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# ELECTRON CAPTURE DETECTION IN GAS CHROMATOGRAPHY

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## I. INTRODUCTION AND DEFINITIONS

In an earlier review[1], electron capture detection (ECD) was briefly discussed as one of many selective detectors available for gas chromatography. The purpose of this review is to present an expanded and more detailed discussion on ECD. The electron attachment phenomenon is examined as a series of discrete events as it is presently understood, and is followed by a discussion of the total system with emphasis on operating parameters and their effects on overall ECD performance.

In order to facilitate the comparison of various ECD designs and their performance characteristics, brief definitions are given which are intended to be primarily descriptive rather than quantitative. The definitions are based on guidelines set by the ASTM E-19 Committee on Chromatography[2].

The development of the ECD stems from studies utilizing argon ionization detectors whose principles were established by Jesse and Sadauskis[3]. They recognized that ionization increased in irradiated gases in the presence of trace amounts of organic molecules. The detection based upon electron affinity, of solutes in an effluent stream of gas, was first reported by Lovelock[4-5] in 1958. Shortly thereafter, it was found that varying the applied electrode potential in an ionization chamber allowed the analyst to differentiate molecular species because of the dissimilarities in free electron attachment[6-7]. The attachment of thermal electrons by molecules was referred to as "electron capture", which is not to be confused with *K* capture, an electron capture process in nuclear reactions[8].

### *A. Response mechanism*

Although a detector senses the variation in the amount of sample passing through it, it can be further classified by its response mechanism as concentration dependent, mass flow-rate dependent, or by a mixed function[1,9]. The concentration detector produces a signal that is proportional to the amount of solute per unit volume of carrier gas passing through the reaction cell. A mass flow-rate detector gives a signal that is proportional to the amount of solute passing through it in unit time but is independent of the volume or carrier gas required for elution. A comprehensive review on the differences between concentration and mass flow-rate dependent detectors has been given by Halász[9].

### *B. Specificity*

Detectors can be classified as either "universal" or "specific". A universal detector responds to most of the solutes passing through it, while a specific detector (also termed selective detector) exhibits a greater response for a particular group of substances with a minimum response to others[9,10].

### *C. Detection limit*

The detection limit is defined as the smallest amount of solute required to produce a signal that is twice the noise level. The units are normally given as C/sec·g of solute. Although a gas chromatographic (GC) peak of such small amplitude is not considered to be a reliable response for good quantitative accuracy, it does represent a reasonable criterion for detector comparison.

### *D. Sensitivity*

The efficiency of the detector as a transducer for converting the sample characteristic into a measurable electrical signal is normally defined as sensitivity[10]. For a concentration-dependent detector, the sensitivity is expressed as the ratio of peak area times flow-rate to the mass of the solute. The sensitivity of mass flow-rate dependent detectors is presented as a proportionality between peak area and solute weight.

### *E. Noise*

The random, fast, peak-to-peak signal fluctuation is called detector noise. Signal noise is quantitated by averaging the peak-to-peak amplitude and is expressed in electrical units (C/sec). Thus, from the detector noise level, the minimum detectable amount of solute can be calculated as well as the lower limit of the linear dynamic range.

### *F. Linearity*

Linearity is the range of sample mass or concentration over which the detector responds in proportional increments within a certain arbitrary deviation. The peak area or height is plotted against a wide range of solute concentrations (or mass) and the curve for the best fit of the data is used to demonstrate linearity.

There are obviously two limits to the linearity curve: the lower concentration limit is set by the limit of detection, and the upper limit is defined by an arbitrary percentage deviation from the linearity curve, normally about 5 %. Thus, the practical meaning of the linearity of a detector is that it provides the analyst with a means of determining the concentrations for which he can be confident of a constant detector calibration factor. Even in those instances where a detector has a small range of linearity, the analyst can have a high quantitative reliability if suitable precautions are taken.

### *G. Response time*

The response time is defined as the time required for the detector output signal to reach about 63 % of the new equilibrium value when the composition of gas entering the detector is changed in an incremental manner.

### *H. Standing or background current*

The constant output signal generated by the ionization processes in the detector when it is operating with no solute passing through it is termed standing current (or sometimes dark current). This output signal is an extremely important diagnostic aid in recognizing malfunctions in the ECD and the overall GC system.

### *I. Electron capture cell configurations*

With one exception, commercially available ECDs employ radioactive isotopes as a means for ultimately generating thermal electrons. The exception (Beckman) produces electrons by means of a rare gas discharge and interaction with the solute vapor occurs in a remote ionization chamber. The potential advantages of this system are that it can be operated at higher temperatures than most conventional detectors, and therefore it should not be so susceptible to contamination.

Primitive ECDs were generally converted argon ionization detectors operating at low applied potentials[1,5,6,11]. Such detectors have coaxial geometry with the anode located along the axis of the cell and surrounded by a cylindrical cathode to which is attached the radioactive source (Fig. 1). Detectors of this type are supplied by some manufacturers, but others now manufacture cells with plane parallel or concentric geometry (Figs. 2 and 3). In the plane parallel configuration, the anode and cathode are arranged parallel to one another at the end of an electrically insulated chamber. In the concentric cylinder ECD[12] (Fig. 3), the cathode houses the radioactive foil, but the anode is removed and isolated by a Kovar glass union. This design presumably is intended to optimize the current conducted through the detector in the d.c. voltage mode[12]. The pin-cup detector represents a fourth geometric design (Fig. 4)[13,14].

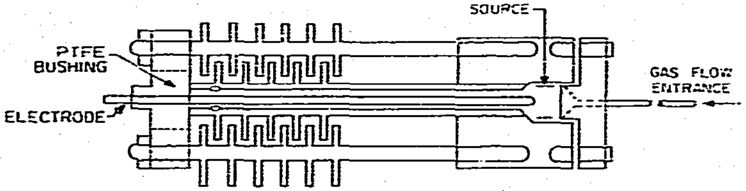


Fig. 1. Coaxial ECD.

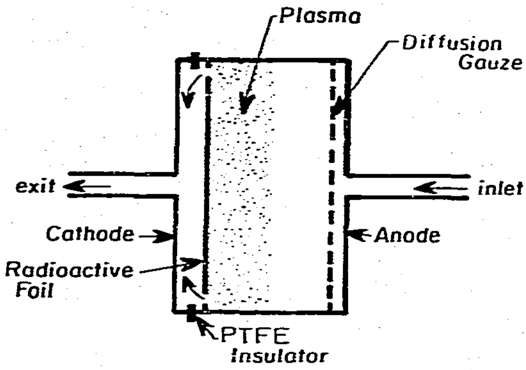


Fig. 2. Plane parallel ECD.

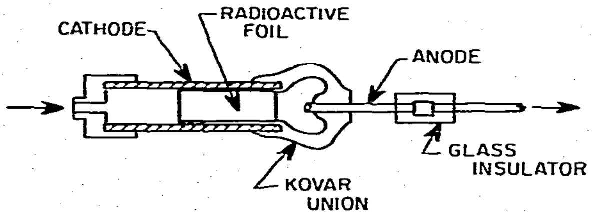


Fig. 3. Concentric cylinder ECD.

These detectors function satisfactorily if due attention is paid to the peculiarities of each, and care is taken to optimize the operating parameters. A comparison between these geometrical types has been reported, but they are difficult to evaluate because a large number of experimental variables affect their overall performance[15,16].

The plane parallel detector has a larger dead volume than the coaxial or concentric cylinder type for equivalent specific activity foils, and therefore it is often necessary to add a purge (scavenger) gas at the exit of the column so that the separation efficiency is not lost. If the time constant for cell purging is too long, the cell may behave as an exponential dilution flask, and peaks will exhibit a large trailing edge (tailing).

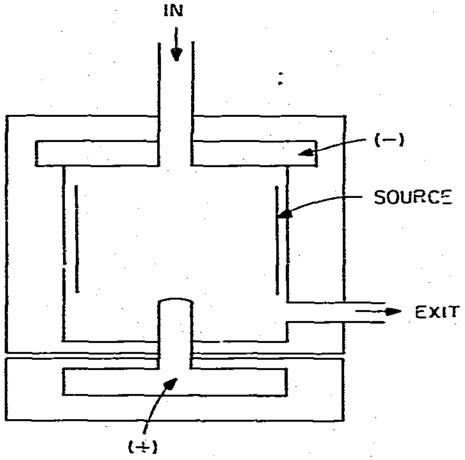


Fig. 4. Pin-cup electron affinity detector.

## 2. THEORETICAL BASIS FOR ELECTRON ATTACHMENT

### A. *Primary radiation*

As pointed out above, ECDs, with the exception of one type, utilize a radioactive source for providing their primary radiation.

When a radiation particle traverses a chamber containing a gas, ionization will occur during collisions along its path. Approximately 36 eV are expended in forming a nitrogen ion pair, while 28 eV are consumed in argon–methane[8]. Perturbation in ion currents generally depends upon the number of primary particles gener-

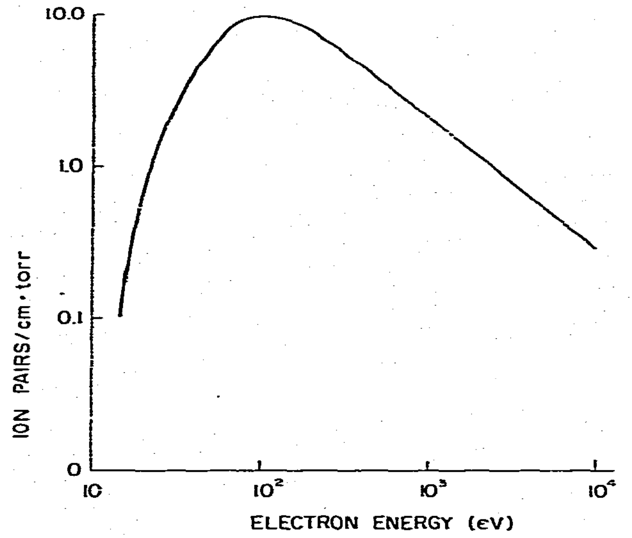


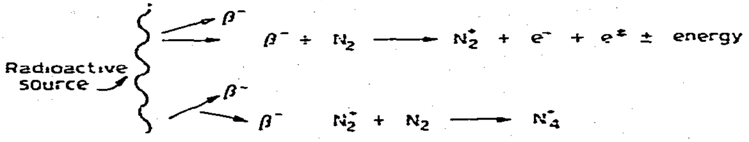
Fig. 5. Ion pair generation rate for nitrogen.

ated in unit time: on this basis, alpha-radiation (*ca.* 3.5 MeV) promotes as much as $10^4$–$10^5$ pairs/cm but for the same ion current would be more noisy than beta-radiation, which produces $10^2$–$10^3$ ion pairs/cm (Fig. 5) of travel[17-19]. Because gamma-radiation yields approximately 1–10 ion pairs/cm, it is generally not considered to be a good source of primary radiation[17,19]. Because large amounts of radioactive material would be required in order to obtain a useful ion current, it is also potentially hazardous.

### *B. Electron capture processes*

#### *(a) Production of thermal electrons*

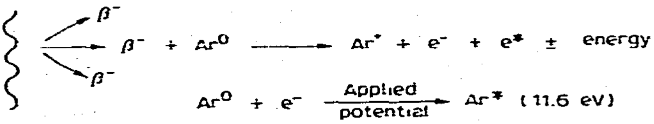
The current produced in an ionization detector arises from secondary electron production through inelastic and elastic collisions between primary electrons, *e.g.*, $\beta^-$ particles, and molecules of nitrogen or atoms of argon or helium carrier gas[19]. These reactions are as follows:



$$\beta^- + N_2 \longrightarrow N_2^+ + e^- + e^* \pm \text{energy} \quad (1)$$

$$N_2^+ + N_2 \longrightarrow N_4^+ \quad (2)$$

or



$$\beta^- + Ar^0 \longrightarrow Ar^+ + e^- + e^* \pm \text{energy} \quad (3)$$

$$Ar^0 + e^- \xrightarrow[\text{potential}]{\text{Applied}} Ar^* \text{ (11.6 eV)} \quad (4)$$

$$Ar^* + CH_4 \longrightarrow Ar^0 + e^- + CH_4 \pm \text{energy} \quad (5)$$

Beta-particles released from a $^{3}H$ source have a maximum energy distribution between 17.6 and 18.9 keV, while those from $^{63}Ni$ are about 67 keV (refs. 17 and 19). The $\beta^-$ particles lose their energy during collision with argon and also possibly with a quench gas until their energy is less than that necessary for the formation of ion pairs.

It is also assumed that the rate of production of thermal electrons is constant and is not enhanced or diminished by the presence of a capturing species[20]. The ionization zone (between $\beta^-$ and argon) is thought to be localized in a concentric region 1–2 mm from the $^{3}H$ source at atmospheric pressure in coaxial detectors[20]. In the parallel plate detector, the electrons form a disk-shaped space, which also extends 2 mm from the cathode surface. The zone probably reaches 6–8 mm for $^{63}Ni$ $\beta^-$ particles[21]. This important property determines the minimum electrode spacing in ECDs.

Pure argon and helium are unsuitable for electron attachment to solute molecules because they are readily converted into metastable forms which would produce undesirable ionization of a solute molecule during its entrance into the detector cell[11,22]. However, if argon containing a quench gas is employed, then the $\beta^-$ particles through collision with carrier gas produce energetic electrons which are thermalized (cooled) during collision with the quench gas[20,23]. The decay of argon metastables (eqn. 5) via the quench gas is also facilitated. Thus, a steady state between production and recombination of ions is reached, yielding a constant plasma level. Positive ions which are also produced in the presence of argon and a quench gas (*e.g.*, methane) are $CH_4^+$, $CH_3^+$, $CH_2^+$, $ArCH_2^+$, etc.[23].

For most inert gases, the lifetime of a metastable atom is short (*ca.* $10^{-9}$ sec) compared with that of other ions. Under constant irradiation, the excited atoms are outnumbered by ionic species. On the other hand, the metastable state of a rare gas has a long lifetime (*ca.* $10^{-6}$ sec) so, in this case, the concentration of metastable atoms is near that of the ions[24]. The excited atoms of pure gases eventually decay to the ground state with emission of energy (eqn. 1), while in the case of metastable rare atoms there may be a transfer of their energy of excitation by collision with traces of solute vapor (Penning reaction). Also, the ionization potentials of the solute molecule are less than the excitation potential of the rare gas atoms, which is the fundamental basis for argon ionization detectors[3,11,22]. From the diffusion coefficient for metastable argon (45 cm$^2$/sec), Biondi[25] determined that during their lifetime they diffuse an average distance of approximately $10^{-1}$ cm. The metastable atoms are therefore probably localized in the region of their initial production[3,25].

A suitable polyatomic gas for thermalization (cooling) of fast electrons is methane at a concentration of 5–10%, depending on the energy of the $\beta^-$ particle colliding with carrier gas atoms[19]. The addition of a quenching gas serves a two-fold function: one function is to reduce and maintain the electron energy at a constant thermal level and the other is to remove argon metastables as fast as they are formed by deactivating collisions[20]. During collision of a fast free electron with a polyatomic gas, a transfer of energy occurs with excitation of low-level vibrational and rotational states of the gas. Thus, a reduction in temperature and decelaration of the fast electrons results.

An estimation of thermalization times has been made by Warman and Sauer[26]. Although ionization of a gas by high-energy radiation produces electrons ($e^*$) with a mean kinetic energy greater than that of the neutral gas molecules, the excess energy decays by inelastic and elastic collisions until their kinetic energy distribution becomes Maxwellian with a mean temperature equal to that of the gas. Warman and Sauer[26] demonstrated that thermalization of electrons occurred in fractions of a microsecond when *n*-hexane is used with monoatomic or diatomic gases; in the absence of a quench gas, the electrons were not completely thermalized even after 50 msec. Using methane, Wentworth *et al.*[20] estimated that an electron with an energy of 10 keV was cooled to 10% above thermal energies ($2-5 \cdot 10^{-2}$ eV) in 0.076 $\mu$sec. Thus, the addition of a polyatomic gas to the carrier gas undergoing ionization increases the thermalization rate of the electrons. As the energy of activation or electron affinity for a solute molecule may be 0–4 eV, it is apparent that the thermalization of electrons occurring from high-energy $\beta^-$ particles (*ca.* 18 keV) is necessary in order to allow or enhance the capturing process while minimizing solute ionization.

Under thermalized conditions, the detector cannot function either as an argon ionization detector nor as an electron mobility detector because the electron energy and the cross-section for attachment cannot be altered by other vapors as it is too low for further reduction in kinetic energy by the solute molecules[23].

The drift velocity of electrons has been estimated to be 6.0 cm/$\mu$sec in argon–5% methane and 0.45 cm/$\mu$sec in argon[20]. Little differences in electron velocities have been observed between argon–5% methane and argon–10% methane[20].

*(b) Electron attachment —Primary and secondary reactions*

When an "electron capturing" solute enters the detector cell, an abundance of low-energy free electrons are available and this plasma is an ideal environment for electron attachment. The following sequence of reactions have been proposed by Wentworth and co-workers[20,23,27].

*Non-dissociative:*

$$e^- + AB \rightleftharpoons AB^- + \text{energy} \qquad (6)$$

$$AB^- + P\cdot \xrightarrow{k_{N_1}} \begin{cases} \rightarrow A\cdot + B\cdot + R\cdot & (7) \\ \rightarrow AB + R\cdot & (8) \end{cases}$$

$$AB^- + R\cdot \xrightarrow{k_{R_2}} \begin{cases} \rightarrow ABR^- & (9) \\ \rightarrow AB + R^- & (10) \\ \rightarrow AR + B^- & (11) \end{cases} \xrightarrow{+P\cdot} \text{neutrals}$$

$$AB^- + AB \longrightarrow \begin{cases} \rightarrow ABAB + e^- & (12) \\ \rightarrow ABA + B^- & (13) \\ \rightarrow ABB + A^- & (14) \end{cases}$$

$$P\cdot + e \xrightarrow{k_N'} \text{neutrals} \qquad (15)$$

$$R\cdot + e^- \xrightarrow{k_R'} R^- \qquad (16)$$

$$AB^- + CH_4 \xrightarrow{k_{-1}'} AB + e^- + CH_4 \qquad (17)$$

*Dissociative:*

$$e^- + AB \xrightarrow{k_{1,2}} A\cdot + B^- \pm \text{energy} \tag{18}$$

$$e^- + AB \xrightarrow{k_1} AB^- \pm \text{energy} \tag{19}$$

$$AB^- + CH_4 \xrightarrow{k_{-1}'} AB + e^- + CH_4 \tag{17}$$

$$AB^- + CH_4 \xrightarrow{k_2'} A\cdot + B^- + CH_4 \tag{20}$$

$$AB^- + P^+ \longrightarrow \begin{array}{ll} \to AB + R\cdot & (7) \\ \to A\cdot + B\cdot + R' & (8) \end{array}$$

$$AB^- + R\cdot \xrightarrow{k_{R_1\cdot}} \begin{array}{ll} \to ABR^- & (9) \\ \to AB + R^- \quad \xrightarrow{+P^+} \text{neutrals} & (10) \\ \to AR + B^- & (11) \end{array}$$

$$B^- + P^+ \longrightarrow \begin{array}{ll} \to BP & (21) \\ \to B\cdot + R\cdot & (22) \end{array}$$

$$B^- + R\cdot \xrightarrow{k_{R_2\cdot}} BR + e^- \tag{23}$$

$$A\cdot + e^- \xrightarrow{k_3} A^- \tag{24}$$

$$A^- + P^+ \xrightarrow{k_{N_3\cdot}} AP \text{ or } A\cdot + P\cdot \tag{25}$$

$$A^- + R\cdot \xrightarrow{k_{R_1\cdot}} AR + e^- \tag{26}$$

$$A\cdot + AB^- \xrightarrow{k_{F_{-1}}} AB + A^- \tag{27}$$

$$e^- + P^+ \xrightarrow{k_N'} R\cdot \tag{28}$$

$$e^- + R\cdot \xrightarrow{k_R'} R^- \tag{29}$$

$$A^- + AB \longrightarrow AB^- + A\cdot \tag{30}$$

$$B^- + AB \longrightarrow AB^- + B\cdot \tag{31}$$

$$A\cdot + AB \longrightarrow A_2 + B\cdot \tag{32}$$

$$B\cdot + AB \longrightarrow B_2 + A\cdot \tag{33}$$

where

$AB$ = capturing solute molecule;
$AB^-$ = negative ion;
$A\cdot$ and $B^-$ = products of dissociation;
$P^+$ = positive ions: $Ar^+$, $ArH^+$, $ArCH^+$, $ArCH_2^+$, $ArCH_3^+$, $ArCH_4^+$, $CH_4^+$, $CH_3^+$, etc.;
$R\cdot$ = radical: $H\cdot$; $CH_3\cdot$, etc.

The solute molecule may attach an electron to form either a negative molecular ion (eqn. 6) or a neutral radical and a negative ion (eqn. 18). In the first case (non-dissociative), the energy of electron attachment is thought to arise from the electron affinity of the molecule and is subsequently either liberated as radiation or translated to other molecules during collisions. In the dissociative capture reaction, the energy balance is maintained by the relative kinetic energy of the reactants before and after collision, the energy released by the formation of a negative ion from a constituent atom or radical of the compound and the energy required or released during the dissociation of the molecule[23]. The net result from either mechanism is a removal of an electron from the plasma with the substitution of a negative ion of a greater mass[1,23]. A net decrease of ion current occurs because of the enhanced recombination rate of negative ions formed by electron attachment with the positive ions in the plasma (eqns. 7, 8 or 21, 22 and 25). Recombination of ions occurs $10^5$–$10^8$ times faster than the recombination of free electrons and positive ions (eqn. 15 or 28). This is the case when an inert gas with a very low affinity for thermal electrons is used, giving a statistically low probability for their recombination.

### *C. Kinetic theory for dissociative and non-dissociative processes*

Wentworth and co-workers[20-23] have also described the electron attachment phenomenon on the basis of kinetic derivations using steady-state approximations. The parameters which characterize the electron capture detector were determined using a pulse sampling technique which allowed the study of dissociative[25] and non-dissociative mechanisms[20-23]. Steady-state conditions were achieved with argon–10% methane using a constant pulse width, applied voltage and pulse period for collection of electrons. Under these conditions, it was assumed that the electrons reached a thermal equilibrium distribution under zero field potential and that the results were independent of pulse voltage amplitude. Wentworth and co-workers[20-23] derived the following expression relating the concentration of capturing species and changes in plasma current:

$$\frac{I_b - I_e}{I_e} = Ka \tag{34}$$

where

$I_b$ = maximum of initial standing current before addition of a capturing species ($I_b = k_p R_\beta^- / k_d$);
$I_e$ = current remaining after the introduction of a capturing species;
$K$ = capture coefficient;
$a$ = concentration of capturing species.

The capture coefficient, $K$, can be obtained by integration with respect to the volume of gas passing through the detector cell during the residence time of a peak[20-23]:

$$\int_0^v \frac{I_b - I_e}{I_e}\,\mathrm{d}v = K \int_0^v a\,\mathrm{d}v \tag{35}$$

where

$$v = \frac{F_r}{C_s} \cdot w; \tag{36}$$

$w$ = peak width;
$F_r$ = flow-rate;
$C_s$ = chart speed.

Therefore

$$\frac{F_r}{C_s} \int_{w}^{w} \frac{I_b - I_e}{I_e}\, \mathrm{d}w = \frac{F_r}{C_s} \cdot A = Kn \tag{37}$$

$$K = \frac{I_b - I_e}{I_e} \cdot (w_{1/2}) \cdot \frac{F_r}{SM} \tag{38}$$

where

$w_{1/2}$ = peak width at half-height;
$S$ = sample size ($\mu$l);
$M$ = molar concentration;
$A$ = peak area;
$n$ = number of moles.

It can readily be shown that the Arrhenius equation can be used to derive a relationship between the temperature dependence of the equilibrium constant and the heat of reaction:

$$\frac{\mathrm{d}(\ln k)}{\mathrm{d}t} = \frac{E_a}{RT^2} \tag{39}$$

On the basis of the kinetic theory model[20], assuming an ideal gas and using the statistical mechanical expression for the equilibrium constant $K_{eq}$, one can write

$$K = \frac{k_L}{k_D} \cdot K_{eq} = \frac{k_L}{k_D} \cdot AT^{-3/2} \cdot \exp\,(E_a/kT) \tag{40}$$

which can be transformed into

$$K = ZT^{-3/2} \cdot \mathrm{e}^{-\Delta E/kT} \tag{41}$$

and rearranged to give

$$\ln KT^{3/2} = \ln Z - \frac{\Delta E}{kT} \tag{42}$$

where

$K$ = capture coefficient;
$Z$ = pre-exponential factor;
$\Delta E$ = activation energy;
$k$ = Boltzman constant;
$T$ = detector cell temperature;
$k_L$ = all reactions removing AB$^-$;
$k_D$ = all reactions removing e$^-$.

The Arrhenius plot of ln $K^{3/2}$ *versus* $1/T$ may be linear with a positive slope for the capturing species undergoing a non-dissociative mechanism[20]. The slope $\Delta E/k$ is related to the activation energy for the mechanism under consideration, and therefore the capture response decreases with increasing temperature for non-dissociative capturing compounds[20].

Attachment of an electron to a solute molecule is related, in addition to electron affinity, to a requirement for sufficient energy to cause attachment at a given temperature. The larger the activation energy necessary for attachment, the slower is the attachment reaction (Fig. 6). The activated complex (AB*) represents an intermediate form during which the electron is being accommodated by the solute molecule.

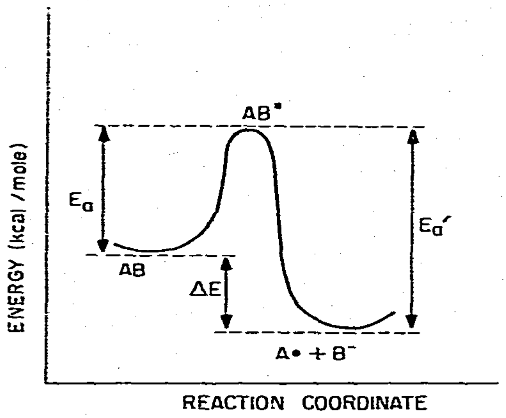


Fig. 6. Relative energies of a molecule undergoing electron attachment.

The energy that must be absorbed by AB to form the activated complex, AB*, is represented by $E_a$. As $A\cdot + B^-$ has a lower energy than AB, heat is evolved in the process and $\Delta E$ is the net heat evolved in the overall reaction. It is also apparent that if $\Delta E$ is positive then, for the reverse reaction to occur, the amount of activation energy becomes $E_a'$, *i.e.*, an endothermic process.

A summary has been given by Wentworth and Chen[29] for the four electron capture mechanisms (Fig. 7) in terms of potential energy diagrams. Mechanism I (eqn. 6) depicts the pure non-dissociative electron attachment, which is characterized by a positive slope and the formation of a stable negative ion. In this case, the overall change in internal energy for the process, $\Delta E$, is equal to the electron affinity. Aromatic hydrocarbons and carbonyl moieties represent this type of mechanism.

Mechanism II (eqn. 18) is represented by alkyl halogens (except C–F). A linear relationship is observed between $E_a$ and $\Delta E$ with a slope of unity[29]. It is possible to differentiate between mechanisms II and III (eqns. 17–20) as $E_a$ is larger in the former[25].

A positive slope in the ln $KT^{3/2}$ *versus* $1/T$ plot may also occur if a solute undergoes capture by either mechanism III or IV. A negative molecular ion inter-

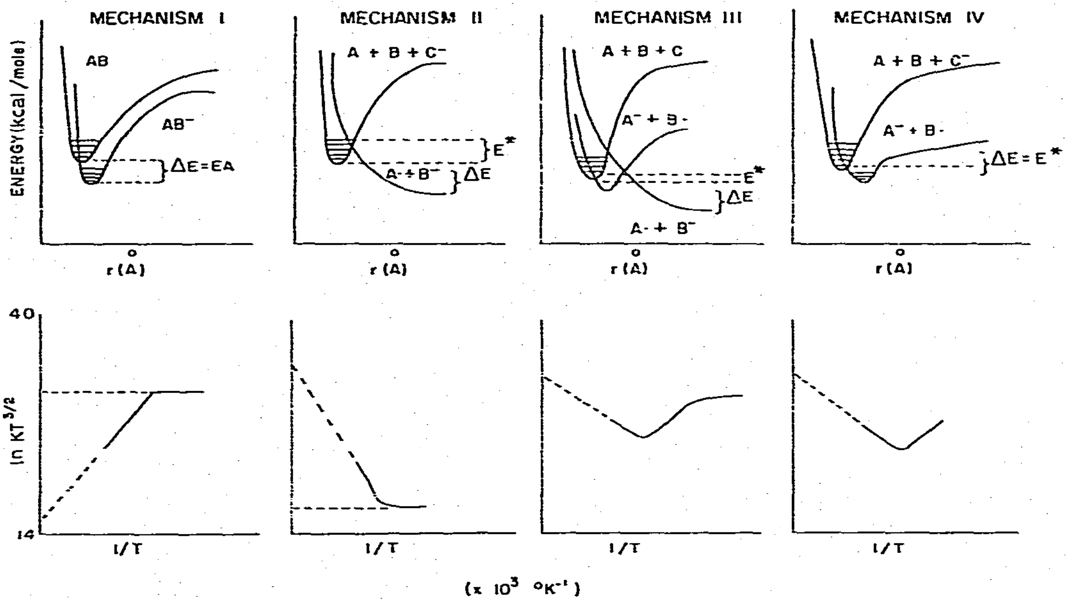


Fig. 7. Summary of electron attachment mechanisms.

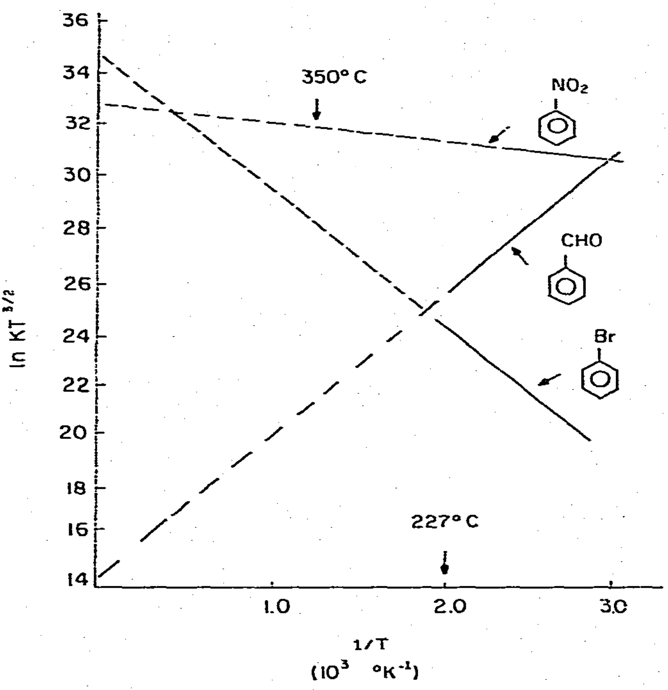


Fig. 8. Relationship between capture coefficient and absolute temperature.

mediate is believed to also occur in these cases[29]. In mechanism III, $E_a$ is greater than $\Delta E$, while they are equal in mechanism IV[29]. Aromatic halogens (Cl, Br, I) are assumed to undergo mechanism III, while acetic anhydride, benzyl acetate and ethyl acetate undergo mechanism IV[29].

Fig. 8 depicts plots of ln $KT^{3/2}$ *versus* $1/T$ for benzaldehyde (non-dissociative, I), bromobenzene (dissociative, II) and nitrobenzene. It can be seen from the slopes that it is important to choose judiciously the detector cell temperature in order to facilitate the electron attachment process. Although the slope with nitrobenzene is small, the fact that it is negative is suggestive of a dissociative process[29].

### *D. Electron affinity, activation energies and electron attachment for organic compounds*

Even though a variety of experimental methods, including ECD, have been employed to determine the electron affinity of molecules the electron affinity measurements have been made only for a few organic compounds[20,23-35].

When an electron moves into a vacant orbital of a molecule, the electron affinity can be described by the Hartree–Fock energy relationship (see ref. 36). If the orbital radius of an electron is larger than other orbitals, then the absolute value of the potential energy for that electron orbital is small. When a electron of the outer orbital penetrates into the orbitals of other electrons, the potential energy commences to acquire a large negative value[36].

TABLE I

ELECTRON AFFINITIES OF SELECTED ATOMS AND MOLECULES[27,28]

| *Atom or molecule* | *Electron affinity (eV)* | *Atom or molecule* | *Electron affinity (eV)* |
|---|---|---|---|
| $NO_2$ | 3.99 | $O_2$ | 2.94 |
| $NO_2$ | 3.88 | $SO_2$ | 1.9 |
| $CO_2$ | ~3.8 | $NH_2$ | 1.21 |
| Cl | 3.61 | $CS_2$ | 0.98 |
| F | 3.44 | $H_2O$ | ~0.9 |
| Br | 3.36 | $O_2$ | 0.45 |
| I | 3.06 | | |

The qualitative aspects of the variation of electron affinities (Table I) can be better understood in terms of the shielding of the nuclear charge by electrons, which is the tendency of atoms to form completed shells. Considering the specific case for a fluorine atom, an electron becoming attached to it will occupy one of its 2p atomic orbitals, which has already five electrons. The fluorine nucleus has a large effect on the incoming electron. The screening constant for the 2p atomic orbital as well as its average radius is relatively small. These relationships are consistent with the large electron affinity for fluorine (Table I). The other extreme case is the argon atom, where all the sp atomic orbitals are already filled. Also, the screening effect on the incoming electron is large and thus the mean radius for the atomic orbital occupied by the electron is large. Furthermore, the electron affinity will be negative.

TABLE 2

ELECTRON AFFINITIES FOR SELECTED AROMATIC COMPOUNDS[20,33,39,38]

| *Compound* | *Electron affinity (eV)* |
|---|---|
| Naphthalene | 0.152 |
| Triphenylene | 0.284 |
| Phenanthrene | 0.308 |
| Chrysene | 0.419 |
| Benzo[*c*]phenanthrene | 0.542 |
| Anthracene | 0.552 |
| Pyrene | 0.579 |
| Azulene | 0.587 |
| Benz[*a*]anthracene | 0.696 |
| Nitrobenzene | 0.850 |
| Chlorobenzene | 0.860 |
| *o*-Chlorotoluene | 1.100 |
| *m*-Dinitrobenzene | 1.430 |
| *sym*-Trinitrobenzene | 1.860 |

For many organic compounds, the electron affinity will be somewhere between those for fluorine and argon[36]. The question remains for those cases where the electron affinity is negative: will negative ions actually exist?

Table 2 depicts the electron affinities for some aromatic hydrocarbons. In general, the values increase as the number of ring fusions increase and are highest for halogen- or nitro-containing aromatic compounds.

Christophorou *et al.*[34] estimated the energy of maximum cross-section for chlorobenzene (dissociative) to be 0.86 eV. Steelhammer and Wentworth[39] calculated the activation energy ($E_a$) to be 9.76 kcal. The molecular adiabatic electron affinity is −6.83 kcal (Table 3). Chlorobenzene serves for the relative comparison of other aromatic compounds, as the bond dissociation energy (87 kcal), and the phenyl radical electron affinity (59.9 kcal) are all well known.

The maximum cross-sections for dissociative electron attachment by *o*-chlorotoluene and *o*-dichlorotoluene are 1.1 and 0.36 eV, respectively[39]. Activation energies for this process have been reported[39] to be 11.10 and 7.46 kcal, respectively. In these

TABLE 3

COMPARISON OF ACTIVATION ENERGIES AND MOLECULAR ELECTRON AFFINITIES FOR HALOGENATED AROMATIC COMPOUNDS[39]

| *Compound* | $E_a$* (*kcal/mole*) | $EA_{MB}$** (*kcal/mole*) |
|---|---|---|
| *o*-Chlorotoluene | 11.10 | 10.00 |
| Chlorobenzene | 9.76 | −6.83 |
| 1-Chloronaphthalene | 8.04 | 6.39 |
| *o*-Dichlorobenzene | 7.46 | 2.16 |
| *o*-Bromotoluene | 6.44 | 3.49 |
| Bromobenzene | 5.53 | −2.27 |
| Iodobenzene | 1.20 | — |

* $E_a$ = activation energy.

** $EA_{MB}$ = molecular adiabatic electron affinity.

determinations, the total radical was assumed to have the same electron affinity as the phenyl radical[39], as it has been also reported that substitution in a phenyl moiety does not alter the electron affinity appreciably[39]. Electron affinities for 2,5-dichlorophenyl, benzoquinonyl and naphthyl radicals appear to be similar to that of phenyl[39].

*o*-Bromotoluene has an energy of 0.95 eV (ref. 39), and $E_a = 6.44$ kcal. The molecular electron affinity is $-3.48$ kcal. Table 3 lists the $E_a$ values for various halogenated aromatic compounds, all of which undergo dissociative electron capture.

The probability of electron attachment can be interpreted also in terms of the cross-section for the formation of a transient or stable negative ion, $AB^-$. For dissociative capturing molecules, the process may occur with a high cross-section and with almost zero energy electrons if molecules contain electrophores whose electron affinity exceeds the bond dissociation energy[33]. In contrast, the electron affinity for a parent molecule which forms a stable negative ion will determine the overall parent ion stability but not necessarily its "electron attachment capacity". For this reason, an absolute measurement of the electron attachment capacity probably is its electron capture cross-section and not its electron affinity. Table 4 gives thermal non-dissociative electron attachment cross-sections, rates of attachment and electron affinities for some aromatic hydrocarbons[33,39]. Although in some instances as the electron capture cross-section increases the magnitude of the electron affinity also increases, there apparently is no direct correlation between these two parameters.

TABLE 4

COMPARISON OF THERMAL ELECTRON ATTACHMENT CROSS-SECTIONS, ELECTRON AFFINITIES AND ELECTRON ATTACHMENT RATES FOR AROMATIC MOLECULES[33]

| *Compound* | *Cross-section* *(cm²)* | *Attachment rate* *(n·sec⁻¹·torr⁻¹)* | *Electron affinity* *(eV)* | *Temperature* *(°K)* |
|---|---|---|---|---|
| Benzene | $<1.3 \cdot 10^{-20}$ | $<3 \cdot 10^{2}$ | $-1.2$ | 298 |
| Naphthalene | $\sim 1.3 \cdot 10^{-19}$ | $<10^{1}$ | 0.1 | 343–398 |
| Phenanthrene | $2.6 \cdot 10^{-18}$ | $7 \cdot 10^{5}$ | $\sim 0.1$ | 453–473 |
| Triphenylene | $1.0 \cdot 10^{-16}$ | $2.7 \cdot 10^{7}$ | $\sim 0.06$ | 443–483 |
| Chrysene | $1.2 \cdot 10^{-16}$ | $3.2 \cdot 10^{7}$ | $\sim 0.35$ | 473–483 |
| Perylene | $1.3 \cdot 10^{-15}$ | $\sim 3.4 \cdot 10^{8}$ | 0.92 | 473–483 |
| Pyrene | $1.6 \cdot 10^{-15}$ | $4.4 \cdot 10^{9}$ | — | 421–503 |
| Azulene | $3.7 \cdot 10^{-15}$ | $1 \cdot 10^{9}$ | 0.66 | 423–488 |

In summary, the probability of electron attachment is related to (1) electron affinity, (2) energy of activation, (3) cross-section for collision and (4) consideration of bond stability *versus* dissociation into stable ions. The electron capture coefficient, *K*, is the net sum of all these processes.

## 3. RELATIONSHIP OF MOLECULAR STRUCTURE TO SENSITIVITY IN ELECTRON CAPTURE DETECTION

### *A. Comparison of relative attachment coefficients*

It is generally recognized by investigators who employ electron attachment techniques that only relatively few organic compounds readily accomodate thermal electrons. The probability of electron attachment for different solute species, as shown in Table 5, covers a very wide range of at least a million-fold[11]. The probability (as seen earlier, a sum of several factors) appears to be dependent upon the presence in the solute molecule of an atom or moiety (electrophore) exhibiting electron affinity and/or favorable bond dissociation energy.

Several reports have described the relative attachment coefficients (*K′*) for different organic compounds[11–16]. The relative attachment coefficient for thermal electrons by compounds are generally made with respect to chlorobenzene, which is assigned a value of unity[11]. As it is believed that the molecular cross-section for

TABLE 5

RELATIVE ATTACHMENT COEFFICIENTS FOR VARIOUS COMPOUNDS[11–15]

| *Chemical classes* | *K′** *scale* | *Selected examples* |
|---|---|---|
| Alkanes, alkenes, alkynes, aliphatic ethers, esters and dienes | 0.01<br>0.10 | Hexane<br>Benzene<br>Cholesterol<br>Benzyl alcohol<br>Naphthalene |
| Aliphatic alcohols, ketones, aldehydes, amines, nitriles, monofluoro and monochloro compounds | 1.0 | Vinyl chloride<br>Ethyl acetoacetate<br>Chlorobenzene |
| Enols, oxalate esters, monobromo, dichloro and hexafluoro compounds | 10.0 | *cis*-Stilbene<br>*trans*-Stilbene<br>Azobenzene<br>Acetophenone |
| Trichloro compounds, chlorohydrates, acyl chlorides, anhydrides, barbiturates, thalidomide and alkyl-leads | 300 | Allyl chloride<br>Benzaldehyde<br>Tetraethyl-lead<br>Benzyl chloride<br>Azulene |
| Monoiodo, dibromo and trichloro compounds, mononitro compounds, lacramators, cinnamaldehyde, fungistatic compounds and pesticides | 1000 | Cinnamaldehyde<br>Nitrobenzene<br>Carbon disulfide<br>1,4-Androstadiene-3,11,17-triene<br>Chloroform |
| 1,2-Diketones, fumarate esters, pyruvate esters, quinones, diiodo, tribromo, polychloro, dinitro compounds and organomercurials | 10,000 | Dinitrobenzene<br>Diiodobenzene<br>Dimethyl fumarate<br>Carbon tetrachloride |

* Values for *K′* are relative to chlorobenzene, which is arbitrarily given a value of 1.0.

electron attachment is proportional to the observed attachment coefficient and the cross-section for chlorobenzene is *ca.* $10^{-16}$ cm$^2$, then an approximate value for the cross-section of thermal electron attachment can be calculated for other compounds[44].

Alkanes, alkenes, alkynes, ethers, amines, esters and simple aromatic compounds have very low coefficients. In those cases where compounds exhibit moderate values, they also posses distinct atoms or moieties such as halogens, nitro and conjugated systems. Two functional groups which alone do not capture can exhibit very high attachment coefficients when bridged by a conjugated system.

TABLE 6

SENSITIVITY COMPARISON OF VARIOUS HALOGENATED ESTERS OF TESTOSTERONE TO ELECTRON ATTACHMENT[2]

| *Derivative* | *C·mole$^{-1}$·$10^{2}$* |
|---|---|
| Trifluoroacetate | 0.012 |
| Monochloroacetate | 0.236 |
| Pentafluoropropionate | 0.330 |
| Heptafluorobutyrate | 1.18 |
| Monochlorodifluoroacetate | 1.67 |
| Perfluorooctanoate | 2.48 |
| Diheptafluorobutyrate | 2.76 |

Many organic compounds that are of biological importance do not exhibit strong electron attachment characteristics. In these cases, investigators have derived methods for incorporating this property into molecules. The preferred route generally involves the use of a fluoro or chloro derivative so that good chromatographic characteristics are maintained in the final product. Table 6 lists some derivatives of testosterone and their sensitivity to electron capture. The most commonly employed derivatives in the alkyl series are the pentafluoropropionates, heptafluorobutyrates and monochlorodifluoroacetates, which appear to represent a compromise between compounds with high sensitivity on the one hand and good chromatographic properties on the other; unfortunately, they have an inverse relationship.

### *B. Predicting sensitivity in electron capture detection*

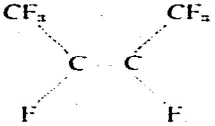
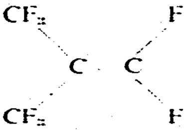
Sufficient information is now available for the formulation of general empirical rules for predicting the magnitude of relative capture coefficients.

For halogen-containing compounds, the magnitude of $K'$ is inversely related to electronegativity and bonding energy. As shown in Table 7, a decrease in $K'$ is observed for the series I $>$ Br $>$ Cl $>$ F. The data in Table 8 indicate that multiple substitution of strong electrophores on the same carbon enhances $K'$ synergistically. The value of $K'$ also depends upon (1) the isomeric form, (2) the frequency of electrophore substitution and (3) the position of substitution of the electrophore with respect to other functional moieties. Table 9 summarizes these effects. Furthermore, allylic substitutions in dienes yield a much larger $K'$ than vinylic substitutions.

Studies have been made on the relative contribution of chloro, nitro and amino substituents and their influence through aromatic ring substitution on overall sen-

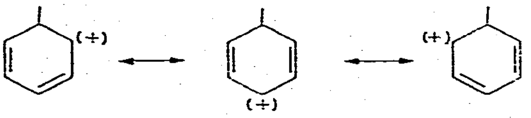
TABLE 7

RELATIVE ATTACHMENT COEFFICIENTS FOR VARIOUS HALOGENATED COMPOUNDS[45]

| *Compound* | *K'** |
|---|---|
| $CF_3Cl$ | 3.3 |
| $CF_3Br$ | $1.3 \cdot 10^2$ |
| $CHF_3$ | 0.3 |
| $CHCl_3$ | $3.3 \cdot 10^4$ |
| $CF_4$ | 1.0 |
| $CCl_4$ | $2.2 \cdot 10^6$ |
| | |
| $CHFCl_2$ | $1.7 \cdot 10^2$ |
| $CF_2Cl_2$ | $3.0 \cdot 10^4$ |
| $CFCl_3$ | $1.2 \cdot 10^6$ |
| | |
| $SF_6$ | $1.9 \cdot 10^6$ |
| $SF_5(CF_2)_2Cl$ | $1.7 \cdot 10^6$ |
| $SF_5(CF_2)_4Cl$ | $1.4 \cdot 10^6$ |
| $SF_5(CF_2)_6Cl$ | $1.5 \cdot 10^6$ |
|  | $1.3 \cdot 10^2$ |
|  | $3.0 \cdot 10^2$ |
| $CF_3CF_2CF_2$-F | 1.0 |
| $CF_3CF_2CF_2$-I | $6.0 \cdot 10^2$ |

* Attachment coefficients are relative to perfluoropropane, which is arbitrarily given a value of 1.0.

sitivity[50–52]. Table 10 depicts this comparison for a few selected compounds. The apparent trends are: (1) *ortho*-chloro enhances sensitivity to a greater extent than *meta*-chloro substitution on aniline, and (2) *para*-chloro significantly diminishes sensitivity on nitrobenzene. These observations can be rationalized on the basis of increased or diminished electron density in the aromatic ring via resonance and the electron-withdrawing and -releasing character of aryl chloro, nitro and amino moieties[50,51]:



On this basis, aromatic compounds with electron-deficient centers would readily undergo electron attachment and the resultant negative ions would also exhibit long lifetimes. Such is the case for mono-, di- and trinitrobenzenes and chloronitrobenzene, which have much larger responses than aniline and chloroaniline[50].

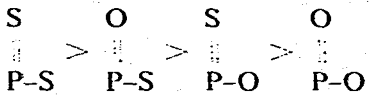
TABLE 8

COMPARISON OF RELATIVE ATTACHMENT COEFFICIENTS FOR STRUCTURAL ISOMERS OF HALOGENATED COMPOUNDS[19]

| *Compound* | K[*] |
|---|---|
| Benzene | 0.0005 |
| Toluene | 0.0027 |
| 2-Fluorotoluene | 0.0073 |
| 4-Fluorotoluene | 0.0073 |
| Chlorobenzene | 1.0 |
| Bromobenzene | 6.0 |
| | |
| 1-Chlorobutane | 0.013 |
| 2-Chlorobutane | 0.027 |
| 1-Chloro-2-methylpropane | 0.023 |
| 2-Chloro-2-methylpropane | 0.16 |
| | |
| 1,2-Dichloroethane | 2.52 |
| 1,1-Dichlorobutane | 1.47 |
| 1,4-Dichlorobutane | 0.02 |
| | |
| 1-Bromopropane | 3.4 |
| 1-Bromobutane | 3.7 |
| Bromocyclopentane | 3.7 |
| 1-Bromopropene-2 | 53.0 |
| 1,1-Dibromoethane | 147.0 |
| | |
| 1-Butanol | 0.013 |
| Di-*n*-butyl ether | 0.008 |
| Acetone | 0.007 |
| Methyl butyrate | 0.012 |
| 2,3-Butanedione | 667.0 |

[*] Capture coefficients are relative to chlorobenzene, which is given a value of 1.0.

The difficulty in predicting relative capture coefficients on the basis of only electrophilic and nucleophic inductive effects is exemplified by the Systox moiety in phosphate pesticides[1,53]. The relative sensitivity changes in the order



$$\overset{S}{\overset{\|}{P}}\text{-}S > \overset{O}{\overset{\|}{P}}\text{-}S > \overset{S}{\overset{\|}{P}}\text{-}O > \overset{O}{\overset{\|}{P}}\text{-}O$$

Many other chemical classes demonstrate high electron capture responses. For example, alkyl di- and trisulfides[54,55] and organometallics[56-58] are good electron-capturing compounds. Table 11 depicts a comparison of sensitivities for some alkyl-lead compounds[56,57]. Some correlation exists between alkyl chain-length (possibly electron-releasing effect by ethyl) and substitution frequency on overall sensitivity.

For polysulfides, some insight is gained by considering their mechanism of electron attachment and subsequent stabilization[54]. Alkyl disulfides demonstrate a non-dissociative mechanism at low detector temperatures and dissociative at high temperatures. Trisulfides, on the other hand, are a non-dissociative type and their relative capture coefficients are larger than those of alkyl disulfides[54]. The explanation

### TABLE 9

### RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND RELATIVE CAPTURE COEFFICIENT[11-45]

| *Parameter* | $K'^*$ |
|---|---|
| *Halogen series* | |
| I | $9 \cdot 10^1$ |
| Br | $3 \cdot 10^2$ |
| Cl | 1 |
| F | ≪1 |
| *Substitution on carbon atom* | |
| Tertiary | 10 |
| Secondary | 2 |
| Primary | 1 |
| *Frequency on carbon atom* | |
| Tetra- | $4 \cdot 10^5$ |
| Tri- | $6 \cdot 10^1$ |
| Di- | $10^2$ |
| Mono- | 1 |
| *Positional isomer (di-, tri-, etc.)* | |
| Alpha- | 10 |
| Beta- | 5 |
| Delta- | 1 |
| *Geometrical isomer* | |
| *Trans-* | 4 |
| *Cis-* | 1 |

* Capture coefficients are relative to the lowest value of series, which is arbitrarily given a value of 1.0.

### TABLE 10

### COMPARISON OF *ORTHO-*, *META-*, AND *PARA*-SUBSTITUTION AND RELATIVE SENSITIVITY OF AROMATIC COMPOUNDS[50-52]

| *Compound* | *Relative response** |
|---|---|
| *m*-Chloroaniline | 0.00003 |
| *o*-Chloroaniline | 0.0001 |
| | |
| *m*-Fluoronitrobenzene | 0.206 |
| *p*-Fluoronitrobenzene | 0.685 |
| *o*-Fluoronitrobenzene | 0.740 |
| | |
| *p*-Chloronitrobenzene | 1.0 |
| *o*-Chloronitrobenzene | 1.7 |
| *m*-Chloronitrobenzene | 2.2 |
| | |
| *o*-Dinitrobenzene | 1.3 |
| *m*-Dinitrobenzene | 1.6 |

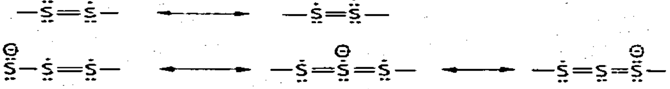
* Values are given relative to *p*-chloronitrobenzene which is given a value of 1.0.

TABLE 11

SENSITIVITY OF ALKYL-LEADS TO ELECTRON ATTACHMENT[56]

| *Compound* | *Moles·sec$^{-1}$·$10^{11}$* |
|---|---|
| Tetraethyl-lead | 240 |
| Tetramethyl-lead | 190 |
| Methyltriethyl-lead | 87 |
| Trimethylethyl-lead | 45 |
| Dimethyldiethyl-lead | 22 |

offered is based upon the role of 3d orbital resonance in the stabilization of the anion radicals for polysulfides. A sulfur atom can accomodate an electron pair and another an odd electron by expansion of the valence shell beyond the octet:



The moiety responsible for imparting electron-capture properties in haloacetate derivatives has also been studied. Landowne and Lipsky[59] proposed that the carbonyl carbon imparted the differences in sensitivity. In contrast, Clarke *et al.*[60] provided evidence which indicated that electron capture occurred in the perfluoroalkyl chain by comparing the responses of trifluoroacetamides and heptafluorobutyramides. A detail study by Matin and Rowland[61] supports the first theory. An amide functionality which can resonate provides an electrophore region for capture:

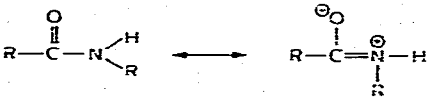


TABLE 12

COMPARISON OF ELECTRON CAPTURE SENSITIVITIES OF VARIOUS PENTAFLUOROBENZAMIDES (PFB) AND HEPTAFLUOROBUTYRAMIDES (HFB)[61]

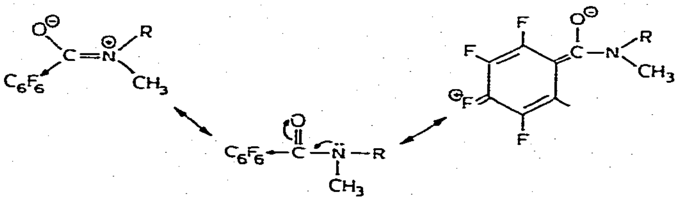
| *Amine** | *Response*** *(C·mole·$10^{12}$)* | | |
|---|---|---|---|
| | *PFB* | *HFB* | *PFB/HFB* |
| Methoxyphenamine (2) | 3.2 | 1.6 | 2.0 |
| Methamphetamine (2) | 6.1 | 4.0 | 1.52 |
| Mephenetermine (2) | 9.2 | 2.2 | 4.20 |
| Phenmetrazine (2) | 28.0 | 8.8 | 3.18 |
| Phentermine (1) | 29.0 | 1.1 | 26.40 |
| *p*-Methoxyphenethylamine (1) | 135.0 | 1.9 | 71.0 |
| Mescaline (1) | 155.0 | 3.7 | 41.9 |
| α-Methylbenzylamine (1) | 180.0 | 2.5 | 72.0 |
| Amphetamine (1) | 225.0 | 2.2 | 102.5 |
| β-Phenethylamine (1) | 300.0 | 2.0 | 150.0 |

* Primary and secondary amines — (1) and (2), respectively.

** All values were obtained at a detector temperature of 320 °C.

As shown in Table 12, the electron capture response of heptafluorobutyramides are significantly different. Tertiary amides exhibit higher responses than secondary amides. This observation is consistent with the concept that tertiary amides provide a better center for electron attachment as the negative ion formed is stabilized by a higher contribution from resonating forms. This effect can be counteracted by steric crowding around the amide group. If coplanarity of O–C–N is prohibited, a reduction in resonance occurs and a decrease in resonance definitely diminishes the overall electron capture response[61].

Further evidence on the involvement of the carbonyl group has been demonstrated. Replacement of the non-resonating heptafluorobutyryl side-chain by an extremely high electron-withdrawing resonating moiety enhances the response[61]. This is confirmed by the data in Table 12. The ratio of pentafluorobenzamide to heptafluorobutyramide sensitivities can differ by as much as 150-fold. Additional resonance can occur between the pentafluorophenyl ring and the carbonyl group, yielding a coplanar, highly electron-delocalized system, which probably accounts for the observed excellent capture characteristics[61]:



Other data also suggest that the order of electron capture sensitivity for primary amines is generally pentafluorobenzamide > pentafluorobenzylidine > heptafluorobutyramide[61].

Predicting coefficients for attachment becomes more complicated as the complexity of the molecule increases with regard to multiple substitution and conjugation. In addition to the structure of the parent molecule, the resultant negative ion stability must be considered in approximating electron attachment probability. In general, a knowledge of the structure of negative ions formed is seriously lacking and much fundamental research in this area needs to be conducted. The solutions to this problem may be accelerated with the advent of the plasma chromatograph[62,63] (operated in the electron capture mode) and negative ion mass spectrometry[64,65].

Durbin *et al.*[27] have identified some products formed during non-dissociative and dissociative type processes. Near thermal electrons were produced by a corona discharge cell for their attachment to electron-absorbing compounds. These authors investigated the electron capture mechanism for benzaldehyde, diethyl maleate, *cis*-stilbene, chlorobenzene and benzyl chloride and the dissociative products were identified by GC–mass spectrometry (MS). Recalling that the non-dissociative and dissociative mechanisms may undergo reactions 7–9, 13, 15, 27–30 and 35, it becomes apparent that the dissociative mechanism potentially could produce products which also could capture (poly-electrophores). Even though a stable radical anion is formed (eqn. 35) and a number of reactions with it can occur, the molecular structure of the original molecule is retained. Products as indicated in reactions 7–9 can occur if the concentration of AB is sufficiently large[27].

Negative species $A^-$ and $B^-$ can transfer their electrons as indicated by reactions 27 and 28, while the radicals $A\cdot$ and $B\cdot$ will react with AB (eqns. 29 and 30). Thus, it is possible to ascertain which mechanism (dissociative or non-dissociative) is occurring by examining the products formed. For example, a predominance of $A_2$ and $B_2$ would imply that dissociative electron attachment is the initial step[27].

Furthermore, Durbin *et al.*[27] derived the following equation, which relates the number of molecules of reactant removed per electron removed from the plasma:

$$R = \frac{WD}{MIT} \tag{43}$$

where

$W$ = weight of solute depleted (g);
$M$ = molecular weight of solute;
$I$ = current (A);
$T$ = time (sec);
$D$ = constant $\left(96{,}500 \frac{\text{C·molecules}}{\text{mole·electron}}\right)$;
$R$ = ability of the compound to react with electrons.

Zlatkis and Lovelock[15] reported that benzaldehyde has an electron capture coefficient of 48. Durbin *et al.*[27] identified acetophenone, benzyl alcohol, phenol, biphenyl, benzophenone and benzil as the reaction products during attachment of thermal electrons, which confirmed a non-dissociative process. The major product was benzil. The $R$ value was 90 molecules/electron when argon plus 2% of carbon dioxide (quench gas) was used.

Upon submitting benzyl chloride (coefficient 110) to near thermal electrons, benzyl alcohol, phenol, bibenzyl, *cis*-stilbene and *trans*-stilbene were identified by GC–MS[27]. For this reaction $R$ was 24 and 34 molecules/electron in argon + 2% of carbon dioxide and argon, respectively. These products indicate that dissociative attachment had occurred. This is partly based on the attachment of an electron followed by formation of a benzyl radical and a chloride anion: the radical subsequently reacts with benzyl chloride to form bibenzyl[27].

Diethyl maleate gave $R$ values of 31 and 18 molecules/electron in the absence of a quench gas[27]. Diethyl succinate and diethyl malate were identified, and thus a non-dissociative mechanism was confirmed.

*cis*-Stilbene, which is a conjugated electrophore, yields bibenzyl, deoxybenzoin and 1,2-diphenylethanol, and possibly *cis*- and *trans*-stilbene were thought to be present in the reaction product mixture, which is consistent with a non-dissociative mechanism.

Finally, Durbin *et al.*[27] also reported that chlorobenzene dissociated to give a chloride anion plus a phenyl radical. The reaction products were biphenyl, and *o*-, *m*- and *p*-chlorobiphenyl. $R$ values of 60 and 64 molecules/electron (no quench gas) were calculated. Although a dissociative mechanism occurs, it has been suggested by Compton *et al.*[66] that chlorobenzene may form a stable radical anion as an intermediate upon attachment of an electron in order to explain the strong loss of electron energy resonance near 1 eV.

In summary, this section has attempted to outline briefly some observations with regard to functionalities that respond to electron attachment and their structural effects on the attachment coefficient.

## 4. CHARACTERISTICS OF DETECTOR OPERATING PARAMETERS

### *A. General remarks*

The application of the electron capture detector is difficult because of the existence of numerous parameters involved in achieving its optimum performance. These parameters can be divided into two categories: firstly those which are related to the chromatographic conditions such as flow-rate of the carrier gas, column temperature and type of stationary phase, and secondly those which are indirectly dependent upon these conditions, such as the nature of the polarizing voltage (pulse continuous), the nature of the radioactive source and the detector cell temperature. Furthermore, some of these parameters are not independent of each other.

### *B. Radioactive source*

Several radiation sources have been examined[17,67]: $^{3}H$ ($\beta^-$, 0.18 MeV), $^{63}Ni$ ($\beta^-$, 0.06), $^{85}Kr$ ($\beta^-$, 0.67), $^{90}Sr$ ($\beta^-$, 0.55), $^{99}Tc$ ($\beta^-$, 0.292), $^{147}Pm$ ($\beta^-$, 0.23), $^{241}Am$ ($\alpha$, 514) and $^{226}Ra$ ($\alpha$, 4.6).

The selection of an irradiation source is determined by (1) the emanation rate of the radioactive material at elevated temperatures, (2) the energy of the radioactive particle, (3) availability of adequate specific activity, (4) radiochemical form and (5) cost. The most commonly used sources are $^{3}H$ and $^{63}Ni$. The high temperature stability of $^{63}Ni$ is well documented[17,67].

Shoemake *et al.*[68] demonstrated that when helium, nitrogen, air and argon–5% methane were used as carrier gases, the standing current increased rapidly when the temperature on the titanium–$^{3}H$ foil exceeded 200 °C, which was interpreted as a loss of $^{3}H$ from the foil. When hydrogen was used as the carrier gas, considerable losses above 140 °C were observed. An exchange between hydrogen gas and bound $^{3}H$ was probably responsible for this phenomenon. The emanation data reported by Shoemake *et al.*[68] provide some guidelines for the selection of operating parameters when employing titanium tritide foils. The generally acceptable temperature limit is 225 °C.

Emanation rates for a new high-temperature source utilizing tritium embedded in a rare earth, scandium, have also been described[69,70]. These studies suggested that the maximum operating temperature should be set at 325 °C. Because of the ability to use high detector temperatures, the problem of source contamination can be readily reduced. The fact that $^{63}Ni$ is a poorer choice than $^{3}H$ means the latter will probably be preferred for most analyses.

Presumably the $^{3}H$ sources (0.018 MeV) are chosen over foil plated with $^{63}Ni$ (0.06 MeV) because of their lower radiation energy[17]. Also, foils of higher specific activity can be manufactured, providing a denser radiation, and as the standing current is directly proportional to the amount of radiation ($I_b = k_p R_\beta / k_D$), greater sensitivities can be achieved.

It is obvious that large variations in day-to-day standing currents may occur when operating at temperatures which cause substantial evaporation of $^{3}H$ from the foil.

### C. Detector temperature

Since the electron attachment coefficients, $K$, may increase (dissociative) or decrease (non-dissociative) with increasing temperature for solute vapors[20,23,71], fluctuations or improper selection of detector cell temperatures would result in erroneous quantitative measurements during chromatographic analysis. For a relative error in $K$ of 1% at a temperature of 400 °K, the temperature variation should not exceed 0.3 °K and at 300 °K it should not exceed 0.2 °K (ref. 29). Likewise, a deviation of ± 3 °K would result in a 10% error in $K$ (ref. 29). Hence it is important that accurate control of detector cell temperature be attained in order to obtain reproducible measurements.

The temperature dependence can be also used to enhance or diminish the sensitivity in some instances in order to minimize unwanted interferences during measurements of a particular solute[29].

Comparison of the sensitivity of various compounds or their derivatives should be made with specific reference to detector temperature[72]. If high electron capture sensitivity is incorporated into a compound via derivatization, the capture process and its temperature dependence should be examined for each potential derivative and their comparison made with respect to $K'$ values. Table 13 depicts the relationship between electron capture mechanism and detector temperature for achieving maximum sensitivity[71-73]. It is readily apparent that derivatization with a reagent does not always yield products that exhibit the same electron capture mechanism, and thus the temperature dependence also varies accordingly.

TABLE 13

RELATIONSHIP BETWEEN ELECTRON CAPTURE MECHANISM AND DETECTOR TEMPERATURE FOR MAXIMUM RESPONSE[71-73]

| *Compound* | *Derivative** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *PFP* | | *HFB* | | *CA* | | *CDFA* | | *PFB* | | *PFPA* | |
| | *Mechanism* | *T*** | *Mechanism* | *T* | *Mechanism* | *T* | *Mechanism* | *T* | *Mechanism* | *T* | *Mechanism* | *T* |
| *n*-Hexanol | IIIA | H | IIIA | H | IIIA | H | IIIA | H | I | L | I | L |
| Cyclohexanol | II | H | II | H | IIIA | H | IIIA | H | I | L | I | L |
| Phenol | I | L | I | L | IIIA | H | II | H | I | L | IIIA | H |
| *n*-Hexylamine | IIIA | H | IIIA | H | IIIA | H | IIIA | H | I | L | I | L |
| Cyclohexamine | IIIA | H | IIIA | H | II | H | IIIA | H | I | L | I | L |
| Aniline | I | L | I | L | IIIA | H | I | L | I | L | I | L |

* PFP = pentafluoroproprionyl; HFB = heptafluorobutyryl; CA = chloroacetyl; CDFA = chlorodifluoroacetyl; PFB = pentafluorobenzyl; PFPA = pentafluorophenacetyl.

** H or L indicates that the highest or lowest feasible detector temperature, respectively, should be used for maximum sensitivity.

### D. Polarizing voltage

The attachment of electrons to molecules can be observed in a simple ionization chamber, with an inert gas, irradiation source and a small applied potential to monitor the liberated ions formed from primary radiation.

Under normal operation of the detector cell, the applied potential may be (1) at constant voltage, (2) under pulsed-constant frequency or (3) under pulsed-variable frequency. A decrease in the current flowing in the chamber is reflected by the presence of a capturing solute which changes the steady-state recombination processes.

The sensitivity of any method of analysis by electron attachment depends upon at least three major factors:

(1) the capture coefficient of the solute molecule;
(2) the $e^-$ concentration in the carrier gas;
(3) the time that is allowed for encounter between absorbing molecules and electrons.

### *(a) Constant applied voltage*

An increase in current from the electron capture cell is observed with increasing applied potential until a saturation plateau is reached (Fig. 7), which represents the total collection of all of the electrons in the detector.

During operation of the detector under constant field potential, the potential chosen represents a fraction of the voltage necessary to collect all of the plasma electrons produced during irradiation. This choice is critical, as it will affect the absorption process[11,71-76,79,80]. Detector configuration and the species to be measured determine the choice of the d.c. potential as well as carrier gas composition and detector contamination[11,71-76,79,80]. To illustrate this point, a comparison of two different instruments reveals that chlorinated hydrocarbon insecticides exhibit greater capture response with a voltage corresponding to *ca.* 90% of the standing current in a Microtek $^{63}$Ni detector, but the same response is at a 20% level for the Carlo Erba instrument[77].

To determine the magnitude of the applied constant potential which will provide the maximum electron capture sensitivity, an initial determination of the detector output current *versus* voltage for a set of analytical conditions is necessary. A general rule is to choose an applied potential which is at approximately 85% of the standing current of the detector ("knee" of curve, Fig. 9). This approach for achieving optimum sensitivity is generally applicable with possible exceptions in those cases where complex dissociative electron capture occurs with a dependence on electron energy.

As the signal of an electron capture detector corresponds to a decrease in standing current, this characteristic easily leads to saturation in the detector when the peak height becomes of the same order of magnitude as the background current. The shape of the chromatographic peak is also modified and the apparent efficiency (HETP) is greatly altered. In order to preserve the efficiency and resolution as well as to keep within the linear dynamic range, the amount of sample that is injected should not produce a decrease of more than 30% in the standing current. Also included, of course, is the decrease resulting from the stationary phase bleed.

Operation of the electron capture cell under the influence of a constant applied voltage produces a migration of ions toward the electrode of opposite polarity[5,41], and a composite current of electrons and ion components results, rather than a pure electron current. Application of a direct potential also prevents the electrons from reaching thermal equilibrium with the carrier gas and therefore decreases the proba-

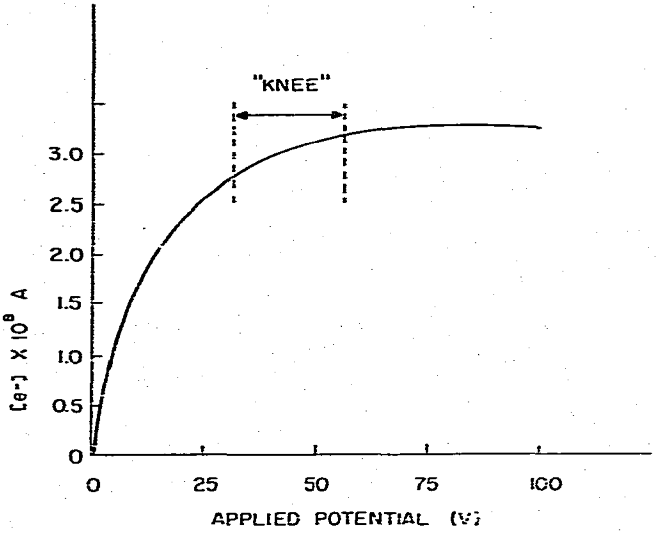


Fig. 9. Electron affinity detector current profile. Source: 240-mC $^{3}$H. Detector temperature, 320 C; flow-rate, 10 ml/min of nitrogen.

bility for capture[5,20]. The electron energy in an ion chamber has a mean value determined by the applied field and nature of the carrier gas (Fig. 10).

Some inherent errors in measurements can occur with a d.c. ion chamber. A space charge may develop under a constant applied potential, affecting current flow[5,22,39]. In a conventional electron absorption detector purged with inert carrier gas, the positive ion concentration may be several thousand times greater than the free electron concentration. An excess of positive ions occurs because free electrons are collected at the anode more rapidly after their liberation than the positive ions,

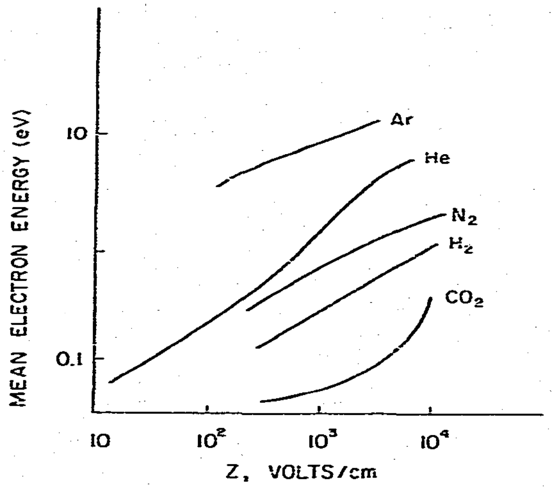


Fig. 10. Relationship between electron energy and applied field strength.

which have a low drift velocity toward the cathode and accumulate as a charge cloud. A potential in opposition to that applied to the chamber is created by this cloud of positive ions, which interferes with the normal collection of free electrons[5,39]. If a polyatomic gas enters the chamber, the electron mobility is altered and also the magnitude of the space charged cloud and observed current flow. As discussed earlier, the probability of electron absorption depends upon the half-life of the electron in the chamber and upon its energy. The combination of these effects can cause a variation with vapor concentration in the probability of electron attachment, thus producing a non-linear response to varying vapor concentration. It has been stated that space charge problems are not as serious when highly asymmetrical electrode configurations are employed[5,41]. The detector response from a small anode should be relatively independent of applied potentials, as the field is weak in the vicinity of the cathode and separation of positive and negative ions cannot easily occur.

As the potential across the chamber is raised, both the probability for electrons to encounter solute molecules and for negative molecular ions to recombine with positive ions decrease. This occurs because under these conditions the time constant or life-time of the ions in the electron capture cell decreases with increasing field strength. Lovelock and Gregory[11] related the fractional loss of ions during the presence of a solute with an affinity for thermal electrons by

$$f = \frac{\alpha N d^4}{N^+ N^- V^2} \qquad (44)$$

where

$N$ = concentration of ions;
$\alpha$ = recombination coefficient(s);
$d$ = electrode distance;
$N^+$ and $N^-$ = mobilities of ions;
$V$ = Voltage.

They pointed out that the potential required for collection of a given proportion of ions is related to $\alpha$. Thus, solutes with weak and strong electron affinities can be determined on the basis of the potential required for collection of a defined proportion of the total ion current.

In addition to recombination processes, it was also pointed out that the production of ions is related to the cross-section for ionization of the solute and carrier gas, the charged species mobility in the gas sample and the mean kinetic energy of the free electrons in the electron capture chamber. The solute affinity for free electrons varies with the electron energy, and therefore the reaction of free electrons and solute vapor is greater under zero field conditions. In fact, this phenomenon has been used to characterize solutes[78] using a potential of constant frequency but variable amplitude.

The magnitude of a constant applied voltage has been also observed to affect the decomposition of the secondary nitrogen positive ions[22]. It is suggested that the second reaction

$$N_2^+ + N_2 \rightarrow N_4^+ \qquad (45)$$

occurs, where $N_4^-$ has a higher mobility than $N_2^+$ because it will not undergo charge exchange reactions. At higher applied field strengths, the $N_4^+$ ion eventually decays.

A simple ion chamber operated at low potential does not necessarily function as an electron absorption detector, but it may operate as (1) an ionization cross-section detector, (2) a detector utilizing metastable atoms for the ionization process (incomplete quenching) and (3) as an electron mobility detector. The degree of participation to which these other detection processes predominate depends upon several factors[14]: (1) composition of gas in the cell, (2) intensity of radiation source, (3) applied potential and (4) detector geometry.

*(b) Constant frequency*

During pulsing, the e$^-$ concentration in the cell is not constant but varies in a saw-tooth fashion (Fig. 11). During the application of a pulse, the e$^-$ concentration decreases to zero owing to the collection of all e$^-$ at the cell electrode (anode). The pulse width ($w$) generally is 0.5–1.0 $\mu$sec[20,23]. The concentration of electrons builds up after each pulse to a plateau as a result of $\beta^-$ particle irradiation of the gas. The magnitude of the e$^-$ concentration is a function of the potential sensitivity and is dependent upon the pulse interval ($P$): as $P$ increases, the detector sensitivity increases to a maximum. In practice, this increase is limited because the pulse interval approaches the time when natural recombination of e$^-$ and positive ions take over[20]. Applying a voltage of between 30 and 50 V for 0.5–1.0 $\mu$sec is usually sufficient to collect all electrons.

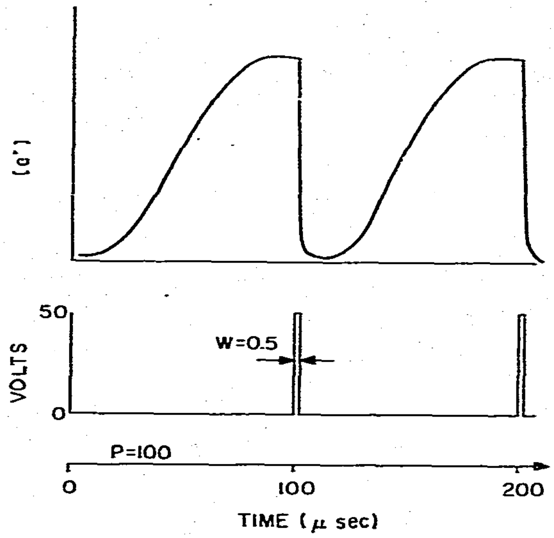


Fig. 11. Electron concentration in ECD during pulsing.

The concentration of electrons, [e$^-$], in the detector cell is related to the pulse period[20,81]:

$$[e^-] = \frac{k_{e^-}}{K_D V_d}(i - e^{-K_D P}) \qquad (46)$$

where

$k_{e^-}$ = rate of electron production by radiolysis of carrier gas;

$V_d$ = detector volume;
$K_D$ = rate of electron removal by all processes;
$P$ = pulse interval.

A typical $[e^-]$ level is $6 \cdot 10^7$ per milliliter (ref. 81).

When no potential is applied to the cell, the electrons are in thermal equilibrium and the migration of large ions does not yield a cell current[18]. The drift of the negative ion is also negligible and thus a negative space charge, *i.e.*, an accumulation of negatively charged ions near the anode, does not occur under pulse conditions[20]. The highest sensitivity and stability are usually obtained by pulsing the detector, and many anomalous responses can be avoided[5,20,41].

The effect of detector temperature and pulse period and width of the polarization voltage on standing current are well known[49]. When the detector temperature is increased, the same standing current plateau is reached but at lower applied voltages. This has been attributed to a decreased gas density, which reduces the probability of collisions between electrons and gas molecules, thus allowing easier collection to electrons.

Altering the pulse width merely effects the relative reduction of standing current and does not modify the sensitivity of the detector if the pulse interval is correctly determined. Hence the pulse interval is a most important parameter in the pulse method. A knowledge of the optimum operating conditions for these two modes of applied polarizing voltage permits the comparison of the sensitivity obtained by the two methods, *i.e.*, the d.c. and pulse method.

A comparison of the sensitivity with constant and pulsed voltage methods has shown that the sensitivity may be three or four times higher in the pulse method than it is in the d.c. method[6]. This phenomenon may be valid only for strong electron-absorbing compounds. The background current noise which limits the sensitivity was identical in the two basic modes[6].

The alternate pulse method utilizes the principle of changes in pulse frequency in order to maintain a constant current[82].

### *(c) Variable frequency*

Maggs *et al.*[82] described a new mode of operation of the ECD in which the detector current is held constant while the frequency ($f$) of the applied pulses is varied. As the electrons are in a steady state into and from the detector chamber, the remaining electrons must be removed by the solute. Furthermore, as the pulse interval increases, so does the $e^-$ concentration (up to the time where recombination takes over):

$$[e^-] \propto 1/f$$

or

$$[\text{solute}] \propto f$$

A pulse power supply which modulates the pulse frequency was designed. Briefly, a reference current, $I_s$, which is compared with the average current, $\bar{I}_D$, and the applied pulsed frequency, maintains via feedback the relationship

$$\bar{I}_D - I_s = 0 \tag{47}$$

As $\bar{I}_D$ begins to decrease due to an electron capturing species entering the detector, a $\Delta I$ is produced. The magnitude of $\Delta I$ is amplified and the amplifier output voltage proportionally changes the applied pulse frequency so as to maintain the above relationship[82].

Thus, the magnitude of change in pulse frequency becomes a measure of the concentration of the electron capturing vapor passing through the detector. The linear dynamic range was $5 \cdot 10^4$ for a 10-mC $^{63}$Ni detector operated in this manner. It also is implied that the limit of detection is increased[82], but its magnitude is not clear.

### *E. Carrier gas flow*

Devaux and Guiochon[83] made extensive investigations into the variations in ECD response with carrier gas flow-rate. The properties were related to a plane parallel ECD ($^3$H) operated in the pulse mode.

#### *(a) Flow vector requirements*

It has been suggested that the gas flow should be arranged to flow in opposition to the negatively charged ions drifting to the anode[83]. Such an arrangement is believed effectively to increase the time of transit for these negatively charged ions and therefore to increase their probability of encountering a positive ion. A large enhancement of current reduction occurs for electron attachment by the sample. In order to achieve this situation, a high gas flow-rate is also normally recommended[12,83].

#### *(b) Effect of flow-rate on peak height and area*

The magnitude of the peak height is greater at higher flow-rates than the magnitude of either peak area of column efficiency[83]. In practical terms, the column flow-rate should be optimized so as to give the best chromatographic characteristics and then, if need be, a scavenger flow should be used to optimize the total flow-rate through the detector to yield the maximum response[83]. The make-up flow-rate cannot be too large, otherwise a dilution occurs.

The degree to which the ECD is a concentration-sensitive detector may depend on the geometric design (plane parallel, pin-cup, coaxial or concentric cylinder)[83].

The peak area per unit mass of a solute is measured by

$$A/m = kI_b/F_r \tag{48}$$

where

$A$ = area;
$m$ = mass;
$I_b$ = standing current;
$F_r$ = flow-rate.

In contrast to other concentration-sensitive detectors in which the area is directly proportional to the flow-rate, the ECD is inversely proportional in this respect[83]. In order to determine the optimum experimental conditions, the flow-rate producing the maximum peak area is selected, *i.e.*, a maximum ratio of peak height to noise.

### *F. Effect of contamination on standing current*

As electron concentration is measured as detector standing current, changes in this parameter (in the absence of a solute) directly reflect changes in the detector sensitivity. There are three main causes of changes in standing current which are related to the electron plasma level: (1) evaporation of $^3H$, (2) contamination of electrode surfaces or radioactive foil and (3) impurities in the gas phase[5,49]. The first problem was discussed earlier.

Contamination of the surface of the radioactive foil will lead to self-absorption of the weak $\beta^-$ particles, consequently reducing the number of $\beta^-$ rays available for carrier gas irradiation. A decrease in the total plasma level of thermal electrons results.

#### *(a) Contact potential*

In addition to a loss in standing current, the temporary or permanent adsorption of a solute in the gaseous effluent from a chromatographic column on to the electrode surfaces can give rise to a contact potential which may oppose or enhance the potential applied to the chamber[5]. If this potential is of the order of a few volts, these effects can cause errors in the electron attachment process. When contact potential develops from temporary adsorption and opposes the applied potential, the chromatographic peak will exhibit a large elution period with severe tailing. Upon enhancement of the applied field, there occurs a diminished response and the peak may be distorted with a large negative deflection on the trailing edge (Fig. 12). Measurement of an incremental response of a second peak closely following the first will probably produce large errors[5]. In either case, *i.e.*, resistance or enhancement, there may also occur false negative or positive responses from a solute that generates the potential at an electrode surface even though it may itself not absorb electrons[5]. Hence it is important to clean the detector frequently in order to minimize the contact potential effects and to obtain accurate and reproducible measurements.

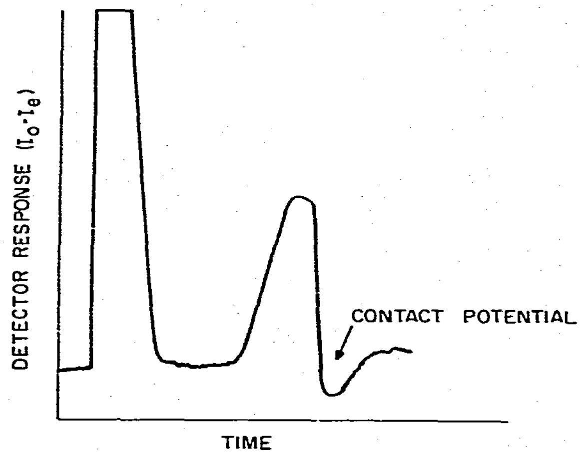


Fig. 12. An ECD exhibiting contact potential.

### *(b) Trace impurities in the vapor phase*

Another major problem stems from impurities in the gas phase. Vapor from samples that emerge at the same retention time as the compound of interest may affect the overall response. The most common example is the situation when a peak emerges on the trailing edge of a large solvent front; less conspicuous is the presence of an unresolved component peak to be measured. Nevertheless, parent solute responce again may be enhanced or decreased depending upon the concentration and electron capturing ability of the impurity[23].

Trace contaminant vapors in the carrier gas can also alter the level of plasma electrons. Karasek and Kane[84] demonstrated that positive $[(H_2O)_nH^+]$ and negative $[(H_2O)_nO_2^-]$ water clustered species are observed when oxygen and water vapor are present in, for example, nitrogen carrier gas. Although the presence of water alone does not change the electron level appreciably, in combination with oxygen a significant decrease does occur. The removal of water is very important if oxygen is present as a contaminant. Similar observations have been reported when argon–methane mixtures were used[84–86].

Depending on the nature of the stationary phase, the standing current of an ECD can be considerably reduced due to "bleed"[1,49]. The reduction may be from the vapor or the decomposition products of the stationary phase having a high electron affinity. This problem is obviously magnified as the column temperature is increased. Therefore, a depletion of thermal plasma electrons occurs, which lowers the probability of reaction for electron attachment between electrons and the solute molecules of interest.

## *G. Signal amplification*

### *(a) Conventional electrometer*

Unlike other ionization detectors, which produce an increase in ion current in the presence of detectable compounds, the ECD, as discussed earlier, exhibits a decrease in current if the compound has an affinity for free electrons. The ECD therefore must operate between the predetermined limits of noise levels at the most sensitive lower end and total detector current at the upper end of this range. It has been generally accepted that the noise level of an ECD ($^3H$) operating under practical GC conditions is about $3 \cdot 10^{-12}$ A. This figure varies depending on the source of ionizing radiation, stationary phase, etc. The linear dynamic range is usually 50 and 500 for $^{63}Ni$ and $^3H$, respectively, which includes the range from noise level to within a 10–30% reduction of total standing current[67].

These criteria are easily satisfied with conventional electrometers for signal amplification. The standing current is displayed as "bucked-out" to a zero baseline, and $I_b - I_e$ is recorded as a positive response. $I$.

### *(b) Linearization by analog conversion*

Non-linearity becomes increasingly apparent as greater reduction in plasma level occurs because the decrease in current output cannot exceed the total plasma current level. As this phenomenon is similar to that encountered in light absorption, initial reports based the electron capture measurements on a Beer's law type of response function[87,88]:

$$I = I_0 \exp(-EcX) \tag{49}$$

where

$c$ = vapor concentration;
$E$ = electron absorption coefficient of vapor;
$X$ = constant related to the geometry of the chamber.

The use of this relationship will extend the apparent linear range; however this expression between response and sample size has no theoretical basis in pulse-operated electron capture detection. On the other hand, recalling eqn. 34, if $I_0$ is the standing current, then

$$\frac{I}{I_0-I} = Ka \tag{50}$$

Fenimore *et al.*[87,88] recognized that the operations of this function could be served by an analog linearizer. Using argon–10% methane as the carrier gas, it is also known that long pulse periods are necessary for utilization of this ratio response function because the steady-state solution of the rate equations for the kinetic model of electron capture requires equilibration of the electron concentration[20].

By employing the analog conversion concept, Fenimore and Davis[88] were able to extend the linear dynamic range of the electron capture responses *versus* sample concentration to $1 \cdot 10^5$. At sufficiently long pulse intervals (> 1000 μsec), the converted response was linear to as high as 87% of detector saturation. The linear function was reported to be valid for dissociative and non-dissociative capturing compounds.

## 5. ESTIMATION OF ELECTRON CAPTURE DETECTION LIMIT

The observed ultrasensitivity of an ECD may lead to speculation as to its projected maximum theoretical limit. A brief exercise is outlined here in an attempt to approximate the theoretical detection limit.

As described earlier, the basis for a displayed response is the amplification of a small signal difference occurring at a high current level. Under these conditions, the absolute sensitivity would probably not depend upon electrical noise but instead upon the noise generated from random emission of $\beta^-$ particles from the radioactive source. The magnitude of this type of noise can be approximated from the Shot relationship[89]:

$$\bar{i}^2 = 2\,e'\,(a+1)\,I_0 B_w$$

where

$e'$ = charge of an electron;
$I_0$ = number of $\beta^-$ particles emitted per unit time;
$a$ = number of electrons formed by ionization per $\beta^-$ ray;
$B_w$ = electrometer bandwidth;
$\bar{i}^2$ = mean square of the fluctuating current generated by random electron collection at the anode.

The noise level has been reported as $3 \cdot 10^{-12}$ A for a 150-mC source[90].

Let us further assume that a signal discernible above background noise is $6\cdot 10^{-12}$ A and that 100% efficiency of electron attachment (*i.e.*, one electron is captured by each solute molecule) is achieved. Furthermore, for every solute molecule present, an electron is depleted from the plasma so that

$$-\frac{\mathrm{d}e^-}{\mathrm{d}t} = \frac{6\cdot 10^{-12}\ \mathrm{c/sec}}{1.6\cdot 10^{-19}\ \mathrm{c/e^-}} = 3.75\cdot 10^{7}\ \mathrm{e^-/sec}$$

As $-\mathrm{d}e^-/\mathrm{d}t = \mathrm{d}N/\mathrm{d}t$ and $\mathrm{d}N/\mathrm{d}t$ represents the number of solute molecules undergoing electron attachment per unit time, then $\mathrm{d}N/\mathrm{d}t = 3.75\cdot 10^{7}$ molecules/sec.

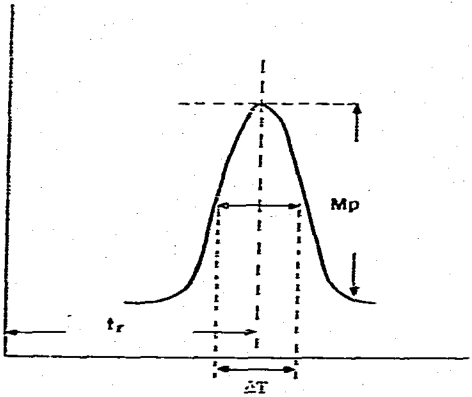


Fig. 13. Symmetrical gas chromatographic peak. $M_p$ = peak maximum; $t_r$ = retention time.

Furthermore,

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{3.75\cdot 10^{7}\ \mathrm{molecules/sec}}{6.02\cdot 10^{23}\ \mathrm{molecules/mole}} = 6.24\cdot 10^{-17}\ \mathrm{mole/sec},$$

where $\mathrm{d}M/\mathrm{d}t$ is the mole rate of attachment. The mole rate can be used to calculate an approximate total number of moles required to produce a GC peak. For a symmetrical peak (Fig. 13), the following relationship may be used[91,92]:

$$m(t) = m_p e^{-a^2(t-t_r)^2} \tag{52}$$

where $m(t)$ is the number of moles as a function of time. For the condition $t_1$, $t_2$, $m(t_1) = m(t_2) = 1/2\, m_p$, it can be shown that

$$a^2 = \frac{2.77}{\Delta T^2}$$

From eqn. 52, we can write

$$m(t) = m_p e^{-\frac{2.77}{\Delta T^2}\cdot(t-t_r)^2} \tag{53}$$

Recalling the function[93]

$$\int_{-\infty}^{\infty} e^{-a^2} x^2 \mathrm{d}x = \frac{1}{a}\sqrt{\pi} \tag{54}$$

then

$$M_T = m_p \Delta T \cdot \frac{\sqrt{\pi}}{1.665} = m_p (1.064 \Delta T) \tag{55}$$

If we assume $\Delta T = 5$ sec, then $M_T = m_p$ (5.32),
$M_T = 6.24 \cdot 10^{-17}$ mole/sec (5.32) and
$M_T \approx 3.32 \cdot 10^{-16}$ mole

Therefore, the theoretical detection limit is near $3.3 \cdot 10^{-16}$ mole.

As an ECD, unless specifically designed to do so, may not operate as a coulometric detector[82], the above calculations should be viewed only as approximations. The question remains as to whether 100% efficiency for electron attachment is achieved for intensely electron-absorbing substances, such as sulfur hexafluoride, carbon tetrachloride and halogenated pesticides, and also whether the net depletion of plasma electrons can ever exceed the total number of solute molecules entering the detector cell.

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## 7. SUMMARY

During the past 15 years, a fundamental understanding of electron capture detection has been gradually developed. This review consolidates and surveys individual research reports into three major areas—the theoretical basis for electron capture detection, the relationship between molecular structure and sensitivity, and operating parameters. In doing so, the strengths and weaknesses of electron capture detection have hopefully been sorted out and thus areas for further research have been brought into focus.

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