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## NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR OPERATING IN THE PULSED MODE

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

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

and

E. C. M. CHEN

*School of Science and Technology, University of Houston, CL., Houston, TX 77058 (U.S.A.)*

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### SUMMARY

This paper describes an electron-capture detector (ECD) which does not require a radioactive source for the generation of electrons and which can be operated in the pulsed mode. Other researchers have developed non-radioactive versions of the ECD; however, all of these have required the application of a constant potential for electron collection. The pulsed mode allows electron attachment to occur under field-free conditions, and is the more commonly used mode of ECD operation. In our detector, electrons are produced by energetic species derived from a microwave-induced discharge in helium. The identity of these energy carriers has not been established definitively, but various possibilities are discussed. The remainder of the apparatus is identical to that used with a normal pulsed-mode ECD with the exception that our detector operates at a pressure of 10–20 Torr. In this paper we report characteristic data for the significant operational parameters (pulse period and pulse width) and measured quantities (rate constants for loss of electrons and for production of electrons) associated with our detector. These are compared to corresponding data typical of a conventional pulsed-mode, radioactive-foil ECD. The detection limit (signal-to-noise ratio = 2) of our detector for carbon tetrachloride, which captures electrons dissociatively with an extremely high capture coefficient, is on the order of 70–80 fg. For methylene chloride, which also captures dissociatively but with a much lower capture coefficient, the detection limit is 8 ng. For hexafluorobenzene, which captures non-dissociatively, the detection limit is 530 fg. These limits were obtained using a prototype detector. We anticipate that improvements in design will result in even better performance.

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### INTRODUCTION

The electron-capture detector (ECD) is generally recognized as the most sensitive detector available for gas chromatographic (GC) measurement of trace levels of chemical compounds. Although it is not a universal detector, it can be used for

a wide range of analyses, encompassing organic as well as inorganic and organo-metallic compounds<sup>1</sup>.

In general, electron-capture detection requires a source of energy which can generate electrons within the ECD cell. Capture of these electrons by analyte molecules as they are eluted from a GC column into the detector produces a change in the electrical conductivity of the previously ionized gas. Initially, a constant voltage was applied to the ECD to measure the change in conductivity<sup>2</sup>. It was noted in this initial study that the ECD response was dependent upon the magnitude of the applied voltage. Later, it was found that the electron capture of many molecules was greatest at low applied voltages (approximately thermal electron energy). Shortly thereafter, Lovelock<sup>3,4</sup> proposed a pulsed mode of operation in which a voltage (*ca.* 40–80 V) is applied only for a short time (*ca.* 0.5–2  $\mu$ s), which is sufficient to collect the free, unattached electrons. Relatively long periods between pulses (*ca.* 100–2000  $\mu$ s) allow the electrons to react under field-free conditions. In this pulsed mode, detector response can be linearized with concentration by varying the pulse interval to maintain a constant current<sup>5</sup>. Commercial detectors generally are operated in the pulsed mode with this constant current/variable frequency method of linearization. However, Aue and Siu<sup>6</sup> express a preference for the application of a constant potential and for linearization of response by varying the applied voltage to maintain a constant current<sup>7</sup>.

From the introduction of the ECD by Lovelock and Lipsky<sup>2</sup> to the present day, commercial detectors have employed a radioactive foil to generate secondary electrons within the ECD cell. The foils used are typically made of stainless steel, containing either scandium tritide ( $\text{Sc}^3\text{H}_3$ ) or  $^{63}\text{Ni}$  which emit soft  $\beta$  particles with an average energy on the order of 5.5–17 keV<sup>8</sup>. These  $\beta$  particles are a convenient source of ionization and impart sufficient energy to secondary electrons so that a substantial population of free electrons is produced.

Despite the convenience of using radioactive foils in the ECD, there are several disadvantages.

(1) *Contamination.* Since analytes come in contact with the radioactive foil, contamination of the foil can occur. If the contaminants are simply adsorbed on the surface of the foil, they frequently can be removed by vaporization at high temperatures. However, if the contaminants are decomposed on the foil, the products of the decomposition may be non-volatile and not easily removed by vaporization. This can degrade detector performance substantially. Evidence for this is commonly found with iodine compounds, where the radioactive foil acquires a dark color after several injections. Since nickel is a well known catalyst, it can promote decomposition especially at temperatures in the range 300–400°C.

(2) *Temperature.*  $\text{Sc}^3\text{H}_3$  and  $^{63}\text{Ni}$  foils have upper temperature limits of 325°C and 400°C, respectively. However, it is well known that the ECD sensitivity for compounds, such as methylene chloride, which capture electrons dissociatively with a low capture coefficient, is greatly increased at high operating temperatures<sup>9</sup>. This effect is even more pronounced when nitrous oxide is used to enhance ECD sensitivity<sup>10</sup>. Consequently, the usefulness of the ECD is limited to some extent by the temperature limit of the radioactive foils.

(3) *Safety.* The use of radioactive foils involves the responsibility and associated costs of protection against radioactive contamination. Detectors containing

$\text{Sc}^3\text{H}_3$  must be vented with care and licensing is required for the use of both  $\text{Sc}^3\text{H}_3$  and  $^{63}\text{Ni}$  detectors. In addition, detectors containing  $^{63}\text{Ni}$  must be given periodic wipe tests to monitor the escape of radioactive material. The disposal of both types of detectors must be handled properly. These precautionary measures add to the cost of an ECD with a radioactive foil.

(4) *Pressure.* The range of the  $\beta$  particles emitted by the commonly used foils requires that detectors of a practical size be operated at or above atmospheric pressure. While this is common GC practice, it is not necessarily optimal. For analytes which capture electrons non-dissociatively with an electron affinity of less than 0.8 eV, the ECD response increases with decreasing temperature<sup>9</sup>. Frequently, the preferred lower temperature is limited by the volatility of the analyte. If the detector were operated at lower pressure, the volatility of the analyte would be enhanced, and lower temperatures could be used when desirable.

There have been several attempts in the past to develop a non-radioactive source of electrons suitable for an ECD. In 1964 the first non-radioactive ECD was developed and briefly marketed by Beckman Instruments<sup>11</sup>. In this detector electrons were formed by electrical discharge in a carrier gas prior to mixing with the GC eluents. Apparently, there were problems, probably due to the need for critical flow-rate control, and the detector did not remain on the market for long.

Ten years later, Wentworth *et al.*<sup>12</sup> described a photoionization ECD. In this detector, the hydrogen Lyman  $\alpha$  emission line was used to produce ionization in the ECD cell. However, due to the low energy of this emission, the population of free electrons produced was small, and the detector could be operated only with a constant potential (d.c. mode). This resulted in a rather low detector sensitivity.

Neukermans *et al.*<sup>13</sup> described an ECD in which a thermionic emitter was the source of electrons. In this detector a platinum wire coated with barium zirconate served as the cathode. A guard gas was passed over the cathode to protect it from contamination by solvents and impurities from the chromatographic system. The electrons were drawn through the guard gas and a mesh anode into a separate chamber, which contained the chromatographic effluent. A detection limit of 0.32 fg was observed for lindane, which is quite impressive. However, the detector has not been commercialized. This may be due to problems encountered in the control of guard gas and column flow-rates.

Kapila *et al.*<sup>14</sup> built a photoionization ECD, using a commercial rare gas resonance line light source (HNU Systems) with a magnesium fluoride window. A dopant gas, tri-*n*-propylamine, was ionized by the light source in a manner similar to that reported earlier by Wentworth *et al.*<sup>12</sup>. The detector could be operated only in the d.c. mode, but detection limits were comparable to those of a conventional, radioactive ECD. The use of the magnesium fluoride window limited the upper temperature of the ECD, and the window tended to become coated, which decreased its optical transmission.

Recently, Simmonds<sup>15</sup> described an ECD in which the electrons were produced from UV irradiation of a metal surface by the photoelectric effect. Since the surface was ionized, only free electrons were generated in the gas phase. To date, only d.c. mode operation of this detector has been reported. The detector showed high sensitivity for sulfur hexafluoride but could not be operated at high temperatures.

None of these non-radioactive detectors have been shown to operate in the

pulsed mode, and none have been developed into a successful, commercial ECD. In a much earlier study<sup>16</sup>, a microwave powered helium resonance lamp was used to ionize an argon-methane mixture in an electron-capture cell. Differential pumping was used in a windowless arrangement, and a pulsed mode of operation was possible. The results of this study were promising, but the disadvantages of differential pumping seemed to prevent its use on a routine basis.

In this paper, we describe a non-radioactive ECD, which uses metastable species produced in a microwave discharge to generate free electrons in the ECD cell. The discharge is coupled directly to the cell. Differential pumping is not required, and there is no window. The metastable species cause ejection of electrons from gas molecules in the cell with sufficient energy so that a large population of free electrons is produced. This mode of ionization is similar to that used in the atmospheric pressure helium afterglow (He-APAG) element-specific GC detector<sup>17</sup>. In that detector, the analyte is added to helium which has previously passed through a discharge, and reaction products are measured by optical emission spectrometry (OES).

## EXPERIMENTAL

A diagram of the non-radioactive ECD used in this study is shown in Fig. 1. The cell was constructed of stainless steel which had been plated inside with 0.001 in. of gold. Cell operating temperatures were in the range of ambient to 360°C. Voltage (negative with respect to ground) was applied to the cell cathode with a pulse generator (Model 102, Datapulse, Inglewood, CA, U.S.A.). The anode current was measured with an electrometer (Model 603, Keithley Instruments, Cleveland, OH, U.S.A.). A quartz discharge tube (4 mm I.D., 6 mm O.D.) and a fused-silica GC

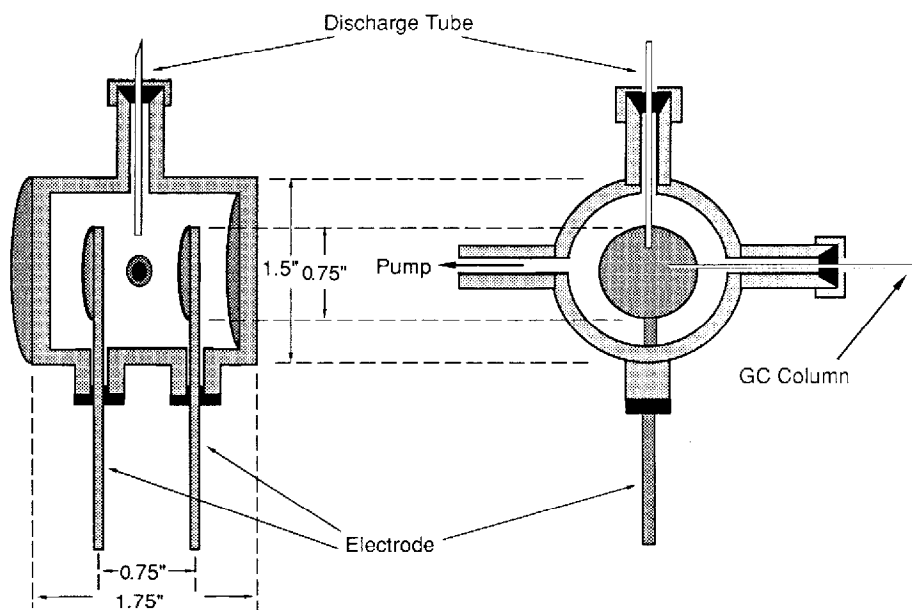


Fig. 1. Schematic diagram of prototype of non-radioactive ECD.

capillary column (cross-linked methyl silicone, 10 m  $\times$  0.32 mm I.D. Hewlett-Packard, Palo Alto, CA, U.S.A.) were connected to the cell so that the gas flow which has passed through the microwave discharge intersected the effluent flow from the column. This intersection was located at the center between the two parallel-plate electrodes (0.75 in. diameter). The "size" of the detector was determined by the reaction volume in which the gas flow from the discharge and the effluent from the capillary column mix and interact before being removed by a vacuum pump (Model HYVAC-7, Central Scientific, a division of Cenco Instruments, Chicago, IL, U.S.A.). The discharge tube was positioned inside an air cooled cylindrical cavity (Broida type, Ophthos Instrument, Rockville, MD, U.S.A.) which was connected to a 2.45-GHz power supply (Model MPG-4M, Kiva Instruments, Rockville, MD, U.S.A.). Under typical operating conditions the forward power to the cavity was 20–44 W and the reflected power was 4–8 W.

A block diagram of the entire apparatus is shown in Fig. 2. In these experiments helium was used, both as the discharge gas and as the GC carrier gas. Helium was zero grade (Big Three Industries, La Porte, TX, U.S.A.) with a stated purity of 99.998%. Water (5 ppm) and hydrocarbons (0.5 ppm total) were the major impurities. The helium was further purified by passage through a charcoal trap which could be cooled with liquid nitrogen. A dopant gas was added to the GC carrier gas through a T piece located between the column end and the ECD cell. In all experiments reported in this paper methane (ultra high purity grade, Union Carbide, Houston, TX, U.S.A.) was used as the dopant gas. The methane gas was purified by passing it through a Drierite ( $\text{CaSO}_4$ ) (W. A. Hammond Drierite, Xenia, OH, U.S.A.) trap followed by an OXY trap (Alltech Assoc., Applied Science Labs., Deerfield, IL,

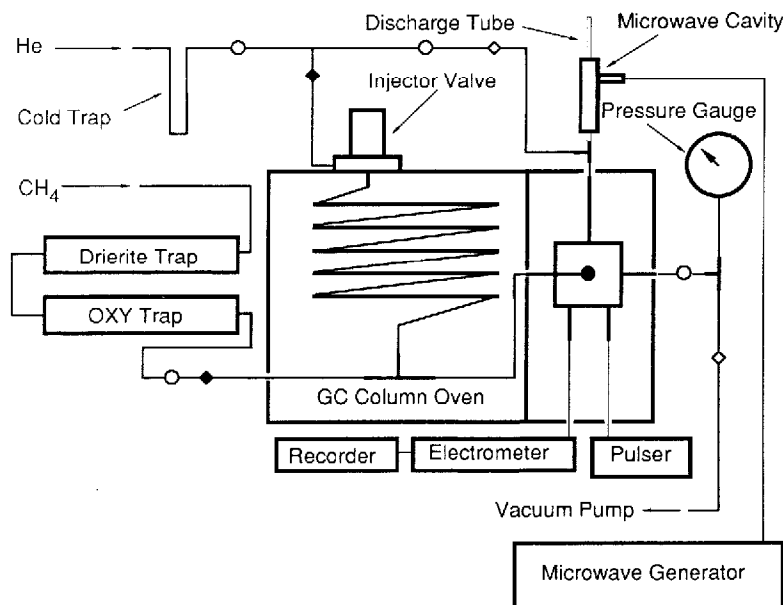


Fig. 2. Block diagram of GC system used to evaluate the prototype non-radioactive ECD.  $\circ$  = Shut off valve;  $\blacklozenge$  = flow controller;  $\diamond$  = needle valve.

U.S.A.). The function of the dopant is discussed below. The use of other dopants will be considered in future investigations.

All analytes were injected as gases through the Series 1200 gas chromatograph (Varian Aerograph, Walnut Creek, CA, U.S.A.). Injections were performed using a six-port valve (Model C6W, Valco Instruments, Houston, TX, U.S.A.) with a sample loop ranging from 2  $\mu\text{l}$  to 5  $\mu\text{l}$ . Analytes were used as received (generally >99% purity). Individual compounds were chromatographed separately to determine the retention times of the major component and detectable impurities. This information was used to prepare mixtures, such that each of the analytes of interest could be completely separated from each other and from any impurities. Gas phase mixtures were prepared by introducing a known volume of liquid into a 250-ml Pyrex flask. The flask had two septa: one for introducing the liquid samples and the other for extracting gas samples. Prior to introducing the liquids into the flask, the empty flask was sampled to assure the absence of residual contamination. This technique eliminates the relatively large solvent peak, which would result from the use of liquid solutions. However, with this technique a non-trivial fraction of the analyte can in some cases be adsorbed on the surface of the flask and the amount sampled may be lower than expected. This would make the "true" minimum detectable quantities (MDQ) lower than reported. Since this was intended to be only a preliminary study, we chose not to use more complicated sampling methods and to be conservative in any claims concerning sensitivity.

The carrier gas flow-rate was 1–2 ml/min. The dopant gas flow-rate varied from 0.21 to 5 ml/min. Each was maintained with a flow controller (Model SA-202, VICI-Condyne, Pasadena, CA, U.S.A.) and was measured through the ECD cell at atmospheric pressure. However, the flow-rates through the flow controllers should be unaffected by downstream pressure and, thus, should have been the same when the ECD was operated at sub-atmospheric pressures. The flow-rate of helium through the microwave discharge was set with a metering valve and was typically 7–15 ml/min when measured at atmospheric pressure. Under operating conditions, sub-atmospheric pressure, this flow-rate would have been somewhat higher. The rate of pumping from the ECD cell could be varied by a needle valve, located between the cell and the vacuum pump. Performance seemed to be best when this valve was fully opened and the pressure in the ECD was typically 15–25 Torr.

## RESULTS AND DISCUSSION

When no dopant is added and the cell contains only nominally pure helium from the column and discharge, the measured standing electron current is on the order of  $1.2 \cdot 10^{-8}$ – $2.0 \cdot 10^{-8}$  A. The source of this current is not entirely clear. Microwave discharges in pure helium at low pressures are known to produce radiation, principally the first resonance line of neutral helium at 584.334 Å (21.22 eV)<sup>18,19</sup>. Experiments<sup>20</sup> at pressures of 5–30 Torr have shown that the transmission of such radiant energy from a discharge through helium to a region some centimeters distant is not a major process and that transport of energy from the discharge is by material particles carried in the gas flow.

The major energy carriers when pure helium is used as the discharge gas have been identified by spectroscopic analysis<sup>20–26</sup> and summarized by Rice *et al.*<sup>17</sup> as:

He( $2^3S$ , 19.81 eV), He $^+$ ( $1S^2S_{1/2}$ , 24.5 eV), He $_2^+$ ( $X^2\Sigma_u^+$ , 18.8–21.6 eV), and He $_2(a^3\Sigma_u^+$ , 14.6–17.4 eV). The relative concentrations of the first three of these were shown<sup>20</sup> to be dependent on the pressure of the helium stream with He( $2^3S$ ) predominant at *ca.* 10 Torr, He $^+$  at *ca.* 20 Torr, and He $_2^+$  at *ca.* 30 Torr. We have not measured the actual pressure in our discharge tube with sufficient accuracy to use this as a basis for identifying the predominant species in our system. To a lesser extent, energetic electrons may also be involved<sup>20</sup>. It has also been established that mutual collisions between He( $2^3S$ ) metastable atoms downstream from a discharge in pure helium lead to the production of He $^+$  and He $_2^+$  ions and electrons<sup>27–30</sup>. If impurities such as nitrogen, oxygen, or carbon dioxide are present in the discharge gas, then the number of possible energy carriers would be even larger since these are known to react readily with the helium energy carriers to form a variety of excited ions<sup>20,31</sup>. The presence of trace amounts of neon results in the production of excited neon atoms<sup>17,20,31</sup>, Ne\*.

Any of these energy carriers would have sufficient energy to ionize the most likely trace impurities in our cell. Reactions of He $^+$  and He $_2^+$  or of the excited impurity ions would result merely in the production of a different positive ion by charge transfer reaction, but reactions of the neutral metastables, He( $2^3S$ ), He $_2(a^3\Sigma_u^+)$ , or Ne\*, could release energetic, but collectable, electrons by Penning ionization reactions. Electrons released by mutual collisions between He( $2^3S$ ) metastables would also be collectable. We tend to favor He( $2^3S$ ) as the primary energy carrier because it has such a long lifetime (*ca.* 150 min at low pressure)<sup>32</sup>. However, we note that the discharge itself appears peach (orange)-colored, whether or not the helium is purified by passage through the liquid-nitrogen-cooled charcoal trap. This color has been associated<sup>17</sup> with the presence of Ne\*. Nitrogen impurity has been associated with a blue color. Identification of the excited metastable energy carrier could, in principle, be made by observing the emission spectrum from the helium flow below the discharge. This remains to be done.

Whatever the active species, the electrons released by their reactions must be too energetic to be captured efficiently even by neutral molecules with high electron affinities, because even when analytes such as chloroform, hexafluorobenzene and methylene chloride are injected, the cell functions as an ionization detector. That is, the anode current increases when the analyte is eluted from the column into the cell. All compounds tested, including hydrogen, oxygen, nitrogen, argon and carbon monoxide, were ionized. This is consistent with Penning ionization of the analyte by either He( $2^3S$ ) or Ne\*. This mode of operation is the subject of a separate investigation which will be reported elsewhere.

### *Characteristics of the ECD*

We were able to operate our cell in the electron-capture mode by adding methane as a dopant to the GC column effluent before it entered the cell. When this was done, the standing anode current was higher than when the cell contained only helium, and the anode current decreased when electron capturing analytes were eluted from the GC column. Presumably, the dopant serves a dual function. It is a source of electrons in that it is ionized by the metastable species, which transfer energy from the microwave discharge to the cell. In addition, it also serves to lower the energy of the resulting electrons through inelastic collisions, making them more readily cap-

tured by analytes with positive electron affinities. Thus, it appears that the use of a microwave discharge is analogous to the use of a radioactive  $\beta$  source. Both create energetic species from the rare gas (helium or argon) which is the major component in the cell, and both produce additional ionization and thermal electrons when a dopant (*e.g.*, methane) is added to the cell.

In order to operate an ECD in the pulsed mode, the proper pulse voltage, width, and interval must be established. For analytical purposes two conditions must be met: (1) a combination of pulse voltage and pulse width ( $T_w$ ) must be selected such that all free electrons produced between pulses are collected within the time  $T_w$ ; (2) the  $T_w$  should be short and the pulse period ( $T_p$ ) long, so that electrons can react with the analytes under essentially field free equilibrium conditions. As we have shown previously using data from a radioactive-foil ECD<sup>8,33</sup>, appropriate values for these parameters can be determined systematically by plotting the average number of electrons collected per pulse ( $N_e$ ) versus a range of pulse widths and versus a range of pulse intervals, using a moderate pulse potential on the order of 50 V.  $N_e$  is calculated from the product of pulse interval times the measured current. Values for  $T_w$  and  $T_p$  are appropriate when small changes in either produce no significant change in  $N_e$ .

Fig. 3 shows plots, constructed from data obtained with the present detector, of  $N_e$  vs.  $T_w$  at three different values of  $T_p$ . The shapes of these plots are similar to the shapes of corresponding plots obtained from radioactive-foil ECD data<sup>8,33</sup>. Both show an initial sharp increase in  $N_e$  as  $T_w$  is increased. In each case this is followed by a plateau region in which further increases in  $T_w$  produce only a gradual increase in  $N_e$ . This general shape can be understood if it is assumed that the total collected electron current consists of at least two components, a relatively large free electron population accumulated between pulses and a smaller free electron population pro-

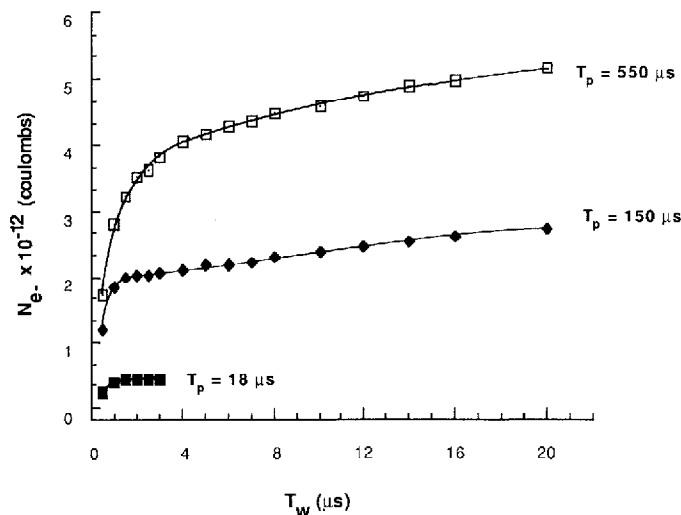


Fig. 3. Number of electrons collected per pulse ( $N_e$ ) vs. pulse width ( $T_w$ ) at different pulse intervals ( $T_p$ ). All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V; cell temperature, 200°C; chamber pressure, 17.5 Torr; methane concentration, 5.1%.



duced while the pulse is on. The initial steep rise in  $N_e$  as  $T_w$  is increased at constant  $T_p$  would then be due to collection of an increasing fraction of the constant free electron population accumulated between pulses as the collection time is increased. Eventually, when  $T_w$  becomes long enough, all of the free electrons produced between pulses are collected, and  $N_e$  changes only slightly as  $T_w$  is further increased, due to collection of those electrons produced while the pulse is on (plateau region). If collection of electrons produced during a pulse were the only reason for the gradual increase in  $N_e$  in the plateau region, then the slope of the curve in the plateau region should be equal to the pseudo zero order rate constant ( $k_p$ ) for free electron production by the metastable species times the reaction volume from which electrons are collected ( $V_r$ ). From the data in Fig. 3, we calculate a value of  $4 \times 10^{11}$  electrons/s for the plateau region slope at 200°C and 5.1% methane. This is significantly higher than the value of  $1.4 \times 10^{11}$  electrons/s calculated for  $k_p V_r$  under similar conditions (see Table I and discussion below). This large a difference is not usually observed with a radioactive-foil ECD. Apparently there exists in the present non-radioactive ECD a process which yields additional collectable electrons only when a pulse is applied. A possible explanation is that  $V_r$  is increased by application of pulses of increasing duration in the present detector but not in a radioactive-foil detector. In any case, this did not appear to adversely affect detector operation.

For a radioactive-foil ECD,  $T_w$  at the point where the plateau region begins (characteristic  $T_w$ ) is typically *ca.* 1  $\mu$ s. As can be seen in Fig. 3, for the present detector this point occurs over a range of  $T_w$  (2–4  $\mu$ s) which depends on the value of  $T_p$ . The reason for this difference is not understood at this time. However, a characteristic  $T_w$  of *ca.* 4  $\mu$ s and a pulse voltage of 50 V satisfy condition 1 and would appear to be appropriate for the present detector. The value of  $N_e$  characteristic of the plateau region (the so-called "standing current") increases as  $T_p$  is increased due to the fact that larger values for  $T_p$  allow more time for the free electron population to build up between electron collecting pulses. Selection of the appropriate value for  $T_p$  is discussed below.

TABLE I

VALUES FOR ELECTRON PRODUCTION RATE CONSTANT ( $k_p$ ) AND ELECTRON LOSS RATE CONSTANT ( $k_D$ ) MEASURED AT SEVERAL TEMPERATURES USING A NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR (NR-ECD) AND COMPARISON TO TYPICAL VALUES FOR A CONVENTIONAL RADIOACTIVE-FOIL ELECTRON-CAPTURE DETECTOR

Detector type	Temp. ( $^{\circ}$ C)	Methane (%)	$k_p V_r$ ( $e^-/s$ )	$K_D$ ( $s^{-1}$ )
NR-ECD	20.0	6.5	$8.1 \cdot 10^{10*}$	$5 \cdot 10^{3*}$
NR-ECD	200.0	6.7	$1.4 \cdot 10^{11*}$	$6.3 \cdot 10^{3*}$
NR-ECD	360.0	7.1	$1.5 \cdot 10^{11*}$	$8.4 \cdot 10^{3*}$
Sc <sup>3</sup> H <sub>3</sub> -ECD	25.0	10.0	$8 \cdot 10^{10***}$	
<sup>63</sup> Ni-ECD	25.0	10.0	$8 \cdot 10^{10***}$	
Sc <sup>3</sup> H <sub>3</sub> -ECD	25.0	5.0		$1.7 \cdot 10^{3***}$

\* This work.

\*\* Ref. 8.

\*\*\* Ref. 33.

We have shown previously<sup>33</sup> that, for a radioactive-foil ECD, both the value of the characteristic  $T_w$  and the magnitude of the standing current are dependent on methane concentration. Fig. 4 shows plots, constructed from data obtained with the present detector, of  $N_e$  vs.  $T_w$  at constant  $T_p$  for five different methane concentrations. These plots show that in general the characteristic  $T_w$  decreases as methane concentration is increased, but that methane concentrations above *ca.* 8% also produce a significant decrease in standing current. This same effect was observed with the radioactive-foil ECD. The variation in  $T_w$  was related to an increase in electron drift velocity with increased methane concentration<sup>33</sup>. The dependence of standing current on methane concentration is not understood but may be related to the concurrent introduction of an impurity, such as oxygen, as methane concentration is changed. For the present detector, a methane concentration between 5% and 8% appears to give the best compromise between a short  $T_w$  and a high standing current. This is about the same concentration normally used with a radioactive-foil ECD.

Fig. 4 also shows that a rather high standing current is produced even when no methane dopant is added to the detector. This was not expected. None of the neutral metastable species considered as the probable transporters of energy from the microwave discharge into the detector cell would have sufficient energy to ionize ground state helium atoms. This current may be the result of electron releasing mutual collisions between two He( $2^3S$ ) metastables, the result of electron releasing interaction between a metastable and a trace impurity (most likely air) in the cell, or the result of electrons carried into the cell from the discharge. The electrons produced, although collectable, must be rather energetic because, as noted above, they are not captured even by molecules with a high electron affinity, and because, as can be seen in Fig. 4, a relatively long (greater than 20  $\mu s$ )  $T_w$  is required in order to collect them

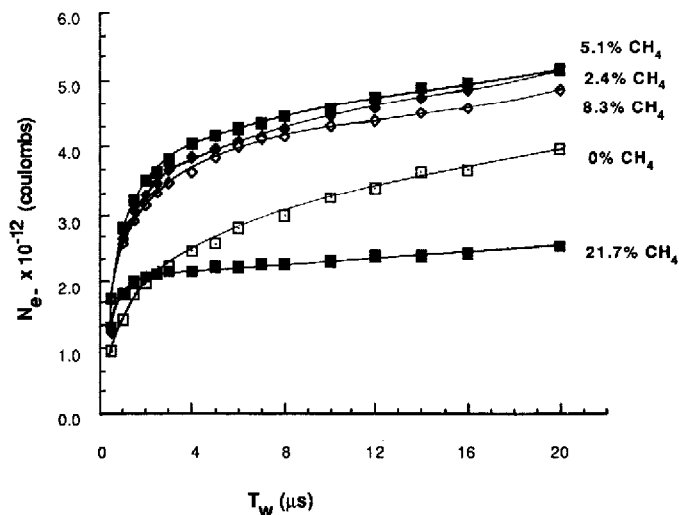


Fig. 4. Number of electrons collected per pulse ( $N_e$ ) vs. pulse width ( $T_w$ ) at different methane concentrations. All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V; cell temperature, 200°C; chamber pressure (no methane), 16.6 Torr;  $T_p$ , 550  $\mu s$ .

efficiently. If trace impurities are the cause, it may be possible to eliminate this current by using a more leak tight cell and gas handling manifold. In any case, this anomaly does not appear to have an adverse effect on the performance of the present detector when methane dopant is used.

Fig. 5 shows plots, constructed from data obtained with the present detector, of  $N_e$  vs.  $T_p$  at constant  $T_w$  for five different methane concentrations. The shapes of these plots are also similar to the shapes of corresponding plots obtained from radioactive-foil ECD data<sup>8</sup>. Both show an initial sharp increase in  $N_e$  as  $T_p$  is increased and in each case this is followed by a plateau region in which further increases in  $T_p$  produce only gradual changes in  $N_e$  (slight increases or decreases). This general shape can be understood if it is assumed that the application of a voltage pulse of duration equal to the characteristic  $T_w$  results in the collection of virtually all of the free electrons and that during the time between pulses,  $T_p$ , the free electron concentration builds up from zero to some steady state value,  $N_e^\infty$ , determined by the rates for electron production and removal by recombination with positive ions. If  $T_p$  is too short, this steady state will not be reached before application of the next pulse and the measured  $N_e$  will be less than  $N_e^\infty$ . As  $T_p$  is increased, the measured  $N_e$  will increase until  $T_p$  exceeds some characteristic value associated with the time required to achieve steady state. Further increases in  $T_p$  should then produce no significant change in the measured  $N_e$  which should be equal to  $N_e^\infty$ . For a radioactive-foil ECD,  $T_p$  at the point where the plateau region begins (characteristic  $T_p$ ) is typically 2000  $\mu\text{s}$ <sup>8</sup>. For the present detector, as can be seen in Fig. 5, this point occurs at about 550  $\mu\text{s}$ . This difference will be discussed further below. The characteristic value of  $T_p$  for the present detector appears to be relatively insensitive to methane concentration. This is true for the radioactive-foil ECD as well<sup>8</sup>. The variation of  $N_e^\infty$  with methane concentration in Fig. 5 is similar to that observed in Fig. 4. For the present detector

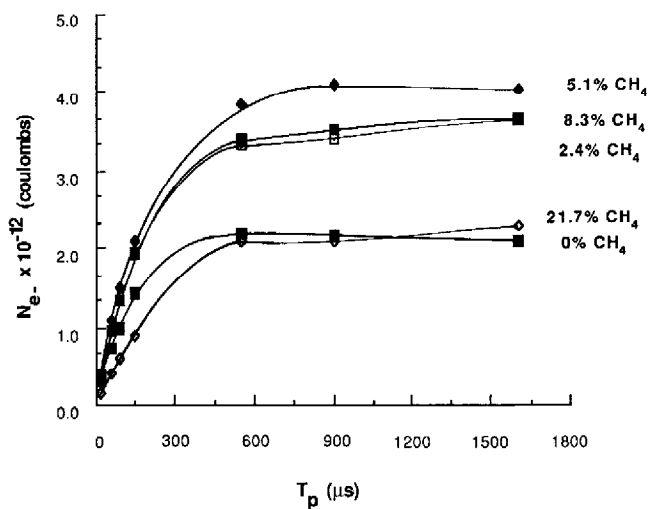


Fig. 5. Number of electrons collected per pulse ( $N_e$ ) vs. pulse period ( $T_p$ ) at different methane concentrations. All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V; temperature, 200°C;  $T_w$ , 1.5–3  $\mu\text{s}$ ; cell pressure, 16.6 Torr (no methane).

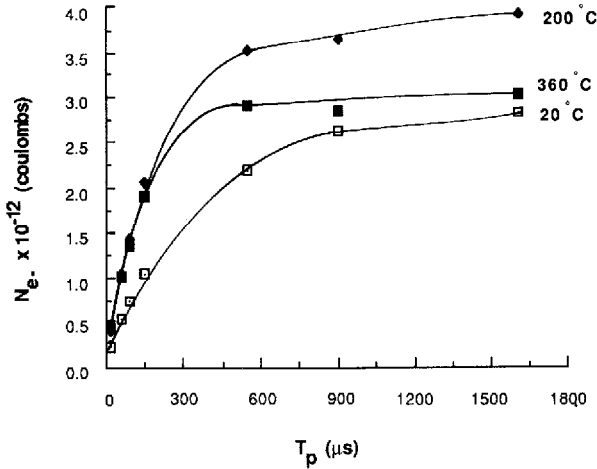


Fig. 6. Number of electrons collected per pulse ( $N_e$ ) vs. pulse period ( $T_p$ ) at different temperatures. All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V;  $T_w$ , 2.5  $\mu\text{s}$ .

operated with 50-V pulses, a characteristic  $T_p$  of *ca.* 550  $\mu\text{s}$  and a characteristic  $T_w$  of *ca.* 4  $\mu\text{s}$  satisfy condition 2.

Fig. 6 shows plots, constructed from data obtained with the present detector, of  $N_e$  vs.  $T_p$  at constant  $T_w$  for three different temperatures. Again the characteristic  $T_p$  is *ca.* 550  $\mu\text{s}$ . It is also insensitive to temperature. However,  $N_e^\infty$  is slightly temperature dependent. It increases as the temperature is increased from 20°C to 200°C and then decreases as the temperature is further increased from 200°C to 360°C. This was not expected.  $N_e^\infty$  should not be strongly temperature dependent. The increase in  $N_e^\infty$  may be due to the presence of an impurity such as oxygen which captures electrons efficiently only at low temperature. The decrease in  $N_e^\infty$  may be due to the release of another impurity as the temperature of the cell is increased above 200°C. The present cell was not specifically designed for high-temperature operation. The epoxy used to seal the electrodes is known to decompose at 120°C. Although an attempt was made to cool these electrode seals during operation at elevated temperatures, there still may have been some outgassing of impurities into the cell. For this reason the present cell was not used for extensive studies at high temperature. Better methods for attaching electrodes are available and will be used in future cell designs which should be capable of operation at temperatures up to at least 450°C.

Characterization of the present detector would not be complete without a study of the pseudo zero order rate constants for production of thermal electrons,  $k_p$  ( $k_p R_\beta$  for radioactive-foil ECD), and for loss of electrons by electron-ion recombination,  $k_D$ . A kinetic analysis of the radioactive-foil ECD has been used to derive the relationships<sup>8,33</sup>

$$k_p V_r = \left( \frac{dN_e}{dt} \right)_{\lim T_p \rightarrow 0}$$

$$N_e^\infty (\lim T_p \rightarrow \infty) = \frac{k_p V_r}{k_D}$$

where  $V_r$  is the reaction volume from which electrons are collected. We have applied these same relationships to the present detector. Although  $k_p$  itself cannot be measured unless  $V_r$  is known, the quantity  $k_p V_r$  can be evaluated from the initial slope ( $T_p \rightarrow 0$ ) of plots such as those shown in Fig. 6. The rate constant  $k_D$  can then be determined by dividing  $k_p V_r$  by  $N_e^\infty$  (also obtained from plots such as Fig. 6 at long  $T_p$ ). The constant  $k_D$  is particularly important, as it provides a measure of the cleanliness of the detector. Moreover, any unusual electron recombinations reaction can be readily ascertained from the values of  $k_p V_r$  and  $k_D$ .

Fig. 7. shows a plot, constructed from data obtained with the present detector, of  $k_p V_r$  vs. temperature at a methane concentration of *ca.* 7% for three cell temperatures. The values for  $k_p V_r$  were determined from the initial slopes of plots similar to those shown in Fig. 6. Slopes were taken over the range  $0 < T_p < 18 \mu s$ . Increasing the cell temperature from 20°C to 200°C causes a rather large increase in the rate of electron production, but increasing the temperature from 200°C to 300°C causes very little change in this rate. Obviously temperature is not affecting the rate as a result of its effect on gas density. Increasing the cell temperature should decrease the gas density. If anything, this should produce a decrease in the rate. The effect of temperature is not understood at present. However, as can be seen in Table I, the values for  $k_p V_r$  obtained with the present detector at sub-atmospheric pressure are about the same as the values obtained with a radioactive-foil ECD at atmospheric pressure under similar conditions (temperature and methane concentration).

Fig. 8 shows a plot, constructed from data obtained with the present detector, of  $k_D$  vs. temperature at a methane concentration of *ca.* 7% for three cell temperatures. The values for  $k_D$  were determined from the same plots used to determine the  $k_p V_r$  values discussed above. To obtain a  $k_D$ , the  $k_p V_r$  value was divided by the

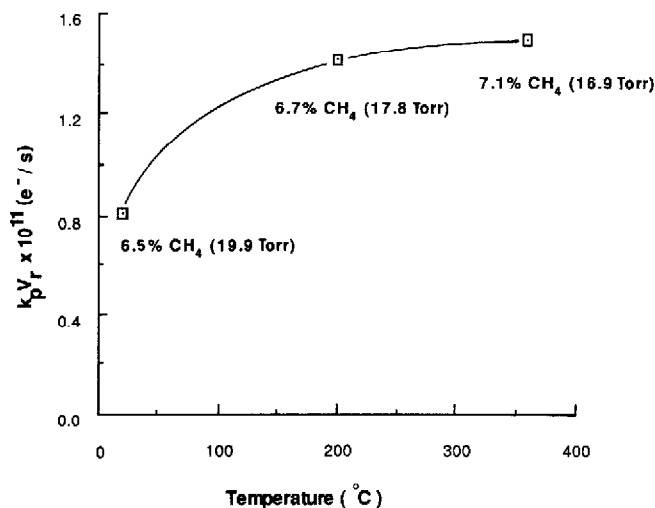


Fig. 7. Pseudo zero order rate constant for rate of electron production ( $k_p$ ) vs. cell temperature. All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V;  $T_w$ , 2.5  $\mu s$ . Total pressure measured without methane and methane concentration were slightly different at each temperature as follows: 20°C, 19.9 Torr, 6.5% methane; 200°C, 17.8 Torr, 6.7% methane; 360°C, 16.9 Torr, 7.1% methane.

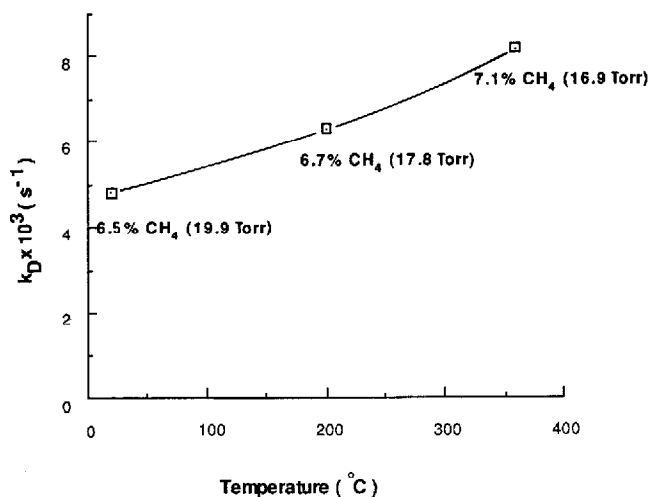


Fig. 8. Pseudo zero order rate constant for electron-ion recombination ( $k_D$ ) vs. cell temperature. All data were measured under the following conditions: discharge power, 26 W; pulse voltage, 50 V;  $T_w$ , 2.5  $\mu$ s. Total pressure measured without methane and methane concentration were slightly different at each temperature as follows: 20°C, 19.9 Torr, 6.5% methane; 200°C, 17.8 Torr, 6.7% methane; 360°C, 16.9 Torr, 7.1% methane.

corresponding  $N_e^\infty$  measured at large  $T_p$ . Increasing the cell temperature from 20 to 360°C produces a factor of 1.7 increase in the rate of electron-ion recombination. This small increase in  $k_D$  is most likely a consequence of cell contamination which increases as the temperature is increased. As can be seen in Table I, the value ( $5 \cdot 10^3$   $s^{-1}$ ) for  $k_D$  obtained with the present detector at sub-atmospheric pressure, 20°C, and 6.5% methane is greater, by a factor of 3, than the value ( $1.7 \cdot 10^3$   $s^{-1}$ ) obtained with a radioactive-foil ECD at atmospheric pressure and otherwise similar conditions. The reason for this is not understood at present. However, the characteristic  $T_p$  for the present detector (550  $\mu$ s) is less, by a factor of 1/3, than the characteristic  $T_p$  for a typical radioactive-foil detector (2000  $\mu$ s). These two facts are self-consistent.

Overall, it would appear that the basic operating conditions for the present non-radioactive ECD are quite close to those used with a conventional radioactive-foil ECD.

#### *Analytical performance at room temperature*

In the initial phase of this study we intended only to investigate the general behavior of our non-radioactive ECD and to get some idea of its sensitivity. Methane was used as the dopant gas, and the ECD was operated at room temperature. Chromatograms obtained from two analyte mixtures are shown in Figs. 9 and 10.

Although the internal volume of the ECD shown in Fig. 1 is considerably greater than that of a conventional ECD, the chromatograms show no apparent broadening due to the larger detector volume. Two features of the present detector account for this. First, unlike conventional, radioactive-foil detectors, the present ECD was operated below atmospheric pressure (typically 15–25 Torr) with a high

gas linear flow-rate through the detector. The total volume flow-rate was typically ca. 20 ml/min when measured at 1 atm pressure. If the flow-rate through the lamp metering valve were to remain unchanged when the cell pressure is reduced to 20 Torr, the equivalent flow-rate under operating conditions (20 Torr) would be 760 ml/min. The actual flow-rate under operating conditions was certainly somewhat higher than this. Second, the actual reactive volume of the present detector is far less than the physical volume of the cell itself.

Minimum detectable quantities (MDQ), at a signal-to-noise ratio of 2, for each of the analytes measured (Figs. 9 and 10) are given in Table II. The standard deviations ( $\sigma$ ), obtained from several replicate determinations of each MDQ, are also noted. With the present detector, the MDQ for carbon tetrachloride is 70 fg.

In Table III are given normalized values for the response of the present detector to each of the analytes measured. From these results, it is clear that at room tem-

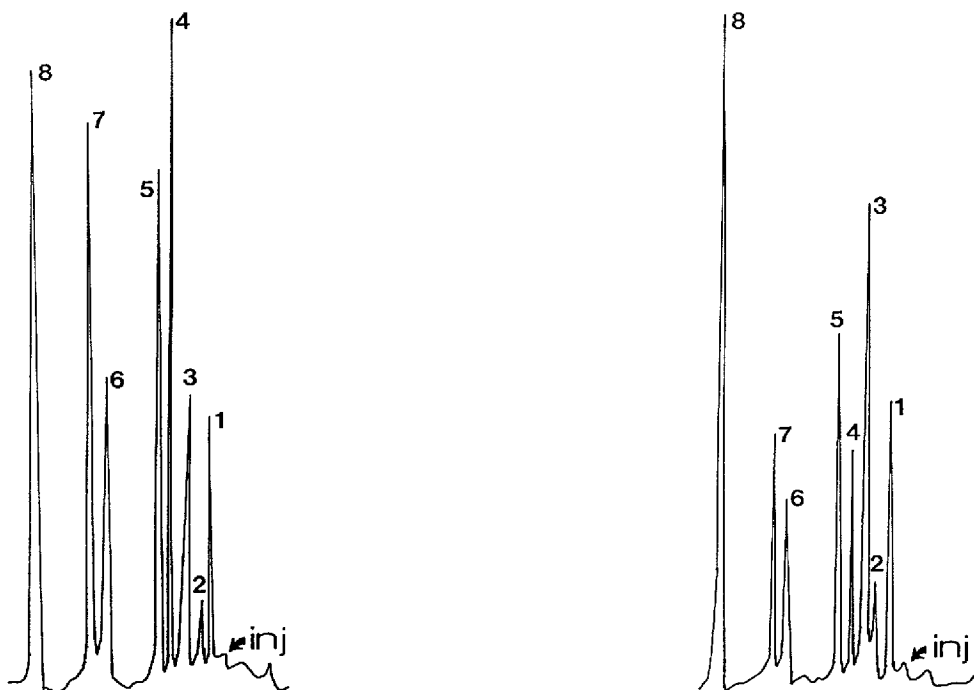


Fig. 9. Chromatogram obtained using non-radioactive ECD under the following conditions: discharge gas, helium; discharge power, 11 W; cell pressure, 15.9 Torr; column, HP cross-linked methyl silicone 8–10 m  $\times$  0.32 mm I.D.;  $T_p$ , 500  $\mu$ s;  $T_w$ , 1.8  $\mu$ s; voltage, 50 V; recorder,  $1.25 \cdot 10^{-9}$  A f.s.d., temperature, 25°C. Peak number, compound, and ng injected as follows: (1) air; (2) methylene chloride, 63.7 ng; (3) chloroform, 0.2 ng; (4) carbon tetrachloride, 0.0053 ng; (5) methylene bromide, 0.025 ng; (6) 1,1,2-trichloroethane, 3.16 ng; (7) chloropentafluorobenzene, 0.018 ng; (8) unknown.

Fig. 10. Chromatogram obtained using non-radioactive ECD under the following conditions: discharge gas, helium; discharge power, 11 W; cell pressure, 15.9 Torr; column, HP cross-linked methyl silicone 8–10 m  $\times$  0.32 mm I.D.;  $T_p$ , 500  $\mu$ s;  $T_w$ , 1.8  $\mu$ s; voltage, 50 V; recorder,  $1.25 \cdot 10^{-9}$  A f.s.d., temperature, 25°C. Peak number, compound, and ng injected as follows: (1) air; (2) *trans*-dichloroethane, 9.6 ng; (3) hexafluorobenzene, 0.028 ng; (4) carbon tetrachloride, 0.0019 ng; (5) methylene bromide, 0.015 ng; (6) 1,1,2-trichloroethane, 1.26 ng; (7) chloropentafluorobenzene, 0.0051 ng; (8) unknown.

TABLE II

MINIMUM DETECTABLE QUANTITIES (MDQ) FOR SELECTED HALOCARBONS MEASURED USING A PROTOTYPE NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR

Fig.	Peak	Compound	MDQ $\pm \sigma^*$ (ng)	MDQ $\pm \sigma^*$ (pmol)
9	2	Methylene chloride	8.0 $\pm$ 0.05	94 $\pm$ 6
	3	Chloroform	0.046 $\pm$ 0.004	0.39 $\pm$ 0
	4	Carbon tetrachloride	6.8 $\pm$ 0.2 $\cdot$ 10 <sup>-5</sup>	4.3 $\pm$ 0.2 $\cdot$ 10 <sup>-4</sup>
	5	Methyl bromide	3.6 $\pm$ 0.4 $\cdot$ 10 <sup>-4</sup>	2.1 $\pm$ 0.2 $\cdot$ 10 <sup>-3</sup>
	6	1,1,2-Trichloroethane	0.080 $\pm$ 0.008	0.59 $\pm$ 0.06
	7	Chloropentafluorobenzene	2.3 $\pm$ 0.3 $\cdot$ 10 <sup>-4</sup>	1.1 $\pm$ 0.1 $\cdot$ 10 <sup>-3</sup>
	10	2	<i>trans</i> -Dichloroethane	0.81** $\pm$ 0
3		Hexafluorobenzene	5.3 $\pm$ 0.3 $\cdot$ 10 <sup>-4</sup>	2.8 $\pm$ 0.5 $\cdot$ 10 <sup>-3</sup>
4		Carbon tetrachloride	8. $\pm$ 1.3 $\cdot$ 10 <sup>-5</sup>	5.4 $\pm$ 0.8 $\cdot$ 10 <sup>-4</sup>
5		Methyl bromide	3.6 $\pm$ 0.5 $\cdot$ 10 <sup>-4</sup>	2.0 $\pm$ 0.3 $\cdot$ 10 <sup>-3</sup>
6		1,1,2-Trichloroethane	0.062 $\pm$ 0.007	0.46 $\pm$ 0.06
7		Chloropentafluorobenzene	1.8 $\pm$ 0.2 $\cdot$ 10 <sup>-4</sup>	9 $\pm$ 1 $\cdot$ 10 <sup>-4</sup>

\* Standard deviation for three replicates unless noted otherwise.

\*\* Two replicates.

perature the response spans five orders of magnitude, from methylene chloride (relative response =  $4 \cdot 10^{-6}$ ) to carbon tetrachloride (relative response = 1). It has been shown, based on a kinetic model, that, at room temperature, the response of the conventional radioactive-foil ECD to a given analyte is determined by the rate constant for thermal electron attachment by the analyte<sup>33</sup>. Many of these rate constants ( $k_1$  or  $k_{12}$  in the references cited) have been measured using a conventional radioactive-foil ECD<sup>34,35</sup> or by other techniques<sup>36</sup>. Similarly normalized values for these are also given in Table III for comparison. The fact that the relative responses measured with the present detector agree very well with the known rate constants for electron attachment indicates that the present detector is truly functioning as an ECD.

TABLE III

COMPARISON OF RELATIVE RESPONSES OBTAINED WITH A NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR TO LITERATURE VALUES FOR THE CORRESPONDING THERMAL ELECTRON ATTACHMENT RATE CONSTANTS

Compound	Relative response (this work)	Electron attachment rate constant (normalized)
Methylene chloride	4 $\cdot$ 10 <sup>-6</sup>	1.4 $\cdot$ 10 <sup>-6</sup> *
Chloroform	4 $\cdot$ 10 <sup>-3</sup>	5.2 $\cdot$ 10 <sup>-3</sup> *
Carbon tetrachloride	1.0	1.0*
Methylene bromide	0.2	0.2*
Hexafluorobenzene	0.5	0.5**

\* Ref. 34.

\*\* Ref. 35.



We believe the analytical performance, demonstrated by these results, is promising and subject to improvement with better operating parameters and/or cell design.

#### *Analytical performance at high temperature*

Since one of the advantages of a non-radioactive ECD is its potential for high-temperature operation, we carried out a preliminary study of the temperature dependence of the response of the present detector to selected compounds. The compounds chosen were: carbon tetrachloride, which has a very high electron-capture coefficient and for which response should show very little temperature dependence, methylene chloride, for which response should increase with temperature, and hexafluorobenzene, which forms a stable negative ion and for which response should be insensitive to changes in temperature at low temperature and decrease at high temperatures. In general, the responses to these compounds observed with the present detector in the temperature range of 25 to 350°C showed the same trends observed with a radioactive-foil ECD<sup>37,38</sup>. Both  $\alpha$  and  $\beta$  regions were observed in the response to hexafluorobenzene. The methylene chloride response increased rapidly with increasing temperature. The carbon tetrachloride response remained relatively constant as temperature was increased. In general, response at high temperature tended to be less precise than at room temperature. This could be attributed to the fact that the prototype cell included some thermally unstable materials. Better materials are available and will be used in future work.

#### CONCLUSIONS

In this investigation we have shown that a detector, in which a microwave discharge is used as the ionizing source, can function as ECD and can be operated in a pulsed mode. Operation as an ECD requires the presence of both helium and methane in the measuring cell. The detector will not function as an ECD if helium alone is used. Other gas mixtures may also work, but this has not been demonstrated. Responses of this detector, at room temperature, to selected analytes have been measured and appear to be comparable to those obtained with a conventional, radioactive-foil ECD. Values for the operating parameters used with the detector (*i.e.*, pulse width, pulse period, methane concentration) are similar to those used with a conventional radioactive-foil ECD, except that the present detector operates most effectively at low pressures (*ca.* 20 Torr). The detector has the potential for operation at higher temperatures than radioactive-foil detectors, but this has not yet been demonstrated.

#### ACKNOWLEDGEMENT

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