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EFFECT OF PRESSURE ON THE PERFORMANCE OF THE FLAME IONIZATION DETECTOR

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SUMMARY

A study has been made of the performance of a flame ionization detector operated under various pressures, at either constant volume flow rates or constant mass flow rates, of the gases fed into the flame. The ionization efficiency was highly dependent on pressure; up to 10% changes in ionization efficiency, depending on the H_2 and N_2 flow rates, resulted from varying the pressure within the range 740–780 mm Hg.

For precise quantitative gas chromatographic analysis it is essential that the pressure in the flame ionization detector should be stabilized. The effects of pressure on the ionization efficiency seem to stem from their respective effect on the ion-producing mechanisms.

INTRODUCTION

The flame ionization detector[1,2] (FID) is one of the most useful gas chromatography (GC) detectors on account of its high sensitivity, small effective sensor volume, and remarkable range of linearity of response. It has therefore been thoroughly studied; of the many existing papers we shall quote only the basic ones[3–5]. The performance of the FID is affected by a number of factors, each having a certain influence on the process of the origination of ions produced on combustion of an organic substance in a diffusional hydrogen flame burning in an electric field. Attempts to utilize the FID for detection under elevated pressures[6] showed that its function is significantly influenced by the pressure in the detector, the effects being significant even at pressures ranging quite close to 760 mm Hg. As we have found only one reference[7] in the literature on this topic, stating the necessity of stabilizing the pressure in the FID when it is employed in a process GC analyzer, we have turned our attention to the pressure effects on the FID performance in the pressure region of 740–780 mm Hg, in which one performs the majority of analyses.

Variation in pressure may bring about changes in the ion-producing reaction mechanisms and have a significant influence on the pattern of the flame. The direct influence of pressure on the ionization mechanisms can hardly be depicted as there is

no consistent description of these mechanisms available as yet[3]. Indirect pressure effects may be associated with the changes of oxygen diffusion into the flame, which may affect the combustion mechanisms in respect of the reactions requiring lesser amounts of oxygen (production of CO instead of CO_2, formation of soot particles, etc.). The pressure in the detector essentially affects the structure and shape of the flame, which are also dependent on the forward fuel velocity in the burner jet and on the overall fuel supply into the flame. If the fuel velocity in the jet is kept constant, the rate of supplying the mass of fuel into the flame is directly proportional to the pressure. If, on the other hand, the mass fuel supply rate is constant, the volume flow rate and forward velocity of fuel in the jet are inversely proportional to the pressure. It follows from what has been said that for the elucidation of the pressure effects on the FID performance the following two conditions of operation should be considered:

(1) Both the fuel (H_2), oxidant (air) and the ionizing substance (C_2H_2) are fed into the detector at a constant mass rate (mole/sec), so that the respective volume flow rates (ml/sec) are inversely proportional to the pressure.

(2) H_2, air, and C_2H_2 are fed into the detector at constant volume flow rates, which causes the rate of combustion of the substance supplied into the flame to be proportional to the pressure.

EXPERIMENTAL

A schematic diagram of the detector employed is shown in Fig. 1. The detector body was made of nickel plated brass, and the seals and insulators were made of teflon. The electrical contacts and the burner jet (0.25 mm O.D.) were of platinum. The detector was inserted in an air thermostat and kept at 140°. The design of the detector has been described in detail elsewhere[6]. The ignition of the flame was carried out by an electrical spark induced, from outside, between the jet and an igniting electrode with the aid of a Ruhmkorff coil. After ignition the igniting electrode was set at the potential of the jet. Both the ignition electrode and the burner jet were electrically insulated from the earth. The polarizing potential, variable within —200 to

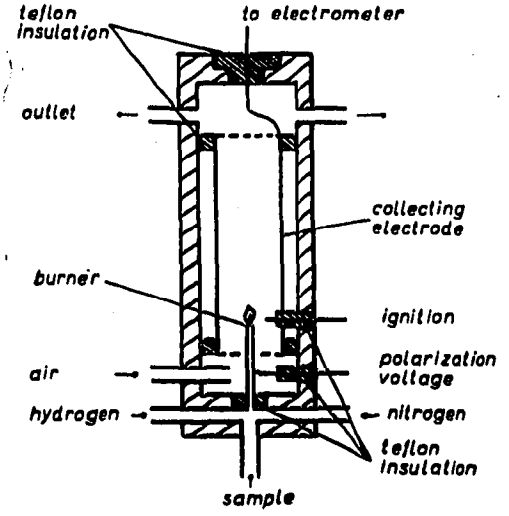

Fig. 1. Schematic diagram of the detector. Inner diameter of the burner jet is 0.25 mm, the collecting electrode is of a cylindrical shape, 120 mm long and 12 mm I.D.

+200 V, was applied to the jet, the collector being connected directly to the electrometer.

The dependence of FID response was followed by measuring the saturated ionization current through the flame fed continuously with sample. The intensity of the current was read out from the volt–ampere curves.

The sample (C_2H_2–H_2 mixture containing 1.20×10^{-7} mole of C_2H_2 in 1 ml at 760 mm Hg and 25°) and the other gases (H_2, N_2, air) were taken directly from the storage cylinders, the respective flow rates being set by needle valves and measured by capillary flow meters. The excess pressure in the detector was maintained by another needle valve controlling the gas emergence from the detector. When working under reduced pressures, the above needle valve was connected to a vacuum pump; the reduced pressure required was obtained by controlling the rate of evacuation. Both the excess pressure and reduced pressure were measured by a mercury pressure gauge. The whole pneumatic system is illustrated schematically in Fig. 2. The volt–ampere characteristics were measured under both the above-mentioned flow conditions.

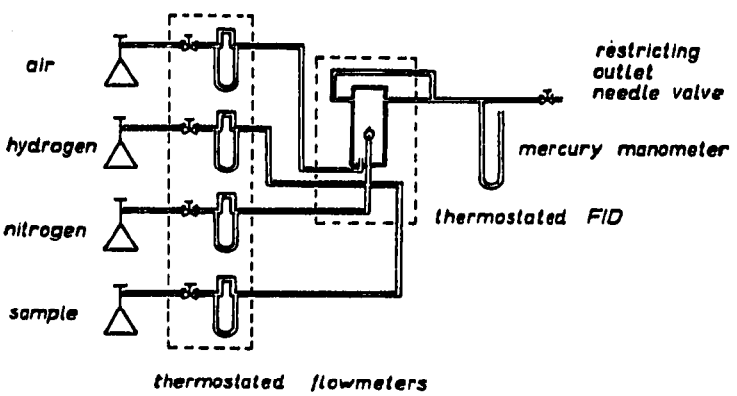

Fig. 2. The pneumatic system.

The constant mass supply rates were effected by setting the flow rates directly by the needle valves on the storage cylinders in which the pressures were kept above 100 atm. Under these conditions, final pressure changes within ±1 atm in the detector during the measurement could cause the gas flow to vary by not more than ±1 %. At constant mass flow rates, the pressure dependence of the saturated ionization current represents a direct picture of the pressure dependence of the molar response (ionization current brought about by feeding the ionizing substance into the flame at a rate of 1 mole/sec, *cf.* ref. 7) and of the molar ionization efficiency (electrical charge transferred by the flame upon the introduction of 1 mole of the ionizing substance into it).

The constant volume flow rates were maintained by setting the needle valves on the storage cylinders in such a way that the differential manometers to the capillary flowmeters should show the same values at all the pressures used. The flow rates of the individual gases are expressed in ml/sec at 760 mm Hg and 25° for the various measurements.

RESULTS

Measurements at constant mass flow rates

Figs. 3 and 4 show the pressure dependence of the ionization efficiency expressed in Coulombs per 1 gramatom of an acetylenic carbon, measured at various flow rates of hydrogen and nitrogen, respectively. The values in Table I of the ionization efficiency, at pressures varying slightly around atmospheric, are expressed as percentages of the ionization efficiency at 760 mm Hg. In all cases the mass supply rate of C_2H_2 was kept constant and amounted to 1.20×10^{-8} mole/sec. The FID response varied within 10^{-8}–10^{-9} A, the background ionization current being less than 10^{-11} A. The mass flow rates of H_2, N_2, and air have been expressed as their corresponding volume flow rates (ml/sec) at 760 mm Hg and 25°.

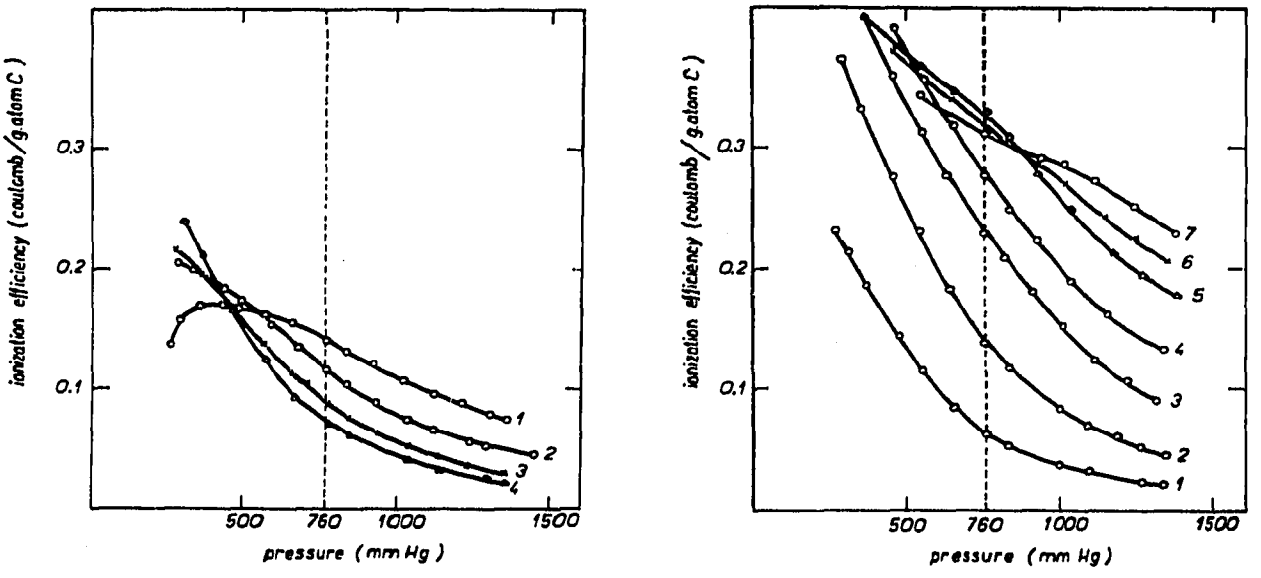

Fig. 3. Dependence of the ionization efficiency on pressure at various mass flow rates of hydrogen and fixed flow rates of air and sample (no nitrogen was added). Curves 1, 2, 3, and 4 correspond to hydrogen flow rates of 0.30, 0.50, 0.70, and 0.90 ml/sec, respectively, the air flow rate was 11 ml/sec, and the C_2H_2 feed rate was 1.20×10^{-8} mole/sec. All the volume flow rates refer to 760 mm Hg and 25°.

Fig. 4. Dependence of the ionization efficiency on pressure at various constant mass flow rates of nitrogen and fixed flow rates of hydrogen, air, and sample. Curves 1, 2, 3, 4, 5, 6, and 7 correspond to nitrogen flow rates of 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 ml/sec, respectively, the hydrogen and air flow rates being 0.9 and 9.0 ml/sec, respectively, the sample feed rate corresponded to 1.20×10^{-8} mole/sec. All the volume flow rates refer to 760 mm Hg and 25°.

Measurement at constant volume flow rates

Figs. 5 and 6 show the pressure dependence of the ionization efficiency at various flow rates of hydrogen and nitrogen, respectively. In all cases the H_2–C_2H_2 mixture was fed into the flame at a rate of 0.1 ml/sec as expressed at the given pressure and 25°. The flow rates of H_2 and N_2 have been expressed in a similar manner. The detector response to C_2H_2 varied within 10^{-9}–10^{-8} A while the background ionization current was less than 10^{-11} A.

TABLE I

DATA ON THE EFFECT OF PRESSURE ON THE IONIZATION EFFICIENCY WITHIN A RANGE CLOSE TO 760 mm Hg

C_2H_2 feed rate of 1.20×10^{-8} mole/sec was maintained throughout, air flow rate being 9.0 ml/sec as measured at 760 mm Hg and 25°.

Flow rates[a] *(ml/sec)*		*Ionization efficiency*[b] *(Coulomb per gram atom C)*	*Relative ionization efficiency at various pressures*[c]				
N_2	H_2		*740 mm Hg*	*750 mm Hg*	*760 mm Hg*	*770 mm Hg*	*780 mm Hg*
0.2	0.3	0.199	101.0	100.5	↑	99.0	98.5
0.2	0.5	0.208	102.0	101.0		99.0	98.0
0.2	0.7	0.175	104.2	102.4		98.2	97.0
0.2	0.9	0.139	105.2	103.0	100.0	97.8	95.5
0.6	0.4	0.300	101.4	100.7		99.6	99.0
0.6	0.5	0.315	100.7	100.4		99.6	99.3
0.6	0.6	0.313	100.7	100.4		100.0	99.6
0.6	0.7	0.306	101.4	100.7		99.3	98.6
0.6	0.8	0.296	102.1	101.1		98.9	98.6
0.6	0.9	0.278	102.6	101.1	↓	98.9	97.4

[a] As measured at 760 mm Hg and 25°.
[b] At 760 mm Hg.
[c] The individual values represent the ionization efficiencies at the given pressures, expressed as percentages of the ionizaton efficiency at 760 mm Hg.

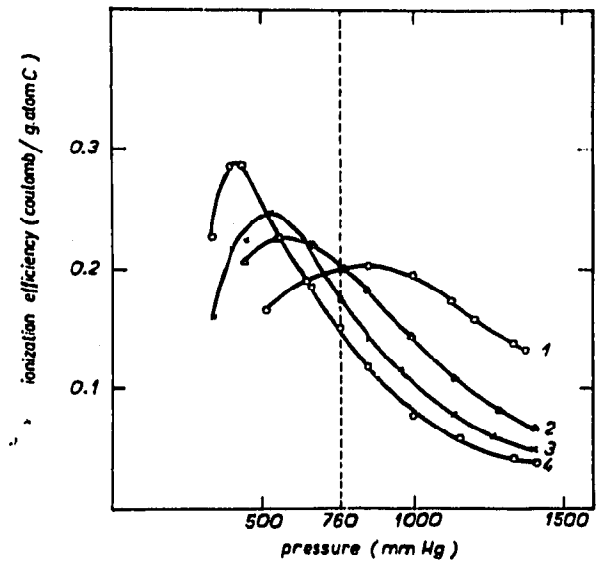

Fig. 5. Dependence of the ionization efficiency on pressure at various constant volume flow rates of hydrogen and fixed flow rates of nitrogen, air, and sample. The nitrogen and air flow rates were 0.20 and 9.0 ml/sec, respectively. Curves 1, 2, 3, and 4 correspond to hydrogen flow rates of 0.30, 0.50, 0.70 and 0.90 ml/sec, respectively. The flow rate of the H_2–C_2H_2 mixture (1.20×10^{-7} mole C_2H_2 in 1 ml of the mixture at 760 mm Hg and 25°) was 0.1 ml/sec. All the flow rates have been measured at the given pressure and 25°.

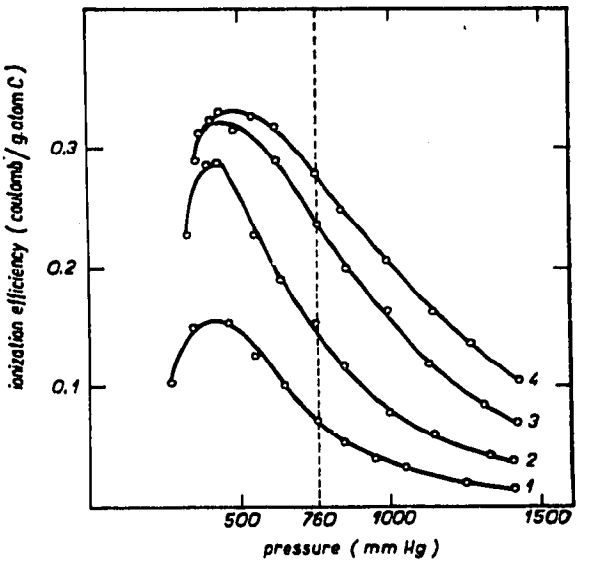

Fig. 6. Dependence of the ionization efficiency on pressure at various constant volume flow rates of nitrogen and fixed flow rates of hydrogen, air, and sample. The hydrogen and air flow rates were 0.80 and 9.0 ml/sec, respectively. Curves 1, 2, 3, and 4 correspond to nitrogen flow rates of 0, 0.20 0.40, and 0.60 ml/sec, respectively. The flow rate of the H_2–C_2H_2 mixture (composition the same as quoted in Fig. 5) was 0.10 ml/sec. All the flow rates have been measured at the given pressure and 25°.

CONCLUSIONS

The measurements under both sets of conditions have shown that the ionization efficiency is strongly dependent on pressure. Normal fluctuations in atmospheric pressure can bring about changes in the ionization efficiency amounting to as much as $\pm 5\%$ of the value measured at 760 mm Hg. Hence it is advisable to stabilize the pressure in the FID when quantitative analysis is to be performed. As the ionization efficiency *vs.* pressure curves obtained under both sets of flow conditions and at various flow rates show similar curves, it seems that the effect of pressure on the ionization efficiency is mainly due to its direct influence on the ion-producing mechanism.

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