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PHOTO-ELECTRON CAPTURE DETECTOR

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SUMMARY

An electron capture detector has been constructed which uses photoionization to produce the electrons, thus eliminating the conventional use of a radioactive source for this purpose. A photo-electron capture detector was investigated using the Lyman-α resonance line of hydrogen with triethylamine. The detector was operated in the d.c. mode and attained a limit of sensitivity for carbon tetrachloride of 50 pg.

INTRODUCTION

The electron capture detector (ECD) has seen extensive application as a sensitive, selective gas chromatographic (GC) detector since its inception in 1960. In the first paper the ECD was operated in the d.c. mode and it was noted that response was dependent upon the d.c. voltage applied and that this dependence on voltage was different for different compounds[1]. Later it was noted that many compounds have a maximum capture cross-section at thermal electron energies and the pulse mode of operation was introduced[2]. In the pulsed mode of operation the electron attachment process takes place primarily between pulses when no voltage is applied. In the pulsed mode a gas, such as methane, is added to the carrier stream prior to the detector in order to remove any excess energy from the electrons. In the absence of a field the electrons are thus allowed to acquire a thermal energy distribution[3] and the electron attachment between pulses is appropriately called thermal electron attachment.

Traditionally radioactive sources, generally in the form of metal foils, have been used to produce the necessary ionization of the carrier gas. Generally these foils are relatively inexpensive and give a constant supply of electrons. Offsetting these advantages are several limitations or disadvantages in using radioactive sources in ECDs: (1) The radioactive source can be contaminated by column bleed or by compounds of low volatility eluted from the GC column. (2) The radioactive sources have an upper temperature limitation which is related to the thermal stability of the foil. (3) The radioactive metal foil appears to react with the electron capturing species as evidenced by discoloration of the surface of the foil after continued use. (4) Use of radioactive sources requires a license and is regulated by some agency such as the Atomic Energy Commission.

The problem of contamination of the foil is a serious one, especially if the radio-

active source cannot be subjected to higher temperatures. This problem exists with tritium foils where the tritium is adsorbed in titanium. The tritium in this foil is released when the temperature exceeds 225°, the release being more rapid as the temperature is elevated[4]. Nickel-63 can be safely used up to 400° and generally less volatile substances can be vaporized at this temperature[5]. Scandium tritide (Sc^3H_3) is another tritium source used in ECDs[6]. Sc^3H_3 has a temperature limitation of 325°[7]. Another radioactive source which has been used satisfactorily in ECDs is promethium-147 (ref. 8). Promethium is plated directly onto gold or platinum foils and the source is thermally stable to 400° (ref. 8). ^{147}Pm has the advantage of low cost compared to a comparable ^{63}Ni foil. Use of ^{63}Ni and ^{147}Pm in ECDs appears to be comparable[9]. For a comparison of the characteristics of possible radiation sources for the ECD, the paper by Shoemake et al.[10] should be consulted.

The temperature of the ECD is also important with regard to the sensitivity of the detector. The response in the ECD for a specific compound may increase, decrease, or remain constant with increasing temperature, depending upon the nature of the capturing process[11]. For those compounds where the response increases with increasing temperature, a higher operating temperature such as attainable with ^{63}Ni or ^{147}Pm would be advantageous.

From the standpoint of thermal stability both ^{63}Ni and ^{147}Pm are superior to ^3H sources. However, the β particles from ^{63}Ni have a maximum energy of 0.06 MeV and those from ^{147}Pm have a maximum energy of 0.23 MeV, both of which are much larger than the maximum energy of 0.017 MeV from ^3H. Consequently, the range of the β particles from ^{63}Ni and ^{147}Pm is large compared to that of ^3H. For this reason a tritium source is more adaptable to miniaturization of the ECD. The advantage of a micro ECD is the use of lower flow-rates in the detector, which leads to higher sensitivity with capillary columns since a smaller flow of scavanger gas can be used. The use of Sc^3H_3 in a micro detector, the volume of which was 0.4 ml, has been demonstrated by Fenimore et al.[12].

Considering all aspects and uses of the ECD, it appears that no one radioactive source is ideal. Furthermore, it is highly improbable that a new isotope will be found that has all the desirable characteristics for an ECD. Finally, any radioactive source will have the disadvantage that it can become contaminated when exposed to the carrier gas flowing from the GC column. For these reasons we have investigated the possibility of using a non-radioactive source to produce the necessary electrons for an ECD.

Initially, different types of sources were considered. It appeared that photoionization with resonance lamps was the most feasible and in this paper we will consider only this type of source. Some of the advantages of using an ionization chamber and an external photon source as a photoionization detector for GC[13,14] have been discussed previously but to date the use of this technique to construct an electron capture type detector has been only tentative[15].

The ultimate objective of our work in this area is to develop an ECD with no temperature restrictions except those of the construction materials and a small reaction volume so that capillary columns can be employed with little or no scavenger gas added.

EXPERIMENTAL

Light source

To obtain electrons for an ECD by means of photoionization requires a light source which produces photons with energy sufficient to ionize the source of electrons. Since suitable electron source molecules must have a relatively high volatility, one expects to use low-molecular-weight substances which would in turn have moderately high ionization potentials. For this reason we set 10 eV as the lower limit for photon energy.

The upper limit for photon energy is determined by the method one chooses to separate the light source and the column effluent. While one may make this interface by means of a differentially pumped connecting chamber[13] or slit system which places no upper limit on photon energy, this is expensive and cumbersome. A solid window seemed more desirable. A thin piece of LiF will transmit to a high energy limit of ≈ 11.9 eV, depending on thickness and temperature[16,17], and was chosen as our window material. Only very thin (≈ 1000 Å) metallic films have been found to provide windows with a higher energy transmission limit. These were considered too fragile for a practical detector. Fortunately the monochromatic resonance emission lines from several permanent gases fall within the energy limits and the techniques for obtaining these emissions from simple lamps have been extensively developed[16,17]. Polychromatic continuum emission sources also exist for this energy range[16], but these are more difficult to produce, are less intense, and offer no apparent advantage. Table I shows the commonly used gases and the energies of their resonance lines which fall within our energy limits.

The simplest resonance line lamp is produced by application of microwave power from a medical type generator through a quartz or Pyrex envelope to excite the appropriate gas. Such lamps work best when the envelope is first evacuated, then filled with the gas, sealed, and finally pumped with a built-in getter to remove trace contaminants. This procedure requires a high-vacuum system for lamp preparation and is necessary only if one wishes to produce a very clean and intense one- or two-

TABLE I

COMMON RESONANCE EMISSION LINES*

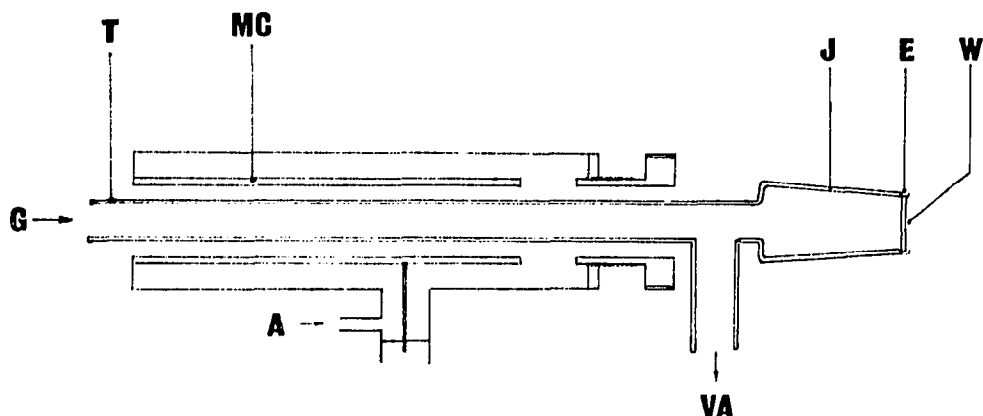| Gas	Line wavelength at maximum (Å)	Line energy at maximum (eV)
He	584.334	21.22
Ne	735.895	16.85
	743.718	16.67
Ar	1048.219	11.83
	1066.659	11.62
Kr	1164.867	10.64
	1235.838	10.03
H₂	1215.670**	10.20**
Xe	1295.586	9.57
	1469.610	8.44

* Taken from ref. 16.
** The atomic Lyman-α line.

Fig. 1. Resonance lamp. G = Gas inlet; T = Pyrex tube; MC = microwave cavity; J = 14/20 glass joint; E = epoxy cement; W = LiF window; VA = outlet to vacuum pump; A = cooling air inlet.

line emission. The desired resonance emission can also be obtained, although usually at reduced intensity and in the presence of other lines, by simply flowing the gas through the lamp. This was considered sufficient for our purposes.

The lamp design used is shown schematically in Fig. 1. It is constructed from 8-mm O.D. Pyrex tubing and a Pyrex standard taper (14/20) ground glass joint. A 10-mm diameter, 1-mm thick LiF disc (McPherson Instruments) is attached to the ground joint with Torr Seal epoxy (Varian). A cylindrical cavity (Ophthos Instruments) slips over the lamp body and microwave power is applied to the cavity from a Microtherm CMD-10 supply (Ratheon Mfg.).

Argon, because of the relatively higher energy of its resonance lines, allows use of a wider selection of electron source gases and was our first choice as a photon emitter. To produce the argon resonance lines, argon is passed through a dry ice cooled activated charcoal trap and into the lamp. A metering valve before the trap and mechanical pump after the lamp allow us to control the gas pressure within the lamp. An operating pressure of ca. 2 torr was found optimum.

The emission produced in this way was observed using a 1-m, near normal incidence, vacuum UV monochromator (McPherson, Model 225) and standard techniques. The monochromator was equipped with a differentially pumped entrance slit system, so the lamp could be checked both with and without its LiF window. Fig. 2 shows the emission spectrum obtained without the window at an optical resolution of better than 1.0 Å. Between 1000 and 1545 Å (8.0 eV) only the two argon resonance lines and the Lyman-α hydrogen line are observed. The latter is due to almost ubiquitous hydrogen contamination. Fig. 3 shows the emission spectrum over the same region observed when a LiF window was added to the lamp. Note that the higher energy argon line is not present with detectable intensity, the lower energy argon line is reduced in intensity with respect to the Lyman-α line, and several more contamination lines are present. We find that to maintain any measurable intensity in the 11.62-eV argon line it is necessary to include the charcoal trap, to use only stainless steel or glass in the flow system, and to make all connections as leak tight as possible. Even then the line is low in intensity and may be completely absorbed by
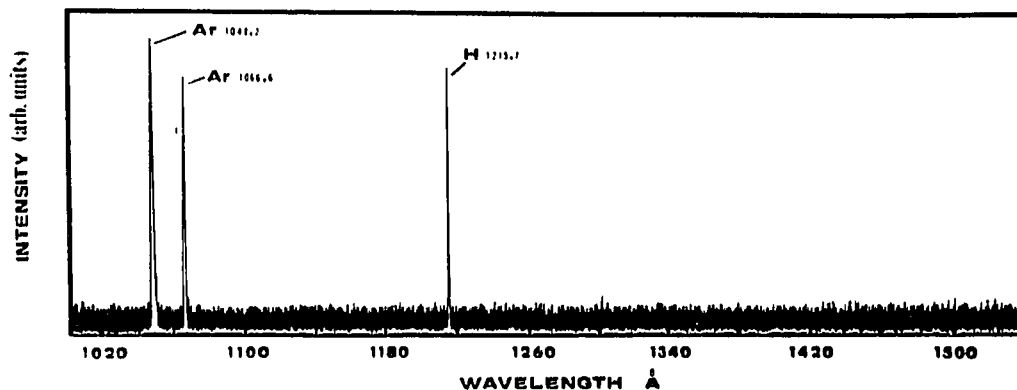
Fig. 2. Argon lamp emission: no window on lamp. *Ca.* 2 torr argon in lamp. 35% microwave power. Obtained with McPherson Model 225 vacuum UV monochromator.

even slight coating of the window on the detector side. It should be possible to increase the intensity of this line by using a thinner LiF window, and by using a quartz lamp envelope which allows more efficient power transmission than Pyrex. It should be possible to reduce contamination of the LiF window on the detector side by operation at high temperature. The epoxy used in the present construction prevents this. A high-temperature ceramic cement is available for use in place of the epoxy but has not yet been tried. While operation at higher temperature may solve contamination problems it introduces another complication also associated with the weak argon emission. As the temperature of the LiF window is raised, its transmission falls off, at least near the high-energy limit where the argon line occurs[17]. With this in mind we also investigated the use of a light source with an emission at lower energy and thus less susceptible to this problem.

Although the lower energy of the Lyman-α line restricts the choice of electron source molecules with which it can be used, the ease with which one can achieve a high intensity in this line made it our second choice as a photon source. Samson[16] has reported that a mixture of 25% hydrogen in helium and a total gas pressure of 200 μ gives a very monochromatic source of Lyman-α radiation. The spectrum he obtained using a microwave discharge lamp is shown in Fig. 4. We used a similar mixture in the same lamp described above. Experiments with both light sources are reported below.
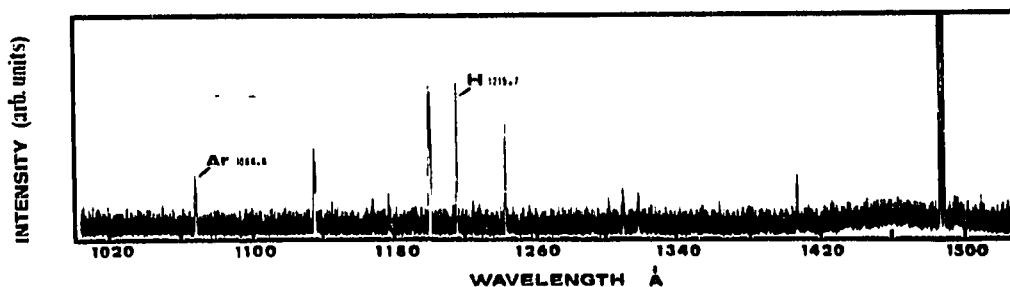

Fig. 3. Argon lamp emission: 1-mm thick LiF window on lamp. *Ca.* 2 torr argon in lamp. 70% microwave power. Obtained with McPherson Model 225 vacuum UV monochromator.
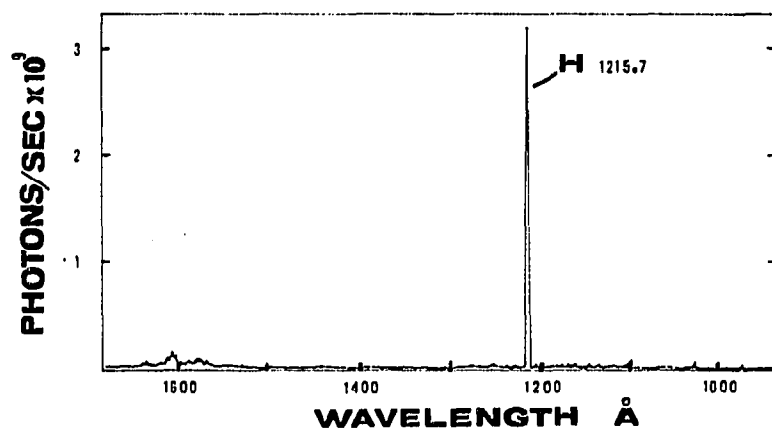
Fig. 4. Hydrogen–helium lamp emission, taken from ref. 16.

Detectors

Two different ECD configurations were used. Detector A_1 is shown in Fig. 5. One end of a PTFE cylinder was machined to receive the ground glass joint of a lamp and provide a 10-mm diameter cavity beyond the end of the window. A 1-mm thick disc of 404 stainless steel is fitted against the flat bottom of this cavity. A section of stainless-steel tubing (0.0625 in. O.D., 0.03 in. I.D.) passes through this disc, to which it is silver soldered, and out through a tight fitting hole to the other end of the PTFE body. The disc and tube form one electrode of the detector and are connected to a vibrating reed electrometer (Victoreen). The stainless-steel tube also serves as the inlet for effluent from the chromatograph column to which it is attached by a length of PTFE tubing which provides electrical isolation. A second electrode is formed by placing a circle of brass wire mesh over the face of the LiF window. A wire soldered to this mesh passes back out of the cavity along the ground glass joint, and connects
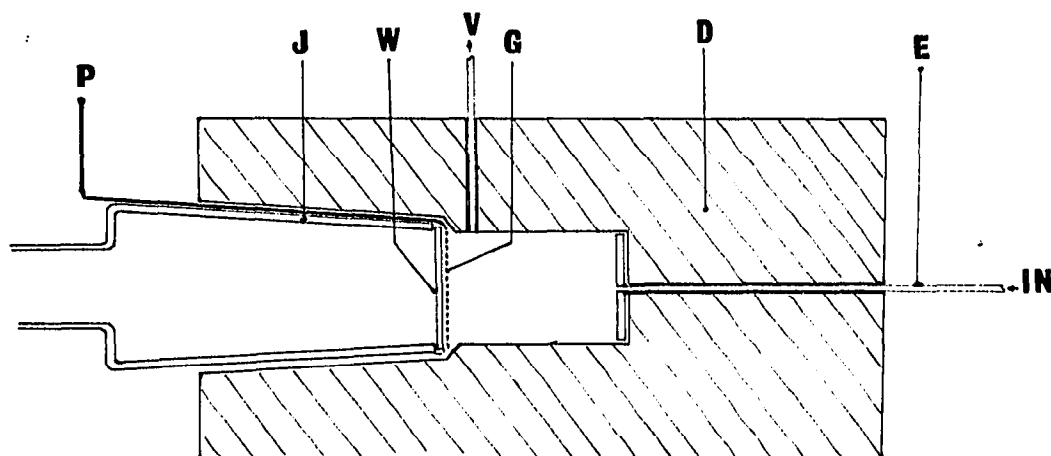
Fig. 5. Detector design A. P = Electrical connection from mesh to voltage supply; J = 14/20 Pyrex glass joint; W = LiF window; V = detector vent; G = brass wire mesh grid; D = PTFE detector body; E = electrical connection to electrometer; IN = inlet for column effluent.

to a pulse generator (Data Pulse 102) or d.c. voltage supply (Mallory Duracell 1.4-V mercury battery). PTFE tape wrapped around the joint and wire holds the mesh in place and provides a suitable gas seal. A piece of 0.0625-in. O.D. PTFE tubing is press fitted into an outlet port drilled through the detector body into the cavity at a point near the window and serves as the detector outlet. The distance between the two electrodes is 12 mm and the total internal volume of the cavity is 0.940 ml. A smaller volume version of this same configuration, detector A_2, was also used. By inserting a PTFE sleeve along the cavity length and a PTFE disc between the steel electrode and the cavity bottom the volume was reduced to 0.200 ml.

The second detector configuration, detector B, is shown in Fig. 6. Again the body was formed from a PTFE cylinder, machined in this case to accept at one end a 0.250-in. O.D. Kovar tube. The other end of the Kovar tube is sealed to a Pyrex joint to form a light path extender which mates with the lamp. The extender is flushed with helium which enters through a sidearm near the lamp window and flows toward the detector. This flow provides a non-absorbing light path for the argon and Lyman-α photons and tends to prevent contamination from reaching the LiF window. The extender also provides some thermal insulation between the lamp and the detector. The Kovar tube forms one electrode of the detector and is connected to the pulse generator or d.c. voltage supply. A 0.0625-in. O.D. stainless-steel tube is positioned inside and along the cylindrical axis of the Kovar tube. This stainless-steel tube extends out the other end of the detector body through a tight-fitting hole and serves as the inlet from the GC column to which it is connected by means of a length of PTFE tubing. The inlet tube again serves as an electrode of the detector and is connected to the electrometer. An outlet port was drilled into the detector body near the end of the Kovar tube. The active volume of this detector is determined by the dynamics of the various gas flows rather than by physical size as in detector type A. The position of the steel inlet tube and the helium flush flow-rate can be varied to optimize sensitivity.
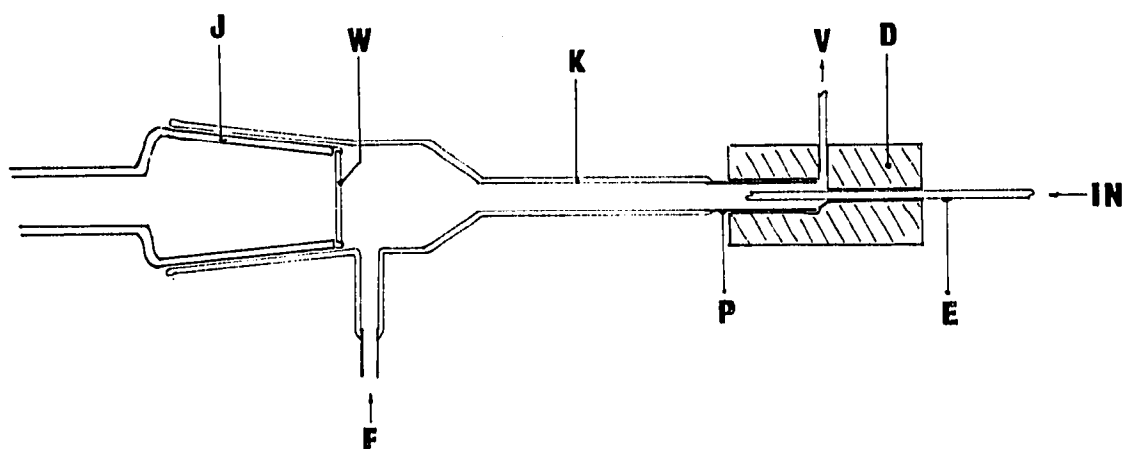

Fig. 6. Detector design B. J = 14/20 Pyrex glass joint; W = LiF window; K = Pyrex tube; V = detector vent; D = detector body; IN = inlet for column effluent; E = electrical connection to electrometer; P = electrical connection to voltage supply; F = helium gas flush.
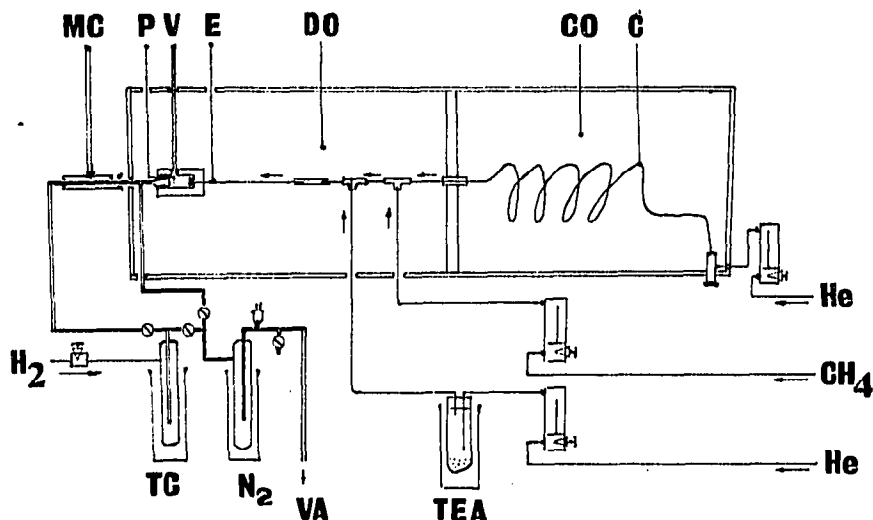
Fig. 7. Schematic diagram of gas chromatograph and gas handling system. MC = Microwave cavity; P = electrical connection to voltage supply; V = detector vent; E = electrical connection to electrometer; DO = detector oven; C = column; He = carrier gas; CH₄ = electron thermalizer gas; TEA = triethylamine vaporizer; VA = outlet to vacuum pump; H₂ = 25% hydrogen in helium; TC = charcoal trap at −78°; N₂ = liquid nitrogen trap; CO = column oven.

Chromatograph and gas handling system

The chromatograph and gas handling system used are shown in Fig. 7. A modified Chromalitics MC-2 mass chromatograph is used. Either detector can be mounted in the detector oven of this unit. When detector A is used, part of the lamp extends into the oven. When detector B is used the lamp is completely outside the oven. In either case the detector oven is held at a temperature of 140 ± 0.2°. A 200 ft. × 0.02 in. I.D. Ni capillary column coated with 10% OV-101 is used.

Detector response is measured for both chloroform and nitrobenzene. For chloroform calibration the column is held at 90° and for nitrobenzene at 160°. Either sample is added to the helium carrier gas through an injector port held at 200°. The carrier gas at an inlet pressure of 20 p.s.i. passes through a 2 in. × 15 in. trap of 8–12 mesh molecular sieve (Supelco, Bellefonte, Pa., U.S.A.) and leaves the column at a flow-rate of 5.4 ml/min. All chemicals are spectroquality (Matheson, Coleman & Bell). For sensitivity calibration, dilutions are made by volume in 10-ml volumetric flasks, and the samples are injected with a 1.0-μl syringe (Hamilton).

A flow-rate of 2.3 ml/min of ultrahigh purity methane, the electron thermalizer, is added to the column effluent through a tee connector before it reaches the detector.

Three electron source compounds are used: ethylene, acetone, and triethylamine (TEA). Any of these can also be added to the column effluent before it reaches the detector. To add TEA helium carrier gas is flushed through a trap containing 3 ml of TEA at −78°.

The lamp gas flows through a micrometering valve and a dry ice cooled charcoal trap (when appropriate) to the lamp and is pumped away by a liquid nitrogen trapped mechanical pump (Cenco Hyvac-14). A thermocouple gauge (Cenco) is used to measure the lamp pressure.

The sensitivity of the Victoreen electrometer is calibrated with a Keithley high-speed picoammeter. The output of the electrometer is recorded on a Honeywell Electronik 194 with 1-mV full scale response.
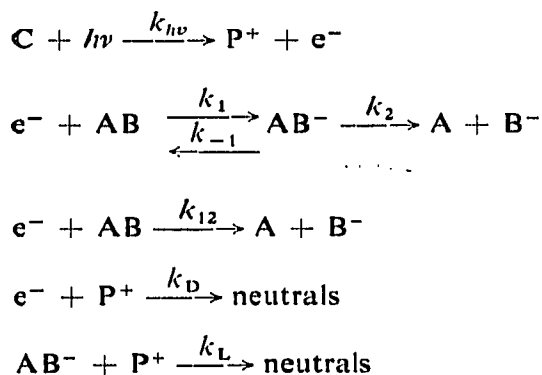
RESULTS AND DISCUSSION

Photo-electron capture mechanism

In the conventional ECD using a radioactive source, such as ^{3}H or ^{63}Ni, the β particles ionize the carrier gas, which is generally argon, helium, or nitrogen. In the photo-electron capture detector (P-ECD) these carrier gases will not be ionized by either the argon or Lyman-α hydrogen resonance lines since the ionization potential (IP) of these gases exceeds the energy from the resonance lamps. The electron source compound (C) with an ionization potential lower than the energy of the resonance line is added to the carrier gas prior to the P-ECD. For the electron source compounds used in this study, a compilation of the maximum excess energy imparted to the electron (E_c^-) upon ionization of C

$$E_c^- = h\nu - IP$$

is shown in Table II. The energy of the electron can be less than this quantity if the positive ion produced becomes vibrationally activated. As will be discussed later, it appears that the energy imparted to the electron is an important factor in the subsequent electron capturing steps.

The added compound, C, is generally at a higher concentration than any electron capturing species, AB. Therefore, the electrons are produced primarily by the ionization of C, even in the presence of AB. After the production of electrons, the remaining electron attachment and neutralization reactions should be similar to the ECD employing a radioactive source[3,18,19]. The mechanism can be written as

$$C + h\nu \xrightarrow{k_{h\nu}} P^+ + e^-$$

$$e^- + AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^- \xrightarrow{k_2} A + B^-$$

$$e^- + AB \xrightarrow{k_{12}} A + B^-$$

$$e^- + P^+ \xrightarrow{k_D} \text{neutrals}$$

$$AB^- + P^+ \xrightarrow{k_L} \text{neutrals}$$

Under steady state conditions, the current obtained while the capturing species is being eluted, I_c^-, is related to the standing current, I_b, by the expression

$$\frac{I_b - I_c^-}{I_c^-} = K[a] \tag{1}$$

TABLE II

MAXIMUM EXCESS ENERGY OF THE PHOTO-ELECTRONS

Compound	IP (eV)	Argon resonance (hv = 11.62 eV)	Lyman-α hydrogen resonance (hv = 10.20 eV)
Ethylene	10.45	1.2	not ionized
Acetone	9.69	1.9	0.5
Triethylamine	7.50	4.1	2.7

where K = electron capture coefficient and $[a]$ = concentration of capturing species, AB. The capture coefficient can be expressed in terms of the individual rate constants. by the expression[19]

$$K = \frac{1}{k_D} \left(k_{12} + \frac{k_1 (k_L + k_2)}{(k_{-1} + k_2 + k_L)} \right) \tag{2}$$

Note that k_D, the rate constant for e^- recombination, is in the denominator. When this recombination rate constant is large, K is universally reduced for all capturing species and the sensitivity is lowered.

Argon resonance lamp with ethylene

The initial experiments in this study used the argon resonance lamp, as described in Experimental, ethylene as the species being ionized (C) in the P-ECD, and a cell design of detector A_2 shown in Fig. 5. The energy of the argon resonance line is in excess of the IP of ethylene by 1.2 eV (see Table II). However, since the intensity of the argon resonance line was decreased by contaminants giving extraneous emission lines (Fig. 3), the standing current was low.

Furthermore, the nature of the photo-electrons produced differed from those formed by β particles. This is best shown by a graph of the standing current, I_b, as
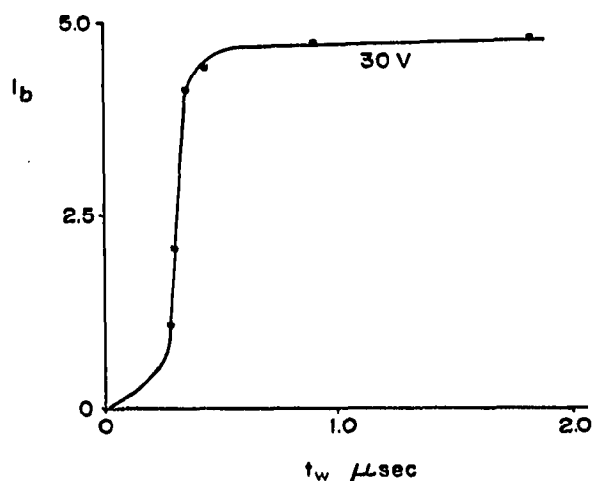

Fig. 8. Standing current, I_b (arbitrary units), produced by β particles versus pulse width, t_w, at 30 V/cm.

a function of the applied pulse width. For comparison, such a graph for the collection of e⁻ formed by β particles is reproduced from ref. 3 in Fig. 8. Only the curve for 30 V is shown. Note that the curve shows an initial steep rise followed by a plateau. This suggests that there is a built-up of the concentration of electrons during the period when no voltage is applied and that electrons are collected completely in a very short pulse of only a few tenths of a microsecond at 20–80 V/cm.

A similar graph is shown in Fig. 9 where the standing current arises from photo-electrons from ethylene and the argon resonance lamp. Note that there is only a small initial rise in the curve followed by a linear increase with increasing pulse width. No plateau is attained. We attribute this result to a rapid rate of recombination of the electrons with the positive ions. The initial energy of the electrons is 1.2 eV if the ionization occurs by the 11.62-eV resonance line of argon. The initial energy of the electron will be less if ionization occurs by longer wavelength lines from the contaminants in the resonance lamp. Apparently 1.2 eV is not sufficient energy to free the electron from the field of the positive ion in a gas at a total pressure of approximately 1 atm. Consequently, only a small concentration of electrons is produced between pulses. However, when an external field is applied, the electrons can be freed
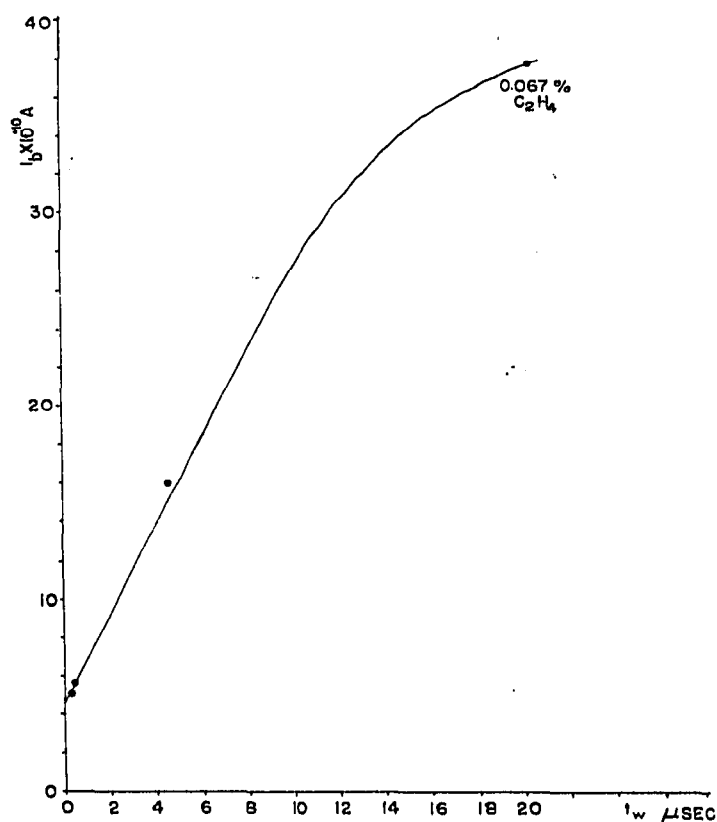

Fig. 9. Standing current, I_b, produced by the argon resonance lamp and ethylene versus pulse width, t_w, at 190 V/cm.

from the positive ions and a measurable current results. Obviously, as the pulse width is increased, more electrons are produced and freed, thus explaining the linear relationship I_b vs. t_w. In contrast, the electrons produced by ionization from β rays have larger initial energies ($\approx 50\%$ in the range 0–6.5 eV)[20], which is sufficient to free the electrons from the positive ion.

The P-ECD is operable with the argon resonance lamp and ethylene, but the sensitivity is quite poor. As mentioned previously, when the recombination rate constant (k_D) is large, the capture coefficient decreases, as described by eqn. 2. This result can also be understood in a qualitative manner by the simple fact that increasing the recombination rate constant does not allow sufficient time for the electron to be captured by AB molecules.

Argon resonance lamp with acetone

In order to impart a higher energy to the photo-electrons, acetone was used in place of ethylene as the electron-producing compound. For direct photoionization the maximum electron energy is 1.9 eV. In addition, it was thought that the addition of argon to the carrier gas would produce metastable argon atoms, which in turn could react with acetone (C) according to the equation

$$Ar^* + C \rightarrow ArC^+ + e^-$$
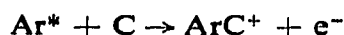
The electrons produced by this reaction could have additional energy equivalent to the bond energy between Ar^+ and C. As with ethylene, detector A_2 was used and the standing current was measured as a function of pulse width. The graph of such data is shown in Fig. 10.

Significantly higher standing currents were attained using acetone. This is apparently due to the lower ionization potential of acetone and ionization by the Lyman-α resonance line of hydrogen in addition to the argon resonance line. Furthermore, note that a higher concentration of electrons is produced during the field free period compared to ethylene as evidenced by the higher current at short pulse widths. This is attributed to a higher energy imparted to the electrons and this is enhanced when argon is added to the carrier gas. Various concentrations of acetone and argon were investigated.

Despite the marked improvement using acetone, the standing current increases with increasing pulse width, suggesting again that not all of the photo-electrons are freed from the positive ions. The recombination rate, k_D, is smaller than with ethylene but still sufficiently large to reduce the sensitivity. The P-ECD with acetone and 1.9% argon added to the carrier gas could be operated in the pulsed mode. However, since some of the electrons collected were produced only when the field was applied, the mode of operation actually is a combination of pulsed and d.c. modes. A mixed mode of operation was not considered advisable and this photo-electron source was not considered further.

Lymanα- hydrogen resonance lamp with TEA

Since it is difficult to obtain the 11.62-eV argon resonance line of argon due to trace contaminants, as discussed in Experimental, it was thought advisable to concentrate our energy in the α-Lyman line of hydrogen (see Fig. 4). TEA was selected
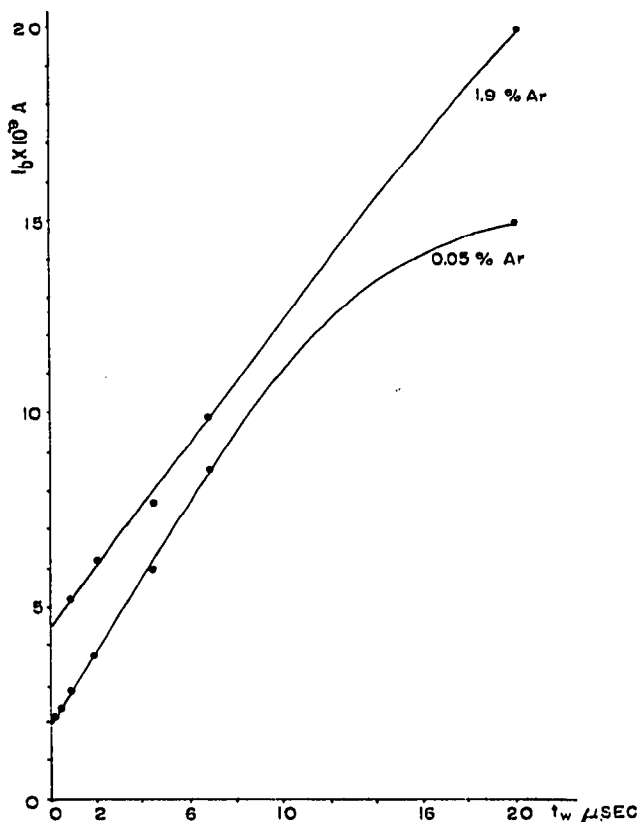
Fig. 10. Standing current, I_b, produced by the argon resonance lamp and acetone *versus* pulse width, t_w, at 190 V/cm.

as the electron-producing gas since it has a very low ionization potential (7.50 eV) and is still relatively volatile. The maximum excess energy of the electrons is 2.7 eV using the Lyman-α line of hydrogen.

P-ECDs of types A and B were used and for both detectors the standing current was extremely high. Maximum currents of the order of 10^{-7} A were obtained. In fact, the current is so large that it was necessary to diminish the current to the region of 10^{-8} A to avoid problems from space charges. Despite the fact that much higher currents were obtained, the collection of electrons still depended upon the applied pulse width and voltage. Consequently, the detector could not be operated effectively in the true pulsed mode. Since high currents are attained even at low applied voltages, the use of the detector in the d.c. mode was investigated. Detector A_1 could be operated satisfactorily with a voltage of 1.4 V applied across an electrode separation of 1.2 cm.

In order to find the optimum conditions at which the detector should be operated in the d.c. mode, the parameters such as flow-rate and concentration were varied. The concentration of TEA was varied by dilution of a helium gas stream saturated with TEA vapor at temperatures of −78° (dry ice), −63.5° (chloroform slush bath),

0° (ice–water bath). The desired current of $\approx 10^{-8}$ A was attained using the saturated TEA vapor at −78°.

The vapor pressure of TEA at −78° is not known exactly, but an estimate of 0.05 torr has been calculated from existing vapor pressure data down to −23°. This is a very small concentration of TEA and is probably insufficient to thermalize the photo-electrons. Methane is frequently used for this purpose with ECDs employing radioactive sources[3]. The exact concentration for this purpose is usually not critical, ranging from a few per cent to 10%.

In the P-ECD the methane will also absorb the Lyman-α line even though it is not ionized. This will attenuate the intensity of the Lyman-α line, thus reducing the ionization of TEA. Furthermore, since the absorption has increased, the region of ionization will be restricted to a shorter path length. The absorption coefficient for methane is 500 cm^{-1} (ref. 21) and 90% of the light is absorbed in a distance of 1 mm at 4.6% methane concentration. Thus 99% of the light is absorbed in a 2-mm path length. In order that the reaction be restricted to a region of 1–2 mm, 4.6% methane was used in the P-ECD. Variation from this concentration showed very little change in sensitivity to chloroform.

The flow-rate in the P-ECD was also varied. The standing current generally increased with increasing flow-rate. However, since the column flow-rate is constant, the additional scavenger flow-rate lowers the concentration of eluted material, making the sensitivity of the detector lower. A compromise between these two effects must be reached. For this detector a flow-rate of 50–60 ml/min seemed optimal, however, the variation in current and sensitivity to chloroform was not great in the vicinity of this flow-rate.
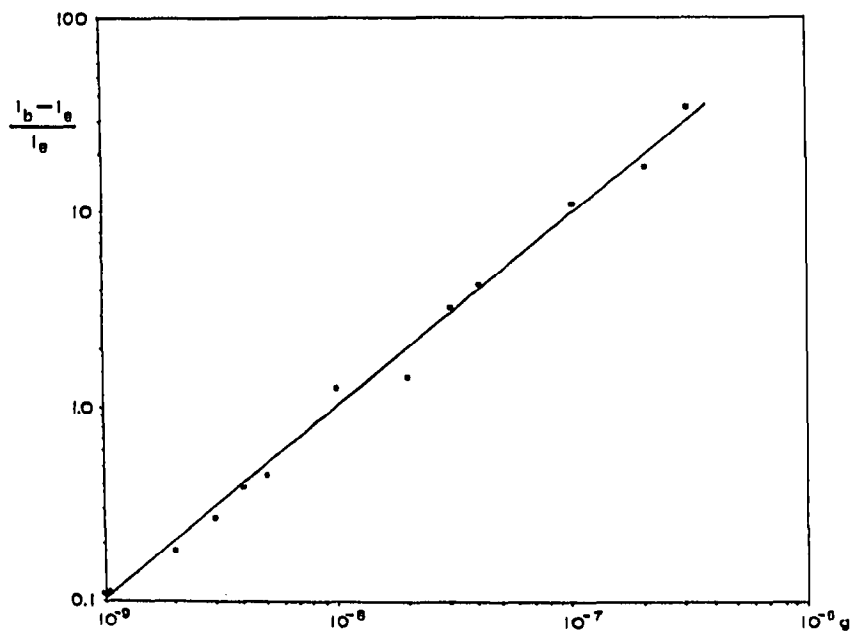

Fig. 11. Concentration dependence for chloroform. Detector temperature, 140°.

The d.c. voltage was changed from 1.4–2.8 V and only a 15% increase in current was observed. Also there was little change in response to chloroform at 2.8 V. In general, the response of the ECD will vary with applied voltage in a different manner for different compounds. Frequently the response is optimized for an analysis of a specific compound. Since we did not have any specific analysis in mind we decided to use as low a voltage as possible, which provides a satisfactory standing current. At 1.4 V the energy distribution of the electrons should be near thermal, so the voltage of 1.4 V was used.

In summary, the specific conditions under which the P-ECD was operated are as follows: flow-rate of column, 5.4 ml/min; of helium + TEA at −78°, 50 ml/min; and of methane, 2.3 ml/min; resulting in a total flow-rate of 57.7 ml/min, with 4.5% methane; potential, 1.4 V; electrode separation, 1.2 cm.

For an ECD operated in the pulsed mode, the concentration dependence of the response is given by eqn. 1. For the d.c. mode of operation the same function frequently applies. The concentration dependence of the P-ECD for chloroform is shown in Fig. 11. The function appears to be obeyed in the range 10^{-9} to 5×10^{-7} g. The highest concentration corresponds to a capture of 97%.

Chloroform undergoes dissociative electron capture whereas nitrobenzene undergoes non-dissociative electron capture. In order to see if eqn. 1 holds for non-dissociative capture the concentration dependence of nitrobenzene was determined and the results are shown in Fig. 12. Again the data seem to obey eqn. 1; the upper concentration of 5×10^{-7} g corresponds to 96% capture. In both Figs. 11 and 12 the straight line is drawn with a slope of one (45°), which is in agreement with eqn. 1.

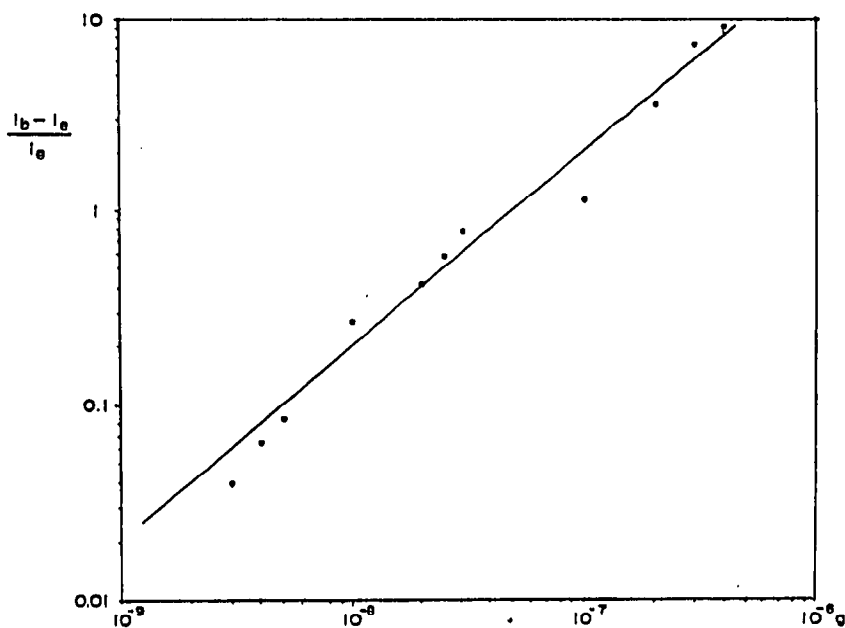The sensitivity of the P-ECD can be measured in terms of the limit of

Fig. 12. Concentration dependence for nitrobenzene. Detector temperature, 140°.

detectability and by the electron capture coefficient for certain compounds. The limit of detectability is a very practical and useful measure of sensitivity; however, it also includes factors not relating to the detector which affect: (1) the peak width such as the GC column, detector volume, and flow-rate and (2) the noise level such as the electrometer, light source, and recorder. The capture coefficient, on the other hand, is a direct measure of the response observed for a given concentration of capturing species. In principle, it should be unrelated to ancillary GC equipment, although it will depend upon the gas flow-rate through the detector, since k_D (see eqns. 1 and 2) can be affected by extreme variations in flow-rate.

The limit of detectability for chloroform and carbon tetrachloride was determined using the system described in Experimental, and the P-ECD A, operated in the d.c. mode under the conditions previously specified. The limit of detectability is defined as the concentration which gives twice the signal-to-noise ratio. The results are: chloroform, 2×10^{-10} g and carbon tetrachloride, 50×10^{-12} g.

Since the peak widths were approximately the same for chloroform and carbon tetrachloride, the limits of detectability can be compared to the electron capture coefficients. For the tritium ECD the ratio of the carbon tetrachloride to chloroform capture coefficients is 27 (ref. 18), which is in good agreement with the ratio of the limits of detectability of 30.

In order to further compare the sensitivity of the P-ECD with that for the tritium ECD, five compounds were investigated which represent a variety of electron capture characteristics. These characteristics are given in the second column of Table III. The photo-electron capture coefficients in column 4 of Table III are to be compared with the tritium electron capture coefficients at 140° (ref. 11) in column 3. Note that in general the tritium values are larger by a factor of ≈ 10–150 as shown in column 5. Therefore one can expect the P-ECD operated in the d.c. mode to be less sensitive than the tritium detector operated in the pulse mode by this factor of ≈ 10–150. This difference in sensitivity is certainly significant; however, there are several modifications that can be made to the P-ECD which should increase the sensitivity and permit working in the pulse mode. There is no reason to conclude at this time that the P-ECD is inherently less sensitive than ECDs using radioactive foils.

The detector design B described in Experimental and shown in Fig. 6 was also used with the Lyman-α resonance line of hydrogen and TEA. This design has the advantage that the LiF window, attached with an epoxy cement, is not located in the ionization and electron capture region and thus would not be exposed to the poten-

TABLE III

COMPARISON OF ELECTRON CAPTURE COEFFICIENTS

Compound	EC characteristics	Electron capture coefficient, K (l/mole)		
		Tritium ECD	P-ECD	Ratio
CCl_4	high capture, dissociative	4.6×10^{10}	3×10^8	153
$C_6H_5NO_2$	high capture, non-dissociative	3.6×10^9	1.3×10^8	28
$CHCl_3$	high capture, dissociative	1.7×10^9	1×10^7	170
CH_2Cl_2	moderate capture, dissociative	1.6×10^6	1×10^5	16
$C_6H_5COCH_3$	moderate capture, non-dissociative	5.3×10^6	5×10^5	9

tially high temperatures at which the detector may be operated. Although it is not fully understood, this detector design did not show the sensitivity of detector A, despite the fact that high currents were observed. Possibly the correct combination of flow-rates and positioning of the electrodes was not used.

Despite the fact that this study was carried out at 140°, there is no reason to believe that the electron attachment process could not be carried out at any temperature up to the limit imposed by the construction of the P-ECD. This has been previously demonstrated using a helium resonance lamp at reduced pressures (≈ 100 torr)[15].

CONCLUSIONS

An ECD using electrons produced through photoionization has been demonstrated. Using the Lyman-α resonance line of hydrogen with TEA added to the gas stream, the P-ECD was operated in the d.c. mode. The limit of detectability for carbon tetrachloride is 50 pg. The electron capture coefficient for five compounds showed the sensitivity to be $\approx 10-150$ times less than a tritium ECD operated in the pulsed mode. It is thought that the sensitivity of the P-ECD can be improved significantly by imparting greater energy to the electrons produced by photoionization so that the electrons are available for capture under field free conditions. This may also be accomplished by lowering the pressure, as was demonstrated using the helium resonance lamp and a detector pressure of 100 torr[13]. This should also permit operation of the P-ECD in the pulsed mode.

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