

CHROMSYMP. 1563

NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR FOR GAS CHROMATOGRAPHY

W. E. WENTWORTH*, T. LIMERO and C. F. BATTEN

Chemistry Department, University of Houston, 4800 Calhoun, Houston, TX 77004 (U.S.A.)

and

EDWARD C. M. CHEN

School of Sciences and Applied Sciences, University of Houston CL, 2700 Bay Area Blvd., Houston, TX 77058 (U.S.A.)

SUMMARY

This paper is an update on the progress made towards developing a practical electron-capture detector which does not require a radioactive source, can be operated in the pulsed mode, and can be used at temperatures up to 800 K. Data obtained using a prototype detector have been reported previously. In this paper results obtained with a "large-volume" but leak-free detector at elevated temperatures are reported, and preliminary data with a practical "small-volume" detector will be discussed. The temperature dependence suggests that the electron-capture mechanisms that have been demonstrated previously are also operative in the non-radioactive detector. The discharge has been examined spectroscopically. Finally, we present characteristic data for the detector under high-purity conditions. These data are similar to those obtained with a radioactive detector and serve as a "base case" for future development.

INTRODUCTION

In a previous publication¹ we presented the rationale for developing a non-radioactive electron-capture detector (ECD) which can be operated at high temperatures and used in the pulsed mode. The original data were obtained on a prototype version of the detector and were obtained to demonstrate the potential of the ionization source. Based on these results, the potential for developing a unique detector for gas chromatography (GC) was good.

We designed a new detector which would simulate a parallel-plate detector and which could be heated to *ca.* 800 K. It was made leak-tight by using flanges. In addition, we examined the spectra of the discharge, using a light pipe. First, the operating parameters of the detector were determined. These data serve as a base case for the non-radioactive detector. Only then were the ECD responses of representative compounds determined as a function of temperature. The general temperature dependence can be used to demonstrate the electron-capture mechanisms when compared with data obtained by using a conventional radioactive ECD. However, in

the course of these studies, when it became obvious that the "large-volume" detector was too large for good, modern chromatography we redesigned the detector with a smaller volume for use with capillary columns.

It should be emphasized that this detector can be used in both an ionization mode and an electron-capture mode so that it can be both selective and non-selective. Only the electron-capture mode will be discussed in detail in this paper, but some representative chromatograms obtained in the ionization mode will be presented.

EXPERIMENTAL

The description of the basic experimental apparatus has been previously given¹ and will not be repeated. Indeed, the only changes that have been made are in the design of the detectors. The detector shown in Fig. 1 has flanges at each end of the six ports so that leaks are kept to a minimum. Low concentrations of air will affect the performance of the detector when operated with helium in the microwave discharge. If air is introduced into the microwave discharge, the lamp will change from a characteristic peach color to a deep blue or violet. This would result in different excited species and noticeably affects the ionization efficiency. Several ports were built into the detector so that a variety of geometries could be investigated. Because of the number of ports and the bulkier flanges, the volume of this detector is unusually large. However, because of the operation at reduced pressures, the "effective" volume is much lower than in atmosphere operation, due to the increased linear flow-rate. This makes the detector suitable for columns with fewer theoretical plates. However, with small-bore

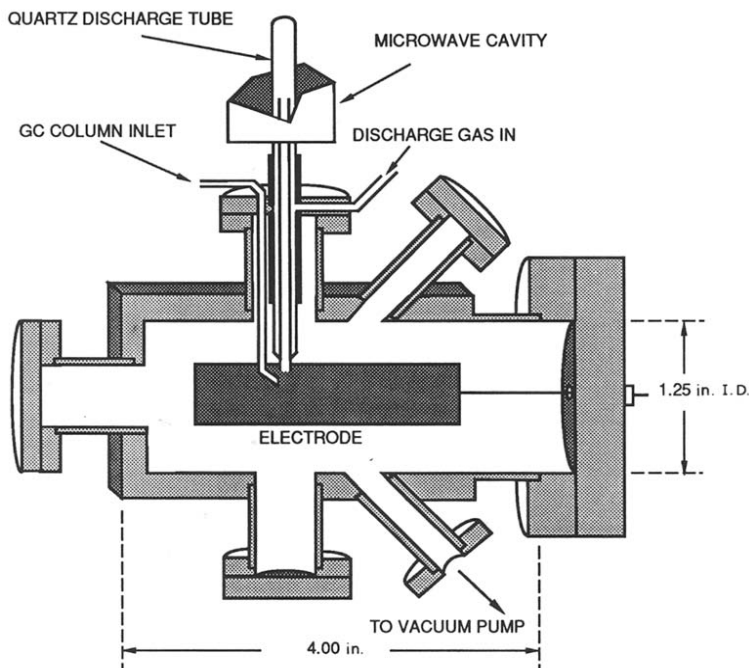


Fig. 1. Schematic diagram of "large-volume" detector.

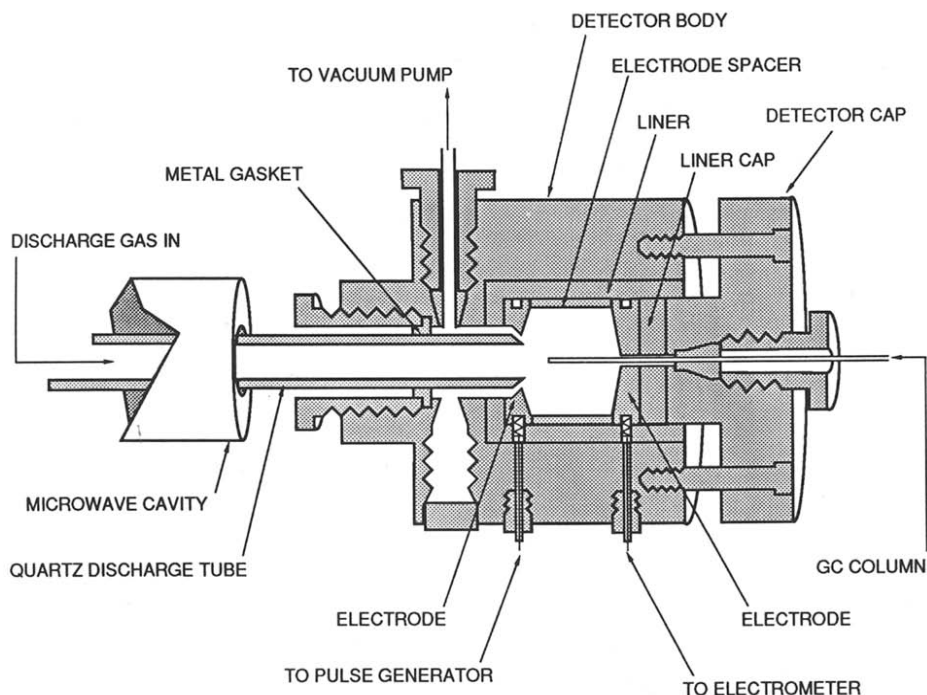


Fig. 2. Schematic diagram of "small-volume" detector.

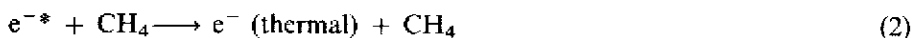
capillaries, peak broadening was obviously occurring. In addition, the column flow was introduced into the detector at the tip of the quartz lamp so that the helium from the discharge lamp and the column flow were approximately parallel. In this configuration, the two gases might not mix completely during the time spent between the electrodes.

In Fig. 2, we describe a first concept of a smaller volume detector, which is a modification of a commercially available radioactive ECD available from Valco (Houston, TX, U.S.A.). This design incorporates two unique features. First, the capillary column flow is directed opposite to the flow from the discharge lamp, and this apparently leads to good mixing, since the ionization efficiency is greater. Secondly, the parallel-plate arrangement, where the lamp flow enters through the negative electrode, results in no charge collection at the anode unless a potential is applied. Collection of extraneous signals is a common problem with other geometries and also with the ^{63}Ni ECD due to the large range of the β particles and the resulting ionization in the vicinity of the anode. This can result in unusual responses and deviations from the expected concentration dependence. The volume of this detector is 0.64 cm^3 . When operated at 40 Torr it has an effective volume of $34\ \mu\text{l}$, compared to operation at 760 Torr. It appeared that the diameter of the discharge lamp can be reduced considerably, and this will allow further reduction in the volume of the detector. We anticipate the next design to be reduced in volume by a factor of 4 or 5.

RESULTS

The major innovation in the non-radioactive ECD is the discharge source. In order to determine some of the species present in the helium discharge afterglow, we measured the emission spectra of the detector. The emission lines were primarily those of helium metastables. A more detailed report on this work will be given in a paper describing the ionization mode.

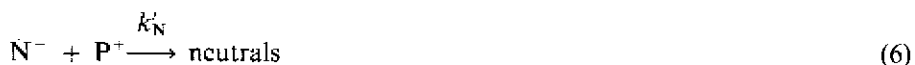
In the non-radioactive ECD, the basic ionization reaction can be described as:



where the overall production rate of thermal electrons is given by k_p . The thermal electrons can then recombine with positive species according to



In the presence of a capturing species, AB, the reactions that take place are



In these reactions, M^* represents any helium metastable (He^* , He^+ , He_2^+ , He_2^*), P^+ is any positive ion, and N^- is any negative ion. The rate constants are indicated above and below the respective reactions. This model is the same as that used for the analysis of the radioactive ECD, and the current studies serve to investigate possible differences in the two detectors³.

Based on this model, the ECD response, expressed as K , can be obtained in terms of the various rate constants as follows

$$\frac{b - [e]}{[e]} \left\{ k'_D [P^+] \right\} = K[AB] = \left\{ \frac{k_1(k_2 + k'_N[P^+])}{(k'_N[P^+] + k_{-1} + k_2)} + k_{12} \right\} [AB] \quad (7)$$

where it is assumed that the extent of capture is small enough that $[AB]$ and $[P^+]$ are essentially constant.

In our preliminary study, operational curves for various parameters were obtained and the similarity between the non-radioactive and the radioactive ECDs

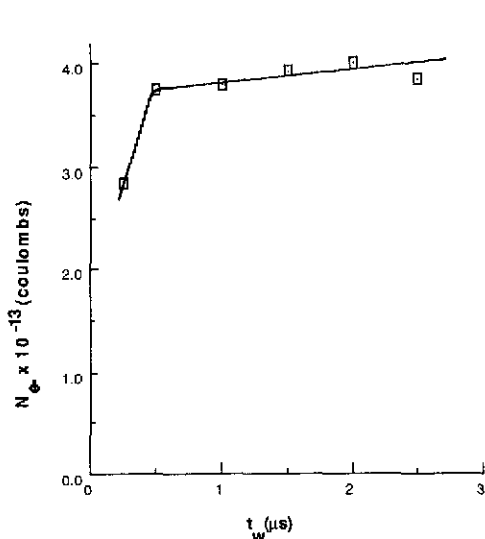


Fig. 3. Number of electrons collected per pulse (N_e) vs. pulse width (t_w): $T = 500^\circ\text{C}$; pressure $P = 29$ Torr; power, 50 W; voltage, 50 V; $t_p = 100$ μs .

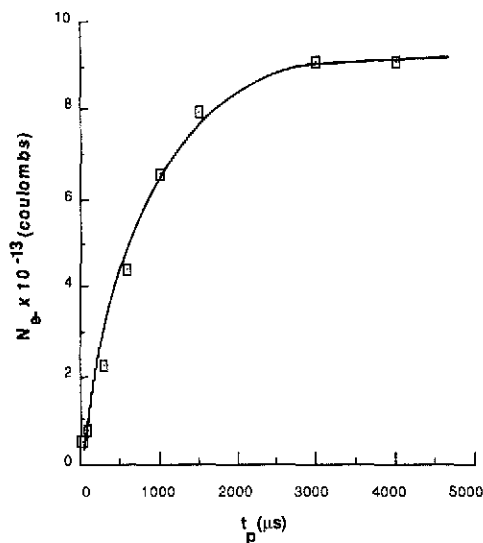


Fig. 4. Number of electrons collected per pulse (N_e) vs. pulse period (t_p): $T = 200^\circ\text{C}$; $P = 28$ Torr; power, 50 W; voltage, 50 V; $t_w = 2$ μs .

were noted. We have obtained improved data, using the leak-free detector, and find that the abnormalities observed in the previous study were artifacts. To illustrate these results, we include plots of N_e (number of electrons per pulse) vs. t_w (pulse width) and N_e vs. t_p (pulse period) in Figs. 3 and 4.

The variation of N_e with t_w shows a plateau at *ca.* 0.5–1.0 μs , which is more like the radioactive FCD. In addition, the slope in the plateau region is lower than reported previously^{1,2} and is more like that found with the radioactive ECD.

The variation of N_e with t_p at temperature $T = 200^\circ\text{C}$ is more like that obtained with a "clean" radioactive ECD, where the plateau is reached at 3000 μs . The effect of impurities on such a curve can be seen in Fig. 5 where data with and without a column are given. With the column, the plateau is reached at about 1500 μs , and the magnitude is reduced by a factor of 3. This column is a "bonded-phase" silica capillary column, where the stationary phase contains polytrifluoromethylsiloxane groups. Apparently, the "bleed" from the column consists of compounds containing the trifluoromethyl group, which cause the reduction in the standing current at long-pulse intervals. Presently, we are using a non-polar bonded-phase silica capillary column, where the stationary phase is polydimethylsiloxane and the effect of the "column bleed" on the non-radioactive ECD is reduced considerably.

These curves can be used to obtain values of $k_p V_r$ (V_r is the reaction volume) and $k'_D[\text{P}^+]$, since the initial slope = $k_p V_r$ and $N_e(\text{max}) = k_p V_r / k'_D[\text{P}^+]$. This has been done as a function of temperature, and the results are given in Figs. 6 and 7. The experiments were performed without a column and with and without methane adjustment. It is believed that the methane adjustment compensated for the temperature effect on the

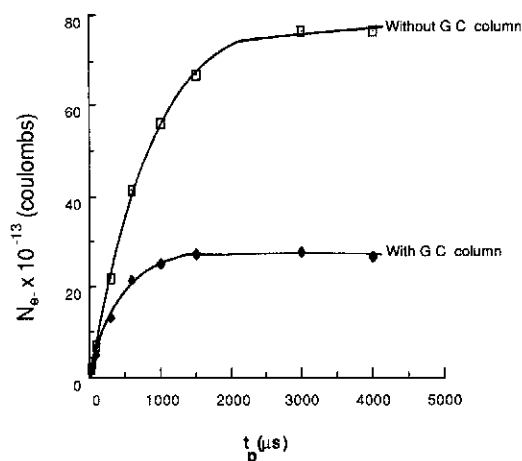


Fig. 5. Number of electrons collected per pulse (N_e) vs. pulse period (t_p), with and without the GC column: $T = 100^\circ\text{C}$; voltage, 50 V; $t_w = 2 \mu\text{s}$; $P = 28$ Torr; power, 50 W (without), 58 W (with). Column, 10 m \times 0.32 mm I.D. cross-linked methylsilicone.

reaction volume. Thus, Fig. 6 shows that by adjusting the methane concentration, the value of $k_p V_r$ could be made constant. However, as shown in Fig. 7, there is an increase in the quantity $k_D = k'_D[\text{P}^+]$ with increasing temperature. The data for the system with the column are given to show the effect of column bleed on the various parameters. Of course, the results are a function of the specific column being used and its prior history.

The normal parameters of interest to those using the ECD for analytical purposes are the minimum detectable quantities and the linearity of the response. In Fig. 8 linearity plots are given for several compounds. Note that the units on the x-axis are femtomoles.

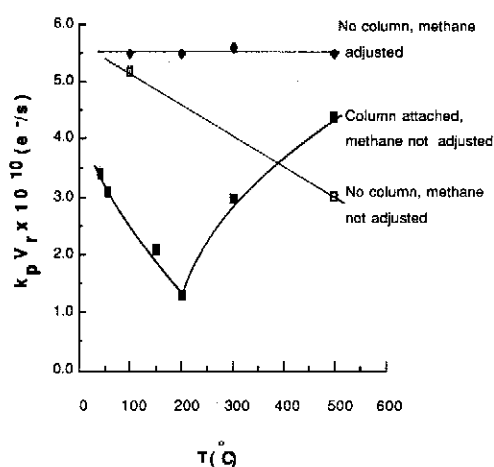


Fig. 6. Electron production ($k_p V_r$) vs. temperature: $P = 28$ Torr; power, 50 W; voltage, 50 V; $t_w = 2 \mu\text{s}$.

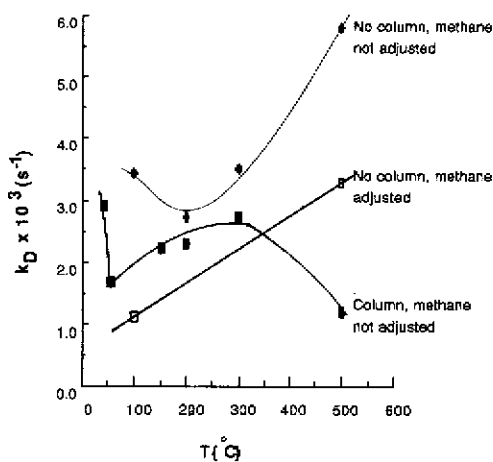


Fig. 7. Pseudo first order recombination rate constant (k_D) vs. temperature: $P = 28$ Torr; power, 50 W; voltage, 50 V; $t_w = 2 \mu\text{s}$.

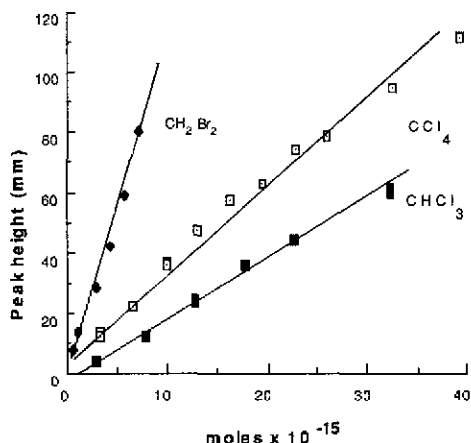


Fig. 8. Concentration dependence for CCl_4 , CH_2Cl_2 and CH_2Br_2 : $P = 23$ Torr; power, 12 W; voltage, 50 V; $t_w = 2 \mu\text{s}$; $t_p = 500 \mu\text{s}$.

In our previous paper, we gave representative values of the minimum detectable amounts at room temperature. It is also important to know the temperature dependence of the response in order to optimize the detector temperature. For example, for the analysis of compounds that have an activation energy for dissociation, a higher temperature is better. On the other hand, for compounds that form stable negative ions, a lower temperature is better. In addition, there are some compounds, such as CCl_4 , where the response is independent of temperature. We have determined the temperature dependence for CCl_4 , CH_2Cl_2 and C_6F_6 . The data are shown in Fig. 9. The general temperature dependence of the capture coefficient is as

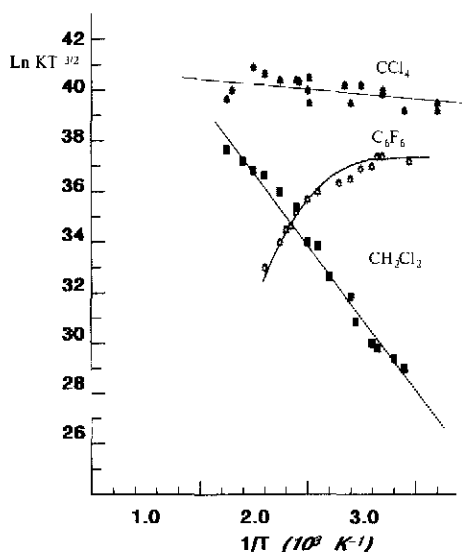


Fig. 9. Temperature dependence for ECD response of CCl_4 , C_6F_6 and CH_2Cl_2 .

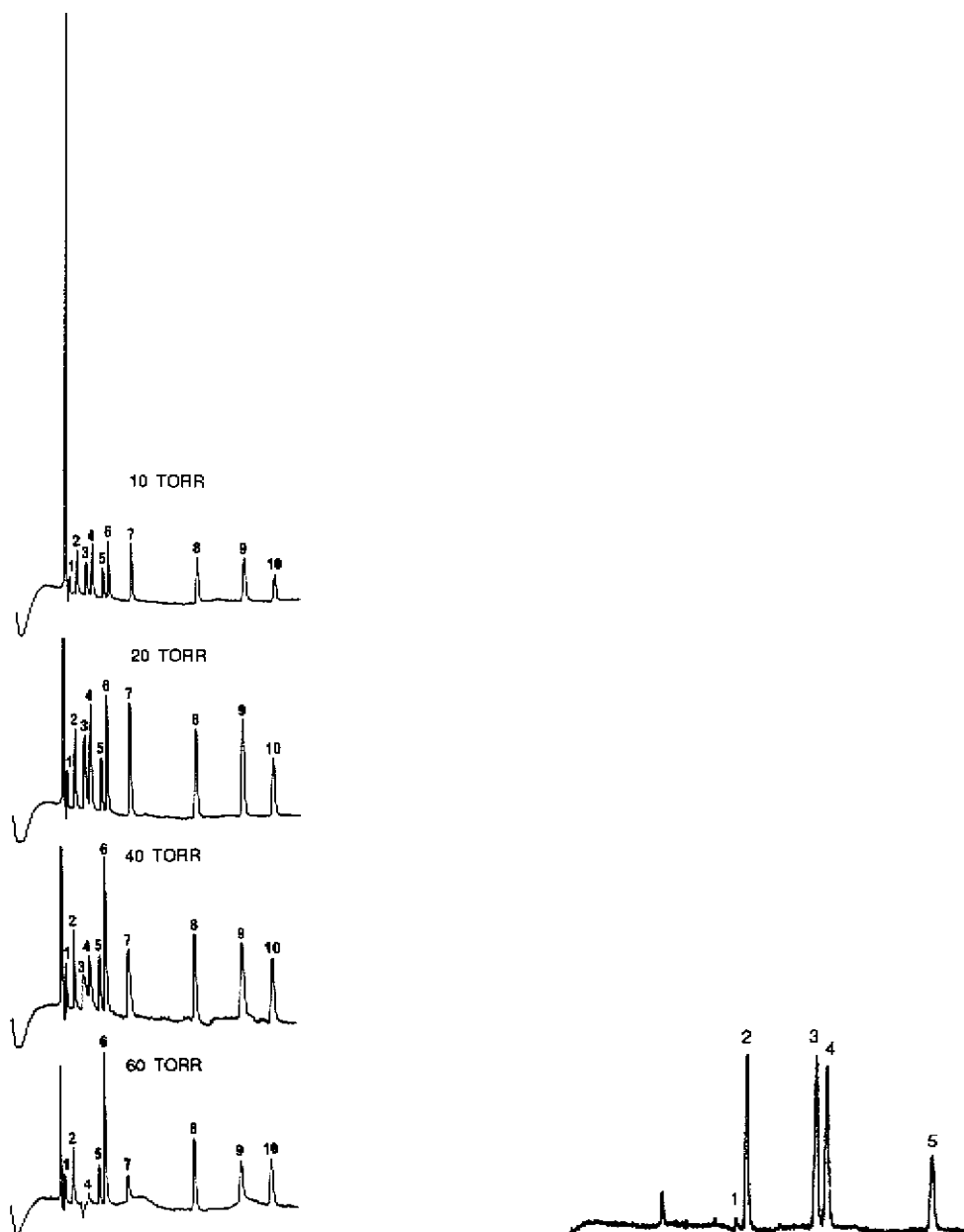


Fig. 10. Ionization mode chromatograms for the "small" detector. Peaks: 1 = C_3H_8 ; 2 = $n-C_4H_{10}$; 3 = CH_3CN ; 4 = $2-C_3H_7OH$; 5 = CH_2Cl_2 ; 6 = CS_2 ; 7 = C_4H_8O (methyl ethyl ketone); 8 = C_6H_6 ; 9 = $C_6H_{14}O$ (*n*-propyl ether); 10 = $n-C_7H_{16}$. The amounts of each component are about the same: 5–10 ng. Column, 30 m \times 0.32 mm I.D., 1 μ m RSL-150 bonded phase; T (column) = 40°C; carrier gas, 3 ml/min helium; discharge gas, helium; discharge power, 100 W; pulse width, 3 μ s; t_p = 30 μ s; pulse voltage, 80 V; T (column) *ca.* 70°C.

Fig. 11. ECD mode chromatogram for the "small" detector. Peaks: 1 = CH_2Cl_2 , 20 ng; 2 = CS_2 , 5 ng; 3 = C_6F_6 , 0.03 ng; 4 = $CHCl_3$, 0.6 ng; 5 = CCl_4 , 0.003 ng. All other conditions are the same as in Fig. 10, except for the addition of methane; t_p = 300 μ s; P = 40 Torr.

expected. Thus, the minimum detectable amount for CH_2Cl_2 is decreased to the fmol range at 500°C , while that for C_6F_6 is increased to the pmol range.

On the basis of these results, it is clear that the discharge source is suitable for use as a GC detector. However, we also discovered that the volume of the detector was seriously degrading the chromatographic performance with extra-column broadening. Thus, we have redesigned the cell with a smaller reaction volume.

We have demonstrated that this detector can be used with capillary columns in the ionization mode. Shown in Fig. 10 are a series of chromatograms, obtained with the "small detector" as a function of detector pressure. In this case, the response is the result of an increase in current due to the ionization of the eluting compound. The non-selective nature of the detector is apparent, since the amount of each component is comparable (5–10 ng). Note that the relative responses change when the cell pressure is changed. The response for CS_2 increases as the pressure is increased while that for the other peaks reach a maximum at 20 Torr and then decrease as the pressure is increased. The percent ionization for heptane is 0.14% in the "small"-volume detector.

The new detector was operated in the ECD mode by adding methane make-up to the helium carrier gas just prior to the detector. The methane concentration and pressure were adjusted to maximize the response for CCl_4 and CS_2 . As the pressure and methane concentration increase, the percent capture for both CS_2 and CCl_4 increases. This pressure sensitivity is probably due to thermalization of the electrons. At higher pressures, smaller amounts of methane were required to produce the same response. At 40 Torr the maximum response could be obtained while maintaining a satisfactory standing current. The results shown in Fig. 11 were obtained under these conditions. The response shown is for 3.2 pg or 21 fmol of CCl_4 . The other compounds in the mixture show less sensitivity in the ECD, as can be seen from the amounts of each compound injected, which are given in the legend. In Fig. 11, the response is a measure of the decrease in the standing current.

The noise, N , which we have observed comes primarily from the microwave power supply and is of two types: one is periodic with *ca.* 30 Hz frequency of *ca.* $4 \cdot 10^{-12}$ A and the other a random noise level of *ca.* $1 \cdot 10^{-12}$ A. Using $2N$ as the detectability, the value for CCl_4 is 128 fg, based on the periodic noise, and 32 fg, based on the random noise. These values are comparable to the 68 fg reported in our earlier paper¹.

CONCLUSIONS

Based on the data obtained from the "leak tight" detector, the operational parameters of the non-radioactive ECD are similar to those of the radioactive ECD. Based on the temperature dependence of the ECD response, the mechanism for ECD response is the same in the non-radioactive and the radioactive ECDs. This clearly demonstrates that the microwave source can be used in an ECD for GC.

The small-volume detector has been demonstrated to be a practical detector for GC. In the ionization mode, it is a non-selective detector with an ionization efficiency for heptane of 0.14%. In the electron-capture mode, it has the typical high sensitivity for CCl_4 . Future work will center on the optimization of the responses.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Robert A. Welch Foundation, Grant EO95 and Valco Co., Houston, TX, U.S.A.

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