FLAME IONIZATION DETECTION UNDER ELEVATED PRESSURES

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SUMMARY

The pressure dependence of the background ionization current in the flame ionization detector has been measured, as well as the ionization efficiency of methane and the relative molar responses of various types of compound at pressures ranging within 1–25 atm. All the above parameters show a strong dependence on pressure; at pressures higher than about 10 atm the ionization efficiency becomes practically independent of pressure. The exceedingly high variability of the response to halogen-containing compounds, depending on the pressure, could be utilized as a principle of selective detection.

INTRODUCTION

It has been shown in a previous paper[1] that the ionization efficiency in an FID is strongly dependent on pressure, the dependence being so pronounced that even variations in the atmospheric pressure may be significant. Since the pressure effects on the ionization efficiency have associated with them the changes in the ionization mechanism, it may be presumed that the influence of pressure on ionization will manifest itself with different substances in different ways. Hence it follows that not only the molar response but also the relative molar response may be dependent on pressure.

The present paper links up with the previous communication; the range of experimental pressures has been extended up to about 25 atm, and the work includes a study of the pressure dependence of the relative molar response.

EXPERIMENTAL

The working procedure as well as the instruments used for the measurement of the pressure dependence of the ionization efficiency were the same as those described previously[1]. The test substance, methane, was used mixed with hydrogen, the methane concentration amounting to 4.60×10^{-7} mole/ml at 760 mm Hg and 25°. The measurement of ionization efficiency was carried out under steady conditions; the sample

and all the necessary gases (H_2, N_2, air) were fed continuously into the detector and the ionization current was measured.

Two sets of working conditions were employed: in the first, constant volume flow rates (ml/sec) of the gases in the burner jet were maintained and in the second, constant mass flow rates (mole/sec) were used. To make the results obtained in both procedures readily comparable, the mass flow rates have been quoted as the corresponding volume flow rates at 760 mm Hg and 25°.

The detector proper, the detailed description of which can be found elsewhere[2], consists of a 25 cm long brass cylinder of 20 mm inside diameter. The burner jet (0.30 mm bore), situated inside the cylinder and insulated from the earthed parts of the detector by teflon, serves as a polarizing electrode. The collector is a 12 cm stainless steel tube, 14 mm I.D., which is bedded in teflon rings and surrounds the burner jet. The flow rates of the gases were controlled and maintained by means of a specially designed unit (cf. ref. 1).

In measuring the pressure dependence of the relative molar response, a 120 cm long stainless steel column, 4 mm I.D., packed with 15 % Carbowax 20 M on silanized Chromosorb G and thermostated at 80°, was inserted between the gas flow controlling unit and the detector. The model substances were: chloroform, tetrachloro-
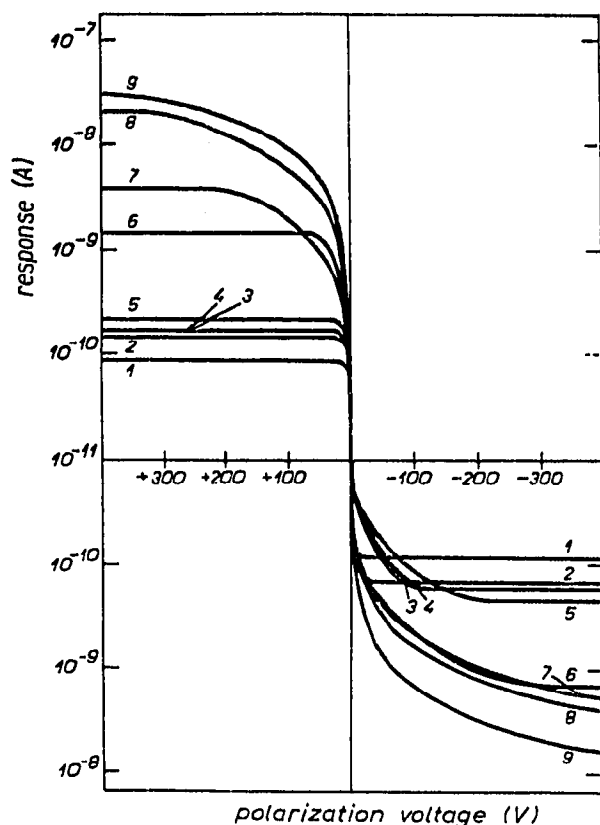

Fig. 1. Volt–ampere characteristics of a pure hydrogen flame. Curves 1, 2, 3, 4, 5, 6, 7, 8, and 9 correspond to pressures of 0.53, 0.79, 1.0, 1.58, 2.1, 9.0, 17.0, 21.0, and 25.0 atm respectively.
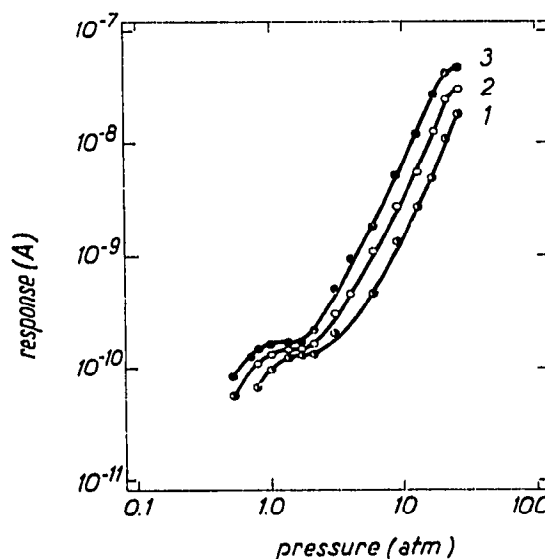
Fig. 2. Pressure dependences of the detector response with a pure hydrogen flame at constant volume flow rates of the gases. Curves 1, 2, and 3 correspond to H_2 flow rates of 0.50, 0.70, and 0.90 ml/sec, respectively; N_2 flow rate was 0.60 ml/sec.

methane, isobutyl alcohol, acetone, butyl acetate, hexane, octane, cyclohexane, and benzene. Six different mixtures of well separated compounds and defined compositions were prepared from the above compounds, each containing benzene as a reference substance. The mixtures were injected into the column via a conventional inlet port with a 1 μl Hamilton syringe, the amounts introduced were in the range of 0.05–0.15 μl. The detector as well as the adjacent parts of the gas inlets were maintained at 140°. The polarizing voltage was + 450 V.

The relative molar responses were determined by the internal standard technique, the measurements of the pressure dependence of the former being carried out at constant volume flow rates of the gases. Under these conditions, the carrier gas (N_2) and hydrogen flow rates were 0.56 and 0.30 ml/sec at 25°, respectively. The air flow rate was 14 ml/sec in all cases.

RESULTS AND DISCUSSION

Pressure dependence of the background ionization current

In this case, no sample was supplied to the flame; the hydrogen was taken directly from a storage cylinder. The polarization voltage necessary to attain a saturation current was determined by measuring the volt–ampere characteristics of the flame at constant volume flow rates of the gases. The respective results are depicted in Fig. 1. It follows from the relationships obtained that both the pressure and sign of polarization voltage have an essential influence on the voltage corresponding to a saturated current. An increase of pressure implies the necessity of raising the polarization voltage. The actual courses of the volt–ampere characteristics in Fig. 1, as well as in Fig. 4, have been drawn on log–linear coordinates, which gives them a slightly modified appearance.

The pressure dependences of the background ionization current of pure hydrogen flame, measured at constant volume flow rates and constant mass flow rates, respectively, are shown in Figs. 2 and 3. The dependences obtained display rather complicated curves; the limiting values on the side of the low pressures correspond to the conditions at which the flame extinguishes itself.
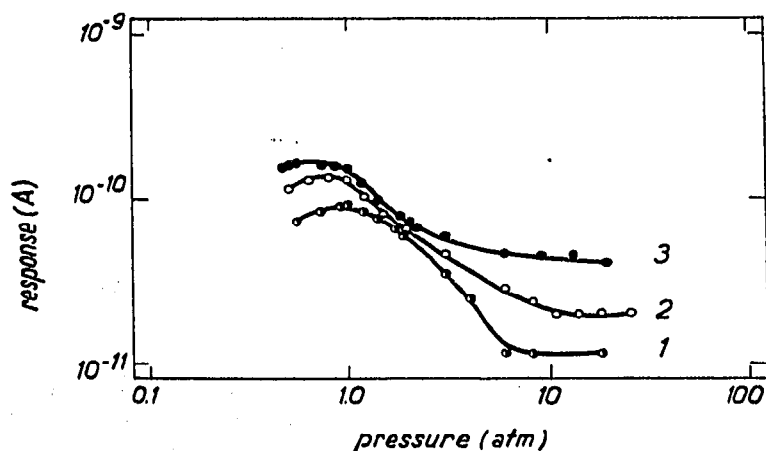

Fig. 3. Pressure dependence of the detector response with a pure hydrogen flame at constant mass flow rates of the gases. Curves 1, 2, and 3 correspond to H_2 flow rates of 0.50, 0.70, and 0.90 ml/sec at 1.0 atm and 25°, respectively; the N_2 flow rate was 0.60 ml/sec at 1.0 atm and 25°.

Pressure dependence of the ionization efficiency of methane

To find the conditions at which the ionization current becomes saturated, it was again necessary to measure the respective volt–ampere characteristics: the results obtained at constant volume flow rates of the gases are shown in Fig. 4.

The ionization efficiency of methane has been calculated from the net ionization gain of methane, *i.e.*, from the difference between the ionization current in the flame fed by a defined stream of the methane and the corresponding background ionization current. The pressure dependence of the ionization efficiency, in Coulombs/g atom, of a paraffinic carbon at constant volume flow rates and at constant mass flow rates, respectively, are shown in Figs. 5 and 6. It is evident from the relationships found that the kind of working conditions has no material effect on the character of the pressure dependence of ionization efficiency. The ionization efficiency *vs.* pressure curves pass through maxima, the positions of which are dependent on the hydrogen and nitrogen flow rates. It is interesting to note that at pressures above approximately 10 atm the ionization efficiency is practically independent of pressure.

Pressure dependence of the relative molar response

The dependences of the relative molar responses (RMR) of the above model substances on pressure follow from the data in Table I. It is evident from the results that the pressure also significantly affects the RMR values. The apparently unsystematic sequence of the values for a given substance stems from the fact that the
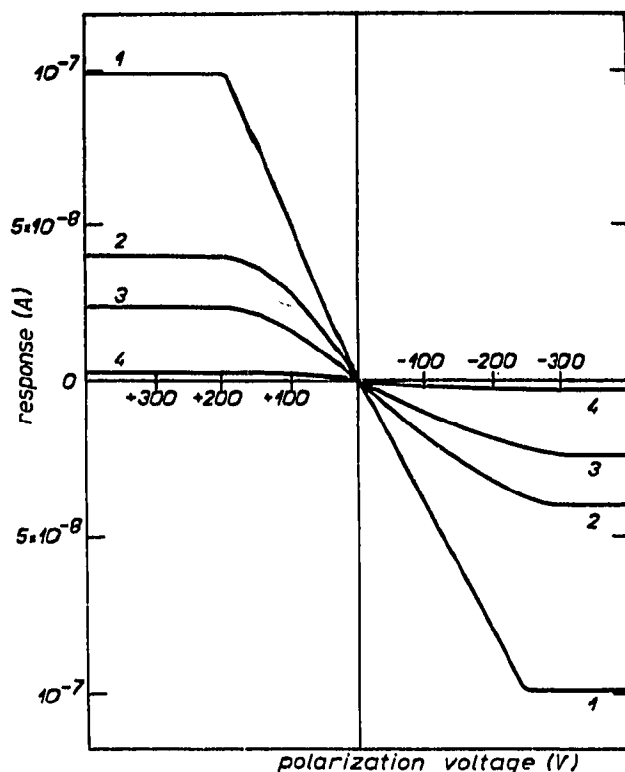

Fig. 4. Volt–ampere characteristics of a hydrogen flame fed with methane at constant volume flow rates of the gases. The N_2 and methane–hydrogen mixture flow rates were 1.0 and 0.70 ml/sec; curves 1, 2, 3, and 4 correspond to pressures of 1.0, 3.0, 13, and 21 atm, respectively.
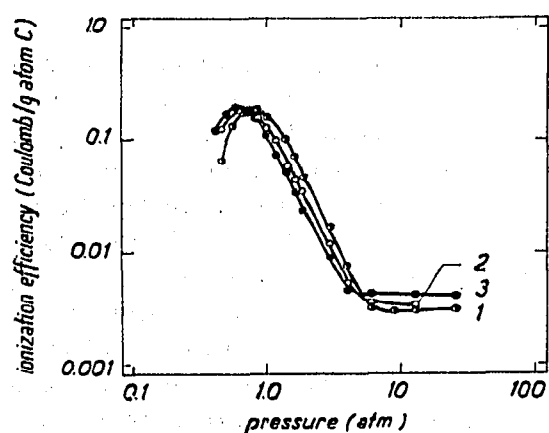
Fig. 5. Pressure dependences of the ionization efficiency of methane at constant volume flow rates of the gases; the N_2 flow rate was 0.20 ml/sec, curves 1, 2, and 3 correspond to the methane–hydrogen mixture flow rates of 0.5, 0.7, and 0.9 ml/sec, respectively.
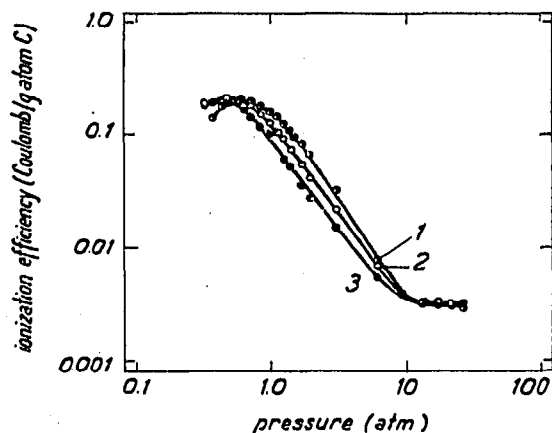
Fig. 6. Pressure dependences of the ionization efficiency of methane at constant mass flow rates; the N_2 flow rate was 0.20 ml/sec at 1 atm and 25°, curves 1, 2, and 3 correspond to the methane–hydrogen mixture flow rate of 0.5, 0.7, and 0.9 ml/sec at 1 atm and 25°, respectively.

molar response vs. pressure curves of the substance in question and of the reference substance display different patterns and, in some cases, intersect each other several times.

A special situation occurs in the case of halogen-containing compounds, the RMR values of which show an extraordinarily high dependence on pressure, especially at pressures close to 1 atm; relatively small changes in pressure bring about substantial changes in the RMR values. The situation is illustrated in Fig. 7, which shows chromatograms of a mixture containing 40.05, 6.00, and 53.95 mole % of tetra-chloromethane, benzene, and trichloromethane, respectively, obtained at an N_2/H_2 flow rate ratio of 0.8. This peculiar behaviour of halogenated substances could be turned to account for their selective identification by flame ionization under controlled pressures.

TABLE I

RMR VALUES OF MODEL SUBSTANCES AT DIFFERENT PRESSURES AND AT H_2, N_2, AND AIR FLOW RATES OF 0.3, 0.56 AND 14 ml/sec, RESPECTIVELY

The coefficient of variation of the RMR values was 2.3%.

| Compound	Pressure (atm)							
	1.0	2.0	3.0	4.0	5.0	7.0	10	15
Octane	1.28	1.36	1.31	1.25	1.25	1.26	1.25	1.04
Cyclohexane	0.97	1.00	0.97	0.94	0.92	0.96	0.96	0.96
Hexane	0.92	0.98	0.98	0.98	0.97	0.95	0.89	0.94
Butyl acetate	0.87	0.79	0.81	0.81	0.81	0.80	0.78	0.65
Thiophene	0.64	0.65	0.65	0.66	0.67	0.68	0.69	0.62
tert.-Butyl alcohol	0.62	0.63	0.63	0.62	0.62	0.62	0.60	0.55
Isobutyl alcohol	0.58	0.64	0.60	0.59	0.59	0.61	0.60	0.51
Acetone	0.34	0.35	0.33	0.34	0.35	0.35	0.33	0.36
Chloroform	0.22	0.13	0.14	0.14	0.15	0.17	0.19	0.26
Tetrachloromethane	0.09	0.12	0.13	0.13	0.14	0.15	0.17	0.30
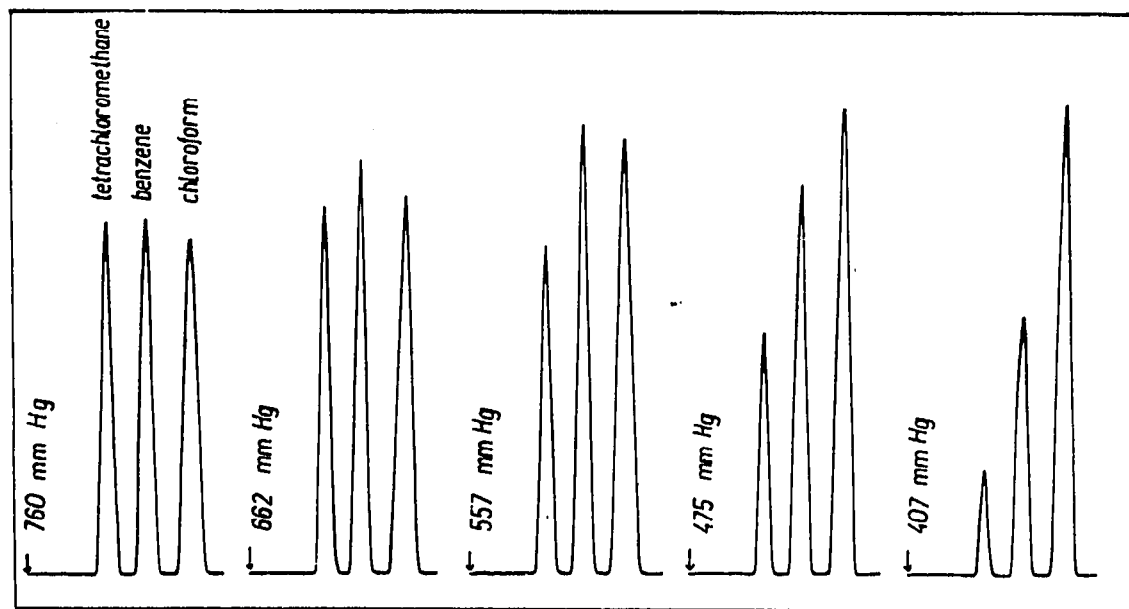
Fig. 7. Chromatograms of a tetrachloromethane–trichloromethane–benzene mixture at various pressures; H_2, N_2, and air flow rates were 0.70, 0.56, and 14 ml/sec, respectively.

CONCLUSIONS

Pressure represents a most important factor in flame ionization detection. The ionization efficiency *vs.* pressure curves display local maxima, the values and positions of which depend on the ratio of the N_2 and H_2 flow rates; an increase in the hydrogen flow rate leads to a shift of the maximum towards low pressures, while increasing the N_2 flow rate shifts the maxima towards the region of higher pressures. For an FID of given geometry, there is certain combination of the pressure and N_2/H_2 flow rate ratio at which the maximum of the ionization efficiency is an absolute maximum. There is no essential difference between the pressure dependences of ionization efficiency measured under constant volume flow rates and constant mass flow rates of the gases.

Though the pressure dependences of ionization efficiency found for different organic substances are very similar to each other, the existing differences cause the relative molar response values to be appreciably dependent on pressure. An exceedingly high sensitivity to pressure has been observed with halogen-containing substances, which renders it possible to detect these compounds selectively by an FID with pressure control.

At pressures higher than about 10 atm, the ionization efficiency is approximately a twentieth as high as that at an atmospheric pressure and remains practically independent of the pressure, *i.e.* the FID behaves as a typical mass-sensitive destructive detector under these conditions.

REFERENCES

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