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THEORETICAL DESCRIPTION OF ELECTRON-CAPTURE DETECTOR CHARACTERISTICS

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SUMMARY

Theoretically determined electron-capture detector (ECD) characteristics, showing the dependences of the ionization current and the relative detector signal on the concentration of investigated molecules, are presented. Calculations take into account the influence of the parameters of the pulsed supply, of the type and purity of the carrier gas, of the activity of the radiation source and of the detector electrode geometry on the characteristics presented. For concentration characteristics, the given equations take into account the physical properties of the investigated particles, described by a constant (k_1).

The general equation describing the detector ionization current derived in this paper includes the empirical equation of Scolnick and the equation of Lovelock *et al.* The mathematical analysis carried out enables one to determine the minimum detectability for a signal deviating by δ from the linear signal of the ECD.

INTRODUCTION

The application of the electron-capture detector (ECD) has permitted us to formulate the conditions for the optimization of its parameters. Despite the fact that the ECD is widely used, considerable work is still being devoted to the theoretical description of the physical processes which take place during its operation.

In this paper, we present an attempt to give a theoretical description of the characteristics of the ECD, giving the dependence of the ionization current of the detector on the parameters of pulsed supply, the type of carrier gas, the geometry of the detector electrodes, sample concentration and other factors.

MATHEMATICAL ANALYSIS

In a detector supplied by voltage pulses of duration t_i , repetition time T and amplitude U_0 , the temporal behaviour of electron concentration between the detector

electrodes is as presented in Fig. 1. During the period the electric field is applied, the electron concentration diminishes from the initial value, $n(0)$, to the value $n(t_i)$, and remains at the value $n(T)$ when the field is off (*i.e.*, between pulses).

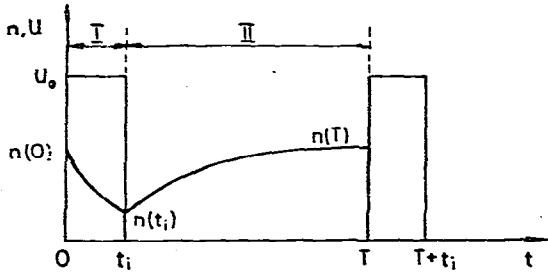


Fig. 1. Temporal behaviour of electron concentration in the detector volume in the presence of supply pulse and during intermission between pulses. Time given from the moment of turning the detector supply on.

In the detector volume, electrons are created by β -particles, the number of which is A_1 ($l/cm^3 \cdot sec$). If we assume that no electric field is present between the detector electrodes and that at a certain moment the radioactive source “begins” to produce electrons (a hypothetical assumption), then the change in electron concentration with time is described by the following dependence:

$$\frac{dn(t)}{dt} = A_1 - k_d \cdot n(t) \quad (1)$$

where k_d is the rate constant describing the loss of electrons in the recombination process with positive ions and in the process of capture by particles of electro-negative impurities of the carrier gas.

Assuming that $n = 0$ at a hypothetical time $t = 0$, the solution of eqn. 1 has the shape

$$n(t) = \frac{A_1}{k_d} (1 - e^{-k_d t}) \quad (2)$$

For $t \rightarrow \infty$, $n = A_1/k_d = n(0)$.

As the detector electrodes are supplied by a pulsed voltage, the electron concentration in the detector changes. For region I in Fig. 1, corresponding to the case when an electric field E_0 appears between the detector electrodes, caused by a voltage pulse of amplitude U_0 , the electron concentration is described by the dependence

$$\frac{dn(t)}{dt} = A_1 - k_d n(t) - k_3 n(t) = A_1 - an(t) \quad (3)$$

where $k_3 = V_d/d$, for a detector with parallel electrodes, V_d being the average electron drift velocity between the detector electrodes in an electric field E_0 , and d the distance between the electrodes.

The solution of eqn. 3 in region I, for $0 < t < t_i$, has the shape

$$n_I(t) = \frac{A_1}{\alpha} + \left[n(0) - \frac{A_1}{\alpha} \right] e^{-\alpha t} \quad (4)$$

The electron concentration at the time $t = t_i$ is then given by

$$n(t_i) = \frac{A_1}{\alpha} + \left[n(0) - \frac{A_1}{\alpha} \right] e^{-\alpha t_i} \quad (5)$$

For region II in Fig. 1, when there is no electric field between the detector electrodes, the electron concentration is described by the equation

$$\frac{dn(t)}{dt} = A_1 - k_d n(t) \quad (6)$$

Because of the boundary condition $n(t_i) \neq 0$ (eqn. 5), the solution of eqn. 6 in region II, for $t_i < t < T$, is different from eqn. 1 and has the shape

$$n_{II}(t) = \frac{A_1}{k_d} + \left[n(t_i) - \frac{A_1}{k_d} \right] e^{-k_d(t-t_i)} \quad (7)$$

The electron concentration at time $t = T$ is then given by

$$n(T) = \frac{A_1}{k_d} + \left[n(t_i) - \frac{A_1}{k_d} \right] e^{-k_d(T-t_i)} \quad (8)$$

In order to define the electron concentration after $m + 1$ cycles, *i.e.*, after the time $(m + 1)T$ (Fig. 2), the following equation is used:

$$n[(m + 1)T] = \frac{A_1}{k_d} + \left\{ \frac{A_1}{\alpha} + \left[n(mT) - \frac{A_1}{\alpha} \right] e^{-\alpha t_i} - \frac{A_1}{k_d} \right\} e^{-k_d(T-t_i)} \quad (9)$$

where $n(mT)$ is the electron concentration in the preceding (m th) cycle.

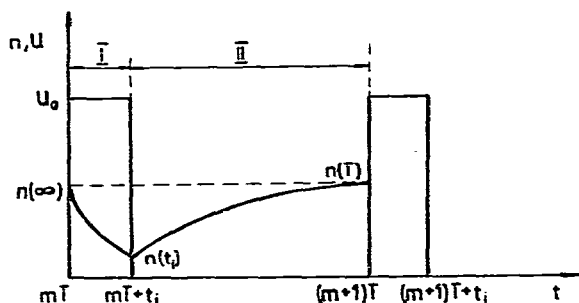


Fig. 2. Change of electron concentration after $(m + 1)T$ time units, at steady state of the accumulation process.

By a certain time after the action of the pulsed voltage on the detector electrodes, a certain value of the electron concentration, $n(\infty)$, is established in the detector (Fig. 2), where

$$n(\infty) = n(\infty + T) \quad (10)$$

The electron concentration for region I is then given by the equation

$$n_1(t) = \frac{A_1}{\alpha} + \left[n(\infty) - \frac{A_1}{\alpha} \right] e^{-\alpha t} \quad (11)$$

Using the eqn. 9 and condition 10, one obtains

$$n(\infty) = \lim_{m \rightarrow \infty} n[(m+1)T] = \frac{D}{1 - e^{-\beta}} \quad (12)$$

where

$$D = \frac{A_1}{k_d} - \left(\frac{A_1}{k_d} - \frac{A_1}{\alpha} \right) e^{-k_d(T-t_i)} - \frac{A_1}{\alpha} \cdot e^{-\beta} \quad (13)$$

and

$$\beta = \alpha t_i + k_d(T - t_i) \quad (14)$$

The average number of electrons collected at the detector electrodes over the period T of the pulsed field in the quiescent state of the collection process is

$$N = \frac{1}{T} \int_0^{t_i} n_1(t) dt \quad (15)$$

After inserting eqn. 11 into eqn. 15, one obtains

$$N = \frac{A_1}{\alpha} \cdot \frac{t_i}{T} + \left[\frac{1}{k_d} - \frac{1}{\alpha} \right] \cdot \frac{A_1}{\alpha T} \cdot \frac{1 - e^{-k_d(T-t_i)}}{1 - e^{-\beta}} \cdot \left[1 - e^{-\alpha t_i} \right] \quad (16)$$

If we let

$$K_1 = \frac{A_1}{\alpha} = \frac{A_1}{k_d + k_3};$$

$$K_2 = K_1 \left(\frac{1}{k_d} - \frac{1}{\alpha} \right) \cdot \frac{1 - e^{-k_d(T-t_i)}}{1 - e^{-\beta}} \quad (17)$$

and

$$K_3 = k_d + k_3 = \alpha$$

eqn. 16 is obtained in the form

$$N = K_1 \cdot \frac{t_i}{T} + \frac{K_2}{T} (1 - e^{-K_3 t_i}) \quad (18)$$

which is known as the empirical equation of Scolnick¹, who gave empirically measured values of the constants K_1 , K_2 and K_3 . The above mathematical analysis enabled us to give the dependence of these constants on the type of carrier gas (described by the parameter k_3), on its purity (described by the parameter k_d), on the activity of the radioactive source (described by the ionization efficiency A_1) and on the pulsed supply parameters (T and t_i).

The ionization current, I , of the detector is

$$I = NesV_d = NeVdk_3 \quad (19)$$

where V is the detector volume, e the electron charge, S the surface area of the collector electrode and $k_3 = V_d/d$ [where V_d is the electron drift velocity and d is the distance between the electrodes (for parallel geometry)].

Inserting eqn. 18 into eqn. 19 and substituting A_1 by a/V , where a is the electron creation rate per unit time (sec^{-1}) we obtain

$$I = K'_1 \cdot \frac{t_i}{T} + \frac{K'_2}{T} (1 - e^{-K_3 t_i}) \quad (20)$$

where

$$K'_1 = ae \cdot \frac{k_3}{\alpha}$$

and

$$K'_2 = K'_1 \left(\frac{1}{k_d} - \frac{1}{\alpha} \right) \cdot \frac{1 - e^{-k_d(T-t_i)}}{1 - e^{-\beta}}$$

For a detector supplied by a constant voltage, $t_i = T$. In this instance the constant $K'_2 = 0$, and the detector current is

$$I = K'_1 = ae \cdot \frac{k_3}{\alpha} \quad (21)$$

After inserting $\alpha = k_d + k_3$, $k_3 = V_d/d$, and $V_d = \mu U_0/d$ (for parallel geometry) into eqn. 21, we obtain

$$I = \frac{AU_0}{B + U_0} \quad (22)$$

where $A = I_0 = ae$ is the saturation current, and $B = k_d d^2/\mu$, where μ is the electron mobility. Eqn. 22 is analogous to the empirical equation of Scolnick¹ describing a detector supplied by a constant voltage.

For a detector supplied by a pulsed voltage of pulse duration $t_i \ll T$, the term $K'_1 t_i/T$ in eqn. 20 can be neglected. As $k_3 \gg k_d$, the term $e^{-K_3 t_i} \ll 1$, and the constant K'_2 , considering that $e^{-\beta} \ll 1$, is of the form $K'_2 = ae \cdot (1 - e^{-k_d T})/k_d$. Eqn. 20 is then simplified to

$$I = \frac{I_0}{k_d T} (1 - e^{-k_d T}) \quad (23)$$

where $I_0 = ae$.

Eqn. 23, describing the current of an ECD supplied by a pulsed voltage, corresponds to the equation of Lovelock *et al.*².

From the above analysis, it follows that eqn. 20 combines the empirical equation of Scolnick and the equation of Lovelock *et al.*

PHYSICAL INTERPRETATION OF THE CONSTANTS A , B , K_1 , K_2 AND K_3

The constant $A = I_0$ in eqn. 22 describes the maximum value of the ionization current that can be obtained in the detector at saturation, with a constant voltage supply. This value is proportional to the radioactive source activity, represented by the factor a , describing the electron creation rate. The factor a is also related to the type of carrier gas, describing the electron creation process by the corresponding ionization cross-section, σ_j .

The constant B in eqn. 22 is related to the purity of the carrier gas (through k_d), the electrode geometry and electron mobility. This constant can be interpreted as a competitive potential, collecting electrons from the active volume of the detector against the constant external potential, U_0 , which creates the detector current, I .

The electron mobility, μ , in the gas in the presence of a constant electrical field depends on the type of gas, on its temperature and pressure and on the field intensity^{3,4}. In general, an increase in pressure or a decrease in the gas temperature leads to a decrease in electron mobility and hence to an increase in the constant B , as demonstrated experimentally by Scolnick¹.

The constant K_1 in eqn. 18 is the concentration of electrons which are collected by the constant voltage U_0 in the active volume of the detector.

The constant K_2 is the limiting value of the electron concentration at the time between field pulses. This takes into account the pulsed supply voltage, and also the fact that between supply pulses electron losses occur in the reaction described by the constant k_d . The value of k_d is 10^3 – 10^4 sec⁻¹ (refs. 2, 5 and 6).

The constant $K_3 = a = k_d + k_3$ is related to the purity and type of carrier gas and its temperature and pressure. This constant is the reciprocal of the time constant of the loss of electrons from the active volume due to a single field pulse. The constant k_3 is defined as

$$k_3 = \frac{SV_d}{V} \quad (24)$$

where S is the surface area of the accumulation electrode of the detector, V_d the average electron drift velocity and V the active volume of the detector.

For a detector with parallel electrodes, k_3 is of the form $k_{3p} = V_d/d$, where d is the electrode separation. In a detector of cylindrical geometry, the corresponding constant, k_{3c} , is

$$k_{3c} = \frac{2\pi}{\ln \frac{R}{r}} \cdot k_{3p} \quad (25)$$

if $V_c = V_p = V$, where R and r are the external and internal radii of the detector electrodes, respectively, and V_p and V_c are the detector active volumes for parallel and cylindrical geometries, respectively.

Table I gives values of the average electron drift velocity, V_d , and values of k_{3p} and k_{3c} calculated for some gases according to Hurst *et al.*⁷ The constant k_{3p} is given for a parallel detector with an electrode spacing of $d = 0.5$ cm. The constant k_{3c} is given for a cylindrical detector with internal and external electrode radii of $r = 0.05$ cm and $R = 0.5$ cm.

TABLE I
CALCULATED VALUES OF k_{3p} AND k_{3c} FOR SOME GASES

| Gas | E/p (V/cm·mmHg) | V_d (cm/sec) | k_{3p} (sec ⁻¹) | k_{3c} (sec ⁻¹) |
|----------|------------------------------------|--------------------------------------|--------------------------------------|--|
| Helium | 10 ⁻² -10 ⁻¹ | 10 ⁵ -10 ⁶ | 2·10 ⁵ -2·10 ⁶ | 5.5·10 ⁵ -5.5·10 ⁶ |
| Argon | 10 ⁻² -10 ⁻¹ | 10 ⁵ -2·10 ⁵ | 2·10 ⁵ -4·10 ⁵ | 5.5·10 ⁵ -1.1·10 ⁶ |
| Hydrogen | 10 ⁻² -10 ⁻¹ | 4·10 ⁴ -2·10 ⁵ | 8·10 ⁴ -4·10 ⁵ | 2.2·10 ⁵ -1.1·10 ⁶ |
| Nitrogen | 10 ⁻² -10 ⁻¹ | 4·10 ⁵ | 8·10 ⁶ | 2.2·10 ⁷ |

RESULTS AND CALCULATIONS

It is convenient to present eqns. 18 and 20 in the form

$$\frac{I}{I_0} = \frac{k_3}{k_d + k_3} \cdot \frac{t}{T} + \frac{1}{k_d T} \left(\frac{k_3}{k_d + k_3} \right)^2 \cdot \frac{1 - e^{-k_d(T-t_i)}}{1 - e^{-(k_d T + k_3 t_i)}} \cdot [1 - e^{-(k_d + k_3)t_i}] \quad (26)$$

However, if $k_3 t_i < 1$, $k_d \ll k_3$ and $t_i < T$, then eqn. 26 can be reduced to

$$\frac{I}{I_0} = \frac{k_3 \cdot \frac{t_i}{T}}{k_d + k_3 \cdot \frac{t_i}{T}} \quad (27)$$

For $k_3 t_i > 1$, $k_d \ll k_3$ and $t_i < T$, eqn. 26 takes the form given by Lovelock *et al.*²:

$$\frac{I}{I_0} = \frac{I}{k_d T} (1 - e^{-k_d T}) \quad (28)$$

Results of calculations of the current ratio, I/I_0 , according to eqns. 26-28 are shown in Fig. 3. The dashed curves represent characteristics calculated by using eqn. 26 with $k_3 = 10^6$ sec⁻¹ and $t_i = 1$ μsec ($k_3 t_i = 1$). The dashed-and-dotted curves were obtained by using eqn. 27, also with $k_3 t_i = 1$. The full curves correspond to the solution of Lovelock *et al.*'s eqn. 28 for $k_3 t_i > 1$. Curves are given for different values of k_d .

Inserting $k_d + k_1 c$ in place of k_d into eqns. 26-28, where k_1 is the constant of electron capture^{8,9} by particles of the measured sample, it is possible to obtain equations relating the detector ionization current to the sample concentration, c . The modified equations are as follows. The complete equation:

$$\frac{I_c}{I_0} = \frac{k_3}{k_d + k_1 c + k_3} \cdot \frac{t_i}{T} + \frac{1}{(k_d + k_1 c) T} \left(\frac{k_3}{k_d + k_1 c + k_3} \right)^2 \cdot \frac{1 - e^{-(k_d + k_1 c)(T-t_i)}}{1 - e^{-[(k_d + k_1 c)T + k_3 t_i]}} \cdot [1 - e^{-(k_d + k_1 c + k_3)t_i}] \quad (29)$$

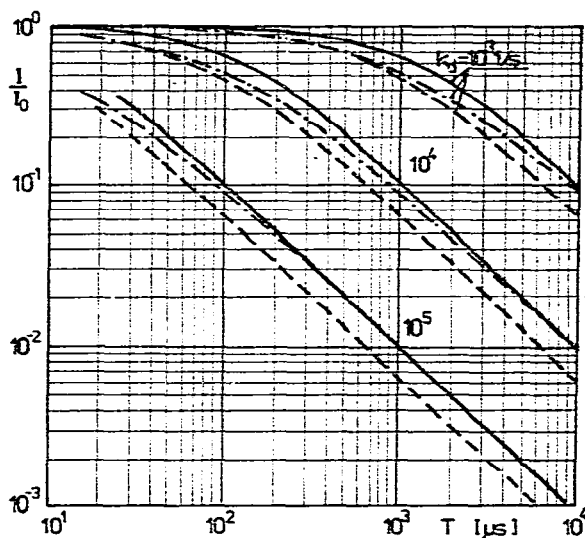


Fig. 3. Dependence of detector ionization current on repetition time of pulsed supply, calculated according to various equations for several k_d values. ---, Eqn. 26; - · - · -, eqn. 27 ($k_3 t_i = 1$); ———, eqn. 28. In calculations, values of $t_i = 1 \mu\text{sec}$ and $k_3 = 10^6 \text{ sec}^{-1}$ were assumed.

The reduced equation, for $k_3 t_i < 1$:

$$\frac{I_c}{I_0} = \frac{k_3 \cdot \frac{t_i}{T}}{k_d + k_1 c + k_3 \cdot \frac{t_i}{T}} \quad (30)$$

The Wentworth *et al.*¹⁰ equation, for $k_3 t_i > 1$:

$$\frac{I_c}{I_0} = \frac{1}{(k_d + k_1 c)T} [1 - e^{-(k_d + k_1 c)T}] \quad (31)$$

The relative detector signal has the form

$$\frac{\Delta I}{I} = \frac{I - I_c}{I} \quad (32)$$

where I is the ionization current of the detector supplied by a pulsed voltage of duration t_i and repetition time T in the absence of investigated particles, and I_c is the ionization current of the same detector in the presence of a concentration c of electro-negative particles in the detector.

On replacing I in eqn. 32 by eqns. 26–28 and I_c by eqns. 29–31, one obtains the concentration characteristics of the detector, given by the full, reduced and Wentworth *et al.*–Lovelock *et al.* equations, respectively.

These characteristics, *i.e.*, the dependences $\Delta I/I = f(c)$, are illustrated in Fig. 4. The full curves correspond to Wentworth *et al.* and Lovelock *et al.*'s equation ($k_3 t_i > 1$), the dashed curves illustrate characteristics calculated using the full

equation for $k_3 t_i = 1$ and the dashed- and-dotted curves were obtained by using the reduced equation with $k_3 t_i = 1$. Despite the contradiction with previous assumptions, one can observe that the behaviour of the last characteristic resembles that calculated using the full equation. This enables us to use the reduced instead of the full equation without introducing large errors, the remark concerning also the reduced form of the basic current eqn. 27. The characteristics presented in Fig. 4 were calculated as an example for detector supply pulses with a repetition time $T = 100 \mu\text{sec}$ and $k_d = 10^3 \text{ sec}^{-1}$. Curves were calculated for different values of k_1 .

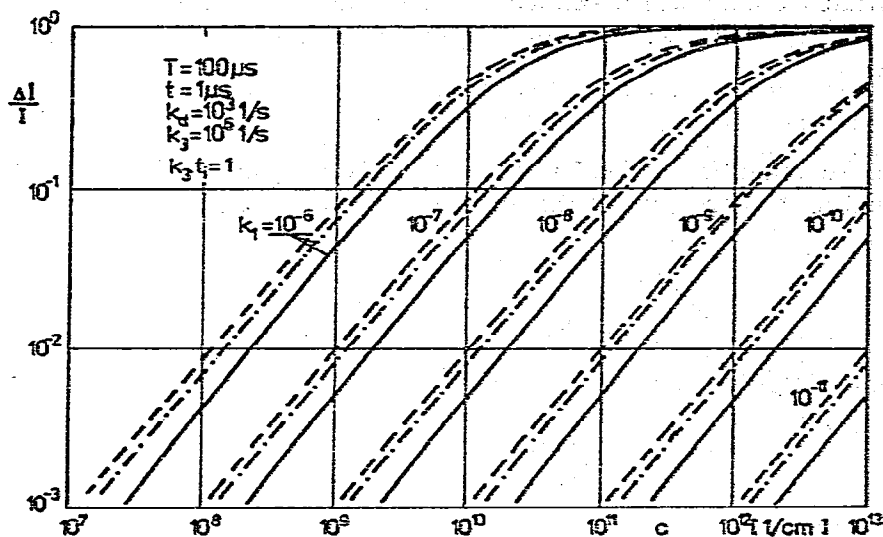


Fig. 4. Dependence of the ECD signal on concentration of investigated particles, for several values of the electron-capture constant, k_1 , calculated according to various equations: — — —, Eqn. 29 ($k_3 t_i = 1$); - - - - -, eqn. 30 ($k_3 t_i = 1$); eqn. 31 ($k_3 t_i > 1$). In calculations, values of $k_d = 10^3 \text{ sec}^{-1}$ and $T = 100 \mu\text{sec}$ were assumed.

The reduced equation for the relative detector signal, calculated using eqns. 27 and 30, is as follows:

$$\frac{\Delta I}{I} = \frac{k_1 c}{k_d + k_3 \cdot \frac{t_i}{T} + k_1 c} = f(c) \tag{33}$$

Using this equation it is possible to calculate the limit of detection with the ECD, assuming that $\Delta I/I = 2I_n/I$, where I_n is the level of fluctuations of the detector ionization current. In this instance

$$\frac{2I_n}{I} = \frac{k_1 c_{\text{min}}}{k_d + k_3 \cdot \frac{t_i}{T} + k_1 c_{\text{min}}} \tag{34}$$

The lowest concentration, c_{\min} , that will give a detector signal equal to double the value of the fluctuation current is then

$$c_{\min} = \frac{2I_n}{I} \cdot \frac{k_d + k_3 \cdot \frac{t_1}{T}}{k_1} \quad (35)$$

Using eqn. 33, it is also possible to determine the dynamic range of the detector and the maximum concentration, c_{\max} , of the investigated substance for which the detector signal does not deviate from a linear dependence by more than δ , as shown in Fig. 5. The function $g(c)$ in Fig. 5 represents the linear part of the detector characteristics and is of the shape

$$g(c) = Kc \quad (36)$$

where $K = \operatorname{tg}\varphi$. The function $f(c)$ in Fig. 5 is calculated by using eqn. 33. The constant K in eqn. 36 is equal to the derivative of the function $f(c)$ for $c = c_{\min}$.

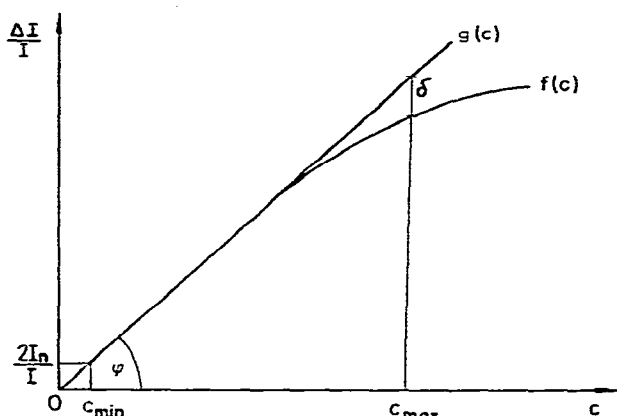


Fig. 5. Ideal detector characteristic, $\Delta I/I = g(c)$, actual behaviour, $\Delta I/I = f(c)$, and deviation, δ , at the end of the dynamic range.

The deviation δ , usually understood as a 5% deviation from linearity, is given by

$$\delta = \frac{g(c_{\max}) - f(c_{\max})}{g(c_{\max})} \quad (37)$$

After inserting into eqn. 37 the function $g(c_{\max}) = f'(c_{\min})c_{\max}$ and the function $f(c_{\max})$ and performing the necessary calculation, an equation is obtained that gives the maximum concentration of the investigated substance for which the detector signal deviates by δ from a linear dependence, *i.e.*

$$c_{\max} = \frac{\delta}{1 - \delta} \cdot \frac{k_d + k_3 \cdot \frac{t_1}{T}}{k_1} \quad (38)$$

Having calculated the relationships that describe c_{\min} and c_{\max} (eqns. 35 and 38), it is now possible to determine the dynamic range of the detector:

$$R_d = \frac{c_{\max}}{c_{\min}} = \frac{I}{2I_n} \cdot \frac{\delta}{1 - \delta} \quad (39)$$

The detector sensitivity is then

$$S = \operatorname{tg} \varphi = f'(c_{\min}) \approx I \cdot \frac{k_1}{k_d + k_3 \cdot \frac{t_i}{T}} \quad (40)$$

As is known, the ECD signal, ΔI , reaches its maximum value at a definite frequency of the voltage pulses supplying the detector. This optimal frequency can be determined by using eqn. 33, according to which the signal, ΔI , for the concentration of sample molecules in the carrier gas c_0 , when $c_{\min} < c_0 < c_{\max}$, is

$$\Delta I = I \cdot \frac{k_1 c_0}{k_d + k_3 \cdot \frac{t_i}{T} + k_1 c_0} \quad (41)$$

After inserting the expression for I from eqn. 27 into eqn. 41, we obtain

$$\Delta I = I_0 \cdot \frac{k_3 t_i}{k_d T + k_3 t_i} \cdot \frac{k_1 c_0 T}{(k_d + k_1 c_0) T + k_3 t_i} \quad (42)$$

When calculating the extreme of the above function with respect to T , one obtains both the repetition time and the frequency of the pulses at which ΔI reaches its maximum value. This optimal repetition time, T_{opt} , can be written as

$$T_{\text{opt}} = \frac{k_3 t_i}{[k_d(k_d + k_1 c_0)]^{1/2}} \quad (43)$$

Eqn. 43 shows that T_{opt} depends on the sample concentration in the carrier gas, the electronegativity of the sample molecules, the type of carrier gas (determined by the constant k_3) and the purity of the carrier gas (determined by the constant k_d). The expression $k_1 c_0$ in eqn. 43, for pure carrier gas (e.g., $k_d = 10^3 \text{ sec}^{-1}$), a small concentration of sample in the carrier gas and strongly electronegative compounds, can be neglected. Then the repetition time of the pulses depends slightly on the type and concentration of the sample and is given by

$$T_{\text{opt}} = \frac{k_3}{k_d} \cdot t_i \quad (44)$$

The optimal repetition time, T_{opt} , depends largely on the sample concentration, for c_0 close to c_{\max} , particularly for compounds with weak electronegative properties.

The important parameters of the ECD connected to the chromatographic

column, such as the optimal pulse frequency ($1/T_{opt}$), minimal detectable concentration (c_{min}) and dynamic range (R_d), can be determined when the values of k_d , k_3 and I_0 are known. These constants can be determined experimentally if the characteristic functions, *i.e.*, $I = I(T)$ and $\Delta I = f(T)$ at $c = c_0 = \text{constant}$, for the chosen test compound (*e.g.*, carbon tetrachloride) are known. Using these functions, one can determine I_{opt} , *i.e.*, the value of the detector current at which the signal maximum, ΔI_{max} , is observed, and ΔI_{max} for $c_0 = \text{constant}$, corresponding to the sample concentration at the peak maximum. When these values are known, one can calculate the following:

$$k_d = k_1 c_0 \cdot \frac{\left(1 - \frac{\Delta I_{max}}{I_{opt}}\right)^2}{\frac{\Delta I_{max}}{I_{opt}} \left(2 - \frac{\Delta I_{max}}{I_{opt}}\right)} \quad (45)$$

$$k_3 = \frac{T_{opt}}{t_i} [k_d(k_d + k_1 c_0)]^{1/2} \quad (46)$$

$$I_0 = I_{opt} \left(\frac{k_d}{k_3} \cdot \frac{T_{opt}}{t_i} + 1 \right) \quad (47)$$

where k_1 denotes the electron-capture constant for the test compound.

Knowing k_d , k_3 and I_0 , it is also possible to determine the sample concentration corresponding to the chromatographic peak maximum for any compound x , when its electron-capture constant, k_{1x} , is known and the analysis is performed under optimal conditions for the test compound. This can be done by using the equation

$$c_x = \frac{1}{k_{1x}} \cdot \frac{\frac{\Delta I_x}{I_{opt}}}{1 - \frac{\Delta I_x}{I_{opt}}} \{k_d + [k_d(k_d + k_1 c_0)]^{1/2}\} \quad (48)$$

with the condition that the concentration of compound x can be found in the linear range of the detector signal. On the other hand, eqn. 48 allows the electron-capture constant, k_{1x} , of compound x to be determined when its concentration corresponding to the chromatographic peak maximum is known.

CONCLUSIONS

This theoretical approach to the calculation of the current and concentration characteristics of the ECD takes into account the relationships between the behaviour of the detector and the type of carrier gas (through the constant k_3), the level of carrier gas pollution (constant k_d) and the pulsed supply voltage (*i.e.*, pulse duration, t_i , and repetition time, T). In this approach, the activity of the radiation source constant, A_1 , and the geometrical configuration of the detector electrodes (constant k_3) are also taken into account.

The general equation 26, describing the detector current characteristics, in-

cludes the empirical equation of Scolnick and also the equation of Lovelock *et al.*². Fig. 3 illustrates the behaviour of the current dependence inside the detector. The detector ionization current measured by a certain measuring circuit can deviate from the values calculated using the above equations owing to some distortions introduced by the circuit itself. In spite of these distortions, the constants k_d , k_3 and I_0 and the concentration of a compound x can be determined (eqns. 45–48), because in these equations a ratio of currents, $\Delta I_{\max}/I_{\text{opt}}$, and not their absolute values, appears.

The theoretical concepts of the operation of the ECD, from which follow the derived dependences describing the detection limit and the dynamic range, are logically connected with practical observations gathered in the application of the ECD, for constant ($t_i = T$) and pulsed voltage supplies. The influence of the electron-capture constant, k_1 , on the behaviour of the detector characteristics clearly demonstrates the influence of the electronegative properties of the investigated substance on its detectability (Fig. 4).

The theoretical description presented does not take into account the influence of space-charge phenomena of positive ions or electron-ion recombination phenomena on the generation of the detector signal. These problems are currently under study.

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