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INFLUENCE OF THE SUPPLY SYSTEM ON THE AVERAGE ELECTRON ENERGY IN THE ELECTRON-CAPTURE DETECTOR

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SUMMARY

Results are presented of mathematical calculations of average electron energies in electron-capture detectors with parallel and cylindrical electrode geometries, for argon and methane and for nitrogen as carrier gases. Calculations were performed with a modified solution of the Boltzmann equation. In the calculations, account was taken of pulsed and continuous systems of detector supply. The calculations show that for pulsed supply systems, where the ratio of pulse duration, t_i , to repetition time, t_r , is smaller than 10^{-2} , the average electron energy in the detector does not depend on the electrode geometry, on the percentage of admixture stabilizing the electron energy or on the pulse repetition time.

INTRODUCTION

The physical principle of the operation of the electron-capture detector (ECD) is the formation of negative ions of the molecules being investigated with free electrons generated in the carrier gas by beta-particles emitted from a radioactive source. This process, called electron capture, proceeds optimally when the value of the average electron energy, ε , taken over the distribution function of the electron energy, $f(\varepsilon)$, reaches the value at which the electron capture cross-section is at its maximum. The latter energy, called the energy of resonance capture, characterizes each chemical compound. Electron capture in dissociative and non-dissociative processes takes place in the range of electron energies between zero and several electronvolts.

Organohalogen compounds, which are the main electron-capture detection agents, are characterized by energies of resonance capture, ε_r , in the range $3/2 kT \leq \varepsilon_r \leq 1 \text{ eV}$.

This paper presents results of calculations of the influence of the detector supply (with a constant voltage or with pulses of duration t_i , and repetition time t_r) on the average electron energy. Values of this energy were calculated for nitrogen and argon-methane mixtures as the carrier gas and for parallel and cylindrical geometries of the detector electrodes. Calculations were performed using experimental

values of cross-sections for elastic scattering, $\sigma_1(\varepsilon)$ and $\sigma_2(\varepsilon)$, given by Laborie *et al.*¹ and the so-called characteristic energy of absorption, $b(\varepsilon)$, given by Christophorou *et al.*² and Uman and co-workers^{3,4}.

THEORETICAL

Average electron energy in the carrier gas

The physical processes that occur in the active volume of the ECD can be described by regarding the plasma present in that volume as a two-component mixture of N_1 atoms of the carrier gas and N_2 atoms of the admixed gas. A mathematical description of the phenomena that occur in such a mixture placed under a constant electric field of intensity E_0 has been given by Uman and Warfield³ and Smirnov⁵. They based their calculations on the phase-space distribution function of electron energy, $f(c, r, t)$, and on the Boltzmann equation given in the following form:

$$\frac{\partial f}{\partial t} + c \nabla_r f + \frac{eE_0}{m} \cdot \nabla_c f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll.}} \quad (1)$$

where

- r is the vector in three-dimensional space;
- c is the vector in three-dimensional velocity space;
- ∇_c is the gradient operator in three-dimensional velocity space;
- ∇_r is the gradient operator in three-dimensional space;
- t is time;
- e is the charge of electron;
- m is the electron mass;

$\left(\frac{\partial f}{\partial t} \right)_{\text{coll.}}$ is the Boltzmann collision integral.

Uman and Warfield³ have given a solution of eqn. 1 for the phase-space distribution function of the form

$$f(c) \approx f_0(c) + \frac{c_x}{c} \cdot f_1(c) \quad (2)$$

as follows:

$$f_0(\varepsilon) = G \exp \left\{ - \int_0^\varepsilon \left[kT + \frac{E_0^2}{3 \varepsilon' F_M(\varepsilon') \sigma_c^2(\varepsilon')} \right]^{-1} d\varepsilon' \right\} \quad (3)$$

$$f_1(\varepsilon) = \frac{E_0}{\sigma_c(\varepsilon)} \cdot \left[kT + \frac{E_0^2}{3 \varepsilon F_M(\varepsilon) \sigma_c^2(\varepsilon)} \right]^{-1} \cdot f_0(\varepsilon) \quad (4)$$

where

G is a normalizing constant;

$$F_M = \frac{N_1 F_1 \sigma_1 + N_2 F_2 \sigma_2}{N_1 \sigma_1 + N_2 \sigma_2} = F_1 \frac{\sigma_1 + \eta \sigma_2 b}{\sigma_1 + \eta \sigma_2} = \frac{H\varepsilon^2 + L\varepsilon + J}{R\varepsilon + W};$$

$$\sigma_c = N_1(\sigma_1 + \eta \sigma_2) = N_1(R\varepsilon + W);$$

- $F_1(\varepsilon)$ is the fractional energy lost by electrons in collision with atoms of gas No. 1, for atomic gas $F_1 = 2m/M$, where M is the atomic mass of this gas and m is the electron mass;
 $F_2(\varepsilon)$ is the fractional energy lost by electrons in collisions with atoms of gas No. 2;
 N_1 is the particle density of gas No. 1;
 N_2 is the particle density of gas No. 2;

$$b(\varepsilon) = \frac{F_2}{F_1};$$

$$\eta = \frac{N_2}{N_1};$$

T = temperature ($^{\circ}\text{K}$);

k = Boltzmann constant;

$R = a + \eta d$;

$W = s + \eta z$;

$H = \eta g d$;

$L = a + \eta d h + \eta g z$;

$J = a + \eta h z$;

a, s, d, z, g and h are parameters resulting from the linear approximation of cross-section for argon and methane included in Table I, where:

$$\sigma_1(\varepsilon) = a\varepsilon + s;$$

$$\sigma_2(\varepsilon) = d\varepsilon + z;$$

$$b(\varepsilon) = g\varepsilon + h.$$

TABLE I

 APPROXIMATION OF CROSS-SECTION (σ , \AA^2) FOR ARGON³ AND METHANE^{1,2}

$$\sigma_{\text{Ar}} = a\varepsilon + s; \sigma_{\text{CH}_4} = d\varepsilon + z; b_{\text{CH}_4} = g\varepsilon + h.$$

Parameter	ε (eV)								
	0-0.05	0.05-0.125	0.125-0.225	0.225-0.5	0.5-0.8	0.8-1.2	1.2-2	2-5.95	>5.95
a	0	0	0	0	1.61	1.61	1.61	1.61	1.61
s	0.5	0.5	0.5	0.5	-0.344	-0.344	-0.344	-0.344	-0.344
d	-188	-188	0	0	0	4.932	4.932	4.932	-0.666
z	23.8	23.8	0.3	0.3	0.3	-3.645	-3.645	-3.645	29.7
g	0	145333.33	0	-22363.64	-7500	-2 750	-560	0	0
h	0	-7266.66	10900	15931.82	8500	4 700	2 100	900	900

Eqns. 3 and 4 are valid for gas mixtures of the type argon + methane, *i.e.*, $N_1 \neq 0$ and $N_2 \neq 0$. For atomic gases, $N_2 = 0$ so eqns. 3 and 4 are transformed into the forms given by Morse *et al.*⁸. For a pure molecular gas, such as nitrogen, $N_1 = 0$ and the parameters in eqns. 3 and 4 assume the following form:

G = normalization constant;

$$F_M = F_1 b(\varepsilon) = \frac{2m}{M} \cdot (g\varepsilon + h);$$

$$\sigma_c = N_2 \sigma_2(\varepsilon) = N_2(d\varepsilon + z);$$

m = electron mass;

M = mass of the atom of the gas with respect to which $b(\varepsilon)$ was calculated;
 g, h, d and z are parameters resulting from the linear approximation of the cross-section for nitrogen, included in Table II.

TABLE II

APPROXIMATION OF CROSS-SECTION (σ , Å²) FOR NITROGEN³

$$\sigma_{N_2} = d\varepsilon + z; \quad b_{N_2} = g\varepsilon + h.$$

Param- eter	ε (eV)					
	0.0-0.8	0.8-1.3	1.3-1.7	1.7-2.4	2.4-3.4	>3.4
d	-12.0	0	15.18	15.18	-15.3	0
z	17.5	7.9	-11.83	-11.83	61.32	9.3
g	0	1292.3	1292.3	0	0	0
h	36.9	-997.9	-997.9	1200	1200	1200

On the basis of eqn. 3, the average electron energy is now represented by the following equation^{3,4}:

$$\bar{\varepsilon} = \frac{\int_0^{\infty} \varepsilon^{3/2} f_0(\varepsilon) d\varepsilon}{\int_0^{\infty} \varepsilon^{1/2} f_0(\varepsilon) d\varepsilon} \quad (5)$$

Influence of the detector supply system on the average electron energy

The ECD can be supplied either with a constant voltage or with square-shaped pulses of duration t_i and repetition time t_r , where $t_r \gg t_i$. For a detector supplied with a constant voltage, the solution of eqn. 1 given by Uman and Warfield can be applied directly in order to determine the average electron energy, as Uman and Warfield's conditions are fulfilled in such a detector. The average electron energy, $\bar{\varepsilon}$, is then given by eqn. 5. However, for a detector supplied with a pulsed voltage, one must consider the average electron energy over the time t , during which the electric field is applied. It was found that the solution of eqn. 1 given by Uman and Warfield can be applied under the condition that the criterion given by Smirnov⁵ is fulfilled in the following form:

$$\frac{\omega}{\nu} \ll 1 \quad (6)$$

where ω is the pulse frequency of the electric field and ν is the frequency of collision between atoms and electrons. For the ECD, $\omega_{\max} = 1$ MHz and ν depends on the type of gas (e.g., for argon, $\nu \approx 10^4$ MHz).

It follows that the criterion given by eqn. 6 is fulfilled and that the frequency range of the voltage supplying the ECD can be assumed to be low. The applicability of Uman and Warfield's solution is also influenced by the relationship between the period during which the field pulse lasts, t_i , and the times t_n and t_{th} , where t_n is the time of "heating up" of electrons to energy $\bar{\varepsilon}$ during the pulse of electric field and

t_{th} is the time of thermalization of electrons to the thermal energy ($3/2 kT$) between the pulses of electric field (according to Warman and Sauer⁶).

When the ECD is used in practice, $t_i = 1 \mu\text{sec}$ and $t_r = 100\text{--}1000 \mu\text{sec}$, so one can neglect t_n and t_{th} , as $t_i > t_n \approx 10^{-8}$ sec and $t_r > t_{th} \approx 10^{-6}$ sec. Under these assumptions, the equation for the average electron energy in a detector supplied by a pulsed voltage over the period t_r is

$$\langle \bar{\varepsilon} \rangle \approx \frac{3}{2} kT + \left(\bar{\varepsilon} - \frac{3}{2} kT \right) \cdot \frac{t_i}{t_r} \quad (7)$$

Influence of the electrode geometry on the average electron energy in the detector

The electric field distribution for different geometries of the measuring electrodes is influenced by the supply voltage (see eqns. 8 and 9). In turn, the average electron energy is a function of the field intensity (see eqns. 3, 5 and 7).

For electrodes of parallel geometry, the intensity of the electric field is

$$E_0 = \frac{U}{d} \quad (8)$$

where

U = detector supply voltage (volts);

d = distance between electrodes (centimetres).

For cylindrical geometry:

$$E_0 = \frac{1}{r} \cdot \frac{U}{\ln \left(\frac{r_2}{r_1} \right)} \quad (9)$$

where

r_1 = radius of the inner electrode;

r_2 = radius of the outer electrode;

r = coordinate of the point at which the field is calculated, where, in all instances, the inequality $r_1 < r < r_2$ holds.

RESULTS AND CALCULATIONS

Figs. 1–5 illustrate the results of calculations of the average electron energy in the carrier gases (argon–methane mixture or nitrogen) for the supply systems mentioned above and for the two geometries of the detector electrodes. For a detector with parallel electrodes, their spacing was assumed to be 1 cm, while for a detector with cylindrical geometry, the size of the ECD currently produced by the Institute of Physics and Nuclear Techniques, Type DNW-600, was assumed⁷; in this detector $r_2 = 0.5$ cm and $r_1 = 0.05$ cm. Calculations were performed using a Wang-700 computer (IBM).

Fig. 1 presents the results of calculations of the average electron energy in a parallel-plate detector with argon–methane as the carrier gas. Calculations were made for a detector supplied with a voltage of amplitude 60 V and pulse duration 1 μsec . In calculations the pressure of the gas was assumed to be 760 mmHg. The

curves in Fig. 1 give the dependence of the average electron energy on the ratio between the duration of the supply pulse, t_i , and the pulse repetition time, t_r . Curve 1 represents pure argon, and curves 2, 3, 4 and 5 represent argon with admixtures of 0.01, 0.1, 1 and 10% of methane, respectively. The behaviour of curves 1–5 illustrates the stabilizing action of methane on the electron energy. Curve 6 in Fig. 1 represents a detector operating with nitrogen as the carrier gas. Over the whole range of t_i/t_r ratios, the energy of electrons in the gas remains constant.

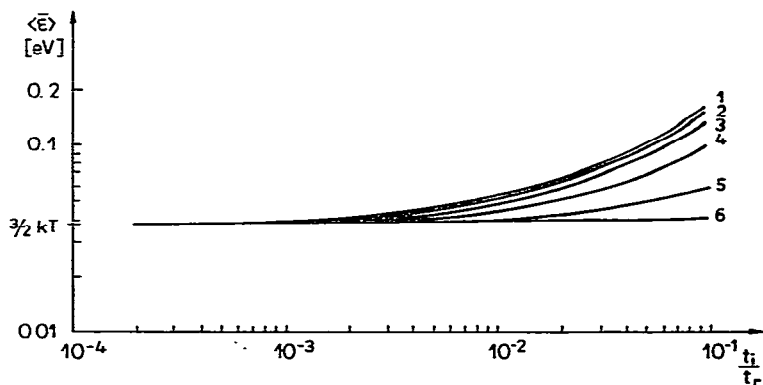


Fig. 1. Dependence of the average electron energy on the ratio of pulse duration, t_i , to repetition time, t_r , for a parallel-plate ECD. Electric field in the detector, 60 V/cm; pressure, 760 mmHg; temperature, 298 °K; $t_i = 1 \mu\text{sec}$. Curves 1–5 represent argon–methane mixtures with 1, 0%; 2, 0.01%; 3, 0.1%; 4, 1%; and 5, 10% of methane. Curve 6 = pure nitrogen.

Fig. 2 shows the dependence of the average electron energy on the ratio t_i/t_r for a detector of cylindrical geometry with the supply conditions given above. Curves 1, 2, 3 and 4 represent points at distances r_1 , $2r_1$, $5r_1$ and $10r_1 = r_2$ from the detector symmetry axis, respectively. Thus, curve 1 represents the surface of the collector electrode and curve 4 the surface of the radioactive source. In practice, the detector is

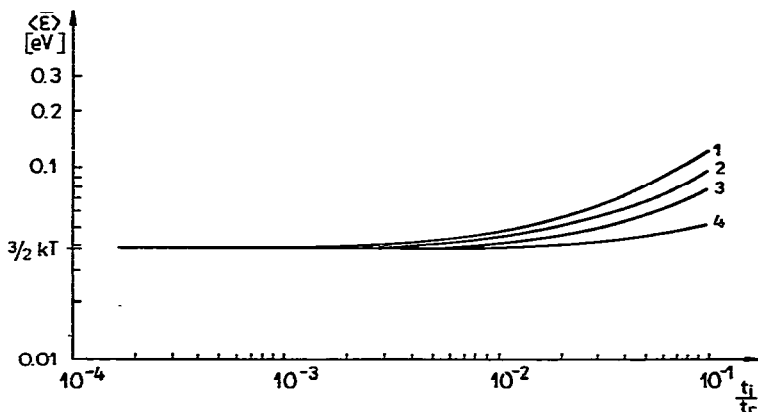


Fig. 2. Dependence of average electron energy on the ratio t_i/t_r , for a cylindrical ECD with $r_1 = 0.05$ cm and $r_2 = 0.5$ cm. Curves: 1 = surface of collector electrode ($r = r_1$); 2 = distance $2r_1$; 3 = distance $5r_1$; 4 = distance $10r_1$. Carrier gas: argon–10% methane.

supplied with a pulsed voltage with a repetition time of 100–1000 μsec , for which the ratio t_i/t_r lies between 10^{-2} and 10^{-3} . For such ratios, the change in electron energy is small and lies around the thermal energy ($3/2 kT$).

In Fig. 3, dependences similar to those illustrated in Fig. 2 are shown for a cylindrical detector operating with nitrogen as the carrier gas. In this instance the change in the average electron energy along the radius connecting the collector electrode with the radioactive source is smaller than that with the argon–methane mixture in the given range of supply pulse frequencies.

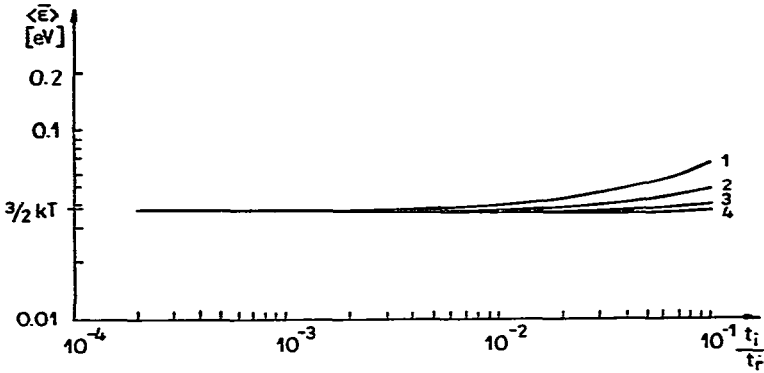


Fig. 3. Dependence of average electron energy on the ratio t_i/t_r in a cylindrical detector with nitrogen as carrier gas. Curves as in Fig. 2.

Fig. 4 gives the dependence of the average electron energy for a parallel-plate detector at various positions between the electrodes. In the calculations the constant supply voltage was assumed to be 10 V, which, for an electrode separation of 1 cm and a pressure of 760 mmHg, gives $E/p = 0.013 \text{ V/cm} \cdot \text{mmHg}$. Curve 1 represents argon–10% methane and curve 2 nitrogen as the carrier gas. Curve 3 illustrates the electron

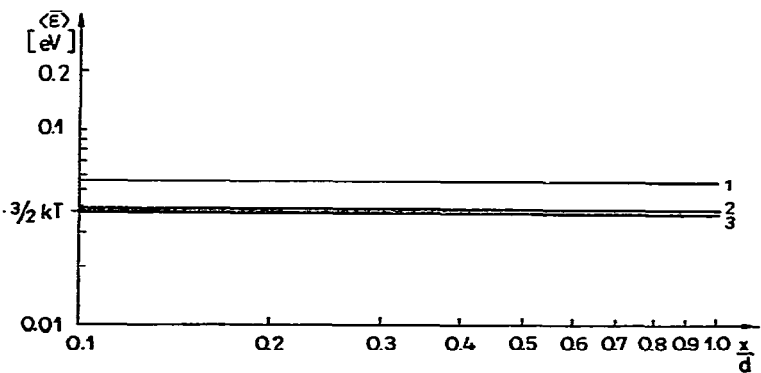


Fig. 4. Average electron energy in a parallel-plate ECD supplied with a constant voltage of 10 V, for argon–10% methane (curve 1) and nitrogen (curve 2) as carrier gases. Curve 3 shows the electron energy of the same detector with a pulsed supply of ratio $t_i/t_r = 10^{-2}$ for argon–10% methane and nitrogen as carrier gases. On the abscissa the relative position at which the electron energy was calculated (x) is given.

energy for a detector supplied with a pulsed voltage where the ratio $t_i/t_r = 10^{-2}$, for argon-10% methane as the carrier gas. With nitrogen as the carrier gas, a curve identical with curve 3 is obtained.

Fig. 5 shows the change in the average electron energy in the cylindrical detector at various distances from the detector anode. Curve 1 represents argon-10% methane and curve 2 nitrogen as the carrier gas. In both instances the detector was supplied with a constant voltage of 10 V. Curves 3 and 4 also represent argon-10% methane and nitrogen respectively, as the carrier gas, for a detector supplied with a pulsed voltage with $t_i/t_r = 10^{-2}$. The broken straight line in Fig. 5 represents the thermal energy level ($3/2 kT$).

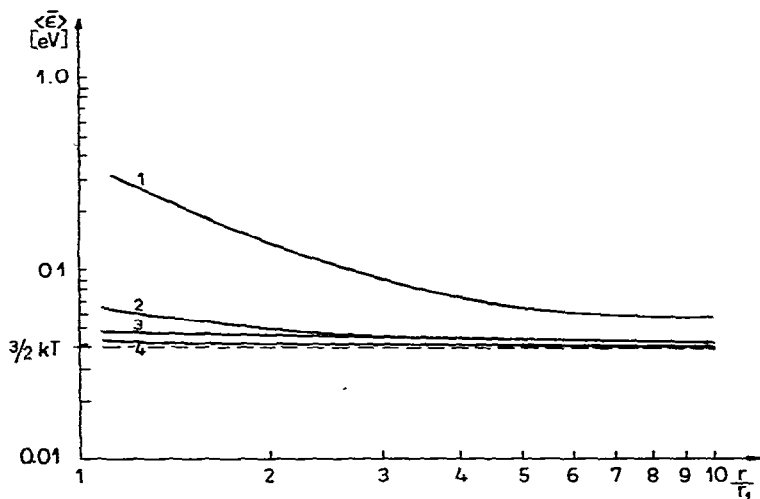


Fig. 5. Changes in the average electron energy along the radius r between the collector electrode and the radioactive source. Detector electrode dimensions as in Fig. 2. Curves: 1, argon-10% methane, detector supplied with a constant voltage $U = 10$ V; 2, nitrogen, $U = 10$ V; 3, argon-10% methane, pulsed supply of $t_i/t_r = 10^{-2}$; 4, nitrogen, pulsed supply of $t_i/t_r = 10^{-2}$. Broken curve 5 = level of thermal energy ($3/2 kT$) for $T = 298$ °K.

CONCLUSIONS

(1) In the range of supply voltages used with ECDs in gas chromatography, transition from a constant voltage to a pulsed supply leads to a decrease in the average electron energy to the energy of thermal motion ($3/2 kT$). This energy is maintained in the whole detector volume for repetition times $t_r > 100$ μ sec, as shown in Figs. 4 and 5, independent of whether the detector has parallel or cylindrical geometry.

(2) For repetition periods of supply pulses larger than 100 μ sec, the influence of the content of molecules stabilizing the electron energy is not large (*cf.*, Fig. 1).

(3) The reason for the constant value of the average electron energy over the period t_r (eqn. 7) for $t_r > 100$ μ sec is that the electron energy distribution $f(\epsilon)$ is also constant. Therefore, the electron-capture constant, k_1 , for compounds in which the resonance capture energy lies in the vicinity of the thermal energy, and defined as⁹

$$k_1 = \left(\frac{2}{m}\right)^{1/2} \cdot \int_0^{\infty} \varepsilon^{1/2} \cdot \sigma_w(\varepsilon) \cdot f(\varepsilon) d\varepsilon \quad (10)$$

where $\sigma_w(\varepsilon)$ is the cross-section for the capture of an electron with energy ε for a given compound and $f(\varepsilon)$ is the electron energy distribution, should be independent of t_r and of the proportion of stabilizer in the admixture.

(4) Adjustment of the average energy of electrons in the detector to the resonance capture energy for the compound being analysed is possible by changing the detector temperature rather than the parameters of the supplying pulses.

(5) The observed influence of the length of the repetition period on the sensitivity of the ECD supports our results.

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