MEASUREMENT OF PERMANENT GASES BY A FLAME EMISSION GAS CHROMATOGRAPHIC DETECTOR

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INTRODUCTION

When using a gas chromatographic detector the following characteristics[1] must be considered: sensitivity of measurement; stability of detection system, *i.e.*, noise and drift, versatility or generality of use for a variety of molecules, linearity of response with respect to amount of molecules, reactivity of detector with molecules being measured, response time of detector to change in composition of gas in the detector, convenience of recording the detector signal, simplicity of operation of detector and interpretation of response, cost of detector, size of detector, and safety of using the detector. Unfortunately, few gas chromatographic detectors display any appreciable sensitivity towards the so-called permanent gases, *e.g.*, O_2, N_2, CO, Ar, He, etc.

The positive mode flame emission detector (positive means the species being measured causes an increase in flame emission) originally described by GRANT[2] and more recently studied in greater detail by BRAMAN[3] and by JUVET and co-workers[4-6] has been shown to be quite sensitive as well as selective in response for a variety of organic molecules containing atoms other than carbon and hydrogen. The positive mode flame emission detector also appears to possess most of the other characteristics mentioned above except for its poor response to the permanent gases. In this manuscript, the decrease in signal resulting from the decreased emission of the OH bands of the flame background is monitored by means of a simple photometric system and is found to be a sensitive measure of the amount of permanent gas introduced into the gas chromatograph. This detector will be designated as a negative flame emission gas chromatographic detector.

EXPERIMENTAL

Spectroscopic apparatus

The experimental system (see schematic diagram in Fig. 1) used was similar to the one used by JUVET AND DURBIN[4,5] and so only the changes from their system will be indicated here. A Beckman No. 4020 aspirator-burner (Beckman Instruments, Inc., Fillerton, Calif., U.S.A.) with a sealed off capillary was used. The concave mirror in the Beckman flame attachment was adjusted for maximum response. The photomultiplier housing of the Beckman DU was removed and replaced with a separate housing (Model 83-012, Jarrell-Ash Co., Waltham, Mas. 02154, U.S.A.) containing an RCA 1P28 photomultiplier tube which was selected for its high gain and low thermionic

emission dark current. The housing was mounted on a bakelite strip the size of the end flange on the Beckman DU monochromator and was connected to the monochromator using the same bolt holes normally used to mount the Beckman DU photomultiplier housing. The phototube voltage of -700 V and the photoanodic current were supplied by and measured by an Aminco photomultiplier microphotometer (No. 10–211, American Instrument Co., Inc., Silver Spring, Md. 20190, U.S.A.). The 50 mV microphotometer output was monitored by a potentiometric recorder (Model SR, E. H. Sargent, Chicago, Ill., U.S.A.) with DISC integrator.

The aspirator-burner was mounted on a microscope stage to allow accurate vertical adjustment of the flame position with respect to the entrance slit of the monochromator (horizontal position was fixed to give maximum signal). This was needed to give a maximum signal-to-noise ratio of the measured radiation. To minimize stray light pickup by the monochromator, the entire flame attachment was enclosed in a light tight box.

Gas chromatographic apparatus

The schematic layout of the gas flow is shown in Fig. 1. The carrier gas for all studies was hydrogen. The hydrogen gas flow was regulated using a two-stage regulator and a needle valve and monitored using a rotameter type flow meter. The flow meter,
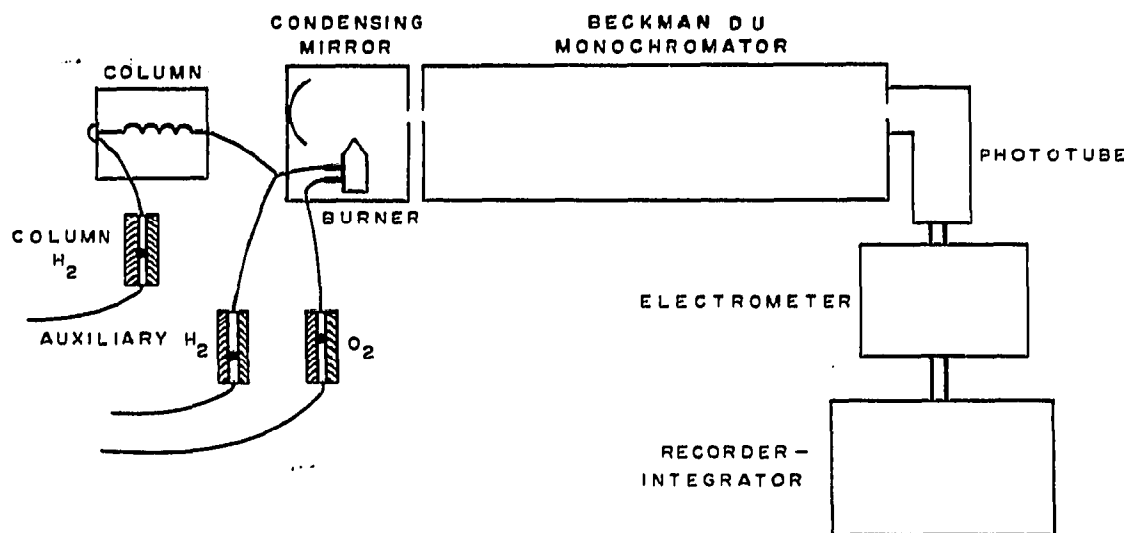

Fig. 1. Schematic diagram of experimental system.

calibrated using a soap bubble flow meter, was connected to the on-column inlet (No. 3500, Carle Instruments, Inc., Anaheim, Calif. 92805, U.S.A.) by means of 1/8 in. O.D. stainless steel tubing. An empty column (1/8 in. O.D. × 2 ft. long stainless steel tubing at 25° was used for samples up to 1 ml in column and a 1/4 in. O.D. × 9 ft. 8 in. long aluminum tubing was used for sample sizes greater than 1 ml) connected the column inlet to the fuel jacket of the burner. The larger column was used strictly to facilitate easier measurement. For volumes larger than 1 ml the delay time between injection and entrance into the flame was so small as to cause difficulty in obtaining accurate response. The oxygen flow to the oxygen port of the burner was regulated using a two-stage regulator and a needle-valve and monitored using a rotameter type

flow meter (the flow meter was calibrated as described above). Copper tubing (1/8 in. O.D.) was used to connect the needle valve to the oxygen port of the burner.

CONDITIONS AND OPERATION

An oxyhydrogen flame was used for all studies. Significantly poorer sensitivities for the permanent gases were obtained using air-hydrogen flames. Measurement of the OH band head emission at 310 mμ was found to be a sensitive indication of the amount of permanent gas introduced into the flame gases. None of the permanent gases studied exhibited characteristic emission within the spectral band width of the monochromator at 310 mμ. The hydrogen flow rate through the column for all measurements was about 50 cc/min. This was supplemented by an auxiliary flow of 70 cc/min. (introduced directly at the fuel port on the burner) added to maintain a flame even though a large sample might temporarily interrupt the carrier gas flow. The oxygen flow rate was adjusted to give maximum OH band emission which resulted for a flow rate of about 30 cc/min. Under these experimental conditions, Gaussian shaped peaks resulted for all samples except ammonia, which resulted in a W-shaped peak.

In order to obtain the most sensitive and selective experimental conditions, the flow rates of hydrogen and oxygen were closely monitored and a small monochromator spectral bandwidth (a monochromator slit width of 0.6 mm results in a spectral bandwidth of 24 Å at 310 mμ) was used. With this spectral bandwidth, the background current signal of the photomultiplier microphotometer was adjusted to be full-scale on the most sensitive scale (1.0 × 10^{-9} A full-scale with an r.m.s. noise level of less than 2.0 × 10^{-12} A and a drift of less than 2 × 10^{-11} A per h of operation) of the microphotometer and also full-scale on the potentiometric recorder.

The instrumental response to the sample gas was calculated as a fractional change, α, in the background current signal, $i°$ according to

$$\alpha = \frac{i° - i}{i°}$$

where i is the current signal due to the sample. For small samples, i.e., samples producing less than about 20% change in the background signal, $i°$, the value of i was evaluated from the lowest depression of the sample current signal. For large samples, i.e., samples producing more than about 80% change in the background signal, $i°$, the values of $i°$ and i were evaluated using a DISC integrator. Samples resulting in more than a 20% but less than a 80% change in $i°$ were evaluated by both techniques. Since the readout signals, i and $i°$, are proportional to the gain of the photomultiplier phototube, γ, which depends on the voltage applied to the photomultiplier phototube, and to the gain of the electrometer, G, any increase in γ or G or both should have no effect on the instrumental response, α.[7]

RESULTS AND DISCUSSION

The negative flame emission detector was usable for measurement of the following permanent gases: N$_2$, O$_2$, CO$_2$, N$_2$O, He, and Ar. Linear responses (the slope of analytical curves for all permanent gases on log–log coordinates was 1.00 ± 0.03 or

better at a 90 % confidence level) up to 4 ml were obtained for all gases studied. In Fig. 2, an analytical curve (log α vs. log sample volume) of CO_2 is given. All other analytical curves are similar to the one in Fig. 2.
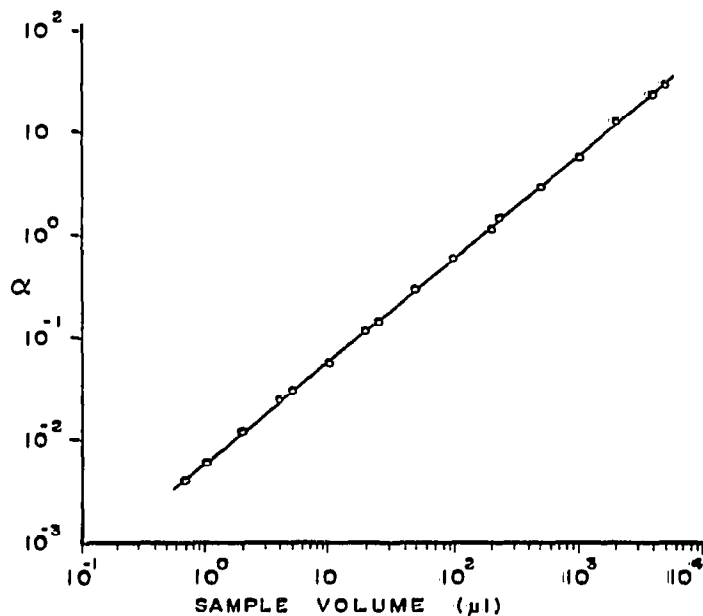

Fig 2. Analytical curve for carbon dioxide.

The limits of detection for N_2, O_2, CO_2, N_2O, He, and Ar were found to be 0.6, 0.26, 0.7, 0.7, 0.5, and 1.5 μl, respectively. The limit of detection was taken as that sample volume resulting in a signal-to-noise ratio of $t\sqrt{2}/\sqrt{m}$, where t is the Student "t" value which can be found in statistics tables and m is the number of sample plus background measurements. For the studies given here, m was 20 and $t\sqrt{2}/\sqrt{m}$ was 1.434. The limits of detection in terms of g/sec are approximately 7.5 × 10⁻⁷, 3.6 × 10⁻⁷, 1.4 × 10⁻⁶, 1.4 × 10⁻⁶, 5.6 × 10⁻⁷, and 2.7 × 10⁻⁶ for N_2, O_2, CO_2, N_2O, He, and Ar, respectively. These values are lower than obtainable when using a thermal conductivity detector or flame ionization detector[8], about the same as those obtainable with the electrodeless discharge detector[9], higher than obtainable when using a helium detector[10-13], but of course, the flame emission detector can be used not only for permanent gas measurement in the negative mode but also for organic vapor measurement in the positive mode.

Sulfur dioxide could not be measured using the negative response of the flame emission detector because the SO radical emits[14,15] in the 310 mμ region. Carbon monoxide also caused an increase in response rather than a decrease at 310 mμ. Carbon monoxide does not emit in the 310 mμ region[14,15], but since it is fuel, it will greatly influence the flame gas composition and temperature. Ammonia, on the other hand, behaved quite anomalously since a decrease in OH emission resulted for small amounts of NH_3 being introduced into the carrier gas whereas for large amounts of NH_3, the response was positive. In addition, with large amounts of NH_3, the peak shape was not Gaussian but rather like a "W". No explanation is proposed for this anomalous behavior although studies involving calculations of flame gas composition and temperature which are now in progress should greatly aid in the interpretation of such results.

A detailed listing of the advantages of the flame emission detector in the positive mode for detection of the emission of molecular and atomic radicals resulting from the flame decomposition of organic materials has already been clearly indicated. The flame emission detector in the negative mode as described in this manuscript is even of more general application than most high sensitivity detectors because of its use for measurement of permanent gases. The flame emission detector, in general, is not as sensitive as many of the ionization type detectors but is certainly more general in use, is more selective than most of the ionization type detectors and is simpler to set up and use. In addition, the detector has most of the other characteristics mentioned previously and is considered desirable for a gas chromatographic detector.

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SUMMARY

The flame emission gas chromatographic detector when used in the negative mode is sensitive to permanent gases, such as O_2, N_2, CO_2, Ar, N_2O, and He. The sample gases are introduced into the hydrogen carrier gas which feeds a Beckman total-consumption aspirator-burner. The flame background emission of the OH bands is then monitored using a monochromator-photomultiplier-amplifier-electrometer-recorder system. The analytical curves of response vs. amount introduced are linear over four decades, and the limits of detection are about 10^{-6} grams per second for the gases listed above.

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