GAS CHROMATOGRAPHIC MEASUREMENT OF HYDROGEN, METHANE, AND NEON IN AIR

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SUMMARY

A gas chromatographic method for methane and hydrogen analysis using a 5A molecular sieve column and a radio frequency discharge glow detector is described. The method allows the detection of 0.003 p.p.m. H_2, 0.02 p.p.m. CH_4, and 0.4 p.p.m. Ne in an air sample of 5 cc. With repeated comparison to a standard the accuracy for natural concentrations of these gases in the troposphere is ± 3 %.

INTRODUCTION

Hydrogen and methane are present in the atmosphere as trace constituents. Earlier measurements[1] gave an average H_2 content in surface air of 0.5 p.p.m. (parts per million by volume); spectroscopic measurements of CH_4 gave an atmospheric average of 1.5 p.p.m.[2]. CH_4 and presumably also H_2 are produced at the earth's surface mainly from biogenic sources. A significant amount of tropospheric H_2 could also be produced during the destruction of CH_4, thus coupling the CH_4 and H_2 cycles. Present estimates give lifetimes of a few years for both gases[3,4] which indicates that the main cycle of production and destruction must take place within the troposphere. However, small fractions of the gases are mixed into the stratosphere where they are eventually oxidized to H_2O and CO_2. The stratospheric phases of the H_2 and CH_4 cycles are particularly interesting because they may contribute about 50% of the water vapor in the upper stratosphere and enter significantly into the water and ozone chemistry at these altitudes.

When the trace gas program was initiated at NCAR in 1964, emphasis was placed upon the study of stratospheric H_2 and CH_4 concentrations and upon their simultaneous measurement. This aim, and the fact that both concentrations are as low as 0.2 p.p.m., presented some difficulties. A detection system with extreme sensitivity and low contamination was required. Fortunately, the required dynamic range was small, since the natural range of the H_2 and CH_4 mixing ratio is narrow. The system finally chosen was a gas chromatograph with a radio frequency glow discharge detector (RF detector).

Gas chromatography (GC) offered the additional advantages of requiring only small amounts of air (5 cc per run) and allowing measurement of the neon concentration as well. Since Ne is uniformly mixed below 100 km altitude, its measurement can be used to determine whether the sampling procedures are free of fractionation, an important aspect of high-altitude sampling.

Since one run with the gas chromatograph requires about 20 min, the sampling rate is one sample in 20 min and there is no advantage in flying a gas chromatograph aboard a balloon or aircraft. Samples were collected in evacuated stainless-steel cans (with a collection time of about 1 min) and analyzed in the laboratory.

The following sections briefly outline the precautions to be taken in the construction of sample containers and discuss in more detail the GC analysis developed to obtain accurate and reliable measurements of atmospheric H_2 and CH_4 concentrations.

MATERIALS AND METHODS

Sample containers

Selection of a material and the construction of the sample containers posed some problems since most materials give off small amounts of H_2 and CH_4.

Stainless steel, which has otherwise attractive properties and was finally used, first appeared to be a poor choice because it releases copious amounts of H_2 (ref. 5). For example, our standard 4-l sample container, freshly fabricated and untreated, added 0.2 p.p.m. of H_2 to the sample of 660 Torr in one week. This corresponds to a release rate of 2×10^{12} H_2 molecules/cm² day. A series of experiments showed, however, that baking in air at 350° for 24 h effectively suppresses the release of H_2. The formation of an oxide layer at the surface appears to be the responsible mechanism, because the same baking sequence in vacuum, reduced but did not eliminate the release of H_2. It has been argued that the thin oxide layer acts as a barrier to the diffusion of gas from the bulk material[6,7]. Another explanation might be that the oxidized surface prevents the recombination of the H-atoms dissolved in the steel and thus prevents the release of H_2 gas from the surface.

Fabrication of the stainless-steel containers was relatively simple. Pairs of commercially available beakers were welded together. Prior to welding, the inner surfaces of the beakers were smoothed and cleaned by electropolishing. The containers were then baked in air at 350° for 24 h. Finally the vacuum valves, Whitey valves type IVM4 S4, proved to be satisfactory, were fitted to adapters which were welded on the top plates. Our standard containers had a volume of 4 l. Table I shows the results of repeated measurements of a sample kept in a container for two years with no increase in H_2 concentration.

Gas chromatograph

The gas chromatograph was designed to be a simple and rugged instrument, suitable for field use; Fig. 1 depicts it schematically. The inlet system consists of a sample injection valve (7 port model from Mikrotek Instruments) and a 5 cc loop, both made of stainless steel. The sample pressure usually 600 Torr, is measured with a 1000 Torr capacitance manometer (MKS Instruments, Inc.), a small-volume instrument with an accuracy of 0.1 %. The sample temperature (close to 25°) is

TABLE I

REPEATED ANALYSIS OF A SAMPLE OF SURFACE AIR

The sample has been collected in Boulder, Colo., 19 August 1969, to check accuracy and reproducibility of the method.

Date of run	H_2 (p.p.m.)[a]	CH_4 (p.p.m.)[a]
19 August 1969	0.56 ± 0.01	1.05 ± 0.02
20 August 1969	0.56 ± 0.01	1.05 ± 0.02
14 October 1969	0.56 ± 0.01	1.06 ± 0.01
22 January 1970	0.57 ± 0.01	1.06 ± 0.01
16 April 1970	0.56 ± 0.01	1.07 ± 0.02
13 July 1970	0.55 ± 0.02	1.06 ± 0.01
17 November 1970	0.56 ± 0.01	1.05 ± 0.02
8 April 1971[b]	0.56 ± 0.01	1.00 ± 0.03
10 August 1971[b]	0.59 ± 0.01	1.06 ± 0.02
Average[c]		
	0.56 ± 0.01	1.05 ± 0.02

[a] Errors are the mean standard variations from four alternate comparisons of sample and standard.
[b] In 1971 samples were compared to a different working standard.
[c] Errors are the standard deviations calculated from the scatter of the individual analyses.
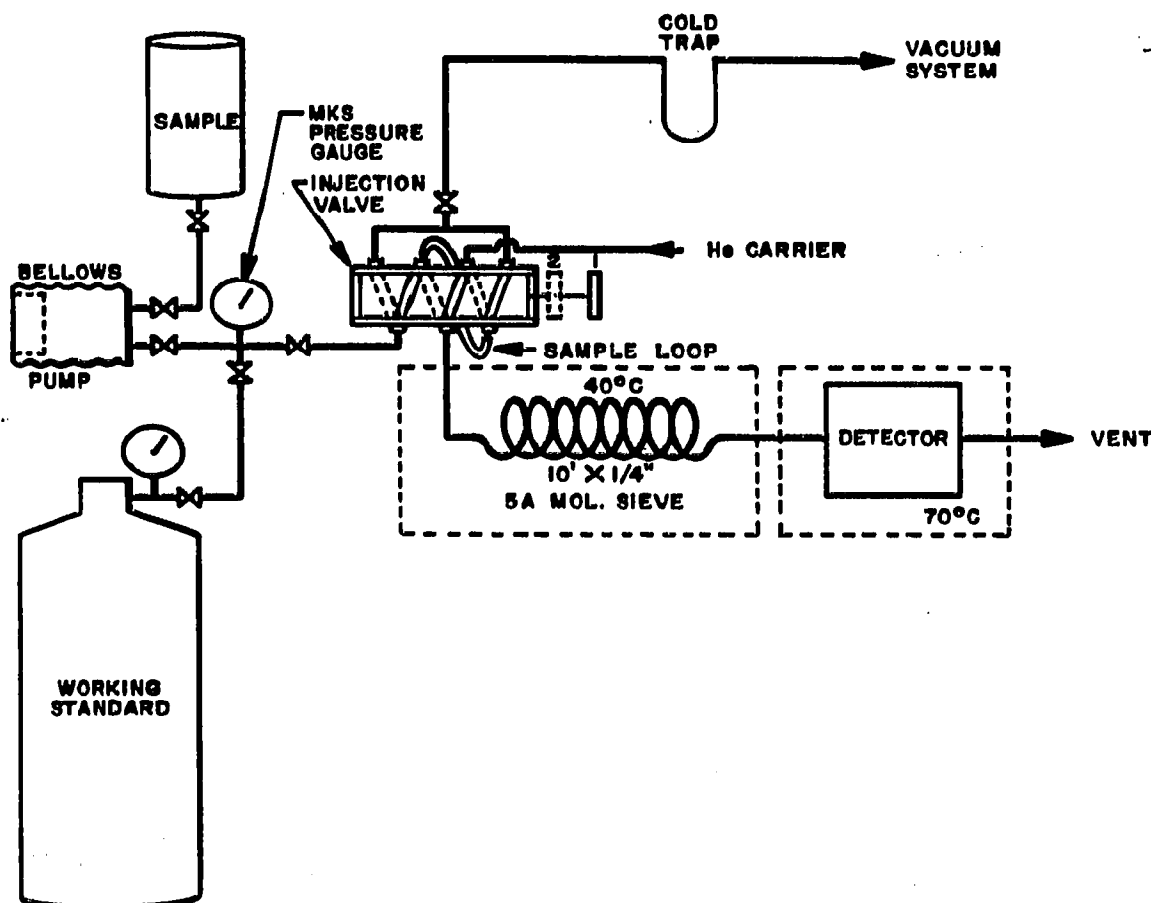

Fig. 1. Schematic arrangement of the gas chromatograph. The ovens housing the column and the detector are outlined by dashed boxes. The two positions of the sample injection valve are indicated by the full and dashed connections. The sample loop has a 5 cc volume.

read from a bi-metal thermometer attached to the sample loop. The tank containing the standard gas mixture is attached directly to the inlet manifold. The sample containers are connected by a swagelok fitting. A bellows-sealed piston pump is used if the low-pressure samples from high altitudes must be compressed to the working pressure of 600 Torr. Nesting bellows and an internal plunger to take up the dead volume when compressed give the pump a compression ratio of 60:1. Thus three strokes of the hand-operated pump are sufficient to attain a pressure of 600 Torr in the loop even when the sample pressure is as low as 10 Torr. (A toepler pump was found unsatisfactory, because it released sufficient amounts of H_2 to contaminate the low-pressure samples from the highest altitudes). All parts of the inlet system are made of stainless steel and are baked in air as described previously.

The 10 ft. $\times$ 1/4 in. molecular sieve column, Linde 5A (60–80 mesh), is operated at 40°. It is preconditioned by heating at 150° for 8 h while purging with dry helium or nitrogen. Helium (grade A from U.S. Bureau of Mines) with an inlet pressure of 30 p.s.i.g. and a flow rate of 100 cc STP/min is used as a carrier gas. No purification of the helium is required; however the tanks are not depleted below a pressure of 500 p.s.i. At the end of every third working day the column is heated to 150° for 30 min to release the CO_2 and water vapor adsorbed from the samples; their accumulation causes a slow degradation of the column's resolution and thus a reduction
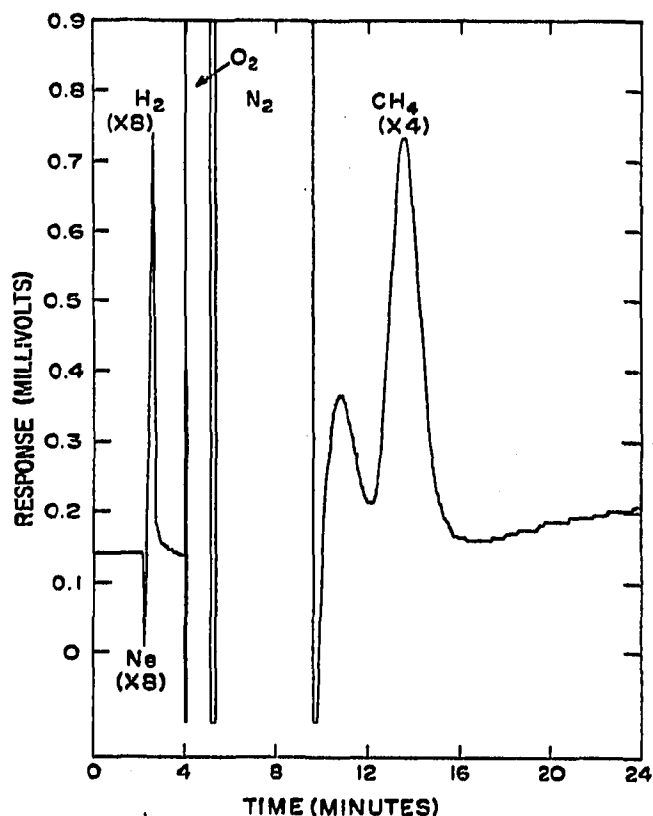

Fig. 2. Chromatogram of the working standard: 500 Torr laboratory air with 0.48 p.p.m. H_2, 2.02 p.p.m. CH_4 and 18.18 p.p.m. Ne. The sequence of elution is Ne, H_2, O_2, N_2, CH_4. The recorder's full scale deflection is 1 mV. The (negative) Ne and the H_2 peak are 8 times attenuated, the CH_4 peak 4 times. The O_2 and N_2 concentrations are so high that they overload and completely quench the discharge in the detector. Inversion peaks occur at the beginning and end of the overload.

in peak height. The resolution of the column and the elution times can be read from the chromatogram in Fig. 2.

The eluting Ne, H_2, and CH_4 peaks are measured with a radio frequency glow discharge detector manufactured by American Instrument Co.; details are described by HAMPTON[9]. The signals are recorded by a Honeywell 1-mV recorder (block diagrams are also given by HAMPTON).

Detector

The detector was chosen for its sensitivity to H_2, Ne, and CH_4. It has the disadvantage that its response depends on a number of parameters besides the partial pressures of the trace gases, which makes it difficult to keep the detector sensitivity constant. One factor which poses a problem, especially for the detection of CH_4, is the input of RF power. The peak heights depend strongly and in a complicated fashion on the RF power applied, the dependence being different for each gas[8]. The RF power is adjusted to obtain a compromise between optimum peak heights for H_2 and CH_4 and a flat base line at the CH_4 peak (cf. Fig. 2). The most pronounced effect of a decrease in RF power is a lowering of the CH_4 peak. In addition, the sensitivity for N_2 increases greatly, shifting the tail of the N_2 which is eluted prior to CH_4 toward the right (cf. Fig. 2) and steepening the base line of the CH_4 peak with a consequent impairment of the detection of CH_4. This characteristic of the RF detector is the major cause for the variation of the sensitivity for CH_4, and results in a steady loss of sensitivity after each tuning. A similar effect, which causes a long-term drift of the sensitivity, is the deposition of foreign material on the electrodes. The detector is, therefore, disassembled and cleaned every six months. To compensate for fluctuations and drift in sensitivity each sample is compared to a standard of known composition. To obtain the desired accuracy of 2 % three alternate runs of sample and standard are conducted for each analysis. For Ne and H_2 the measurements of the peak height are more accurate than measurements of the peak area; for CH_4 there is no difference. Thus the average ratios of the peak heights for the samples and standards are used to calculate the trace-gas concentrations in the samples.

RESULTS AND DISCUSSION

Linearity

As is the case for many sensitive ionization detectors, the response of the RF detector is linear over a relatively small range. When the detector is properly adjusted this range is 0–10 p.p.m. for both H_2 and CH_4 in a 5-cc, 600-Torr sample. Fig. 3 shows the linearity for the lower part of this range, which is the concentration range in air samples from unpolluted areas. The partial pressures of H_2, CH_4, and Ne were varied by addition of increasing amounts of pure N_2 to an air standard of known composition (H_2, 0.48 p.p.m.; CH_4 2.02 p.p.m.; Ne, 18.18 p.p.m.). The total pressure was kept at 600 Torr. The purity of the N_2 had been checked with the gas chromatograph prior to the mixing. The straight lines represent a least-squares fit to the data. Expressed in mV/p.p.m. the fit yields the following slopes: H_2, 9.0 $\pm$ 0.4; CH_4, 1.30 $\pm$ 0.03; and Ne, 0.084 $\pm$ 0.003. The standard deviations allow an estimate of the deviation from linearity. Obviously the deviation is a few percent at most and

the linearity is quite good. The responses in A/mole derived from the slopes are sum-marized in Table II, together with the background noise and the detection limit.
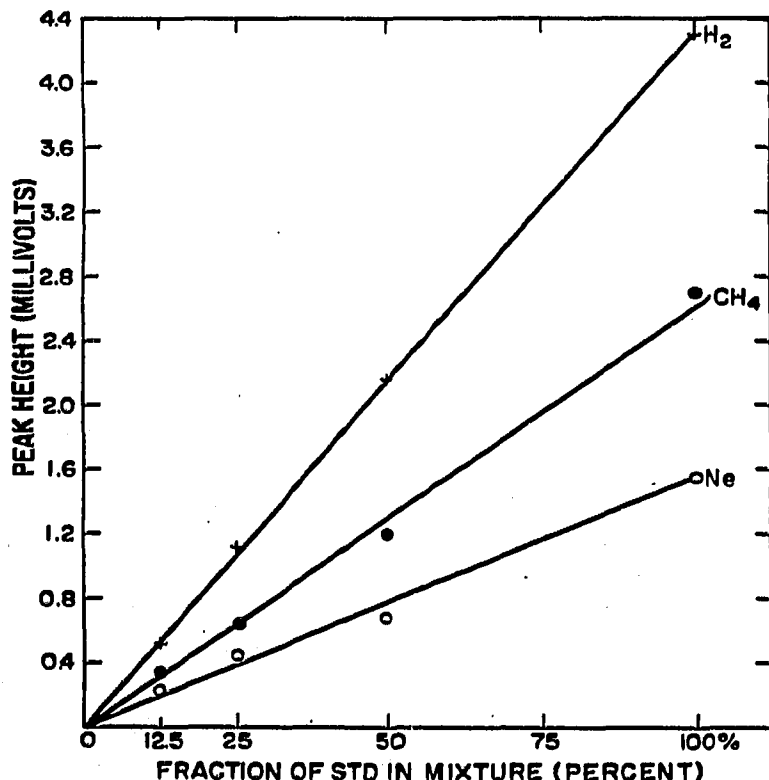

Fig. 3. Peak heights (mV) *vs.* the partial pressures of H_2, CH_4, and Ne in the sample, given as the percent of those in the standard. The partial pressures were varied by diluting the standard with various amounts of pure N_2. The total pressure was kept constant at 600 Torr. The standard (laboratory air) contained 0.48 p.p.m. H_2, 2.02 p.p.m. CH_4 and 18.18 p.p.m. Ne. The peak heights are linear with the partial pressure.

TABLE II

RESPONSE (PEAK HEIGHT), BACKGROUND CURRENT, AND DETECTION LIMIT OF THE GAS

CHROMATOGRAPH FOR Ne, H_2, AND CH_4

Gas	Response (A/mole)	Background current (A)	Noise level (A)[a]	Detection limit	
				mole	p.p.m.[b]
Ne	2.6×10^2	1.5×10^{-5}	0.5×10^{-8}	6×10^{-11}	0.4
H_2	2.8×10^4	1.5×10^{-5}	0.5×10^{-8}	5×10^{-13}	0.003
CH_4	0.4×10^4	1.5×10^{-5}	0.5×10^{-8}	4×10^{-12}	0.02

[a] Noise, corresponding to 0.01 mV as it appears on recorder after being filtered.
[b] For a 5-cc sample at 600 Torr; larger samples would improve detection limit proportionally.

One peculiarity is caused by the very high N_2 peak in the air sample (*cf.* Fig. 2). The peak quenches the detector and its tail continues to influence the detector while the CH_4 peak is passing through, causing a drop in sensitivity for CH_4. Thus when the amounts of CH_4, Ne, and H_2 in the sample loop are varied by varying the sample

pressure, we obtain the response shown in Fig. 4. Whereas the responses for H$_2$ and Ne are still linear with the total amounts of these gases in the sample loop, the slope of the CH$_4$ curve decreases at higher pressures. The decrease indicates a relative loss of sensitivity which is due to the increased partial pressure of N$_2$. This is shown by the fact that if the same experiment is conducted with a H$_2$–CH$_4$–Ne mixture in He, CH$_4$ also has a linear response curve whose slope agrees with the slope in Fig. 4 for small pressures. It is therefore important that the samples measured have the same N$_2$ pressure, or, since they are compared to a standard, that the standard and sample are measured at the same pressure and have a similar N$_2$–O$_2$ composition. Under
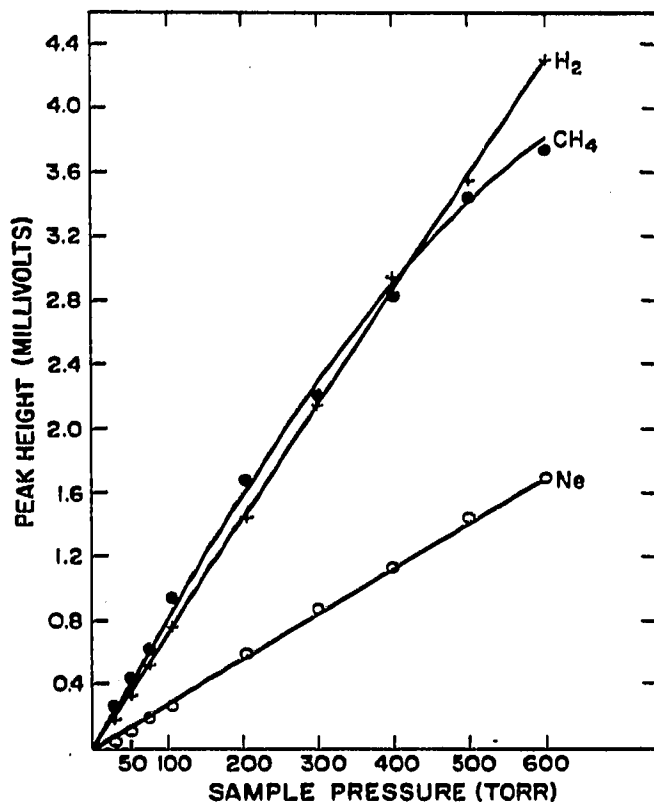

Fig. 4. Peak heights (mV) of H$_2$, CH$_4$, and Ne vs. the pressure (Torr) of the air sample in the loop. The peak heights of H$_2$ and Ne increase linearly with their concentrations in the sample loop, whereas the peak height of CH$_4$ increases more slowly.

these conditions the ratio of CH$_4$-peak height in sample and standard is indeed independent of the sample pressure in the loop, as verified by the measurements shown in Fig. 5. Actually, the mixing ratio of N$_2$ and O$_2$ can vary within certain limits without changing the relative sensitivity for CH$_4$. Thus it was found that a mixture of 80 % N$_2$–20 % O$_2$–1.5 p.p.m. CH$_4$ (i.e. close to the composition of air) when compared to a mixture of pure N$_2$–1.5 p.p.m. CH$_4$ had the same peak heights for CH$_4$; this circumstance simplified the mixing of calibration standards described below.

It should be noted that with proper tuning, the CH$_4$-peak height vs. total sample pressure can also be made linear. However, a slight decrease in RF power changes the form of the curve to that shown in Fig. 4. Maintaining the necessary degree of tuning seems impractical, especially when comparison to a standard eliminates the need to do so.
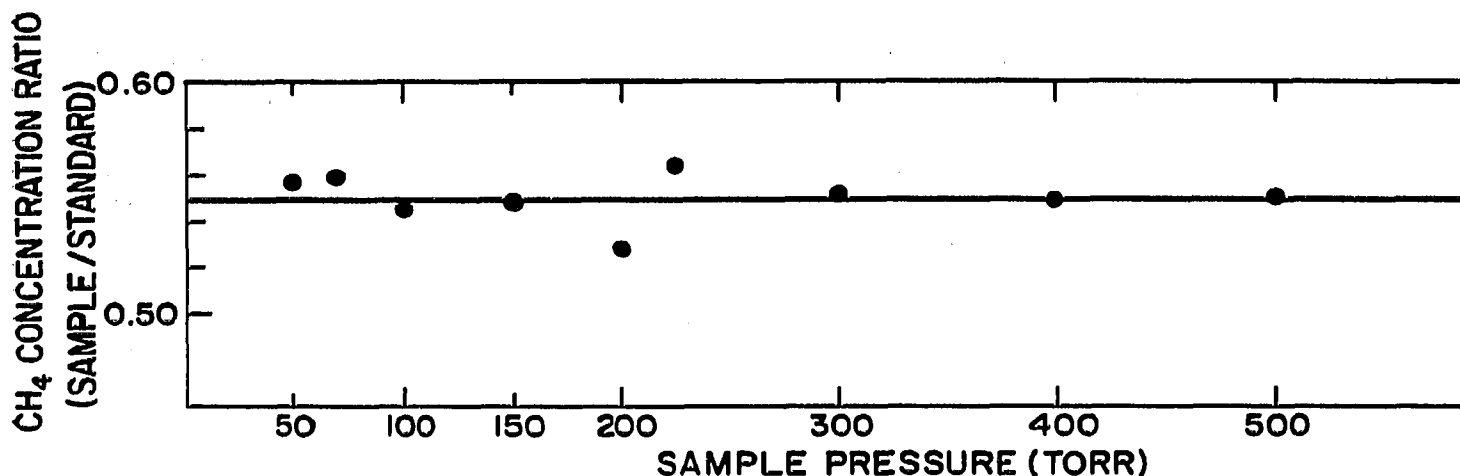
Fig. 5. Ratio of the CH_4-peak height in sample and standard *vs.* the pressure in the sample loop. The ratio is independent of the pressure. At lower pressures the scatter of the data points becomes larger. Note that the origin of the ordinate is suppressed.

Detection limit

The detection limit and accuracy have been improved over the years through modifications in the detector's construction and operation. The detector volume was decreased through installation of an outer electrode with narrower bore, and the power output of the RF generator was increased by 50 %. Both changes increased the peaks for H_2 and CH_4 by a factor two. At the same time the noise level and long-term drift were decreased by enclosing the detector in an oven, to improve the thermo-statting and to eliminate the drift caused by changes in room temperature and by drafts. A further improvement was the installation of alignment pins to allow re-producible assembly of the detector after cleaning. The present detection limit can be estimated from the response obtained from the slopes in Fig. 3 (*cf.* Table II) or directly from the peak heights in Fig. 2. The noise level is 0.01 mV corresponding to 0.5×10^{-8} A (Table II). Assuming that a peak of three times the amplitude of the noise would be detected, we obtain a detection limit of 0.4 p.p.m. for Ne, 0.003 p.p.m. for H_2, and 0.02 p.p.m. for CH_4 (*cf.* also Table II).

Standard and standard calibration

Air from the laboratory's compressed air system, from which H_2O and CO_2 are largely removed, is filled into cylinders of about 12-1 volume to a pressure of 100 p.s.i.g. The air is stored for one half year before being used as a working standard. A cylinder lasts for about two years.

The absolute concentrations of H_2 and CH_4 in the working standard are de-termined by comparison with calibrated samples in the gas chromatograph. Since we could not obtain reliable calibration standards in the required p.p.m. range commercially, the calibration standards are prepared in the laboratory using the vacuum line shown in Fig. 6. Small amounts of H_2 and CH_4 are mixed in the line by successive dilution with pure N_2, which contains less than 0.003 p.p.m. H_2 and less than 0.02 p.p.m. CH_4 as measured with the gas chromatograph. (As mentioned above, the gas chromatograph has the same sensitivity for CH_4 in air as in pure N_2, and the same is of course true for the H_2 sensitivity.)

The mixing proceeds as follows: Volume C (*cf.* Fig. 6) is filled with pure H_2 or CH_4 to a few tens of Torr, and pressure and temperature (p_1, T_1) are measured.

Pure N_2 is added to about 1000 Torr, pressure and temperature (p_2, T_2) are measured, and the mixture is expanded into volume A. After evacuation of C, the mixture in A is expanded back into C, giving a pressure of about 25 Torr (p_3, T_3). Finally
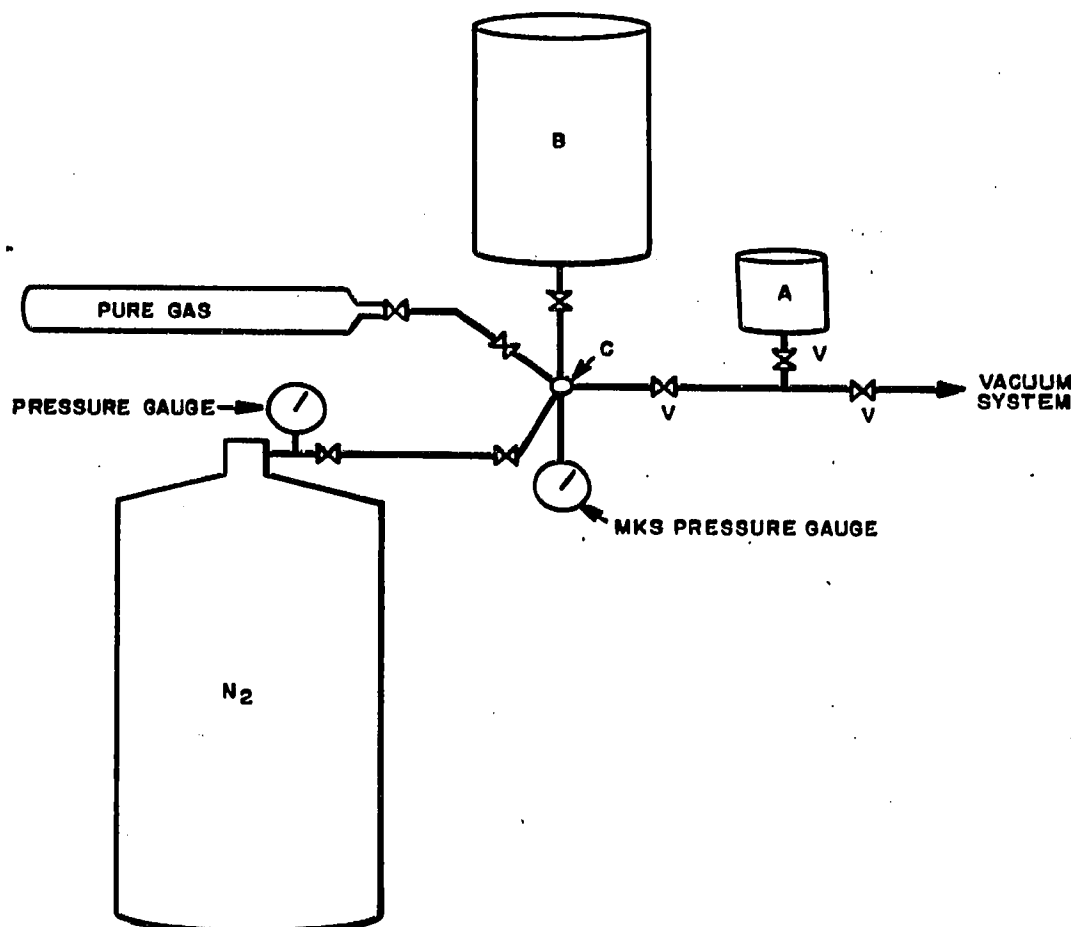

Fig. 6. Schematic of the vacuum line for the mixing of the standards. The volumes are A $\cong$ 600 cc; B = 4022 cc; C = 14.96 cc.

the mixture in volume C is expanded into volume B and N_2 is added to a total pressure of about 1000 Torr (p_4, T_4). The volume ratios (cf. Fig. 6, caption) yield the required p.p.m. range of the trace gas in the mixture. The resulting mixing ratio of the trace gas is

$$m = \frac{p_1 \cdot T_1}{p_2 \cdot T_2} \cdot \frac{C \cdot p_3 \cdot T_3}{(B + C) \cdot p_4 \cdot T_4}$$

where terms which contribute less than 10^{-3} to the result have been neglected. The volumes B and C were determined gravimetrically (by filling the volumes with water) to an accuracy of better than $\pm$ 1%. The baratron allows measurement of the lower pressures (p_1, p_3) to $\pm$ 1%, and the higher pressures (p_2, p_4) to about 0.2%. The temperature is measured to 0.5°. Thus the overall error in the trace-gas mixing ratio in the prepared standards is $\pm$ 2%, discounting reading errors. For H_2 and CH_4 five standards were prepared to cover the expected range of uncontaminated air. The standards were compared on the gas chromatograph to confirm the consistency

and reliability of their preparation[9]. Results are shown in Tables III and IV. The agreement between measurements is usually better than 5 %; the larger error now includes the GC measurement. There is excellent agreement between the average mixing ratios in Tables III and IV and those calculated from the dilution; this reaffirms that the detector response is linear to about 1 %.

TABLE III

COMPARISON OF H_2 CALIBRATION STANDARDS

The mixing ratios of the "samples" were calculated from the peak height ratio of the "sample" to the standard and the mixing ratio of the latter as calculated from the dilution. These absolute mixing ratios are shown in parentheses.

Standards run as "samples"	Standards run as "standards" (p.p.m.)					Averages (p.p.m.)[a]
	I	II	III	IV	V	
I	(0.36)	0.38	0.36	0.34	0.37	0.362 ± 0.015
II	0.65	(0.67)	0.59	0.70	0.68	0.658 ± 0.042
III	0.82	0.85	(0.89)	0.95	0.96	0.894 ± 0.061
IV	1.09	0.99	1.00	(1.08)	1.10	1.052 ± 0.053
V	1.36	1.38	1.24	1.32	(1.34)	1.328 ± 0.054

[a] Error is the standard deviation of the sample runs.

TABLE IV

COMPARISON OF CH_4 CALIBRATION STANDARDS

Arrangement identical to Table III.

Standards run as "samples"	Standards run as "standards" (p.p.m.)					Averages (p.p.m.)[a]
	I	II	III	IV	V	
I	(0.83)	0.83	0.77	0.85	0.80	0.816 ± 0.031
II	1.16	(1.15)	1.19	1.15	1.23	1.176 ± 0.034
III	1.41	1.53	(1.48)	1.48	1.56	1.492 ± 0.057
IV	1.70	1.78	1.65	(1.75)	1.82	1.740 ± 0.067
V	2.60	2.44	2.43	2.58	(2.50)	2.510 ± 0.078

[a] Error is the standard deviation of the sample runs.

All five calibration standards are compared to the working standard and the results averaged. The trace gas concentrations in the working standard (at present 0.48 p.p.m. H_2, 2.02 p.p.m. CH_4, 18.18 p.p.m. Ne) are then known to ± 2.5 %. A large part of this error is due to the error in the volumes of B and C of the dilution system (± 1 %). Each time a new working standard is used the calibration standards are compared to both the old and the new working standards. The working standard is also compared repeatedly to calibration standards throughout its use to insure that its composition does not change. No changes were observed (cf. also Table I).

Accuracy of the sample measurement

An analysis consists of repeated comparisons of the sample to the working standard. Standard and sample runs are alternated (starting with the standard)

until four standard runs are completed. This sequence allows determination of the tropospheric mixing ratio of H_2 and CH_4 with an average accuracy of $\pm$ 2 % relative to the standard. The absolute mixing ratios in the sample are then $\pm$ 3 %, since the mixing ratio in the working standard is known to $\pm$ 2.5 %. The relative accuracy is illustrated by Table I which shows analyses of the same sample on different dates. The errors given for the individual analyses are the mean standard deviations, calculated from the alternate sample and standard runs. They range between 1 % and 3 %, averaging 2 %. The reproducibility of the individual analyses is about 2 % as is seen from the standard deviations for the averages for H_2 and CH_4 (0.01 and 0.02 p.p.m. respectively) given at the bottom of Table I.

CONCLUSION

GC provides an accurate and reliable method for routine determination of natural concentrations of CH_4 and H_2 in the atmosphere. The relatively time-consuming analysis is the only drawback. Omission of one sample and one standard run would reduce the time by 40 min at the expense of an error increase of 1.5 times. This reduced accuracy is sufficient, since the natural range of mixing ratios in the troposphere is 0.2–1.0 p.p.m. for H_2 and 0.8–1.6 p.p.m. for CH_4.

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