank approaches ambient pressure before the NDIR indicates that combustion is complete, it must be quickly replaced with a new tank by closing the tank shutoff valve and connecting the sample line to the new tank, then opening the new tank. When the sample is completely collected, place the CO_2 vent valve in the vent position, close the collection tank shutoff valve, and remove the collection tank from the condensate module.

Turn off the electrical probe heater. Pressurize the collection tank. Read and record the pressure (P_f) of the collection tanks using a manometer accurate to the nearest 1 mm Hg.

3.5.2.4 Shutdown of the Condensate Module

Shutdown of the condensate module to a standby state saves warm-up time and equipment wear, and is appropriate when samples are being received on a frequent basis.

To shut down to a standby state, turn off the trap heating furnace and turn the oxidizing furnace to the 500^{o}C standby setting.

Clean out the water trap by removing it from the dry ice, disconnecting the tube at the outlet of the water trap, and heating it with a Bunsen burner to drive off the water.

Set the oxygen and carrier flow rates to the standby setting of 5 ml/min. Power must always go to flow controllers or they will revert to full open. If it becomes necessary to shut off the flow controllers power, the gas supply to the flow controllers must be shut off.

3.6 Sample Analysis

The summary of the instrument parameters for analysis can be found in Table 25.1-2.

3.6.1 Speciation of Tank Contents

Equilibrate each of the chromatographic columns (the silicone oil and Porapak Q column) in a dry ice/isopropyl alcohol bath (-80^{o}C). Set flow in the forward direction (i.e. from silicone oil to Porapak), and select the large loop for the initial conditions.

Inject a 50 ml sample into the sample port to flush the loop. Switch the loop valve to the position that flushes the sample into the columns. Under these analytical conditions, CO elutes before CH_4, and CO_2 is trapped on the Porapak column.

After seven minutes, or when all the CH_4 has eluted, immerse the Porapak column in room temperature water, and the silicone oil column in ice water. Under these conditions CO_2 will elute first; followed by ethylene, acetylene, and ethane. The ice water bath on the silicone column holds any higher-boiling organics on that column while releasing any residual CO_2 that may have been trapped.

When the lighter compounds have come off the column, set a boiling water ($100^{o}C$) bath on each column and immediately set the backflush valve to the backflush setting. Under these conditions the heavier compounds will elute off the silicone oil column. A copy of a typical chromatogram is shown in Figure 25.1-8.

If any of the individual compounds of the sample are greater than 1 percent equivalent CO_2, inject the sample again using the small loop.

If any of the individual compounds of the sample injected on the large loop show an area count of 5 percent equivalent CO_2, dilute the sample to less than 1 percent equivalent CO_2 on the small loop. Run each sample or its dilution in duplicate. Follow the sample injection with the appropriate standards as described in Section 3.9.

3.6.2 Recovered Condensate (CO_2)

The CO_2 that has been collected in the intermediate tanks from condensate recovery must be quantified. Bypass the columns, since speciation will not be necessary. Using the appropriate sample loops and dilutions as specified above, make replicate injections of each intermediate tank, followed by the appropriate standard as described in Section 3.9.

3.7 Calculations

3.7.1 Sample Tank

Concentrations of gaseous effluent components present in the gaseous phase are reported as concentrations of carbon in parts per million by volume (ppm v/v):

$$C_{sa} = \frac{C_{st} \times A_{sa} \times P_f}{A_{st} \times P_i} \times D$$

where:

C_{sa} = CO, CH_4, CO_2, or backflush concentration corresponding to peak being measured, ppm v/v

C_{st} = Concentration of CO, CH_4, or CO_2 in the standard, ppm v/v

A_{sa} = Area of charted response curve for the CO, CH_4, CO_2 or backflush sample in units identical to A_{st}

A_{st} = Area of charted response curve for the standard in units identical to A_{sa}

P_f = Final pressure to which the sample in the tank was pressurized, Torr

P_i = Initial pressure of the sample in the tank, as received after sample collection, Torr

D = Dilution factor

Peak height can be used instead of areas when the compound used in the calibrating mixture is the same as the compound being measured (i.e. CO, CH_4, CO_2). Since backflushes are almost always mixtures of several compounds, area must be used for calculations.

3.7.2 Condensate

The concentration of effluent components present in the condensate trap are reported as ppm v/v carbon:

$$C_{sa} = \frac{C_{st} \times A_{sa} \times P_f \times V_f}{A_{st} \times P_i \quad V_i} \times D$$

where the variables in addition to those described in Section 2.7.1 are:

V_i = Volume of the bulb, tank, or bag sample to which the trap was originally attached, ml

V_f = Volume of the tank in which the oxidized contents of the trap were collected, ml

A convenient laboratory worksheet is shown in Figure 25.1-9.

3.8 Calibrations

3.8.1 Tank Volume

Calibrate the tank or bulb volume by weighing it empty and full of water. Measure the temperature of the water by using a mercury-in-glass thermometer accurate to 0.1^{o}C. Calculate the volume according to the formula:

$$V = \frac{W1 - W2}{D_t}$$

where:

V = Volume of the tank or bulb, ml

W1-W2 = Weight of water, g

D_t = Density of water in g/ml at temperature t

Report the volume to the nearest 10 ml.

Under ordinary circumstances a density of 0.9971 is representive for water 25^{o}C. The uncalibrated volume of the connections on the tank side of the valve is estimated to be less than 10 ml and considered as negligible.

3.8.2 Gas Concentrations

Check the instrument response by injecting a check standard before performing any analyses. If the response is acceptable, proceed with sample tank and condensate analysis. Immediately calibrate each sample component against CO_2 standards that are within 5 percent of the sample peak areas when working in the non-linear range of the NDIR. (This must be determined beforehand.) Make a standard injection for every concentration. Follow the last sample analysis with replicate injections of the check standard. A drift of more than 10 percent invalidates the results and requires sample reanalysis.

3.9 Quality Control

3.9.1 Balances

Used to calibrate tank volumes.
Must be accurate and repeatable.

3.9.2 Gas Standards

Must be NBS traceable.

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4. Engineering Calculations

Calculate the mass emission rate using the form as shown in Figure 25.1-11.

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Table 25.1-1

TCA SAMPLING INTERVAL TABLE (ΔP SETTING FOR MINIHELIC)

TEMPERATURE (°F)

time - minutes

°F Min.	70	200	400	600	800	1000	1200	1400	1600
15	2.65	2.90							
20	2.20	2.45	2.70					ΔP	
25	1.90	2.15	2.30	2.70				MINIHELIC	
30	1.65	1.85	2.00	2.40	2.85			SETTINGS	
35	1.40	1.60	1.80	2.10	2.50	2.85		("H_2O)	
40	1.20	1.40	1.60	1.90	2.25	2.50	2.95		
45	1.05	1.25	1.40	1.70	2.00	2.25	2.60	3.00	
50	0.95	1.15	1.25	1.50	1.85	2.05	2.40	2.70	
55	0.85	1.05	1.15	1.35	1.65	1.85	2.15	2.45	2.80
60	0.80	0.95	1.05	1.25	1.55	1.70	2.00	2.30	2.55
65	0.70	0.85	0.95	1.15	1.40	1.60	1.90	2.15	2.40
70	0.65	0.80	0.90	1.05	1.30	1.50	1.75	2.00	2.25
75	0.60	0.75	0.80	1.00	1.25	1.40	1.65	1.90	2.15
80	0.55	0.65	0.75	0.90	1.15	1.30	1.55	1.80	2.05
85	0.50	0.60	0.70	0.85	1.10	1.25	1.50	1.75	1.95
90	0.50	0.55	0.65	0.80	1.05	1.25	1.50	1.65	1.90

TABLE 25.1-2

SUMMARY OF INSTRUMENT PARAMETERS: TCA/NDIR

Gas Module

Sample Loop Volume (ml): 1.5, 3.0

Analytical Columns: Grade 316 stainless steel tubing.
(1) 7 ft x 1/8 inch. OD, (2) 10 ft x 1/8 inch OD.

Partitioning Media: (1) 10% Silicone oil W-98 on 80-100 mesh
Chromosorb W; (2) 100-200 mesh Parapak O.

Carrier Gas: Air

Flow Rate: 80 ml/min

Pressure Upstream to Column (psig): 100

Column temperature (°C): -80, 0, -20 (ambient), 100, all isothermal.

Combustion Temperature (°C): 950

Detector: Non-Dispersive Infrared Radiation (NDIR),
3/8-in. dia. x 3/8-in. length cell.

Oxidizer: 30-40 Mesh Quartz in an 3/8 inch Inconel Tube.

Condensate Module

Carrier Gas: Air

Flow Rate (ml/min): 80

Combustion Gas: 36% oxygen, 64% nitrogen

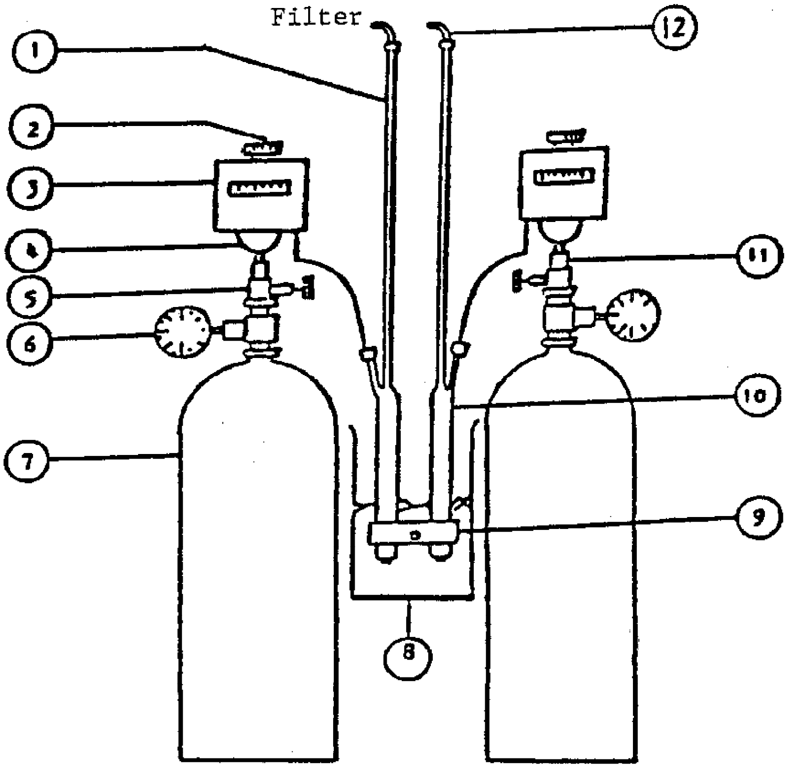
Flow Rate (ml/min): 20

Trap Heating Temperature (°C): -80 to 600 (dull red).

Combustion Temperature (°C): 850

Detector: Non-Dispersive Infrared Radiation,
3 3-in. dia. x 3/8-in. length cell.

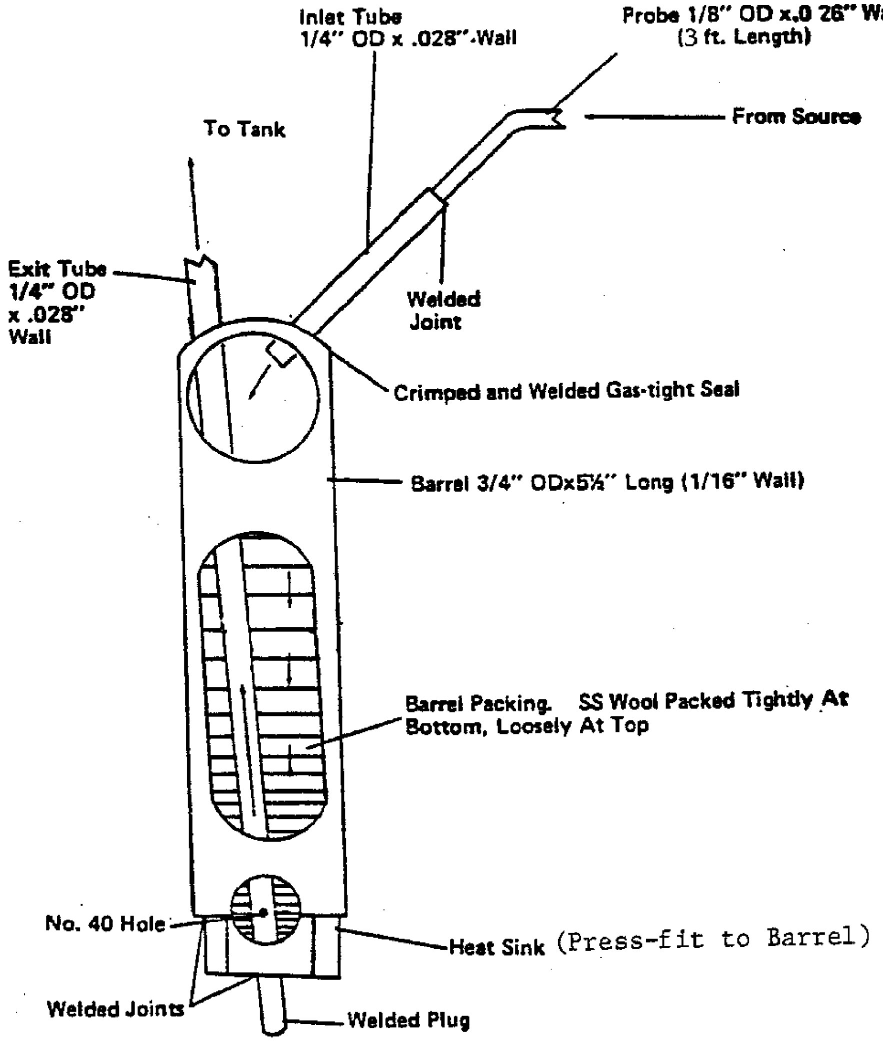
Oxidizer: 30-40 Mesh Quartz in an 1/4 inch Inconel Tube.



1. Sampling Probe
2. Flow Rate Control Valve
3. Minihelic Differential Pressure Gauge
4. Vacuum Regulator
5. Sample Flow Valve
6. Vacuum Gauge
7. Evacuated Tank
8. Condensate Trap Container
9. Heat Sink Clamp
10. Condensate Trap
11. Quick Disconnect
12. Flow Nozzle

Figure 25.1-1

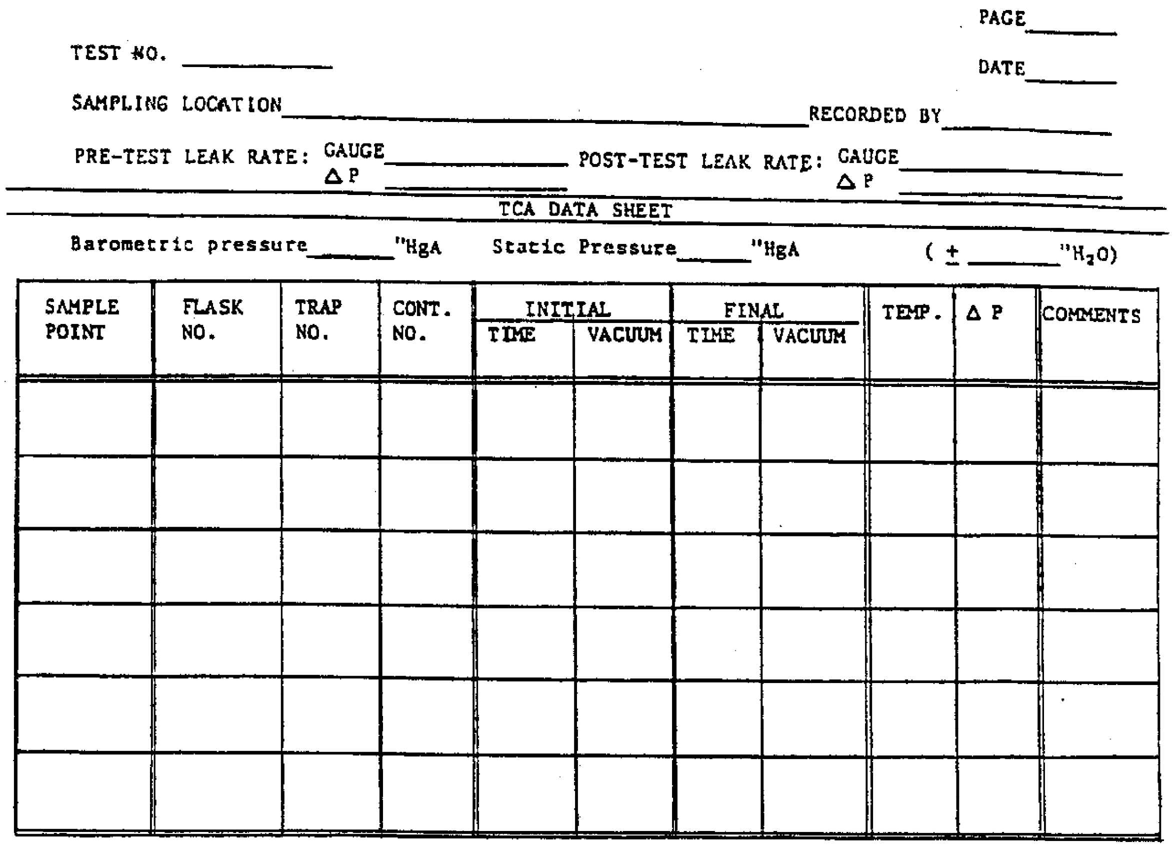
Sample Apparatus for Organics



Material: Type 316 Stainless Steel

Figure 25.1-2

Construction Details of Condensate Trap



PAGE ______

TEST NO. ______

DATE ______

SAMPLING LOCATION ______ RECORDED BY ______

PRE-TEST LEAK RATE: GAUGE ______ POST-TEST LEAK RATE: GAUGE ______

Δ P ______ Δ P ______

TCA DATA SHEET

Barometric pressure ______ "HgA Static Pressure ______ "HgA (± ______ "H_2O)

SAMPLE POINT	FLASK NO.	TRAP NO.	CONT. NO.	INITIAL		FINAL		TEMP.	Δ P	COMMENTS
				TIME	VACUUM	TIME	VACUUM			

Figure 25.1-3

TCA Data Sheet

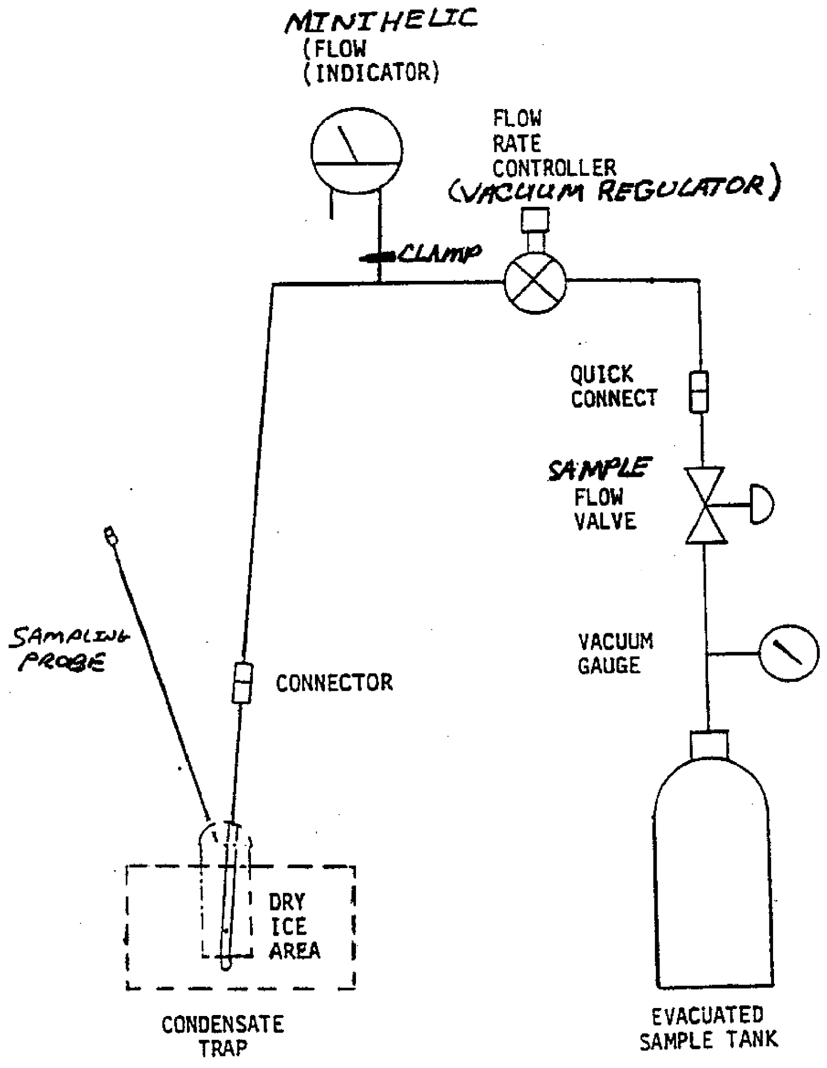


Figure 25.1-4

TCA Sampling Train Setup

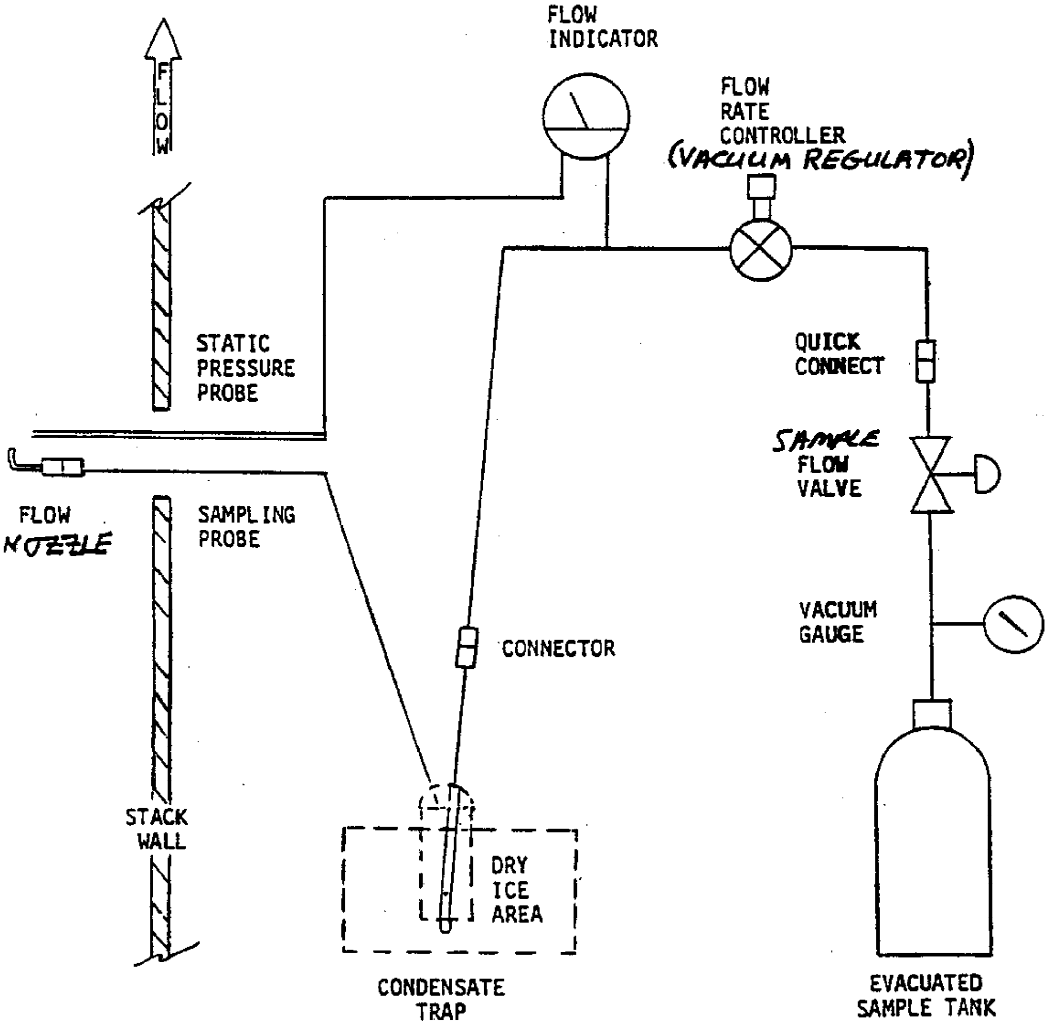
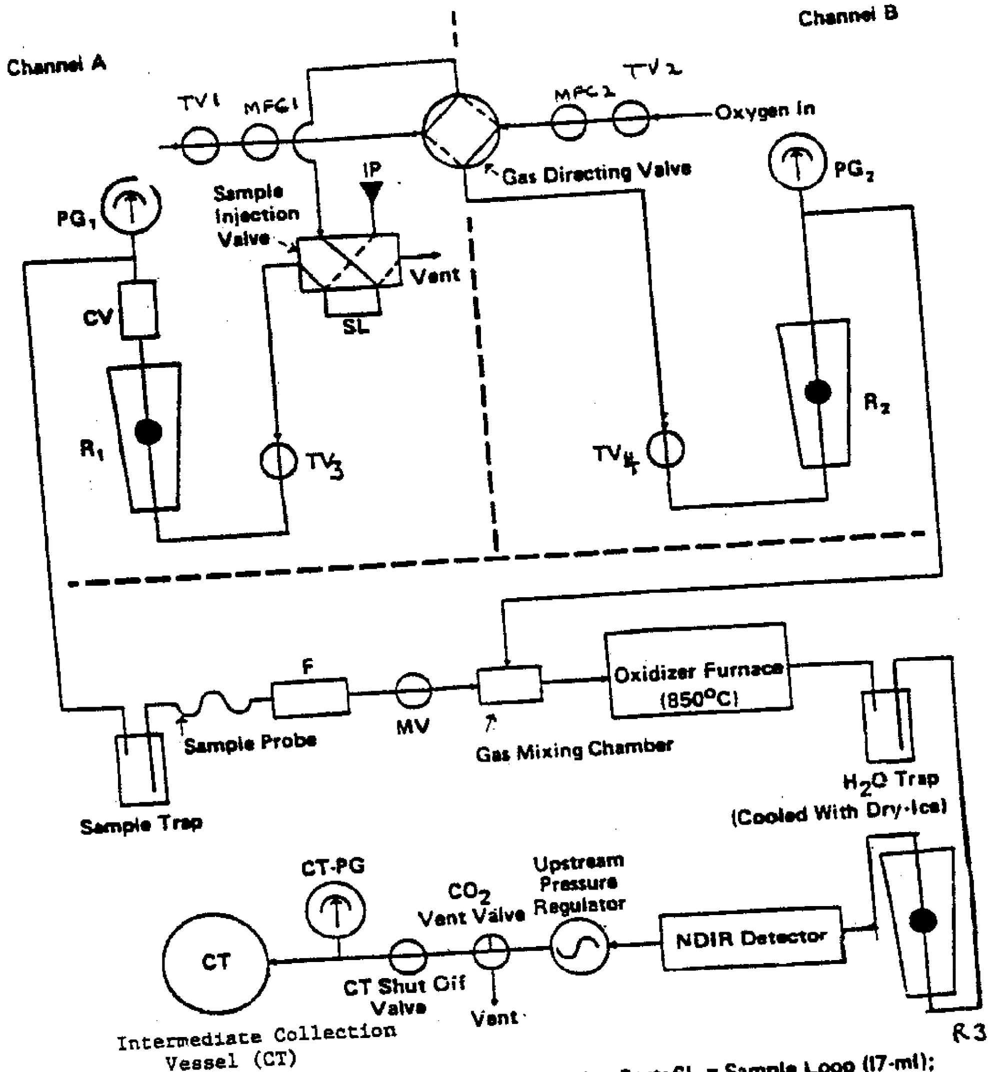


Figure 25.1-5

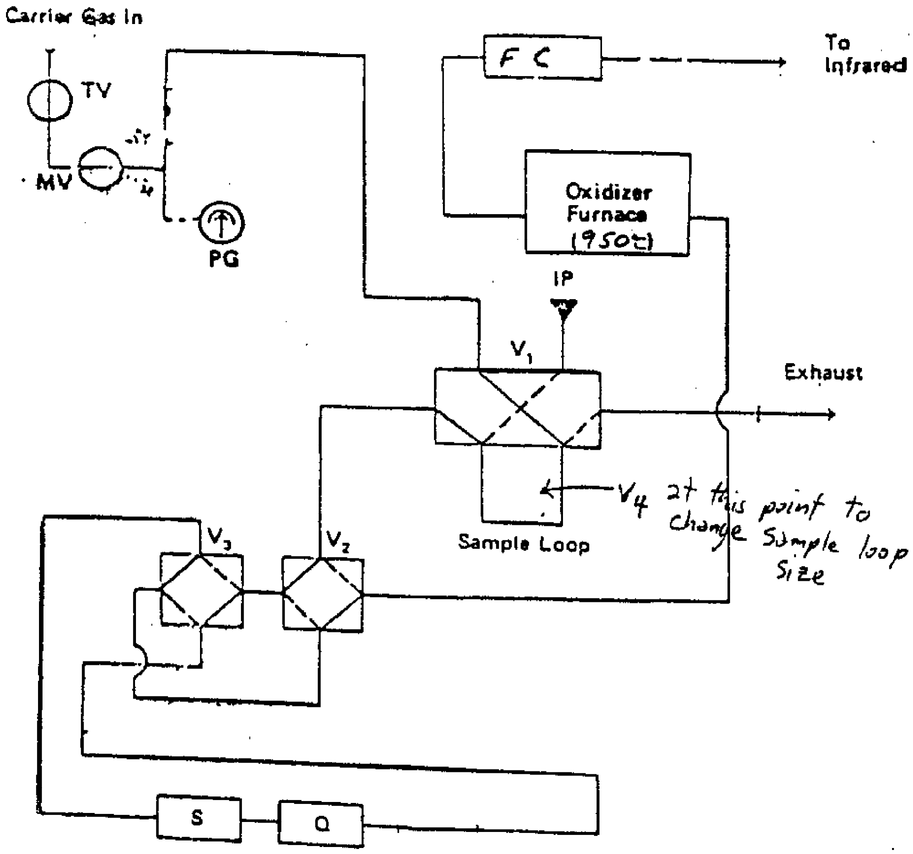
TCA Sampling Setup with Static Pressure Probe



LEGEND: PG = Pressure Gauge; IP = Injection Port; SL = Sample Loop (17-ml); CV = Check Valve; TV = Toggle Valve; MV = Metering Valve; R = Rotameter; CT = Collection Tank (2-liter); NDIR = Non-dispersive Infrared; F = 50-Micron Sintered Filter; — — = Channel Boundary; ——→ = Direction Of Flow.
MFC = MASS FLOW CONTROLLER

Figure 25.1-6

Fundamental Flow Layout of a Total Combustion Analysis Condensate (or Trap) Module for Processing the Trap Portion of an Emission Sample



LEGEND: IP = Injection Port; TV = Toggle Valve; MV = Metering Valve;
R = Rotameter; PG = Pressure Gauge; FC = Flow Controler
V_1 = Sample Injection Valve; V_2 = Column Bypass Valve;
V_3 = Column Flow Reverse Valve; S = Silicone
Oil W98 and Q = Porapak Q.

Figure 25.1-7

TCA Gas (or Chromatographic) Module Flow Diagram Shows Valves in Proper Position for Introducing Loop Sample in Forward Direction and Eluting Through Column to Analyzer

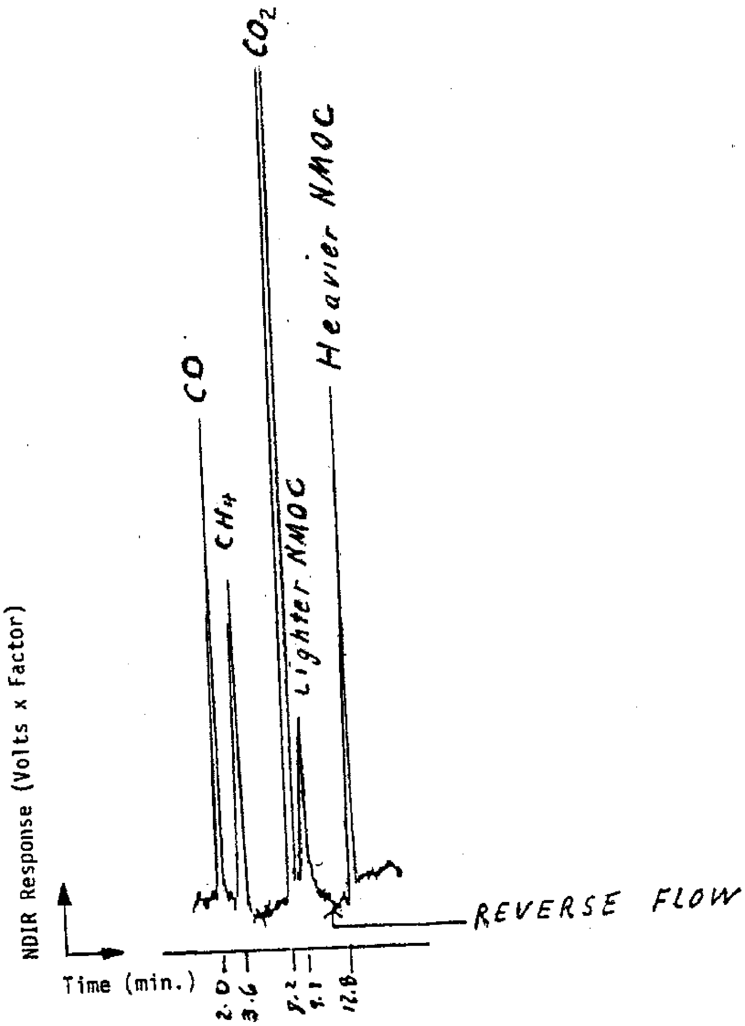
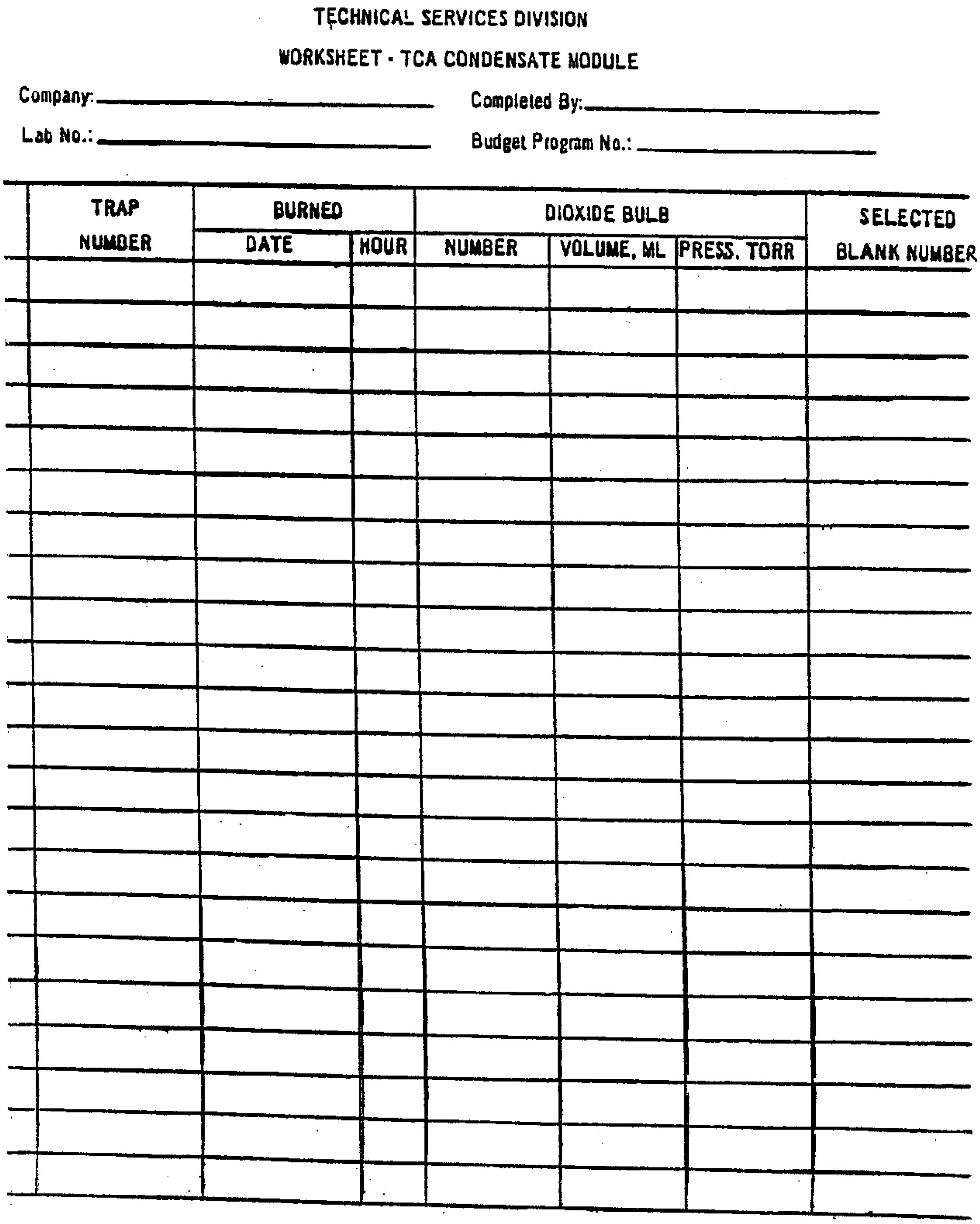


Figure 25.1-8

Typical Chromatogram: TCA/NDIR Gas Module



TECHNICAL SERVICES DIVISION

WORKSHEET - TCA CONDENSATE MODULE

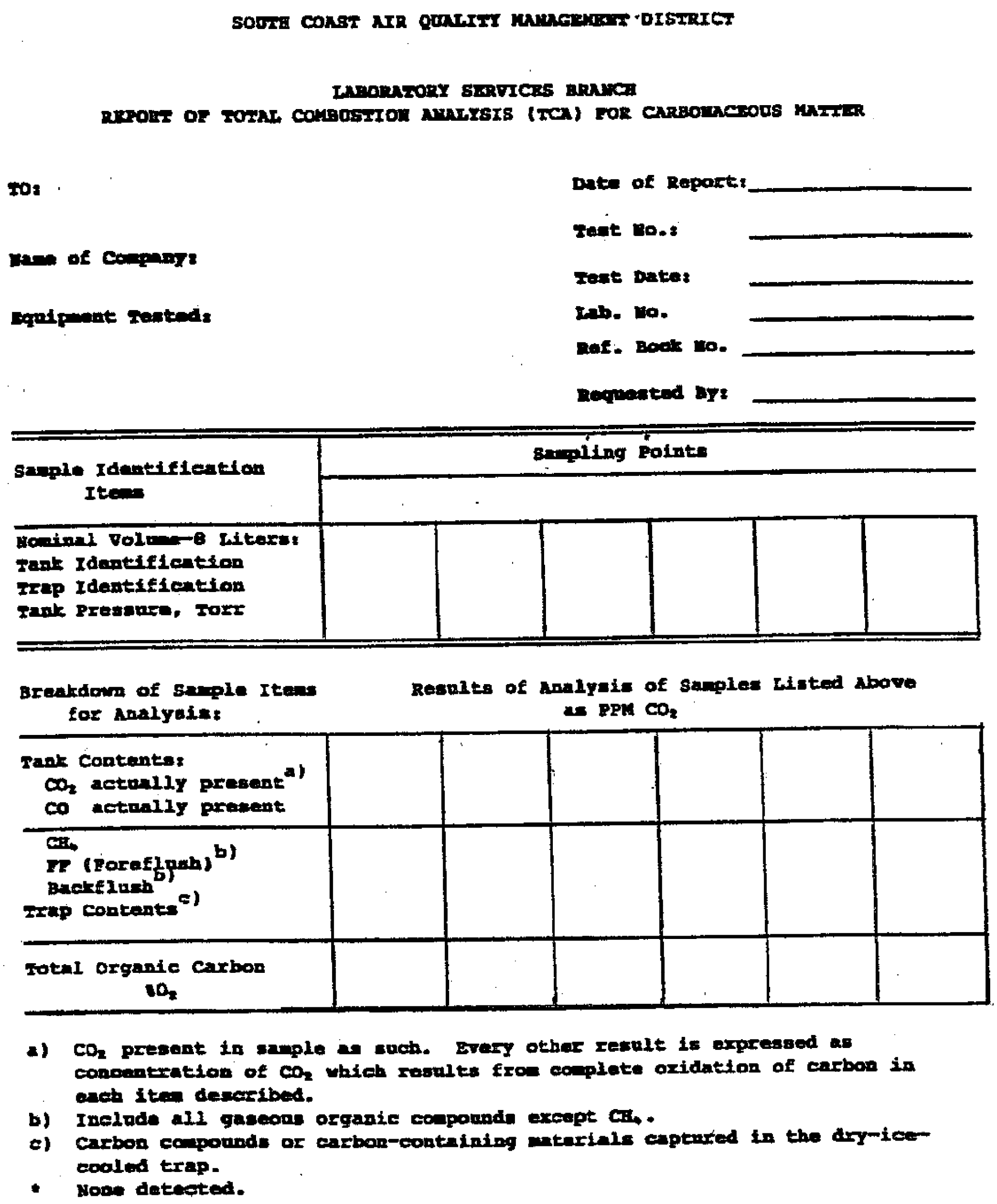
Company: ____________________ Completed By: ____________________

Lab No.: ____________________ Budget Program No.: ____________________

	TRAP NUMBER	BURNED		DIOXIDE BULB			SELECTED BLANK NUMBER
		DATE	HOUR	NUMBER	VOLUME, ML	PRESS. TORR	

Figure 25.1-9

Laboratory Worksheet



SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

LABORATORY SERVICES BRANCH
REPORT OF TOTAL COMBUSTION ANALYSIS (TCA) FOR CARBONACEOUS MATTER

TO:

Name of Company:

Equipment Tested:

Date of Report: ____________

Test No.: ____________

Test Date: ____________

Lab. No. ____________

Ref. Book No. ____________

Requested By: ____________

Sample Identification Items	Sampling Points					
Nominal Volume—8 Liters: Tank Identification Trap Identification Tank Pressure, Torr						

Breakdown of Sample Items for Analysis:	Results of Analysis of Samples Listed Above as PPM CO_2					
Tank Contents: CO_2 actually present[a)] CO actually present						
CH_4 FF (Foreflush)[b)] Backflush[b)] Trap Contents[c)]						
Total Organic Carbon %O_2						

a) CO_2 present in sample as such. Every other result is expressed as concentration of CO_2 which results from complete oxidation of carbon in each item described.
b) Include all gaseous organic compounds except CH_4.
c) Carbon compounds or carbon-containing materials captured in the dry-ice-cooled trap.
* None detected.

Figure 25.1-10

Laboratory Report Sheet

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Page______

Test No.____________ Date____________

Calculated By________

Sampling Location______________________________ Checked By________

ORGANIC FLOW RATE CALCULATIONS

NOTE: All concentrations in ppm volume as CO_2, dry basis, unless noted otherwise.

SAMPLE POINT	FLASK					TRAP	TOTAL ORGANICS		% O_2
	CO_2	CO	CH_4	FORE-FLUSH	BACK-FLUSH			LESS CH_4	
(Average)									
(Average)									
(Average)									

1. Gas Flow Rates: SAMPLE POINT FLOW

____________________ ____________________dscfm

____________________ ____________________dscfm

____________________ ____________________dscfm

2. Organic Flow Rates, as____________________:

SAMPLE POINT MASS FLOW RATE

__________ $= 1.583 \times 10^{-7}$x(____A/B)x(________ppm)x(__________dscfm) = __________lb/hr

__________ $= 1.583 \times 10^{-7}$x(____A/B)x(________ppm)x(__________dscfm) = __________lb/hr

__________ $= 1.583 \times 10^{-7}$x(____A/B)x(________ppm)x(__________dscfm) = __________lb/hr

(Where A = hydrocarbon molecular weight, and B = carbon number)

3. Efficiency of Control Device:

$$100 \times \left[1 - \left(\frac{\text{outlet mass flow}}{\text{inlet mass flow}}\right)\right] = 100 \times \left[1 - \left(\frac{\text{\_\_\_\_\_\_ lb/hr}}{\text{\_\_\_\_\_\_ lb/hr}}\right)\right] = \text{\_\_\_\_\_\_\_\_\_\_}\%$$

Figure 25.1-11

Emission Calculation Sheet

METHOD 25.1

DETERMINATION OF CARBON MONOXIDE, METHANE, AND TOTAL NON-METHANE ORGANIC COMPOUNDS AT LOW CONCENTRATIONS BY TOTAL COMBUSTION ANALYSIS (TCA/FID)

Section 5 of 5

5. **Alternative Laboratory Procedures**

5.1 Apparatus

5.1.1 Sample Collection Train Preparation

For sampling apparatus refer to Section 3.1.1.

5.1.2 Sample Recovery

a. Gas Pressurization System

b. Manometer

Capable of measuring pressure to the nearest 1 mm Hg in the 1 to 900 mm range. Manometer must be NIST traceable.

5.1.3 Sample Analysis

The NMO analyzer is a GC with back flush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. TGNMO sampling equipment can be constructed from commercially available components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

The NMO analyzer is a semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from NMO compounds, (2) oxidizing the NMO to CO_2, and CO to CO_2, and (3) reducing the CO_2 to CH_4 and quantifying as CH_4. See Figure 25.1-12 for a flow chart of the instrument. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement. The analyzer consists of the following major components:

a. Oxidation Catalyst

A catalyst system capable of oxidizing CH_4 to CO_2 with at least 95 percent efficiency is acceptable.

b. Reduction Catalyst

A catalyst system capable of reducing CO_2 to CH_4 with at least 95 percent efficiency is acceptable.

c. Separation Column(s)

Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds. (See Section 5.2 for column types).

d. Sample Injection System

A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer. (A2 ml loop is recommended.)

e. FID with a linear response (± 5 percent) over the operating range of 0.5 to 500 ppm C_3H_8.

f. Data Recording System

Digital integration system compatible with the FID for permanently recording the analytical results.

g. Syringe

Gas tight syringe, 30 ml.

h. Dewars

Size sufficient to surround the chromatographic column.

5.2 Reagents

5.2.1 Sample Collection Train Equipment Preparation

See Section 3.2.1.

5.2.2 Sample Analysis

a. Oxidation Catalyst

Hopcalite (MSA Part No. 41566) is satisfactory. Pack 6 in. of granular Hopcalite in the center of a 12 in. x 1/4 in. Inconel tube. Plug both ends with quartz wool.

b. Reduction Catalyst

Finely divided nickel on 60 to 80 mesh firebrick substrata, is satisfactory.

Prepare by dissolving nickel nitrate in deionized water. Stir ten times (by weight) as much firebrick 40 to 60 mesh into solution. Heat to dryness in an oven at 200^{o}F. Pack the center of a 12 in. x 1/4 in. Inconel tube with 6 in. of this catalyst. Plug both ends with quartz wool.

c. Carrier Gas

Helium, chromatographic grade.

d. Hydrogen, Reagent Grade

For reduction of CO_2 and FID fuel.

e. Air, USP Breathing Grade

For FID combustion.

f. Column Packing

1-1/2 ft. x 1/8 in. of 10 percent SE 30 on Chromosorb W 80 to 100 mesh, and 4-1/2 ft. x 1/8 in. of Porapak Q 80 to 100 mesh. Column may be made symmetric by adding another 1-1/2 ft. of S E30 on Chromosorb W at the other end of the column.

g. Calibration Gas

50 ppm CO, 50 ppm CH_4, 25 ppm ethane, 10 ppm isopentane in nitrogen, and other separate standards as required.

h. Water Baths

Water baths at 0°C (ice water), 20°C (nominal-ambient) and 100°C (boiling water) are required.

5.3 Pretest Preparation

See Section 3.3.

5.4 Preparation of Sample Collection Train

See Section 3.4.

5.5 Sample Recovery

See Section 3.5.2 (Tanks).

5.6 Sample Analysis

Set instrument parameters as follows:
Detector : 250°C
Oxidation catalyst : 650°C
Reduction catalyst : 350°C
10 port valve oven : 150°C
Heated transfer lines : 105°C
Gas flow rates

Carrier : Helium, 25 ml/min

Air : 180 ml/min
Hydrogen : 24 ml/min

Reproduce exactly the timing of valve switching and column temperature changes for each blank, sample, and standard run in a series. Analyze low concentration samples before high concentration samples. Prior to sample analysis, determine system background for non-methane hydrocarbons by injecting pure (99.999 percent) nitrogen into the system and following the timing sequence as for an actual sample. Table 25.1-3 shows a listing of the timing sequence.

Figure 25.1-13 shows where the step number appears on a plot of response vs. time. Step one establishes the $0^{o}C$ column temperature required for separation of CO, CO_2, CH_4, and non-methane hydrocarbons. Step two injects the sample and switches carrier flow in the forward direction. (See Figure 25.1-14.) Step three allows CO_2 to be eluted quickly from the columns. Switching the sample injection valve and immersing the column into boiling water for Step 4 reverses carrier flow direction and elutes NMO as a back-flush peak. Detector output for the back-flush peak is sent to a where a response vs. time curve is plotted and the area under the backflush peak is integrated.

Since NMO are a mixture, this back-flush peak may not be symmetrical; however, the area under a response vs. time curve is due to the presence of methane and is proportional to the amount of carbon present in the sample.

5.7 Calculations

Methane, carbon monoxide, and total NMO are quantified by integrating a response vs. time curve from a sample and comparing areas with a standard gas within the linear range of the instrument.

$$H = \frac{C_{std} \times R_{spl} - R_B}{R_{std} - R_B}$$

where:

H = Component as ppm methane equivalent

C_{std} = Concentration of standard as ppm methane equivalent

R_{spl} = Response from sample (area)

R_{std} = Response from standard (area)

R_B = Response from blank (area)

TABLE 25.1-3

COLUMN TEMPERATURE PROGRAM

Step No.	Time	Position	Description
1	0 min	2	Immerse the analytical column in ice water.
2	2 min	1	With ten port valve in position 2 flush sample loop with 20 ml of sample. Inject 2 ml of sample, standard, or blank N_2 by switching the 10 port valve to position 1.
3	4 min	1	Immerse column in room temperature water.
4	8.5 mi	2	Remove the room temperature water bath from the analytical column. Switch the 10-port valve to position 2, and immediately immerse the analytical column in boiling water.

5	12 min	2	Remove the boiling water bath and immerse the analytical column in ice water, beginning the sequence again at Step 1 and time zero.

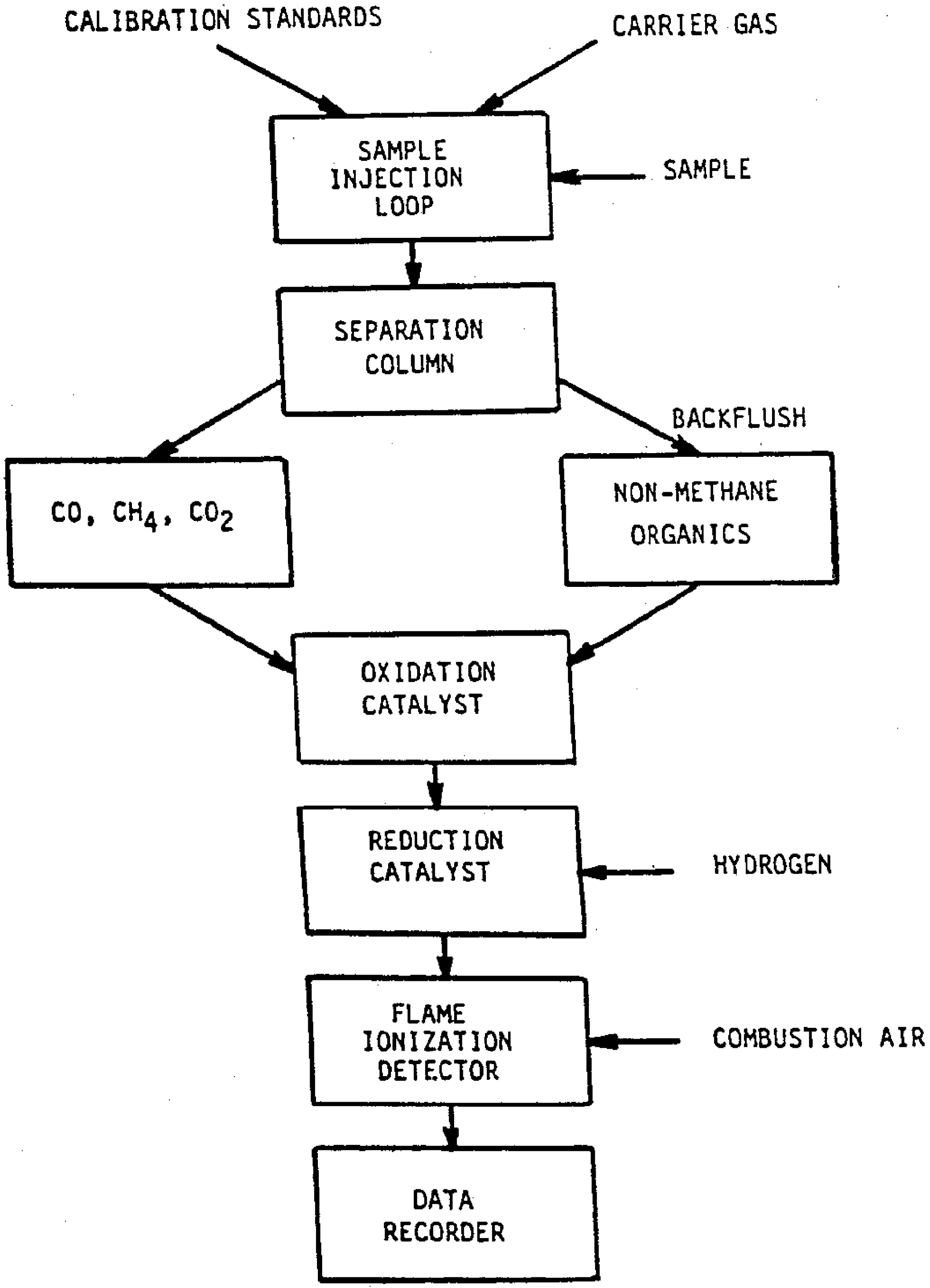


Figure 25.1-12 Flow Diagram TCA/FID

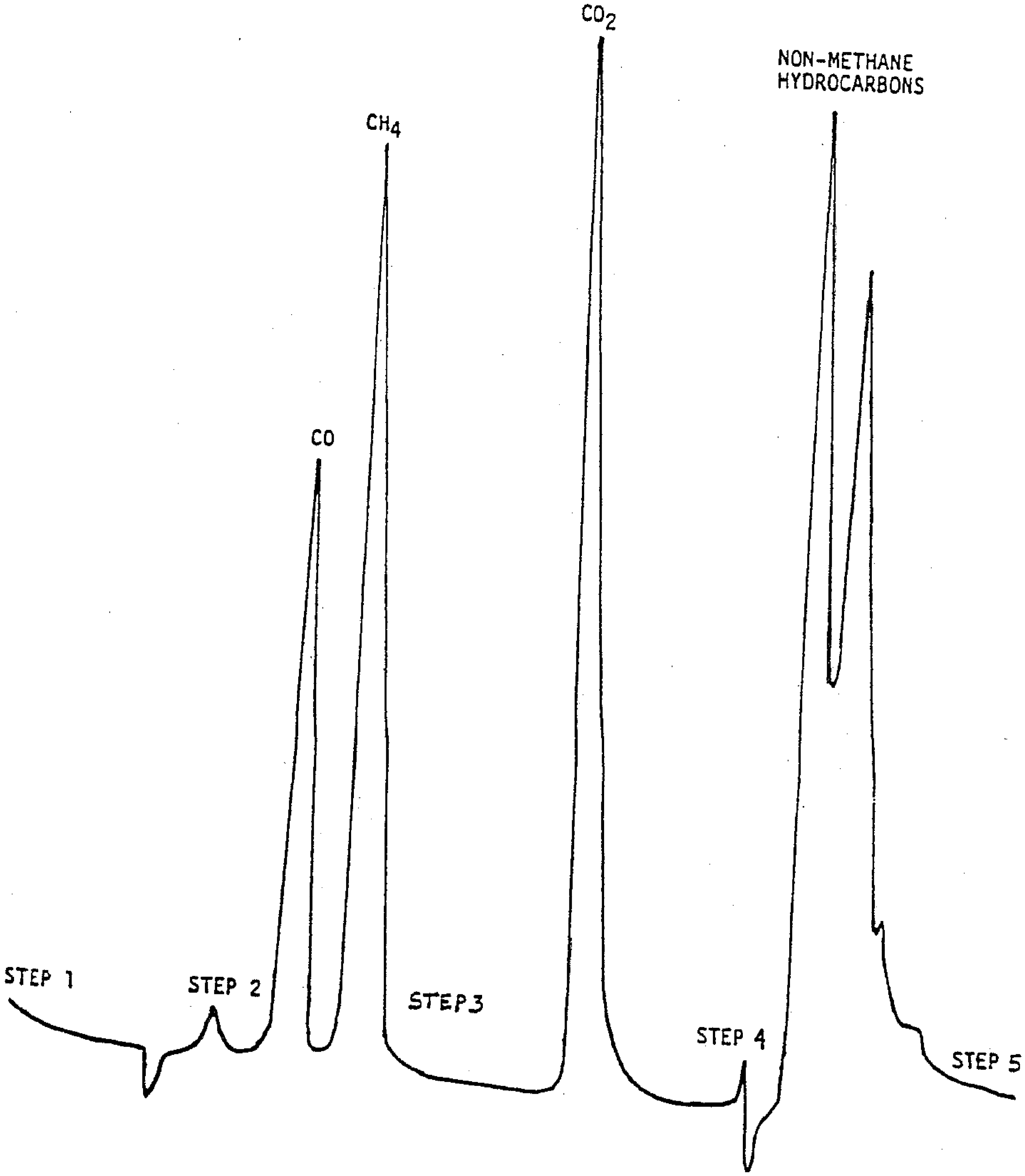


Figure 25.1-13 Analytical Chromatogram TCA/FID

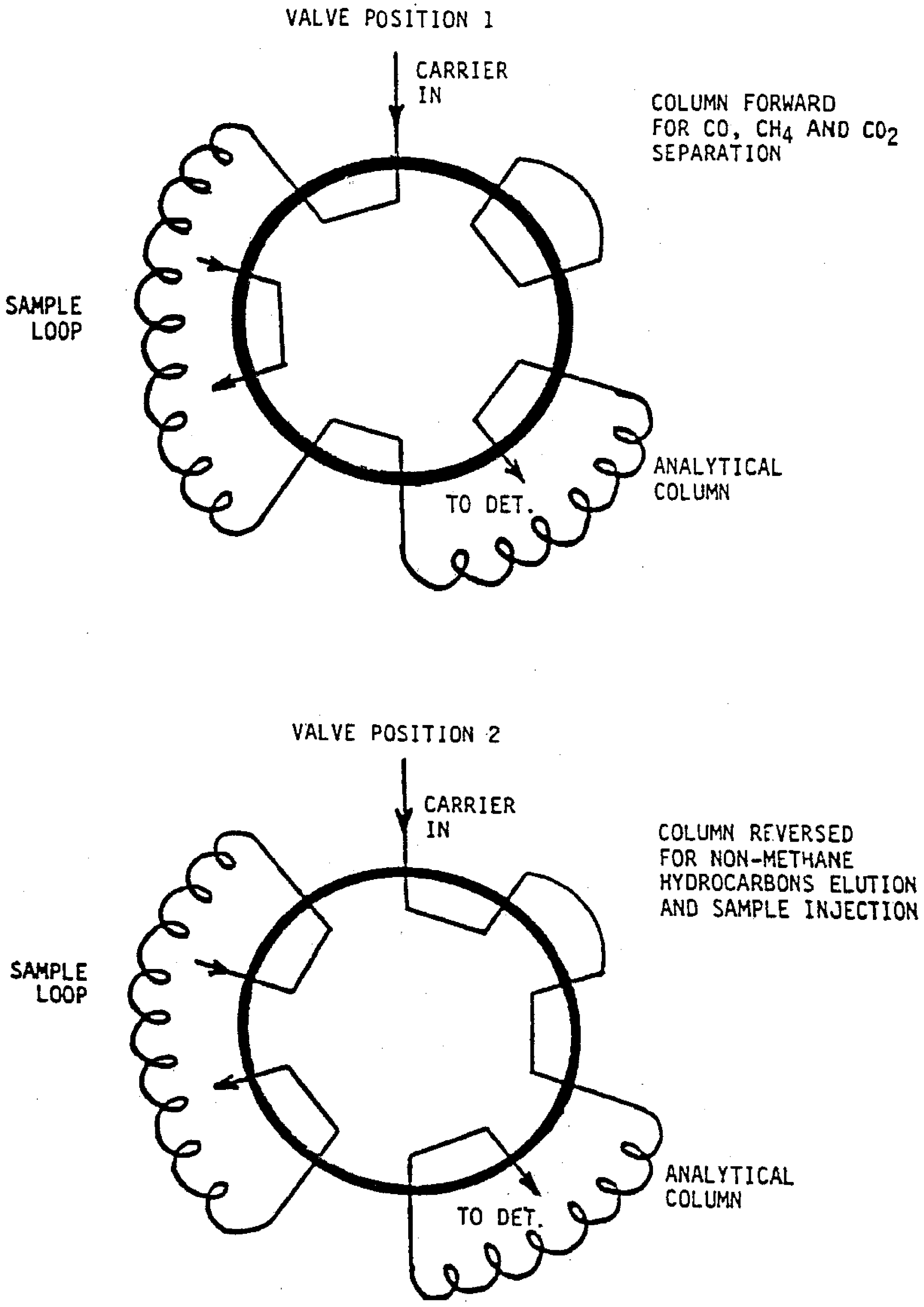


Figure 25.1-14 10-Port Valve. TCA/FID