A SENSITIVE DETECTOR FOR GAS CHROMATOGRAPHY

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The growing importance of gas chromatography as a method for the analysis and separation of complex mixtures of volatile substances has increased the need for physical methods of measuring the concentration of vapours in the gas stream emerging from the chromatography column.

A critical comparison of the methods at present in use together with a discussion of desiderata for an ideal detector has been given by JAMES[1] and of the detectors at present in practical use, namely the Katharometer, the hydrogen flame detector SCOTT[2], the ionisation cross section detector DEAL *et al.*[3] and the gas density balance MARTIN AND JAMES[4] only the last approaches the ideal requirements. The others are either insensitive or have responses which are non-linear, and unrelated to any simple molecular parameter so that calibration for each substance to be detected may be necessary.

The continuing quest for an ideal detector has stimulated interest in other possible physical methods of detection. The most fruitful of these have been methods based on the ionisation properties of gases. In addition to the detector already mentioned which depends for its action on the differences in the ionisation cross section of different molecular species, two methods have recently been described which use the well known sensitivity of a low pressure gas discharge to small changes in the composition of the gas, HARLEY AND PRETORIUS[5], RYCE AND BRYCE[6]. Both of these devices have sensitivities many orders of magnitude greater than those so far described. This paper describes a detector whose method of operation is based on the unique ionisation properties of argon. It has a sensitivity which can be varied over a wide range and which will permit the detection of as little as $2 \cdot 10^{-12}$ moles of most organic substances. In spite of its high sensitivity to vapour composition the device is relatively insensitive to temperature, pressure and gas flow rate. In addition to these desirable properties the detector is simple to construct, and has a response which is closely similar for different molecular species.

General principles of operation

The absorption of ionising radiation by gases produces ions and excited but unionised atoms and molecules. With most gases the life time of the metastable atoms is short, *ca.* 10^{-9} secs., consequently under constant conditions of irradiation the ions which have a comparatively long life time greatly outnumber the excited but non-ionised atoms. The rare gases are unusual in their possession of long lived metastable

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atoms, and in these gases the concentration of metastable atoms approaches that of ions during steady irradiation. In the pure gas the metastable atoms eventually decay to the normal state with the emission of radiation. In the presence of small traces of other gases the metastable rare gas atoms can, during their lifetime, transfer their energy of excitation by collision. If the ionisation potential of the gas molecules is less than the excitation potential of the rare gas atoms the transfer of energy on collision leads to the ionisation of the added gas. The molecules of most organic compounds have ionisation potentials lower than the excitation potential of helium, neon, and argon, and are ionised on collision with the metastable atoms of these noble gases.

The steady level of ionisation in an irradiated gas is easily measured in an ionisation chamber and so is any increase following the addition of another gas or vapour. It follows that a simple gas chromatography apparatus can be based on the use of a rare gas as the carrier gas and an ionisation chamber containing a source of ionising radiation as the detector.

In practice only two rare gases are available in cylinder form and at prices which would permit the economic use of such an apparatus namely helium and argon. By a fortunate coincidence the cheaper of these gases, argon, functions well in the device when used directly from commercial cylinders. Carefully purified helium would do even better but the commercial gas contains sufficient impurity, probably neon and argon, to discharge the metastable helium atoms shortly after their formation. Commercial argon is not necessarily purer than helium, but the excitation potential of metastable argon is lower than that of helium and neon; collision with these gases as impurities does not therefore cause the discharge of the metastable argon.

There follows a description of the construction of a practical detector based on the use of argon as a carrier gas. An account is given of its response under a wide

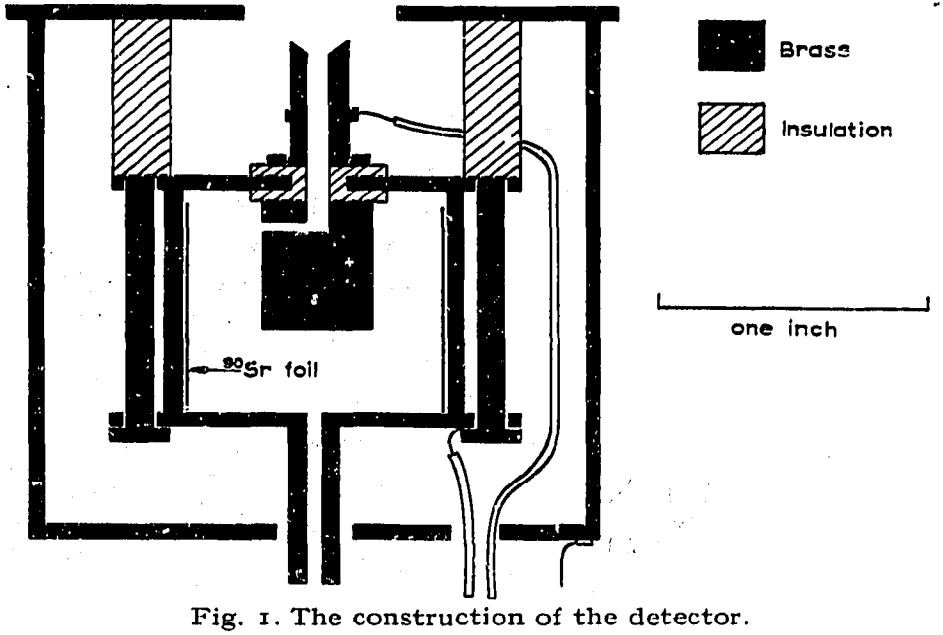

Fig. 1. The construction of the detector.

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variety of operating conditions and with many different substances. The theoretical aspects of its operation are also discussed.

Details of construction

Fig. 1 illustrates the design and dimensions of a typical ionisation chamber suitable for use as a detector. It consists of a central brass collecting electrode, which also serves as the entry port for the gases emerging from the chromatography column. This electrode is insulated from the body of the chamber by means of a poly-tetrafluorethylene washer. The chamber itself is also made of brass and thick enough to shield the radiation source contained within it. The gas is led from the chamber through a short length of brass tubing. In use the outer part of the chamber is at a relatively high potential with respect to earth and frequently at temperatures as high as 200°. The whole chamber is enclosed in an outer jacket of brass or aluminium at earth potential.

Source of ionising radiation

Sealed sources of a wide variety of radio-active isotopes are available commercially for use with industrial thickness gauges. They consist of a small quantity of a compound of some radio-active element firmly bonded in silver foil. Most of the radiation from the element is free to escape the foil but the escape of the isotope itself is virtually impossible. For satisfactory operation with an ionisation chamber of the type just described sufficient radiation to give an ionisation current of 10^{-8} to 10^{-9} amperes is required. With currents smaller than this, expensive amplifiers may be needed and with higher currents the operation of the detector may be impaired by space charge effects. A ten millicurie ^{90}Sr source of β radiation and a 80 microcurie radium source of α radiation have both been found satisfactory. The ^{90}Sr source is to be preferred since the noise level of the device is inversely related to the mean number of ionising particles entering the chamber in unit time and this is nearly 100 times as great from the ^{90}Sr source as from the radium α particle source.

The external radiation from the assembled detector is less than 10 mR per hour at the surface, so that the completed apparatus does not present an external radiation hazard. The exposed sources however are distinctly hazardous and all precautions appropriate to the handling of radio active material should be taken during the assembly and dismantling of the detector.

Amplifier and high voltage supply

The ionisation current of the order of 10^{-8} amperes is most conveniently conveyed to a milliammeter or to a simple pen recorder by a D.C. current amplifier of the type developed by SCROGGIE[7] modified for use with ionisation devices, WELLMAN AND LOVELOCK[8]. The input resistance of the amplifier was $2 \cdot 10^9$ ohms and the steady voltage developed across it by the ionisation current with pure argon flowing in the detector was approximately 20 volts. An equal and opposite voltage was applied to the input of the amplifier from a potentiometer chain so that the indicating meter

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read zero for pure argon, and gave a positive deflection with argon containing organic compounds.

Calibration

The high sensitivity of the detector made calibration a formidable problem. Static methods in which the chamber was filled alternately with pure argon and with a mixture of argon and test vapour were found unsatisfactory. The adsorbtion and desorbtion of small traces of vapour from the walls of the chamber gave unsteady and unreproduceable readings particularly at low vapour concentrations.

Dynamic methods of calibration were therefore used. In these a known quantity of a pure organic substance or mixture of substances was introduced into a stream of pure argon flowing at a constant rate through either a mixing chamber of known volume or a gas chromatograph column, and then through the detector. The rise and fall of ionisation current as the slug of vapour passed through the detector was recorded graphically using a recording milliammeter. The response of the detector to known quantities of different substances was determined from measurements of the area of the peak drawn on the recording paper. The method of introducing known quantities of vapour into the gas stream was as follows. With volatile substances argon was saturated with the vapour by passage through a vessel containing cotton wool soaked with the test substance. The saturating vessel was maintained at 0° in a Dewar flask containing crushed ice and water, the argon saturated at 0° with the test substance was allowed to warm to room temperature by passage through a coil of metal tubing. The vapour issuing from this tubing was drawn several times into a hypodermic syringe to allow the walls of the syringe to equilibrate with the vapour and then a quantity between 0.5 and 10 ml of vapour injected into the gas stream.

With substances of low volatility a known quantity of liquid was transferred using a micro pipette, volume 0.2 microlitres, to the top of a chromatography column, and the vapour passed through the column to the detector by a stream of argon flowing at a constant rate. For these tests the column and the detector were both enclosed in solid aluminium rod maintained at between 100° and 240° according to the rate of emergence of the test substance.

All tests were made at atmospheric pressure; the relative insensitivity of the detector to changes in temperature and pressure, made unnecessary any special precautions to maintain these quantities constant during the course of an experiment. Flow rates were measured with a soap bubble flowmeter, and the potential applied to the ionisation chamber was varied in different tests between 0 and 2000 volts.

RESULTS AND DISCUSSION

JESSE AND SADAUSKIS[9] found that an increase in ionisation occurs when traces of foreign gas are added to the rare gases under conditions of constant irradiation. They reported that the increased ionisation followed the collision of the foreign gas

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molecules with excited but unionised rare gas atoms, and varied with foreign gas concentration according to the relationship developed by STERN AND VOLMER[10]:

$$\frac{1}{\Delta I} = \frac{1}{C}\left(\frac{K_d}{yK_i}\right) + \frac{1}{y} \qquad (1)$$

where ΔI is the increase in ionisation at a concentration of foreign gas C, y is the concentration of excited argon atoms when $C = 0$ and Kd and Ki are constants relating to the cross sections for radiation and ionisation respectively for the excited argon atoms. This relationship predicts an increase in ionisation with increasing concentration of foreign gas rising linearly at first but tending to a constant level at which the excited atoms are discharged by collision immediately they are formed. The response of the detector was found to follow this relationship when the applied potential was less than 300 volts. At higher potentials, in the region of 500 volts the response became linear over a much wider range of concentration, and the sensitivity increased. At still higher potentials the sensitivity increased still further and the response with concentration became non-linear once more but in the opposite sense to that observed at lower potentials so that the ionisation current increased more rapidly than did the concentration and indeed tended to infinity at a finite gas concentration. In practice at voltages above 1000 sparks appeared in the detector chamber when foreign gasses were introduced into the argon stream.

The observed relationship between ionisation current, applied potential, and vapour concentration using methanol as the foreign gas is illustrated in Fig. 2. The improved linearity and sensitivity at higher potentials and the instability at very high potentials can be explained as follows: the negative ions in argon are free electrons and these even at low field strengths have unusually high velocities of agitation, TOWNSEND[11]. As the field strength in the detector is raised the agitation velocities of the free electrons increases until a significant proportion of them

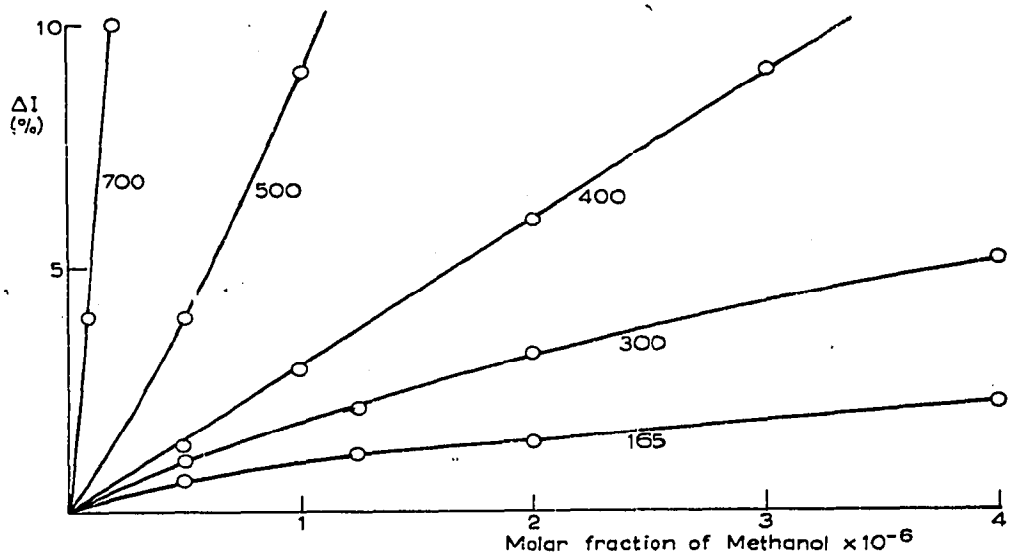

Fig. 2. The increase in ionisation current (ΔI) when argon containing various concentrations of methanol is introduced into the detector. The lines shown are drawn for various applied potentials the values of which are shown against each line in the figure.

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have enough kinetic energy to excite further argon atoms to the metastable state. The ionisation potential of argon is 15.7 ev, the excitation potential of metastable argon is 11.6 ev, this considerable difference allows a great increase in the concentration of metastable atoms without a corresponding increase in the concentration of ions. This is illustrated in Fig. 3 which shows the ionisation current in the detector

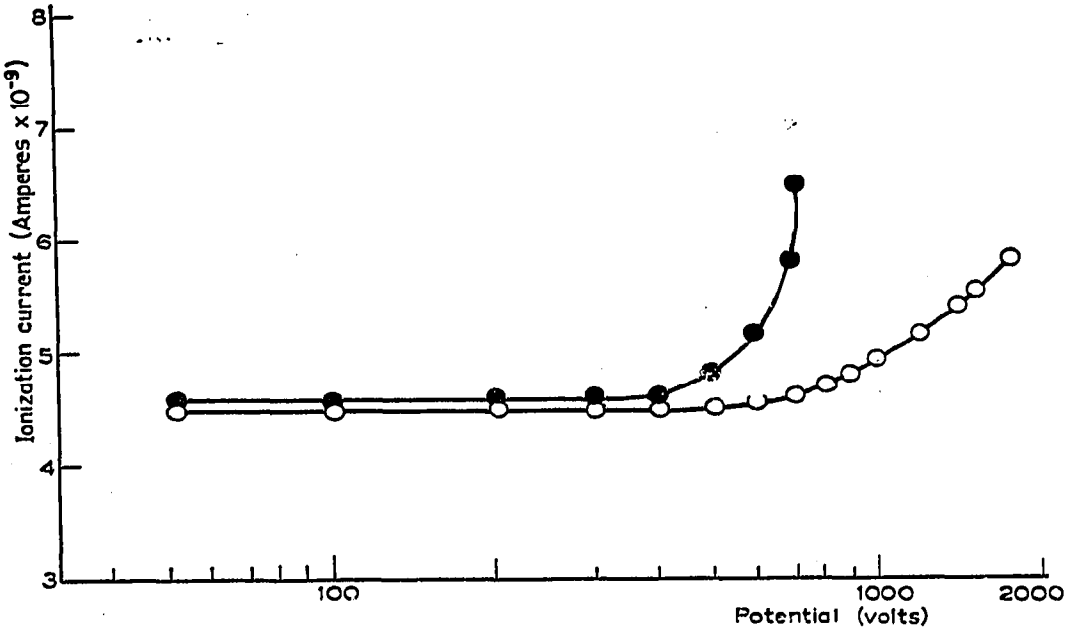

Fig. 3. The ionisation current in pure argon (○) and in argon containing pentanol (●). The pentanol concentration was one part in 10^6 by volume.

with pure argon flowing and with argon containing pentanol vapour at potentials between 50 and 1200 volts. In the pure argon the ionisation current is practically unchanged until the highest voltage is reached. Here the free electrons have sufficient energy to produce ions on collision. In the impure argon the ionisation current commences to rise at 300 volts and tends to infinity at 1100 where sparking occurs. The difference between the ionisation current in the impure and in the pure argon is 100 times greater at 1000 volts than at 300 volts so that presumably the concentration of metastable atoms has increased in this proportion.

The multiplication of metastable atoms by electron collision explains the increased sensitivity at high voltages. The improved linearity and the instability at very high potentials can also be explained if it is assumed that the electrons set free when foreign gas molecules are ionized are themselves free to enter the chain of multiplication.

Using the STERN-VOLMER equation as a basis it is possible to derive an expression for the increase in ionisation current for various concentrations of foreign gas at different applied potentials, namely:

$$\Delta I = \frac{K_i C\,(\Phi x + y)}{K_i C\,(1 - \Phi) + K_d} \qquad (2)$$

where x is the concentration of ions when $C = 0$, Φ is the multiplication factor for

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the concentration of metastable argon atoms. The other quantities are the same as those described for equation (1).

This relationship for different values of Φ corresponding to different applied

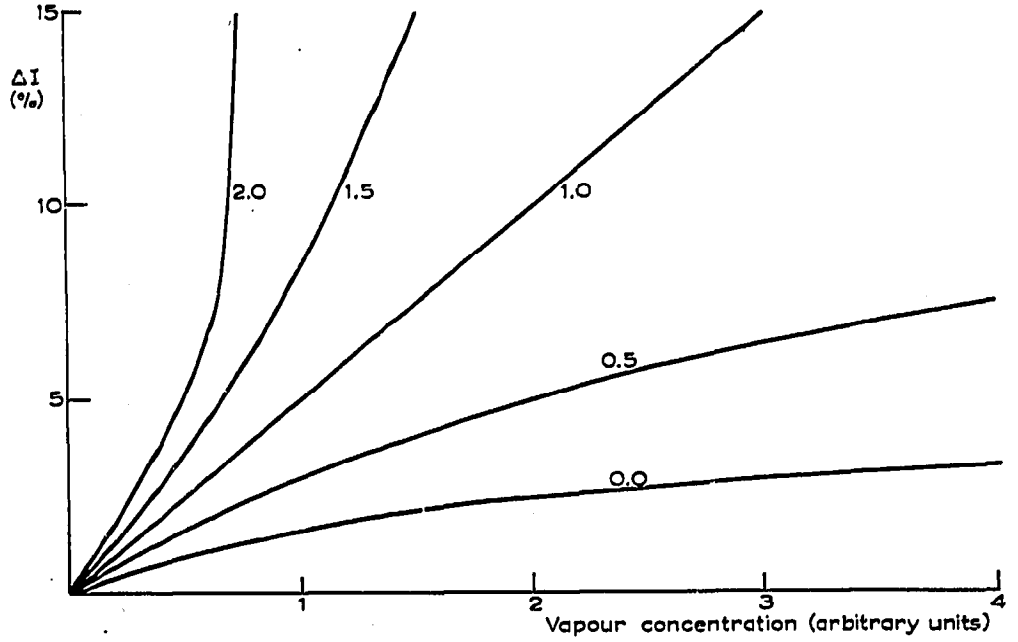

Fig. 4. The calculated increase in ionisation current (ΔI) when argon containing various concentrations of vapour is introduced into the detector. The lines are drawn for different values of the multiplication factor (Φ) of the initial concentration of excited argon atoms.

voltages is shown in Fig. 4 and can be seen to be closely similar to the observed response at different voltages shown in Fig. 2.

Response to various molecular species

One of the more important features of a practical detector is that it should regard the different molecular species presented to it either equally or in a simple predictable manner.

The response of the detector here described for different substances might be

TABLE I

THE SENSITIVITY OF THE DETECTOR TO COMPOUNDS WITH DIFFERENT IONISATION POTENTIALS

Compounds with ionisation potentials below 11.6 eV Compound	*I.P.* eV	*S*	*Compounds with ionisation potentials above 11.6 eV* Compound	*I.P.* eV	*S*
Methanol	10.9	0.9	Nitrogen	15.5	0.00
Ethanol	10.6	0.9	Carbon dioxide	14.4	0.01
Hexane	10.6	1.2	Oxygen	13.6	0.00
Ethyl acetate	10.0	0.9	Methane	13.2	0.07
Benzene	9.5	1.5	Water	12.8	0.03
Bromobenzene	9.4	0.9			
Cyclohexane	9.2	1.4			

I.P. = ionisation potential in electron volts, S = molar sensitivity of the detector relative to pentanol ($S = 1$). Excitation potential of metastable argon atoms 11.6 electron volts.

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expected to be a function of, the ionisation potential, the cross sectional area, and the velocity of approach for the collision between the test molecules and the metastable argon atoms. Table I shows the sensitivity of the device for the same molar fractions of a series of substances whose ionisation potentials are known with precision, MORRISON AND NICHOLSON[12]. The Table illustrates that those substances with ionisation potentials markedly greater than the excitation potential of argon do not respond whereas those with ionisation near of below the argon excitation potential give closely similar responses.

In practice all but a very few low molecular weight organic compounds have ionisation potentials lower than 11.6 ev. An attempt was therefore made to account for the small differences in response of different compounds in terms of the expected frequencies of collision between the organic molecules and argon atoms using the kinetic theory of gases as a basis for calculation.

According to the kinetic theory of gases the number of collisions per second in a gas which is a mixture of two different molecular species is:

$$(r_1 + r_2)^2 n_1 n_2 \left\{3\,RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right\}^{1/2} \tag{3}$$

where r, n and M denote the radius, molar fraction, and molecular weight respectively of each molecular species. R is the gas constant and T the absolute temperature.

If the ionisation current in the detector is related to the frequency of collision between argon atoms and the foreign vapour molecules, then the relative response to different molecular species at the same molecular concentrations will be proportional to:

$$(r_A + r_x)^2 \left\{\frac{1}{M_A} + \frac{1}{M_x}\right\}^{1/2} \tag{4}$$

where r_A and M_A and r_x and M_x refer to the radius and molecular weights of argon and the test substance respectively.

For substances with molecular weights considerably greater than argon, and assuming that the radius of the molecules is approximately proportional to $M^{2/3}$ this expression reduces approximately to: $\frac{1}{M^{1/6}}$ (5)

This last expression would suggest that only small changes in the sensitivity of the detector for different compounds are to be expected. The mass sensitivity, that is the response to a given mass of substance, is the more convenient practical unit and is obtained from expressions (4) and (5) by dividing by the molecular weight. The observed mass sensitivities of different classes of organic compound plotted against their molecular weights are shown in Fig. 5; also shown as a solid line is the expected mass sensitivity using expression (4). In the calculations the radii of the molecules were assumed to be approximately equal to:

$$\left(\frac{3M}{4d}\right)^{1/3}$$

where (M) is the molecular weight and (d) the density in the liquid or solid state at low temperatures. Nearly all of the compounds whose mass sensitivities are shown

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in Fig. 5 have low temperature densities close to 1, and this value was chosen in calculating the expected response. Both the observed and the calculated sensitivities are referred to that of a standard substance 1-pentanol. Fig. 5 illustrates that with low molecular weight compounds there is good agreement between observation and theory. For the higher molecular weight alcohols and fatty acid esters the sensitivity falls less rapidly than the expression predicts. This divergence might

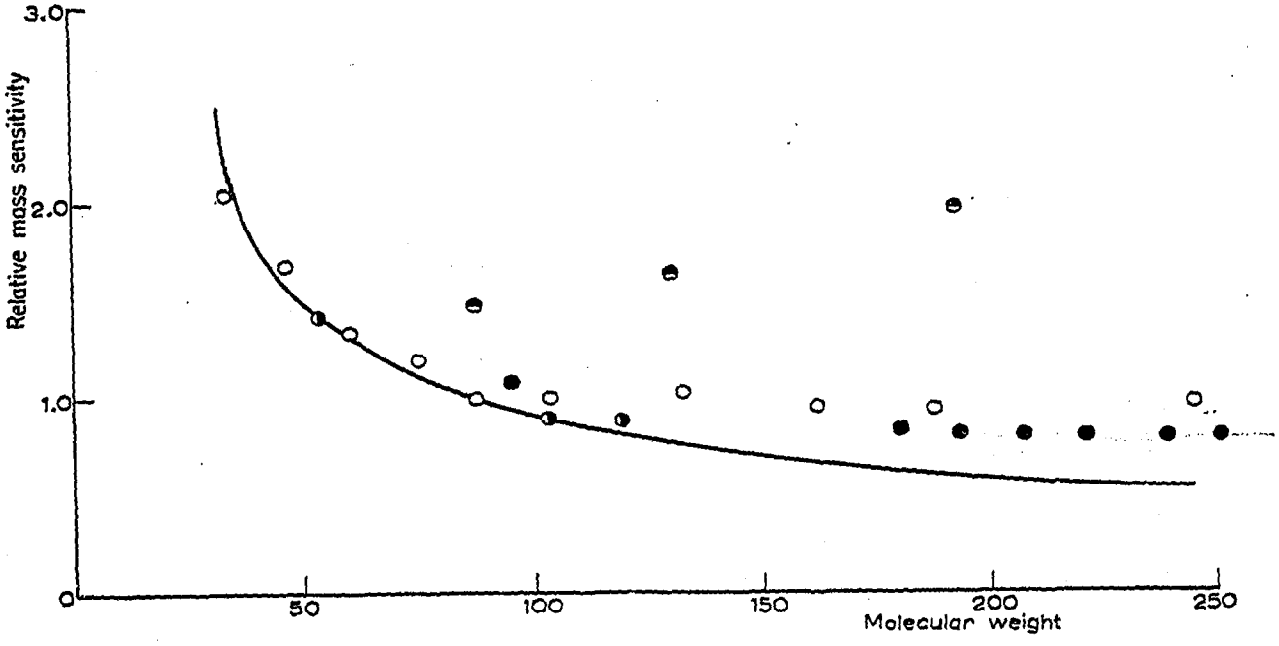

Fig. 5. The mass sensitivity of the detector to different organic substances. The solid line is the calculated mass sensitivity, and the points are the observed values for various classes of organic compounds as follows:
(○) *n*-primary alcohols (◐) ketones and ethers
(●) *n*-primary fatty acid methyl esters (◒) aromatic hydrocarbons.
Both the observed and calculated values of the mass sensitivity are relative to 1-pentanol, mass sensitivity 1.

be due to the partial or complete uncoiling of their hydrocarbon chains in the gas phase, so that the molecular radii are greater in the gas phase than in the liquid or solid state. Even greater divergences are shown by the aromatic hydrocarbons, benzene, naphthalene and phenanthrene. With these planar molecules the discrepancy is probably attributable to their large effective cross section when free to rotate in the gas phase. If in expression (4) the calculated sensitivities are determined from the cross sections of molecular models a much closer agreement between theory and practice is obtained. In general the detector does not discriminate between the different molecular species. With the methyl esters of the higher fatty acids and the alcohols, which compounds are most conveniently analysed by gas chromatography, the mass sensitivity is constant within the limits of precision of the method.

PERFORMANCE

Sensitivity

The sensitivity of any electrical transducer is a function of the signal to noise ratio at given input level and to its time of response. With the detector here described the response time was determined by the requirements of resolution in gas chromatography and was set at 2 seconds, this was done by choosing appropriate values in the input circuit of the amplifier. At this time of response the random fluctuations

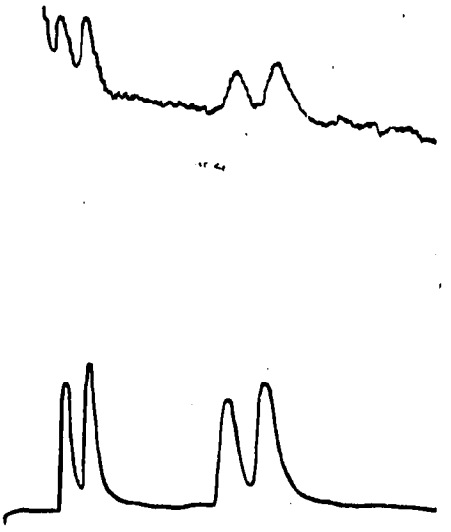

Fig. 6. A chromatogram illustrating the separation of a mixture of isomeric ethyl diphenyls. In the upper chromatogram the quantity of each component was 0.05 microgram and in the lower chromatogram 5.0 microgram.

in the current flow in the ionisation chamber was 0.05 % of the total current and this high level of noise is a consequence of the stochastic nature of the emission of the radio-active source. The sensitivity of the detector is therefore the concentration of vapour which would increase the ionisation current by 0.1 %, that is twice the noise level. Fig. 6 shows a record of a chromatogram taken with the detector operating at its highest sensitivity with an applied potential of 1200 volts. 0.05 microgram each of a mixture of isomeric ethyl-diphenyls (dissolved in 200 millimicrolitres of chlorobenzene) were added to the chromatography column and a separation made at 200°. The record illustrates the random fluctuations of the signal and the responses to the components of the mixture. The maximum deflection given by each component is approximately 20 times the noise level. At this sensitivity level therefore $5 \cdot 10^{-9}$ g of organic substance could just be detected. There is of course a considerable dilution of the vapour in the retention volume of the column; with the separation illustrated in Fig. 6 the sensitivity of the detector itself is rather more than ten times greater than that of the complete chromatographic apparatus. It would just respond to $5 \cdot 10^{-10}$ g or $2.5 \cdot 10^{-12}$ moles. There is good reason to believe that sensitivities considerably higher than this could be obtained if care were taken in the design of the detector to avoid sharp points and edges.

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It is rarely necessary or desirable to operate the detector at these extreme sensitivities and with operation at 400 volts, loads of between 10 micrograms and 1.0 mg give satisfactory results. For example in Fig. 6 there is also shown a record of the separation of the same mixture of diphenyls using an applied potential of 400 volts and a column load of 20 micrograms.

Stability and linearity of response

In normal use the amplifier gain is adjusted to a level at which the noise generated by the detector cannot be seen on the recorder tracing. At this level of amplification the maximum deflection of the recorder is given by an input signal of between two and five volts. This is high compared with that of most electrical transducers and no trace of instability or of long term drift attributable to the amplifier was expected or found. The ionisation current in the detector itself remains constant during small changes in the ambient temperature and pressure, and no special precautions, such as enclosing the detector in a thermostatically controlled environment, appear to be necessary. Ionisation devices similar to the detector form the basis of highly sensitive flowmeters, LOVELOCK AND WASILEWSKA[13], the detector was however designed to have a low sensitivity to gas flow rate; in practice alterations in the gas flow rate between 5 and 100 ml per minute did not sensibly affect the ionisation current.

Fig. 2 illustrates that the response of the instrument is linear over a considerable range of methanol vapour concentration, provided that the applied voltage is sufficient to provide some multiplication of the metastable argon atoms. The non-linearity at high voltages can be prevented by including a high resistance, 10^{10} ohms in series with the ionisation chamber. With some substances particularly low molecular weight halogenated hydrocarbons, for example CCl_4 and $CHCl_3$, the response becomes non-linear at high concentrations even when the applied voltage is sufficient for a linear response with most other compounds. This effect is probably a consequence of electron capture by these vapours. For the same reasons it is important to ensure that no air leaks into the detector during its operation; oxygen is particularly effective in capturing electrons and prevents the multiplication of the metastable argon atoms.

Although in the interests of linearity of response it is best to operate the detector at low vapour concentrations no "poisoning" of the detector or memory effects following the use of a gross excess of any compound have been observed.

Decomposition in the detector

With this and other ionisation devices the ionisation of any organic vapour molecule passing through the detector is inevitably followed by its destruction. The proportion of molecules destroyed by ionisation is closely related to the observed increase in ionisation current, since the detector operates under conditions where almost all ions produced in the chamber are collected. If it is assumed that not more than ten times as many molecules are damaged by radiation as are ionised, and this estimate is likely to include a large factor of safety, then the fraction of a gram mol-

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ecule destroyed per second is $A/M \times 10/96{,}500$ where A is the observed increase in ionisation current in amperes and M the molecular weight of the compound. Simple calculation indicates that the proportion of molecules destroyed varies from one in 10^6 at the maximum sensitivity to one in 10^9 under normal conditions of operation. Losses of this magnitude are clearly negligible. With other ionisation devices where much higher currents flow the complete destruction of the sample is possible.

Operation at high temperatures

Within the limits of the thermal stability of the materials of its construction the only effects of high temperatures on the operation of the detector is a small decrease in the ionisation current. The detector has been maintained for many months at 200° and for several days at 245° without appreciable change in its response. The small and regular change in ionisation current with temperature makes possible the continuous alterations in temperature during the course of a chromatographic separation.

ACKNOWLEDGEMENTS

I am indebted to Dr. A. T. JAMES for drawing my attention to the need for the device and for his helpful suggestions concerning the application of the detector to gas chromatography. I am most grateful to Mr. E. A. PIPER and to Mr. L. WOODGET, both of the Instrument Division of the National Institute for Medical Research, who constructed the detector and other apparatus ancillary to it.

SUMMARY

The unique ionisation properties of argon form the basis of a sensitive and stable detector for use with gas chromatography apparatus The detector is capable of responding to as little as $2 \cdot 10^{-12}$ moles of most organic compounds and its response to different molecular species is closely similar, and linear with concentration over a considerable range.

Details of construction and performance are given. The theory of operation of the device is dicussed, and depends on ionising collision between excited argon atoms and molecules of the test substance in the vapour phase.

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