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AN IMPROVED LIGHT HYDROCARBON ANALYSIS SYSTEM.(U)
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Gas calibration methods	Dry ice-acetone baths	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A system for extracting and measuring ambient levels of C_1-C_4 hydrocarbons and carbon monoxide (CO) in seawater is described. The analytical instrument is a gas chromatograph with flame ionization detectors that incorporates a catalytic conversion of CO to CH_4 (methane). The samples are concentrated prior to introduction to the chromatographic system. The volatile hydrocarbons are extracted from the seawater by the use of a helium flow stream and concentrated on dry ice-acetone cold traps. Air samples can be processed in a similar way.

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AN IMPROVED LIGHT HYDROCARBON ANALYSIS SYSTEM

INTRODUCTION

This report describes in detail the procedures and equipment used to measure ambient C_1-C_4 hydrocarbons and carbon monoxide (CO) in seawater and in samples of clean air. The analysis procedures and apparatus are modeled after that used by Swinnerton et al. [1-4]. The improvements to the system were in the areas of calibration, air sampling, and chromatographic columns.

The original calibration method used gas-saturated water (analyzed using the existing system) to determine the calibration factor. This method was laborious and susceptible to operator error due to sample transfer with a syringe. The modification included using gas standards introduced directly to the system via valves with changeable volume calibration loops.

The air sampling component was modified so that a fixed volume loop was used to admit the sample into the analysis system rather than variable volume glass sampling flasks. The air sampling component was constructed so that samples could be introduced into the system by either continuous pumping or by an air sampling flask.

The chromatographic column for the C_2-C_4 hydrocarbons analysis was improved by changing the percentage of column loading and increasing the rate of the temperature increase in the column oven. The percentage of Nujol loading on the alumina support was increased from 5% to 10% until quantitative separation between the saturated and unsaturated hydrocarbons was achieved.

The system comprises several components as shown schematically in block diagram in Fig. 1. The system is designed to analyze both water and air samples. Two modes of calibration are included in the system: (1) a *quick* calibration; (2) sample procedure calibration.

Since the hydrocarbons in question are present in nl/L quantities (10^{-9} liter of gas/liter of H_2O), and since this removal from seawater is not instantaneous (the gas chromatographic column requires introduction of the sample as a very small coherent addition), concentration of the sample is necessary. In regard to air samples, the low concentration of CO (0.2 part per million by volume (ppmv)) also

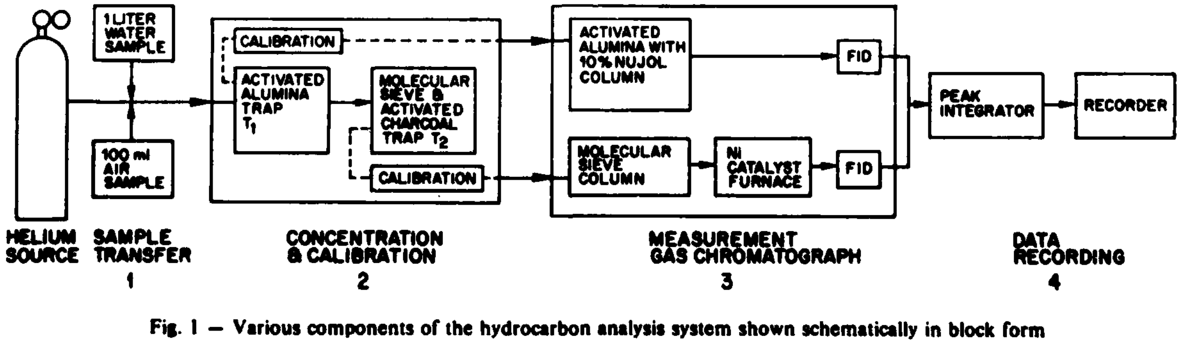

Fig. 1 — Various components of the hydrocarbon analysis system shown schematically in block form

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Manuscript submitted February 11, 1982.

necessitates concentration before introduction to the gas chromatograph. The concentration is accomplished by using two cold traps (−77°C) in series. The gas chromatographic output is fed into an electronic integrator which calculates the total area under the peaks and prints the data on paper tape. The processed signal is then sent to a 1-mV strip chart recorder.

SAMPLE TRANSFER AND EXTRACTION

Figure 2 shows in detail the flow pattern for this system. Water samples are collected in 1.2-l glass bottles with ground-glass stoppers. The bottle is attached to a transfer tee (upper right-hand portion of Fig. 2) where He overpressure is applied above the water. A 1-liter water sample is transferred from the bottom of the sample bottle to the purging chamber via a stainless steel tube in the transfer tee. Prior to filling, the purging chamber is drained to a residual level of 400 ml while an excess of He is passed through it to ensure a *clean* atmosphere and *clean* H_2O in the chamber. This residual *clean* H_2O acts as a *cap* to the sample which is added at the bottom of the chamber (just above the glass frit). The *cap* prevents the sample gases from diffusing into the He atmosphere above the water. It takes approximately 4 to 5 minutes to completely transfer the H_2O sample. The pressure in the sample bottle is released before purging of the sample begins.

There are two valves which control the flow of He to the extraction chamber. One, H_2O drain valve, is a coarse adjustment valve which allows a large amount of He to flow into the chamber to facilitate the draining of the chamber in a reasonable time and maintains a positive pressure of He in the system to prevent contamination by air. The second valve is a needle valve and is in series with a stainless steel toggle valve. They are used to control the flow of He through the glass frit during the extraction procedure. The glass frit at the bottom of the extraction chamber, through which the He must pass, has a medium porosity which produces finely dispersed bubbles in the 25 to 50-μm range.

Air samples are passed through a 100-ml loop which is connected to a 6-way Perkin-Elmer valve located in the main He line for the purging and trapping procedure. The air sample can be introduced into the loop by either a continuous pumping system or by an air sampling flask in which the sample has been collected and returned to the laboratory.

Once the air sample has been isolated, the valve is turned so as to direct the He flow through the sampling loop and to the 3- and 4-way valves shown in Fig. 2. The 4-way valve either directs the sample to exhaust or to the 3-way valve, where it can be transferred to the concentrating traps or to bypass and vented off. The gases purged from the seawater sample follow the same basic pathway. In this case, the 4-way valve would be turned to accept the flow coming from the extraction chamber rather than from the air sampling loop.

CONCENTRATION AND CALIBRATION

A flow rate of 60 ml/min of He is used both to purge the gases of interest from the seawater and to transfer the air sample to the concentrating traps, T_1 and T_2. Prior to sample transfer, the T_1 and T_2 traps are cooled to −77°C in a dry ice-acetone bath. The 3-way valve is turned to the trap position which directs the flow of He either from the purging chamber or air sampling loop to the traps. This mode of operation is maintained for 10 minutes to allow for the quantitative removal of the C_1-C_4 hydrocarbons from the water sample. The traps are then isolated by closure of the appropriate toggle valves, and the 3-way valve is turned to bypass. Next, the traps are individually heated for 1 minute at 90° C and sequentially backflushed into the gas chromatograph for analysis.

Trap T_1 concentrates CO_2 and the hydrocarbons heavier than CH_4. CH_4, CO, and air pass through to the T_2 trap which concentrates the CH_4 and CO while allowing the major atmospheric gases to pass through. Each cold trap is made of a stainless steel tube approximately 30 cm long × 3 mm ID formed into a U-tube approximately 14 cm long. T_1 is filled with activated alumina, 42/60 mesh, while T_2 is a

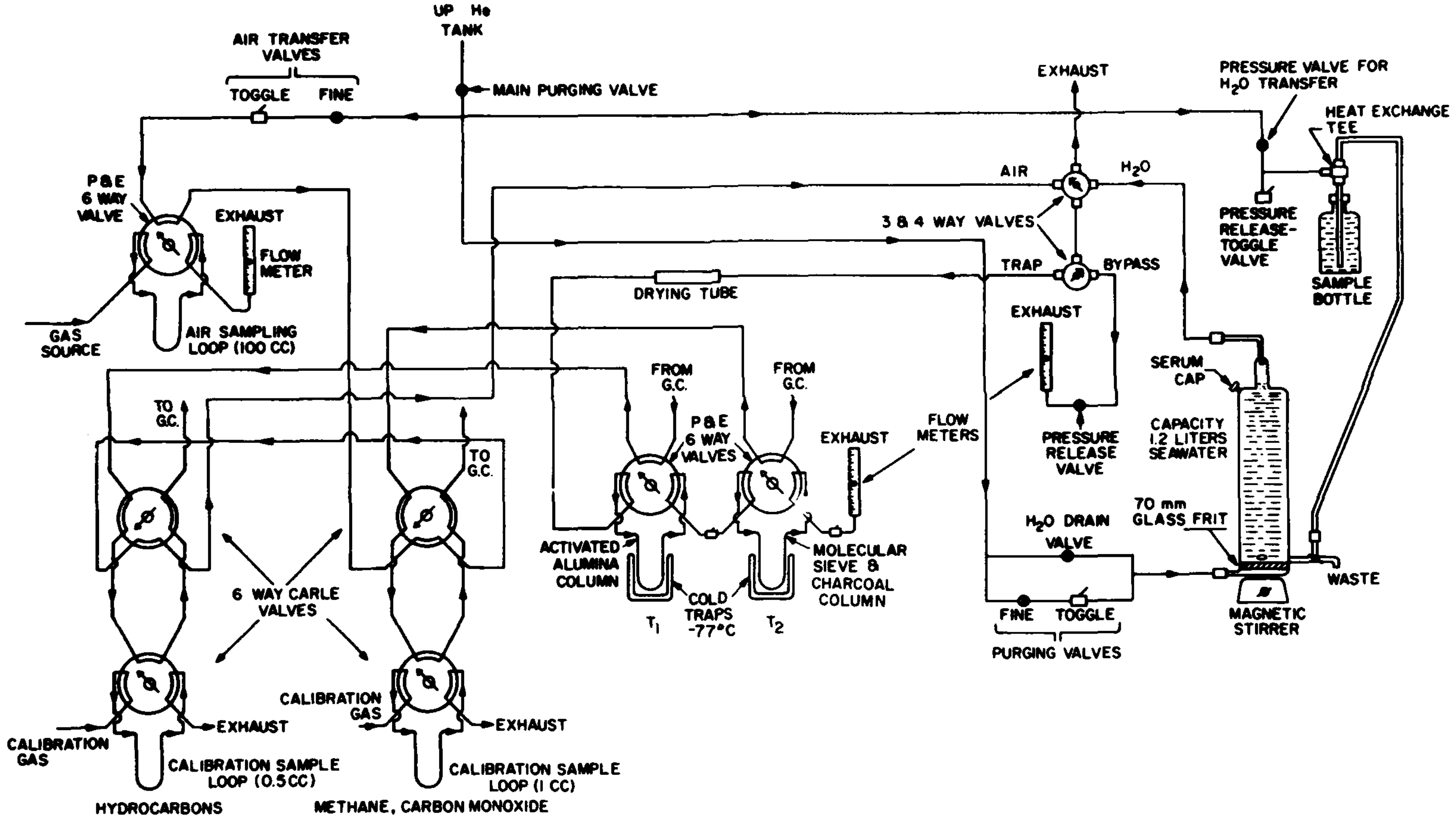


Fig. 2 — Flow pattern for hydrocarbon analysis system

mixture of 1/4 by weight activated, 30/60 mesh charcoal and 3/4 5A molecular sieve, 42/60 mesh. Prior to the traps, there is a glass drying tube which is approximately 10 cm × 1 cm OD and is filled with magnesium perchlorate, $Mg(ClO_4)_2$.

As stated previously, there are two modes of calibration: a quick mode and a sample mode. Figures 3 and 4 demonstrate these modes for calibrating both of the flame ionization detectors (FID) in the gas chromatograph. Also, the sample mode can check the integrity of the traps (i.e., retaining the sample during purging and quantitative release of sample upon heating). Figure 3 shows those valves used to calibrate the "B" side of the gas chromatograph. The "B" side separates and determines the concentrations of CH_4 and CO in the sample. Figure 4 shows those valves used to calibrate the "A" side of the gas chromatograph which analyzes hydrocarbons heavier than CH_4.

As demonstrated in Figs. 3 and 4, the quick calibration consists of directly injecting the calibration sample into the gas chromatograph for analysis. The sample mode treats the calibration sample as if it were an air sample and subjects it to all the rigors inherent in the system. Calibrations can also be made via the main air sampling loop. In this instance, only a trap calibration can be run and the calibration gas must approximate the concentrations found in the air sample.

Commercial gas standards in the 1 to 10-ppmv range are now available in aluminum tanks, and they are stable over long periods of time. Previously, low concentrations of the calibration gases were unstable in steel cylinders, making it necessary to work with a much higher concentration. The small calibration loops (0.5 ml, 1 ml) are used when calibration concentrations are in the 1- to 10-ppmv range.

MEASUREMENT

A Varian Model 1700 gas chromatograph, with dual FID and with two columns in parallel, is used for the analyses. Any good gas chromatograph equipped with FIDs could be used. Helium from a second tank transports the sample from the traps to the chromatograph for analysis.

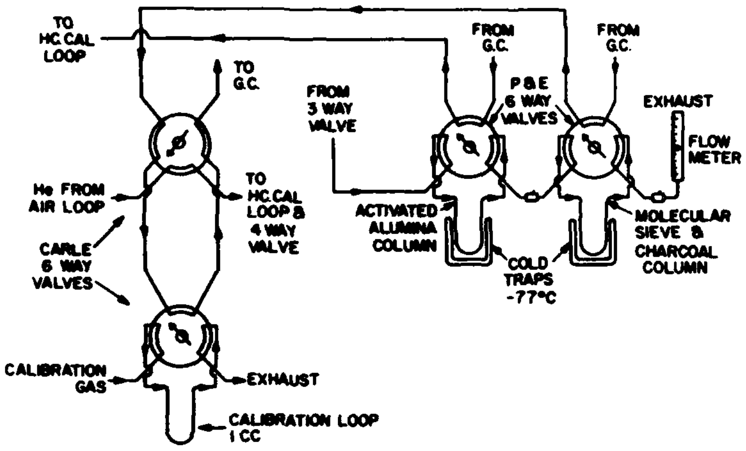
The T_1 trap is connected to the "A" side of the chromatograph. The column for this analysis consists of a 1.5 m × 3 mm ID aluminum tube filled with 10% Nujol on activated, 42/60 mesh alumina. When the sample (containing hydrocarbons heavier than CH_4) has been backflushed off trap T_1 and onto the column, the temperature-programmed oven is heated from 25° to 80°C at a rate of 15°/min and maintained at the upper temperature until the analysis is completed. The analysis time is about 10 minutes.

The T_2 trap is connected to the "B" side of the chromatograph. Here the column consists of a 1.5 m × 3 mm ID aluminum tube filled with 5A molecular sieve, 42/60 mesh. The sample from the column passes into a special nickel catalyst tube which reduces the CO to CH_4 just before the FID. The nickel catalyst used for these analyses [5] is supported on 30-60 mesh Silocel firebrick packed into a 10 cm × 3 mm ID length of stainless steel tubing. The molecular sieve column is not temperature programmed. The analysis time for this column is approximately 7 to 8 minutes.

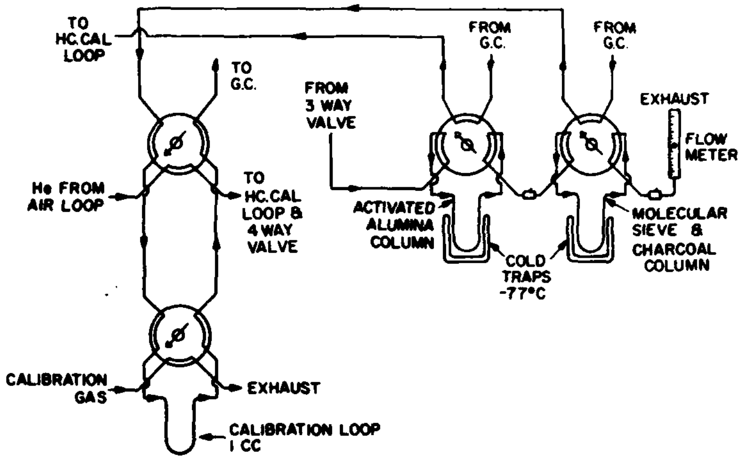
DATA REDUCTION

The data from the gas chromatograph are channeled to a Columbia Scientific Instruments integrator; the processed signal is then sent to a 1-mV strip chart recorder. Peak areas are computed by the integrator and printed on paper tape along with the time for maximum peak height. Standards of known concentrations are analyzed and the peak area for each individual component is computed. A calibration factor is obtained which can be updated conveniently during analysis by use of the *quick* calibration techniques.

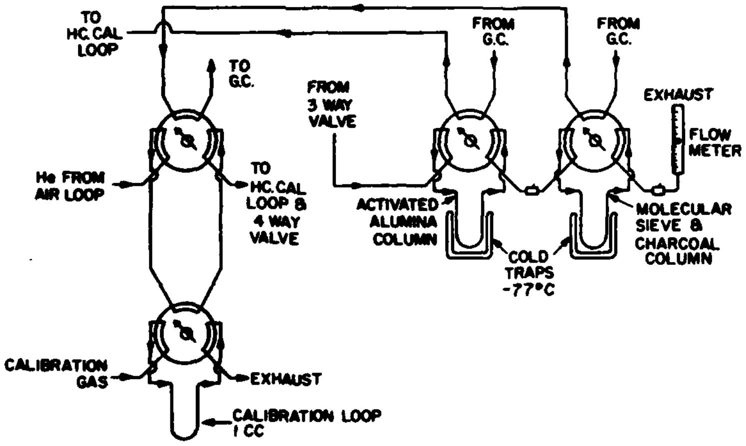
① He FROM G.C. VIA MOLECULAR SIEVE TRAP; BYPASSING CALIBRATION LOOP AND TRAPPING SYSTEM



② He FROM G.C. VIA MOLECULAR SIEVE TRAP INCORPORATING CALIBRATION LOOP AND INJECTING INTO G.C.



③ INCORPORATING He FROM AIR LOOP AS MAIN CARRIER GAS AND PROCEEDING TO TRAPPING SYSTEM WHILE BYPASSING CALIBRATION LOOP



④ INCORPORATE CALIBRATION LOOP INTO TRAPPING SYSTEM WITH He FROM AIR LOOP AS MAIN CARRIER

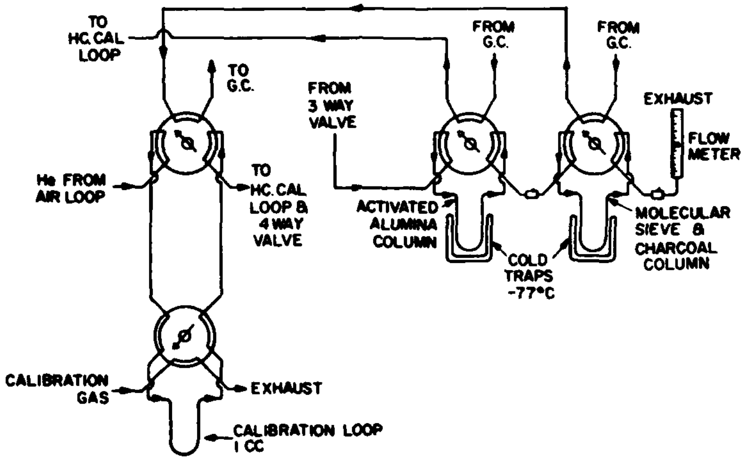
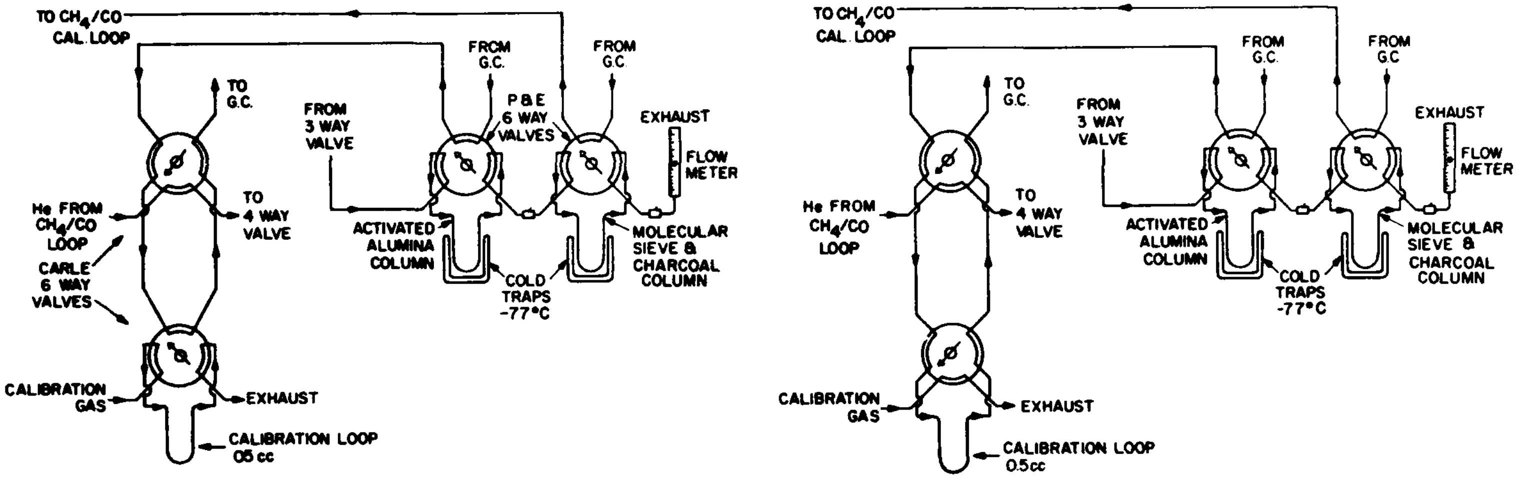


Fig. 3 — Various calibration modes for T_2 trap (CH_4/CO)

① He FROM G.C. VIA ACTIVATED ALUMINA TRAP; BYPASSING CALIBRATION LOOP AND TRAPPING SYSTEM

② He FROM G.C. VIA ACTIVATED ALUMINA TRAP INCORPORATING CALIBRATION LOOP AND INJECTING INTO G.C.



③ INCORPORATING He FROM AIR LOOP AS MAIN CARRIER GAS AND PROCEEDING TO TRAPPING SYSTEM WHILE BYPASSING CALIBRATION LOOP

④ INCORPORATE CALIBRATION LOOP INTO TRAPPING SYSTEM WITH He FROM AIR LOOP AS MAIN CARRIER

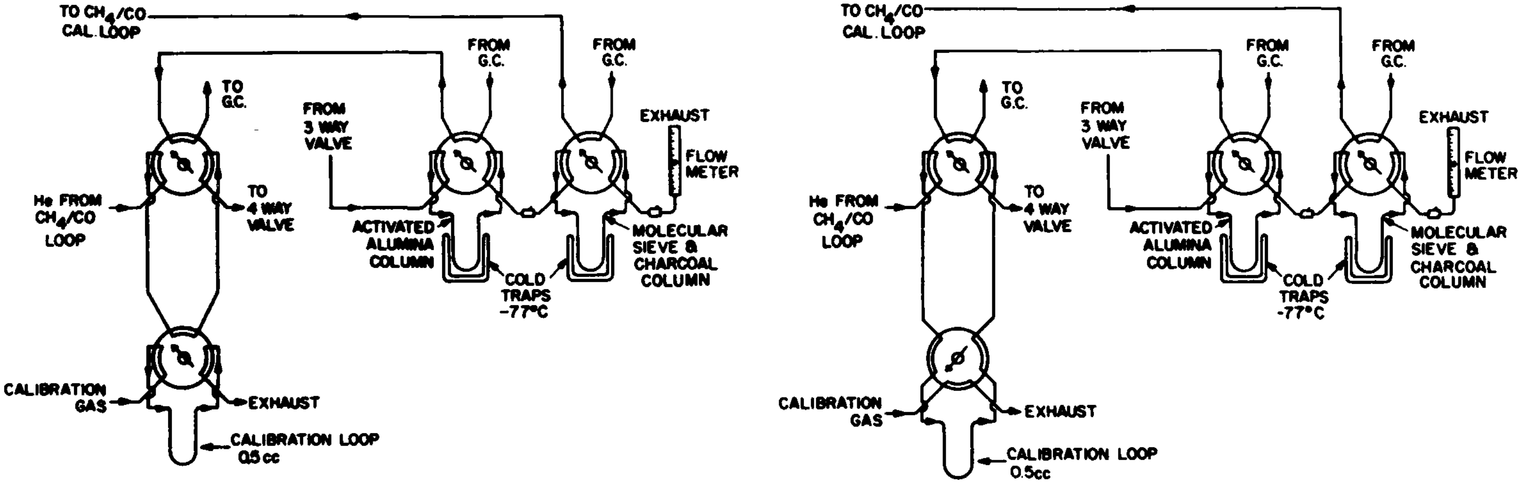


Fig. 4 — Various calibration modes for T_1 trap (hydrocarbons heavier than CH_4)

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