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GAS CHROMATOGRAPHIC DETECTION MODES FOR THE PLASMA CHROMATOGRAPH

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SUMMARY

The use of a plasma chromatograph as a gas chromatographic (GC) detector is described. It not only duplicates the capabilities of many known detectors, but also gives low-resolution qualitative detection of chosen compounds. Detection of GC effluents comparable to the flame ionisation and electron capture detectors is demonstrated using positive and negative modes of operation of a research-oriented instrument. A tunable mobility detection of both positive and negative ions selected in the mobility spectra of given compounds provides highly sensitive, and low-resolution qualitative detection of GC effluents. The use of this technique is facilitated by the availability of a number of reference spectra of different classes of compounds previously reported. Further development of the plasma chromatographic instrumentation for multi-mode detection of GC effluents is suggested.

INTRODUCTION

Plasma chromatography[1,2] was first introduced as an analytical technique in 1970[1,2]. Operating on the principles of charge transfer ionization, positive reactant ions produced in nitrogen at atmospheric pressure by the ionizing emission of beta rays from a ^{63}Ni source react with the sample to form positively charged species characteristic of the sample. Thermal electrons formed from the beta particles may also react with the sample to produce characteristic negatively charged species. These positive or negative product ions are separated according to their drift velocities in an electric field at atmospheric pressure using an ion-drift spectrometer. A plot of ion current *versus* drift time results in a positive ion mobility spectrum (PIMS) or a

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negative ion mobility spectrum (NIMS) which is characteristic of the component being analyzed. A complete review of this technique has been reported previously[3].

Analysis for the most part has required the introduction of pure samples to obtain reproducible ion mobility spectra. In order for the plasma chromatograph to be practically applied to mixtures in a wide variety of analyses, it must be used in conjunction with an efficient separation method. The sensitivity of the plasma chromatograph (less than 10^{-9} g for most organic compounds), its atmospheric pressure operation, and its use of nitrogen as the reactant and drift gases in the ion-drift spectrometer are factors which point to gas chromatography (GC) as the most suitable separation technique for use with plasma chromatography.

On the other hand, GC is an efficient separation technique which benefits much from a sensitive, selective multi-mode detection system. Any analyst who has faced the problem of selecting GC detectors from the numerous choices available feels the desire for a single detection system capable of analyzing the wide variety of trace compounds separated by GC methods. Plasma chromatography offers such a system by combining the characteristics of a number of currently used GC detectors.

The complementary aspects of the plasma chromatograph and the gas chromatograph have been realized previously and their combination has been reported several times in the literature. Cram and Chesler[4] separated a number of the E-series freons and recorded their ion mobility spectra as each eluted from the column. Karasek and Kim[5] have reported ion mobility spectra of phthalic acids introduced into the plasma chromatograph via a gas chromatograph. In both of these applications the plasma chromatograph was used to obtain selected PIMS scans and not, as conventional GC detectors, to produce data in the form of chromatograms. A flame ionisation detector (FID) was required to supply retention time data.

Also, a method for analyzing resmethrin from peanut oil has been reported in which the plasma chromatograph continuously monitors the column effluent[6]. The plasma chromatograph is permanently tuned to the drift time which corresponds to the molecular ion (MH^+) produced by resmethrin. This mode of detection was shown to be significantly more sensitive than the FID and provided a response tracing typical of a conventional chromatogram.

However, the use of these GC–plasma chromatography coupled systems has been limited. This has primarily been due to two major technical problems. First, the sensitivity of the plasma chromatograph is so great that residual solvent, unseparated components, background bleed from the column, or contamination of the carrier gas changes, complicates, or completely eliminates the response. Secondly, the cell volumes of the presently available plasma chromatographs are so large that diffusion and adsorption effects cause serious loss of the plasma chromatographic quantitative reproducibility and of chromatographic resolution and sensitivity.

This work presents data to illustrate use of the plasma chromatograph as a multi-mode detection system for GC. Several modes of operation are described which are fundamental for the versatile use of the instrument as a GC detector. Test mixtures are analyzed to point out sensitivity and selectivity characteristics of the different detection modes. Methods which allow successful interfacing of the two instruments are discussed.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard 7620 gas chromatograph was interfaced to a Beta VI plasma chromatograph via a 0.030 in. I.D. stainless-steel transfer line. This transfer line was connected directly to the GC column through the side panel of the oven. The injection port of the plasma chromatograph was modified to accept the transfer tube. The tube must be inserted into the plasma chromatograph with caution, since the first ring of the reaction chamber is under high voltage ($\pm$3000 V). For safety the transfer line was grounded and a 2-in. gap was allowed between it and the first ring of the reaction chamber.

The GC column was a 4 ft. $\times$ 4 mm I.D. borosilicate column packed with a highly inert, 0.2% specially prepared Carbowax 20M film on Chromosorb W, 100–120 mesh (ref. 7 and references quoted therein). It was continuously conditioned at 175 °C when not in use, run at 150 °C for isothermal operations, and temperature programmed either from 60–150 °C at a rate of 10 °C/min for positive mode operation or from 50–80 °C at 6 °C/min for negative mode operation. The injection port of the plasma chromatograph and the transfer line were wrapped with heating tape and held constant at 175 °C. Nitrogen (Linde high-purity grade, 99.996%) was used as the GC carrier gas with a flow rate of 30 ml/min.

Plasma chromatographic drift and carrier gases were also Linde high-purity grade nitrogen and had respective flow-rates of 560 and 310 ml/min. The temperature throughout the plasma chromatograph was held constant at 155 °C for the positive mode and at 140 °C for the negative mode. The pressure was 733 torr for the positive mode and 728 torr for the negative mode. The voltage gradient throughout the drift and reactor sections of the instrument was held constant at 214 V/cm. Ion mobility spectra were taken with 2-min scans and with gate widths of 0.2 msec (positive mode) or 0.5 msec (negative mode) for both the first and second gates. Gas chromatograms were obtained by constantly opening the second gate at a specific time after the first gate to monitor the abundance of ions with that specific mobility. The repetition rate of the gates was at a 20-msec interval. Specific changes from these general operating conditions are given with the experiment to which they apply.

Test compounds

Microliter amounts of the headspace vapors from selected test compounds were used to demonstrate and test the various analytical modes of the GC–plasma chromatographic system. These test compounds along with their amounts per microliter of headspace vapor at 22 °C and atmospheric pressure are listed in Table I.

Modes of operation

Mobility spectra were obtained by injecting headspace vapors of the compounds of interest into the gas chromatograph with the column held isothermally at 150 °C. Scans of the 2-msec time base were used to record mobility spectra and to determine the major product ions formed and their drift times. Drift times were also determined by calculation from literature values of reported reduced mobilities. Reduced mobilities (K_0) and drift time values used in these experiments are summarized in Table II.

TABLE I

SAMPLE CONCENTRATION ESTIMATED FROM VAPOR PRESSURE DATA[21]

Test compound	*Headspace concentration (ng/μl)*
Iodobenzene	6*
Bromobenzene	33
Chlorobenzene	36*
Toluene	125
p-Chlorotoluene	22

* Calculated for an equal volume binary mixture of iodobenzene and chlorobenzene.

TABLE II

REDUCED MOBILITY AND DRIFT TIME VALUES

Ion monitored	*Reduced mobility ($cm^2/V \cdot sec$)*	*Drift time (msec)*
Positive reactant ion	2.35	7.48
Positive product ion		
p-Chlorotoluene	1.96	9.00
2,4-Dichlorotoluene	1.81	9.75
2,4,5-Trichlorotoluene	1.67	10.54
Negative product ion		
Chlorobenzene (Cl^-)	2.92	6.07
Bromobenzene (Br^-)	2.63	6.73
Iodobenzene (I^-)	2.53	7.14

The major positive reactant ion at a drift time of 7.48 msec ($K_0 = 2.35$) was continuously monitored while a mixture of three test compounds, *p*-chlorotoluene, 2,4-dichlorotoluene, and 2,4,5-trichlorotoluene, was chromatographed and the separated peaks then introduced into the inlet of the plasma chromatograph (Fig. 2). The mixture of these three components was prepared by separately drawing 0.1 μl of *p*-chlorotoluene, 0.2 μl of 2,4-dichlorotoluene, and 4 μl of 2,4,5-trichlorotoluene of their headspace vapor into a 5-μl syringe.

Under essentially the same conditions used when monitoring the major reactant ion peak, the product ion peaks of each of the three test compounds in the mixture were the monitored selected ion chromatograms seen in Fig. 3. The drift time for the major product ion of *p*-chlorotoluene was 9.00 msec, for 2,4-dichlorotoluene it was 9.75 msec, and for 2,4,5-trichlorotoluene it was 10.54 msec.

In the negative mode (*i.e.*, the voltage gradient is reversed so that negative ions are collected) the plasma chromatograph was tuned to continuously monitor the electron current by setting the second gate so that it monitored the first 0.5-msec increment of a 20-msec time base. The vapor in the headspace from an equal volume mixture of chlorobenzene and iodobenzene was used as a test mixture. 5-μl injections of this headspace were used to produce the data. The gas chromatograph was programmed from 50–80 °C at 6 °C/min. All other operating conditions were similar to those in the positive mode.

The negative product ions were monitored in the same manner as were the

positive product ions. Chromatograms were obtained for the mixture of chloro- and iodobenzene under the same conditions as the electron current had been monitored, except that the spectrometer was tuned to the drift times which corresponded to the mobilities Cl^- and I^-.

Two operating parameters were investigated using this electron current mode. The effect that the plasma chromatographic carrier gas had on the shape of the chromatographic peak was investigated by repetitive injections of 1-μl headspace vapors by holding the GC carrier gas flow-rate at 30 ml/min and the PLC drift gas flow-rate at 560 ml/min, while the PLC carrier flow-rate was varied from 0–310 ml/min. Also, the voltage gradient of the drift tube was varied from 2–214 V/cm to determine its effect on the response of 1 μl injection of the headspace from bromobenzene.

RESULTS AND DISCUSSION

The ion mobility spectra produced by the plasma chromatograph serve only as low-resolution fingerprint data for known compounds. For unknown compounds in GC peaks these ion mobility spectra can be used to provide semi-qualitative information. Introduction into the plasma chromatograph through a GC interface is a desirable technique to insure sample purity when known compounds are being studied to establish reference ion mobility spectra.

Fig. 1 shows three positive ion mobility spectra which were obtained by introducing the test compounds via a gas chromatograph. Tracing (a) is a blank and shows a typical positive reactant ion spectrum. The strong response and the absence

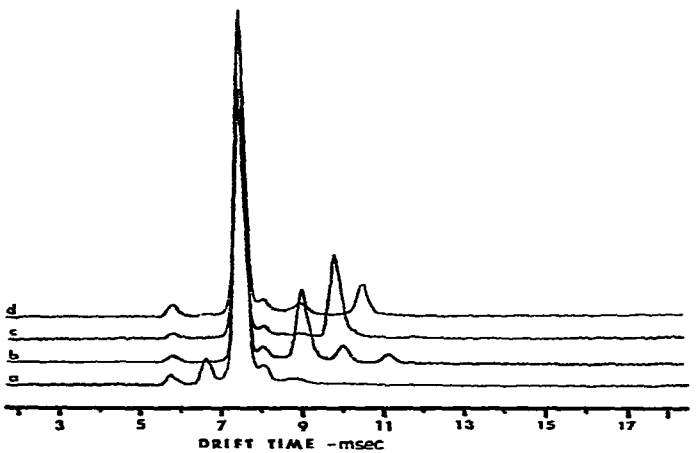

Fig. 1. GC–plasma chromatographic positive ion mobility spectra (PIMS) of (a) reactant ions, (b) a 0.2-μl injection of *p*-chlorotoluene headspace vapor ($\approx$4 ng), (c) a 0.4-μl injection of 2,4-dichlorotoluene headspace vapor, and (d) a 5-μl injection of 2,4,5-trichlorotoluene headspace vapor. GC–plasma chromatography conditions were as follows: column, 4 ft. $\times$ 4 mm I.D. borosilicate glass tube packed with Ultra-Bond 20 (100–120 mesh); injection temperature, 200°C; column temperature, 150°C; transfer line temperature; 175°C; plasma chromatography temperature, 155°C; atmospheric pressure, 733 torr; GC carrier gas, nitrogen, at 30 ml/min; plasma chromatography carrier gas, nitrogen at 310 ml/min; plasma chromatography drift gas, nitrogen at 560 ml/min; drift times scanned, 0–20 msec in 2 min; gate widths, 0.2 msec; voltage gradient, −214 V/cm.

of extraneous unidentified ion peaks indicate that the system is virtually free of contamination. Tracing (b) the positive ion mobility spectra of *p*-chlorotoluene with its major product ion at 9.00 msec ($K_0 = 1.96$), tracing (c) shows the major product ion for 2,4-dichlorotoluene at 9.75 msec ($K_0 = 1.81$), and tracing (d) shows the major product ion at 10.54 msec ($K_0 = 1.67$) for 2,4,5-trichlorotoluene.

In order to produce these product ions, a certain portion of the reactant ion concentration is depleted. By tuning the plasma chromatograph to continuously respond to the major reactant ion, the presence of eluting compounds can be detected by a reduction in reactant ion current. Fig. 2 illustrates this technique for a mixture of 2,4,5-trichlorotoluene, 2,4-dichlorotoluene, and *p*-chlorotoluene. When the plasma chromatograph is tuned to 7.48 msec, the major reactant ion is continuously detected and a tracing of its charge transfer activity results in a chromatogram of the three components. This is analogous to the function of an electron capture detector (ECD) in which standing electron current is depleted to give a GC peak.

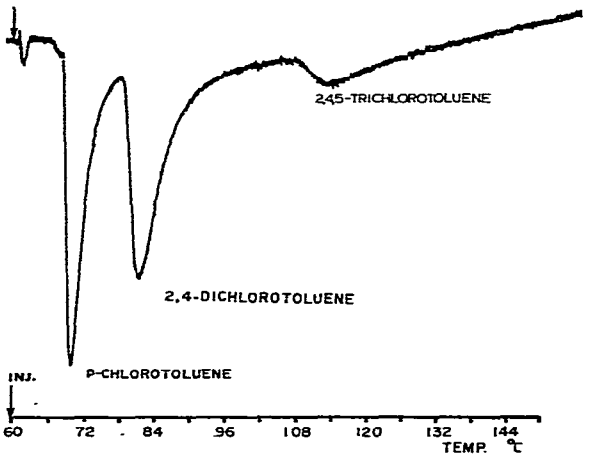

Fig. 2. GC–plasma chromatographic positive reactant ion mode. Single injection of a mixture of 0.1 μl of *p*-chlorotoluene headspace vapor ($\approx$2 ng), 0.2 μl of 2,4-dichlorotoluene headspace vapor, and 4 μl of 2,4,5-trichlorotoluene headspace vapor. GC–plasma chromatography conditions were the same as in Fig. 1, except that the column was temperature programmed from 60–150°C at 10°C/min, and a drift time of 7.48 msec was monitored.

To date, the positive reactant ions of the plasma chromatograph have always reacted when any organic component was introduced into the reaction chamber. By monitoring these ions, the plasma chromatograph is a non-selective, universal GC detector. The type of information gained is essentially that obtained from a FID except that the detection limits for the plasma chromatograph have been reported to the three orders of magnitude lower than those of the FID[3]. From Fig. 2, the peak height detection limit (two times the baseline noise level) for *p*-chlorotoluene is calculated to be approximately 40 pg.

The plasma chromatograph becomes a selective GC detector when it is tuned to continuously monitor a product ion instead of a reactant ion. Only those compounds capable of producing an ion which migrates at a selected drift time will

respond in the detector. The chromatograms given in Fig. 3 show the selective detection of each of the three components in the test mixture. *p*-Chlorotoluene is selectively detected when the plasma chromatograph is tuned to 9.00 msec. (The small peak in chromatogram c can be attributed to a secondary product ion of 2,4-dichlorotoluene with a drift time of 9.00 msec.) Similarly, chromatograms for drift times of 9.75 and 10.54 msec respond selectively to 2,4-dichlorotoluene and 2,4,5-trichlorotoluene, respectively, when the mixture of the three test compounds is injected.

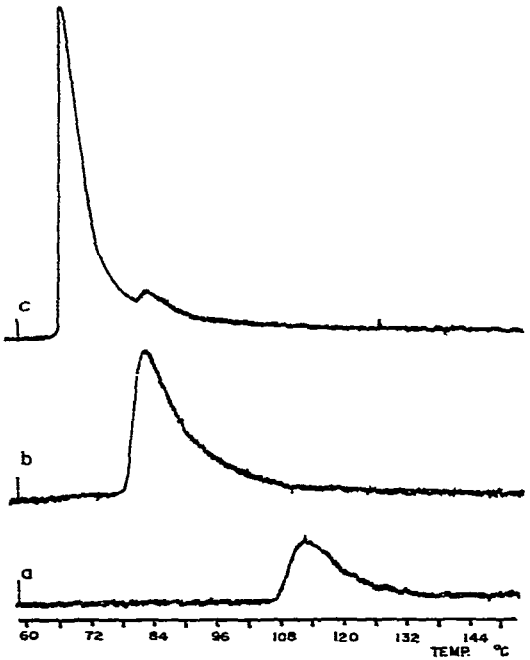

Fig. 3. GC–plasma chromatographic positive product ion mode. Chromatograms a, b, and c are produced from separate injections of the test mixture of (c) 0.1 μl of *p*-chlorotoluene headspace vapor ($\approx$2 ng) (drift time, 9.00 msec), (b) 0.2 μl of 2,4-dichlorotoluene headspace vapor (drift time, 9.75 msec), and (a) 4 μl of 2,4,5-trichlorotoluene headspace vapor (drift time, 10.54 msec). GC–plasma chromatography conditions were as in Fig. 2, except for monitoring of the drift times given above.

Chromatograms analogous to those shown in Figs. 2 and 3 for the positive mode can be made in the negative mode (Fig. 4). The information gained, however, is quite different. When the plasma chromatograph is tuned to the electron current, the plasma chromatographic detector's mode of operation is almost identical to that of the commonly used d.c. ECD. The electron current is measured until a compound capable of capturing electrons enters the detector. Then, the current decreases and the response appears as a negative peak. Unlike the positive reactant ion mode, the electron current mode is a semi-selective detector which responds only to those compounds which can capture electrons. For example, a 5-μl injection of the headspace

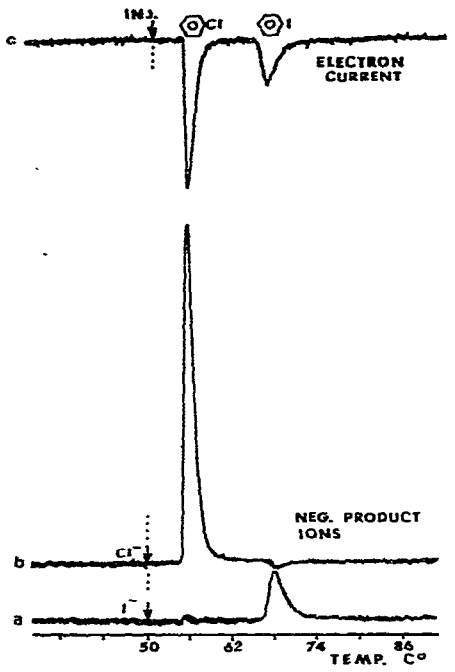

Fig. 4. GC–plasma chromatographic electron current and negative product ion modes. Chromatograms are of identical injections of a mixture of approximately 30 ng of iodobenzene and 180 ng of chlorobenzene. GC–plasma chromatography conditions were as follows: column, 4 ft. × 4 mm I.D. borosilicate glass tube packed with Ultra-Bond 20 (100–120 mesh); injection temperature, 200°C; temperature program, 50–80°C at 6°C/min; transfer line temperature, 175°C; plasma chromatography temperature, 140°C; atmospheric pressure, 728 torr; GC carrier gas, nitrogen, at 30 ml/min; plasma chromatography carrier gas, nitrogen, at 310 ml/min; plasma chromatography drift gas, nitrogen, at 560 ml/min; drift times monitored, (a) 7.14 msec, (b) 6.07 msec, and (c) 0.2 msec; gate widths, 0.5 msec; voltage gradient, +214 V/cm.

of toluene will not produce a response in the electron current mode. By contrast, this toluene sample will completely deplete the positive reactant ions and produces a strong response.

When a compound does capture an electron, it forms negative product ions either by associative or dissociative reactions[8]. Thus, its response can also be determined by monitoring the drift times corresponding to the negative product ions. Fig. 4 illustrates both the electron capture mode and the negative product ion mode with chromatograms of a mixture of chlorobenzene and iodobenzene. The negative product ion mode is essentially an added dimension of the electron current mode, which provides a method to identify various electron capturing compounds. Conventional ECDs give no such qualitative information about the compounds to which they respond.

Notice in Fig. 4 that the Cl^- and I^- peaks are larger than the electron current reduction peaks. The reason for this is not completely clear. It may be that some of the electrons formed in the reactor diffuse to the stainless-steel walls of the plasma chromatograph while the product ions formed migrate more completely to the col-

lector electrode. Whatever the case, the effect was seen repeatedly and indicates that under these conditions, the negative product ion mode is more sensitive than the electron current mode.

The drift times which were selected to monitor Cl^- and I^- ions can be determined literature values. K_0 values for these negative ions have previously been reported as 2.90 $cm^2/V \cdot sec$ for Cl^- and 2.50 $cm^2/V \cdot sec$ for I^- (ref. 9). Appropriate drift times are found by solving the following equation using experimental conditions of temperature and pressure

$$\tau = \frac{d}{K_0 E} \times \frac{273}{T} \times \frac{P}{760}$$

where τ is the drift time in seconds, K_0 is the reduced mobility of the ion in $cm^2/V \cdot sec$, E is the electric field gradient in V/cm, d is the drift length in cm (6 cm for the Beta VI instrument), T is the temperature in °K, and P is the pressure in torr.

K_0 values for a number of compounds have been reported in the literature, which facilitates the selection of drift times for both the positive and negative product ion modes of detection. Some of the compounds and compound classes for which K_0 values have been compiled include *n*-alkyl halides[9], substituted aromatics[10], isomeric halogenated nitrobenzenes[11], TNT[12], *n*-alkanes[13], phthalic acids[5,14], LSD and Δ^9-THC[15], *n*-alkyl acetates[16], heroin and cocaine[17], *n*-alkyl alcohols[18], and aliphatic *n*-nitrosamines[19].

It should be emphasized that the purpose of this paper is to demonstrate the various modes available to GC–plasma chromatography. Interfacing techniques are in the early stages of development and the conditions of the interface and plasma chromatographic tube used in this work are not ideal. For example, the transfer line was a 3-ft.-long stainless-steel tube which emptied into a large cell volume of the Beta VI instrument. These conditions lead to excessive compound adsorption and residence time in the plasma chromatographic ionizer in a loss of sensitivity and component resolution. Nevertheless, the components are separated sufficiently to demonstrate the advantages of the various detection modes and the limits of detection are substantially lower than most commercially available GC detection systems.

Adsorption effects of the interface were reduced somewhat by using higher than normal flow-rates for the carrier and drift gases in the plasma chromatograph. Fig. 5 shows how the symmetry of a chromatographed peak increases as the GC–plasma chromatographic carrier gas flow-rate is increased from 30–340 ml/min. Peak symmetry or "tailing factor"[20] is measured by dropping a vertical line from the maximum of the peak to the baseline. The ratio of the baseline width measured from this intersection to the leading edge of the peak and the baseline width from this intersection to the trailing edge of the peak serves as an indication of peak symmetry. This ratio is then multiplied by 100 so that a symmetrical peak has a tailing factor of 100. In Fig. 5 the tailing factor increased from about 25–30 as this flow-rate is increased from 30–340 ml/min. This 17% decrease in tailing is not large for such a great change in flow-rate and it suggests that fundamental modifications of the ionization cell region and interface surfaces are required before adsorption and diffusion effects can be eliminated.

The difficulty in coupling a plasma chromatograph to a gas chromatograph is

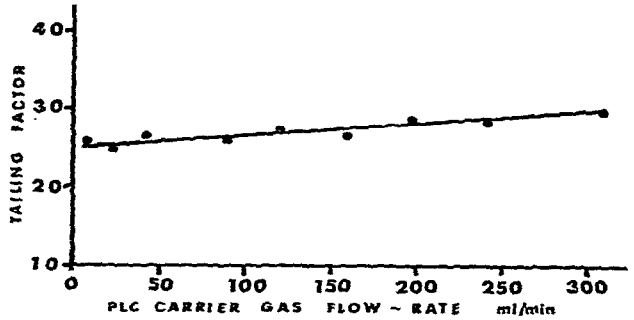

Fig. 5. Peak symmetry (tailing factor) *vs.* plasma chromatography carrier gas flow-rate. Injections of 30 ng of bromobenzene were used to obtain the data. GC–plasma chromatography conditions were the same as in Fig. 4 (drift time, 0.2 msec) except for variation of plasma chromatography carrier gas from 0–310 ml/min. A symmetrical peak has a tailing factor of 100.

not only due to effects of adsorption and gas diffusion, but also due to the high sensitivity of the technique. The detector can be easily overloaded (as is the case for an ECD, and in the past the principal difficulty in interfacing the plasma chromatograph to a gas chromatograph has been the continuous elution of "bleed" from the GC column which saturates the ionizer and reduces the detector's response. The success of the interface discussed in this paper is due chiefly to scrupulous cleaning of the entire GC–plasma chromatographic system before assembling, maintaining a leak-free system once assembled, and using a column with no detectable bleed.

The presence of strong reactant ions with no contamination product ion peaks attests to the lack of column bleed at 150 °C (Fig. 1). Also, the ability to temperature program the column without a baseline shift for both the positive reactant ion and the electron current modes indicates that the system is uncontaminated (Figs. 2 and 4). Although Fig. 4 only shows the temperature program up to 85 °C, no change in the baseline current was seen when the program was allowed to continue to 150 °C.

In general, the operating parameters for the plasma chromatograph chosen for these experiments are those customarily used for best results when obtaining ion mobility spectra. They do not necessarily reflect the optimum conditions for GC detection. For example, when the voltage on the tube is lowered from 3000–150 V, the negative mode response for bromobenzene increases almost two orders of magnitude (Fig. 6). These results are not surprising when analogies to the d.c. electron capture detector are made, but they do point out the necessity for further investigations of the modes of detection of the plasma chromatograph to increase the ability to function as desirable GC detectors.

With its six modes of operation (positive and negative ion mobility spectra, continuous positive and negative product ion monitoring, continuous electron current monitoring, and continuous positive reactant ion monitoring), the plasma chromatograph can supply a wealth of information about trace components eluted from a gas chromatograph. This information is similar to that obtained with FID, ECD, and other GC detection systems. Because of this multimode aspect, the plasma chromatograph has the potential for development into a consolidated GC detection system which is sensitive and selective for a wide variety of compounds. The major

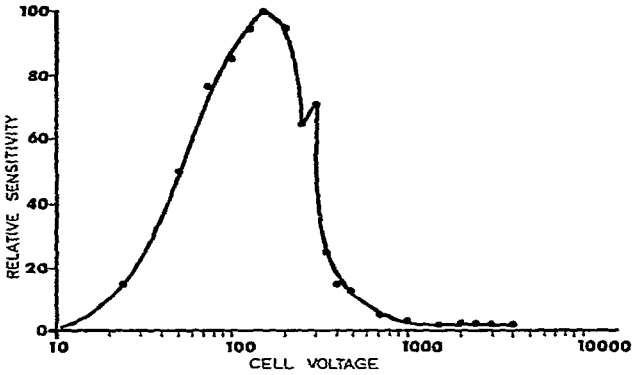

Fig. 6. Electron current mode sensitivity *vs.* plasma chromatography drift voltage. Injections of 30 ng of bromobenzene were used to obtain the data. GC–plasma chromatography conditions were the same as in Fig. 4, except for variations in the voltage gradient from +2–+214 V/cm.

instrumental design problems to be solved are to reduce considerably the size and surface area of the ionizer of the plasma chromatograph and to use a short interface of inert construction.

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