OPTIMUM CONDITIONS IN CONSTANT-FREQUENCY ELECTRON-CAPTURE DETECTION

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SUMMARY

The equations describing the dependence of sensitivity, linearity and minimum detectable concentration of an electron-capture detector working in the constant-frequency mode on pulse period t_p were derived, on the basis of the Wentworth kinetic model. The dependence of the optimum supply parameter, $k_D t_p$, on the standardized sample concentration, $x = k_1 c/k_D$, was calculated and presented graphically. Predictions and calculations were verified experimentally for sulphur hexafluoride.

INTRODUCTION

Since the introduction of the electron-capture detector (ECD) into laboratory practice, there have been many reports relating to theory and analytical applications. However, less attention has been paid to deriving from existing theories conclusions that could be helpful in analytical work, in particular the dependence of fundamental detector parameters such as sensitivity, linearity and minimum detectable concentration on the supply parameter. In the d.c. mode of operation it is commonly accepted that the detector response achieves its maximum value at a certain voltage[1,2] and this phenomenon has also been observed in the constant-frequency system[3-5]. Only a few workers, however, have attempted to determine the requirements under which it appears. Śliwka et al.[6], in their work on the coulometric ECD, presented a simplified solution of the Lovelock stirred reactor model and obtained an expression for the optimum pulse period in the form

$$t_{p(opt)} = \frac{k_3 t_i}{[k_D(k_D + k_1 c)]^{1/2}}$$ (1)

where k_D = pseudo-recombination rate constant (sec^{-1}); t_i = pulse width (μsec); k_1 = electron-capture rate constant (l/mole · sec); c = sample concentration in the detector (mole/l); k_3 = rate constant for the collection of electrons by the incoming pulse voltage (sec^{-1}).

For small samples, *i.e.*, $c \to 0$, eqn. 1 takes form

$$k_D t_{p(opt)} = k_3 t_i$$ (2)

When taking into consideration the assumption of limiting $k_3 t_i$ to values less than 1, one finds out that for $c \to 0$, $k_D t_{p(opt)}$ should be less than 1. Unfortunately, the equation for a detector current given by Śliwka et al.[6] does not make possible the determination of k_3 or k_D directly from the basic detector characteristic, i.e., from the dependence of the detector current in a sample free mode, I_b, on the pulse period, t_p. The method proposed for the calculation of k_3 and k_D requires the execution of a whole series of measurements and a knowledge of k_1. Connor[7], in a paper on the theory and practice of the ECD, also considered the existence of the optimum pulse period of the voltage pulses supplying the detector and arrived at the conclusion that for small samples $k_D t_{p(opt)} = 1.79$.

Performance parameters of the ECD

As a starting point for the following consideration we accepted the equation for the concentration of the electrons in a detector in the absence of capturing species[6], [b], given by Wentworth et al.[8] in the form

$$[b] = \frac{k_p R_\beta}{k_D} [1 - \exp(-k_D t_p)] \tag{3}$$

where $k_p R_\beta$ = rate of production of the ion–electron pairs in the detector (mole/l · sec).

When there are sample molecules entering the detector and, consequently, taking part in the electron-capture reaction with the electrons present, the process is accompanied by a reduction in the detector current and thus the concentration of electrons reaches the value

$$[e^-] = \frac{k_p R_\beta}{k_D + k_1 c} \{1 - \exp[-(k_D + k_1 c)t_p]\} \tag{4}$$

The detector response can be defined as the difference between the detector current in the absence of capturing species and the current when there are some capturing species in the carrier gas:

$$R = \frac{NqV}{t_p} \cdot \Delta[e^-] = NqV \frac{[b] - [e^-]}{t_p}$$

$$= \frac{NqV k_p R_\beta}{k_D t_p} \left\{ 1 - \exp(-k_D t_p) - k_D \cdot \frac{1 - \exp[-(k_D + k_1 c)t_p]}{k_D + k_1 c} \right\} \tag{5}$$

where N = Avogadro's number (6.0248 · 10^{23} molecules/mole); q = electron charge (1.603 · 10^{-19} C); V = detector volume (l).

If we let $x = k_1 c / k_D$ and introduce x into eqn. 5, we obtain

$$R = \frac{NqV k_p R_\beta}{k_D t_p} \left\{ 1 - \exp(-k_D t_p) - \frac{1 - \exp[-(1 + x)k_D t_p]}{1 + x} \right\} \tag{6}$$
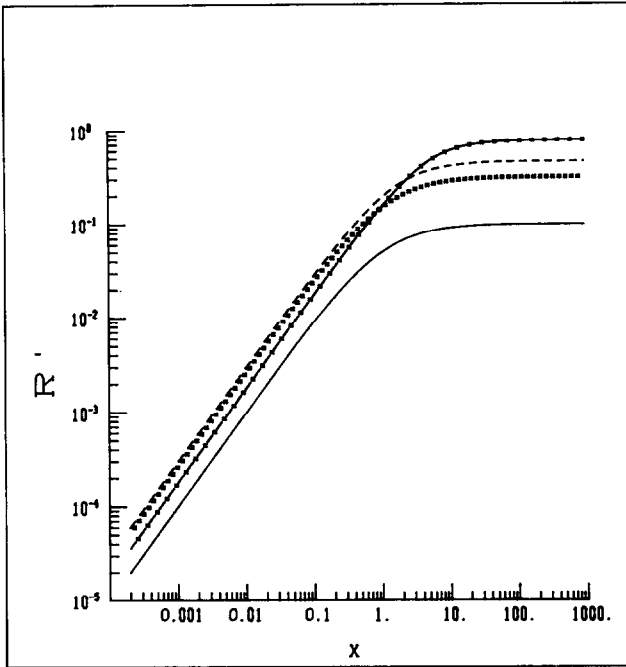
Fig. 1. Standardized ECD response, R', *versus* standardized sample concentration, x, for different values of the supply parameter, $k_D t_p$: × – ×, 0.5; - - - - - -, 1.8; × × ×, 3.0; ———, 10.0.

The detector response, R, can be related to the maximum detector current, $I_0 = NqVk_pR_\beta$, by

$$R' = \frac{R}{I_0} = \frac{1}{k_D t_p} \left\{ 1 - \exp(-k_D t_p) - \frac{1 - \exp[-(1 + x)k_D t_p]}{1 + x} \right\} \tag{7}$$

The plot of eqn. 7 is shown in Fig. 1. All calculations and figures appearing in this paper were executed with help of the Cyber 70 computer library.

As can be seen from Fig. 1, both the course and the shape of the function depend significantly on $k_D t_p$. This graph, being in fact a standardized calibration curve of the ECD, can serve as the basis for the determination of the fundamental detector performance parameters. R' vs. $k_D t_p$ at certain values of x is presented in Fig. 2. This plot reveals that the maximum response occurs at certain values of $k_D t_p$. It can also be clearly seen that the optimum value of $k_D t_p$ depends on x. Fig. 3 shows this dependence for a wide range of x values. From Fig. 3 it follows that $k_D t_{p(opt)}$ tends to 1.79 for small samples, which is in agreement with Connor's findings. For x greater than 200, $k_D t_{p(opt)}$ remains constant at 0.1. The detector sensitivity, S, can be defined as $S = dR/dc$. Appropriate differentiation of eqn. 5 gives

$$S = \frac{NqVk_pR_\beta k_1}{k_D^2 t_p} \cdot \frac{1 - [1 + (1 + x)k_D t_p]\exp[-(1 + x)k_D t_p]}{(1 + x)^2} \tag{8}$$
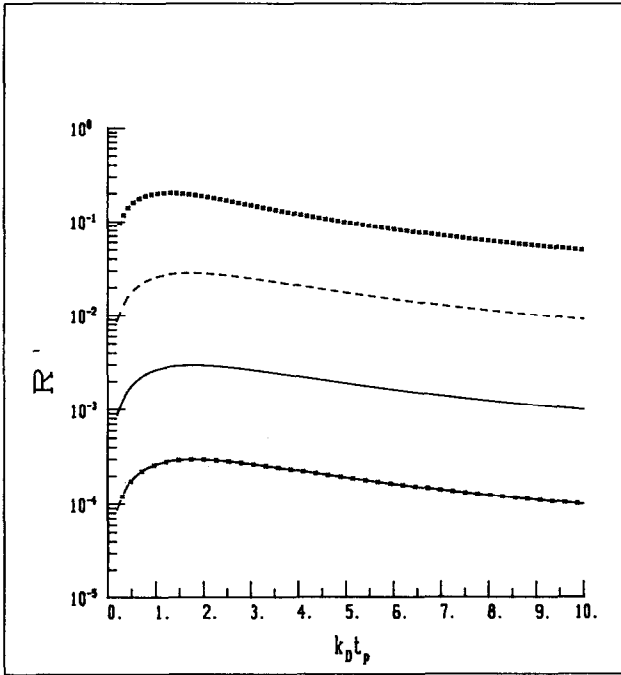
Fig. 2. Standardized ECD response, R', *versus* supply parameter, $k_D t_p$, for different values of standardized sample concentration, x: $\times - \times$, 10^{-3}; ———, 10^{-2}; --------, 10^{-1}; $\times \times \times$, 10^0.
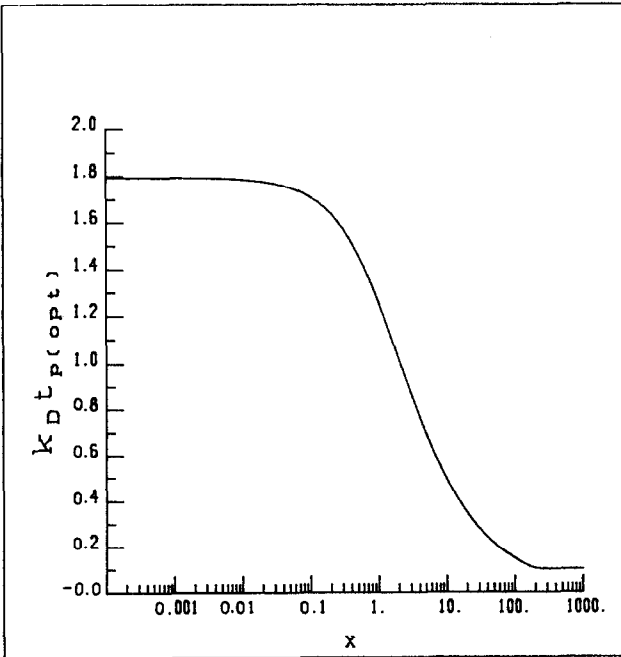

Fig. 3. Optimum supply parameter, $k_D t_p$, *versus* standardized sample concentration, x.

If we substitute 1.79 for $k_D t_p$ in eqn. 8 and consider a small sample, we obtain for the maximum value of S

$$S_{max} = 0.298 \cdot \frac{k_p R_\beta N q V k_1}{k_D} \tag{9}$$

When applying a standardization procedure similar to that used with R', we find that

$$S' = \frac{S k_D}{k_p R_\beta N q V k_1} = \frac{1 - [1 + (1 + x)k_D t_p]\exp[-(1 + x)k_D t_p]}{k_D t_p (1 + x)^2} \tag{10}$$

Figs. 4 and 5 illustrate the dependence of S' on x and $k_D t_p$, respectively.

The minimum detectable concentration (MDC) is usually defined as the concentration of a sample that causes the generation of a detector response R equal to twice the noise current $2I_n$. Fig. 6 represents the dependence of the standardized MDC, *i.e.*, x_{min}, on the supply parameter $k_D t_p$ for different values of $2I_n/I_0$. Fig. 6 is a graphical representation of the non-linear equation $R = 2I_n$, which was solved for different values of $k_D t_p$ in the range 0–10 and for three arbitrarily chosen $2I_n/I_0$ values showing typical ECD conditions. As shown in Fig. 6, any change in $2I_n/I_0$ leads to a corresponding proportional change in x_{min}. It can be noted that despite the wide range of variability of x_{min} the optimum value of $k_D t_p$ remains constant according to Fig. 3.
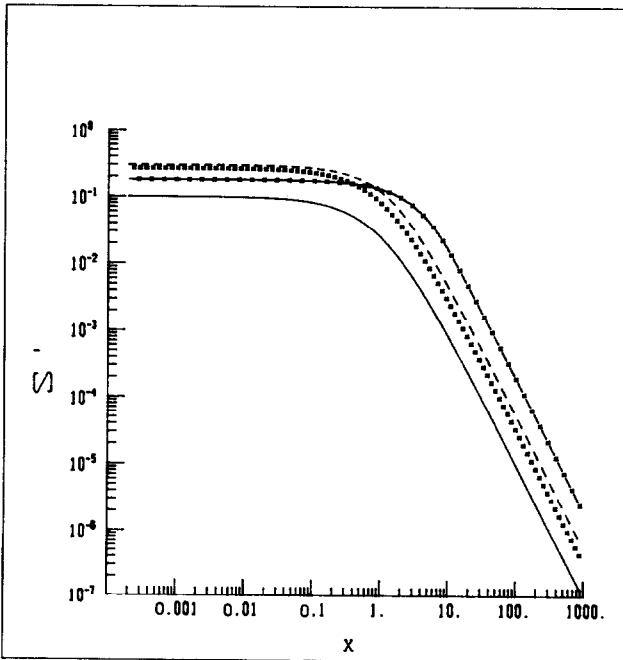

Fig. 4. Standardized ECD sensitivity, S', *versus* standardized sample concentration, x, for $k_D t_p$ values as in Fig. 1.
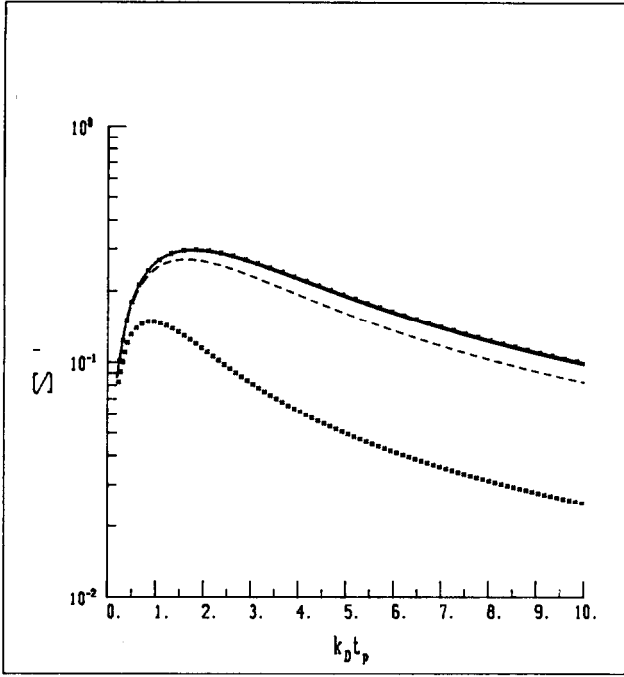
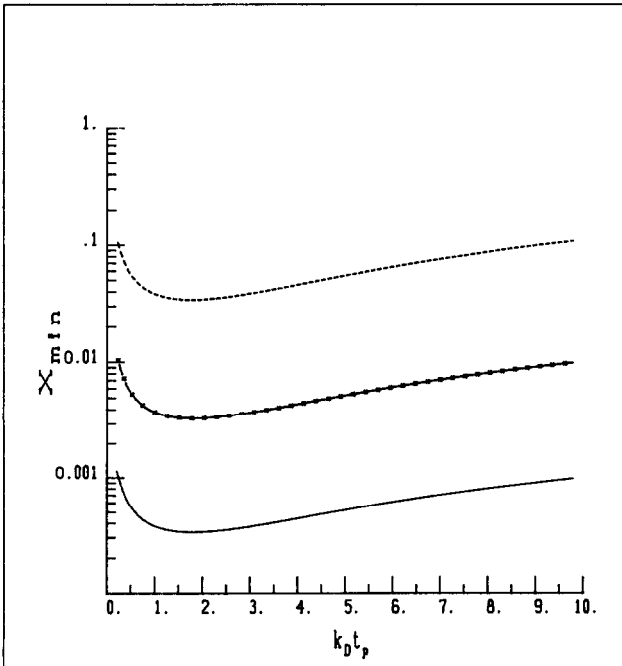Fig. 5. Standardized ECD sensitivity, S', *versus* supply parameter, $k_D t_p$, for x values as in Fig. 2.

Fig. 6. Standardized minimum detectable concentration, x_{min}, *versus* supply parameter, $k_D t_p$, for the following values of $2I_n/I_0$: ———, 10^{-4}; $\times$–$\times$, 10^{-3}; ---------, 10^{-2}.

There is, in fact, a certain ambiguity in the determination of x_{max}, *i.e.*, the maximum concentration of the sample that can be detected without a significant decrease in linearity. An alternative approach to the problem seems possible. One can take for x_{max} a concentration of sample that causes a deviation from linearity not greater than 5%[5]. One can also assume that the ECD system works linearly at a concentration of the sample that leads to a reduction in the detector current not exceeding 30% of the current measured in the absence of capturing species[9]. In the following considerations the alternative approach was adopted. The dependence of x_{max} on k_Dt_p for three $2I_n/I_0$ values is presented in Fig. 7. Values of x_{max} were obtained by solving the non-linear equation $S(x_{max}) = 0.95 \, S(x_{min})$ for three given $2I_n/I_0$ values. If by any chance x_{max} calculated by the procedure given above appeared to be greater than the x value corresponding to a 30% reduction in the standing current, calculations for greater values of k_Dt_p were not made and the last x value was taken as x_{max}. With all the k_Dt_p and $2I_n/I_0$ values used in calculations of x_{max}, the second part of the calculation procedure has never been used. As can be seen from Fig. 7, the x_{max} values are not as sensitive to the change in $2I_n/I_0$ as are the corresponding x_{min} values.

The linear range of the detector, LR, can be defined as the ratio x_{max}/x_{min}. The LR values calculated in this way are represented in Fig. 8. As with x_{min}, the linear range depends significantly on $2I_n/I_0$ and decreases monotonically along the k_Dt_p axis. Of the three parameters essential in determining the performance of the ECD system, only sensitivity and minimum detectable concentration can take maximum
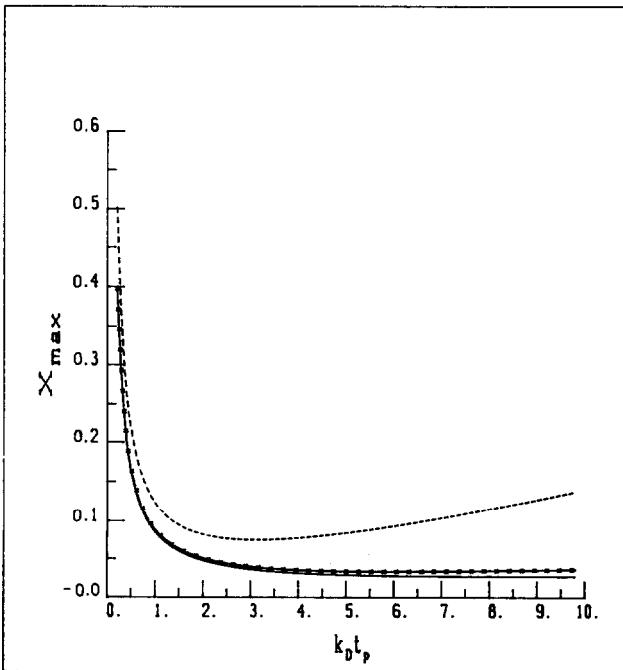

Fig. 7. Standardized maximum concentration, x_{max}, *versus* supply parameter, k_Dt_p, for $2I_n/I_0$ values as in Fig. 6.
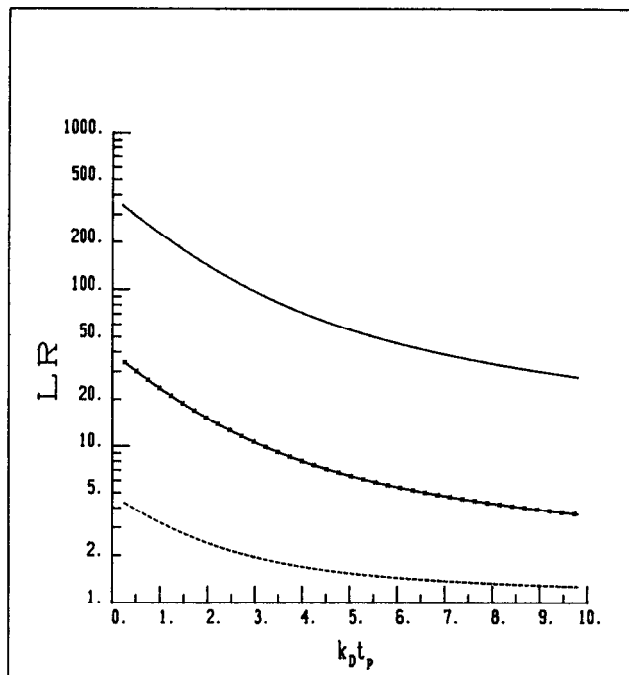
Fig. 8. Linear range of the ECD *versus* supply parameter, $k_D t_p$, for $2I_n/I_0$ values as in Fig. 6.

values depending on the supply parameter $k_D t_p$. As can be seen from Fig. 6, x_{min} is strongly dependent on $2I_n/I_0$, which implies that the last value should be measured prior to the preliminary set of the optimum pulse conditions. This value can seriously affect the choice of the appropriate pulse period.

EXPERIMENTAL

Apparatus

A sulphur hexafluoride (SF_6) analyser equipped with an ECD operating at 473°K connected to a stainless-steel chromatographic column (1.5 m × 4 mm I.D.) filled with silica gel and operating at room temperature was used. The SF_6 analyser and the ECD itself were constructed in our laboratory. The ECD was of a cylindrical geometry, equipped with ^{63}Ni ionization source with an activity of 10 mCi. The carrier gas was purified nitrogen (oxygen content less than 5 ppm), which was additionally purified using a two-stage filter filled with molecular sieve 5Å and active carbon (Merck). The pulse voltage generator used for the measurements was also built in our laboratory and had the following parameters: pulse amplitude, 50 V; pulse period range, 10–10,000 μsec; and pulse width range, 1–100 μsec. A pulse width of 9 μsec appeared to be sufficient to ensure the collection of all the electrons present in the detector. For the measurement of the detector current an electrometer from an N-504 chromatograph (Mera-Elmat, Poland) was employed. The measurement results were recorded on a TZ-4100 recorder (Laboratorni Pristroje, Czechoslovakia). SF_6 was supplied by Merck-Schuchard with a specified purity of 99.7%.

Procedure

Samples with different concentration of SF_6 in nitrogen were prepared in 2-1 stainless-steel bottles by the static dilution method. Mixtures were prepared just before the measurements. On-column injections were made with help of a six-way injector (Valco, U.S.A.). Approximately 1 cm^3 of the sample was injected several times in order to minimize the standard deviation of the detector response. The range of concentration covered in the measurements was 2–200 ppb (v/v) of SF_6 in nitrogen.

RESULTS AND DISCUSSION

Values of the rate constants k_D and $k_p R_\beta$ were determined according to the procedure proposed by Wentworth *et al.*[10]. Just before each measurement the characteristic function of the ECD, *i.e.*, $I = f(t_p)$, was measured and corresponding electron concentration values *vs.* $k_D t_p$ were plotted, as shown in Fig. 9 (solid line). The value of $k_p R_\beta$ was calculated as the slope of this plot at $t_p \rightarrow 0$, *i.e.*, $k_p R_\beta = (db/dt_p)_{t_p \rightarrow 0}$, whereas k_D was calculated as $b_{max}/k_p R_\beta$. The dashed line was used in order to plot eqn. 3 with k_D and $k_p R_\beta$ determined from the experimental curve (solid line). The maximum concentration of thermal electrons, b_{max}, was determined at $t_p = 10,240$ μsec according to the shape of the function as well as Connor's suggestion[6] that a steady state in the electron concentration can be obtained for pulse periods exceeding 5000 μsec.

Mentioned below are some ECD parameters, with their standard deviations,

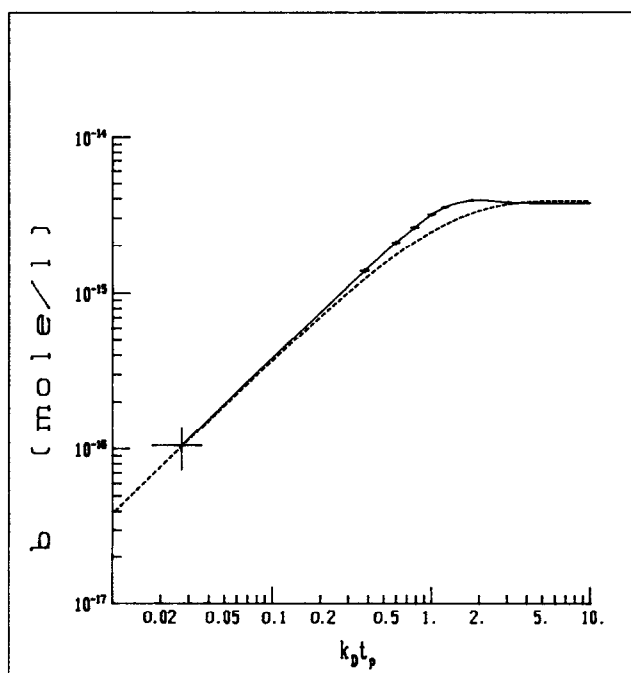Fig. 9. Concentration of electrons in the ECD *versus* supply parameter, $k_D t_p$: ————, experimental curve; --------, eqn. 3. The error bars shown are equal to 2 standard deviations (2σ).
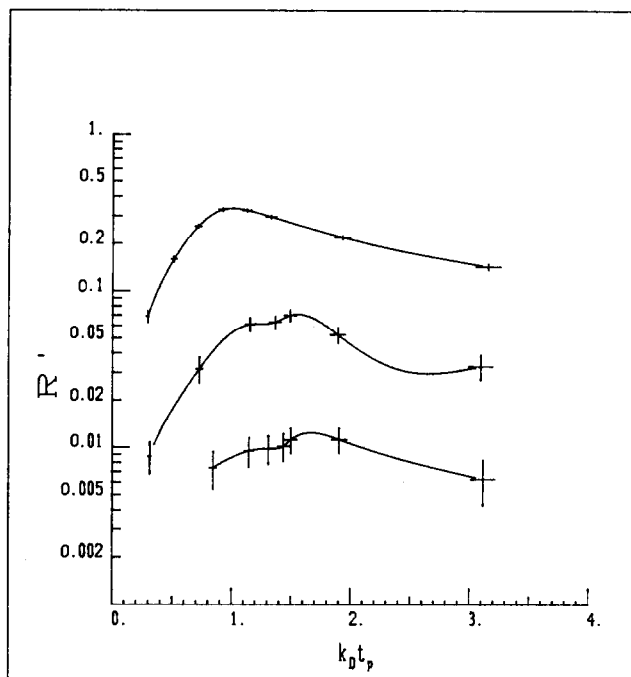
Fig. 10. Standardized ECD response, R', *versus* supply parameter, $k_D t_p$, for SF_6 concentrations of 2.2 · 10^{-16}, 2.4 · 10^{-15} and 2.1 · 10^{-14} mole/l with increasing order of R' values. The error bars shown are equal to 2σ, except for the lowest SF_6 concentration, when only 1σ was plotted.

which illustrate the variations with time during 14 days of a measurement run. All the errors given are equal to 2 standard deviations:

(i) rate of production of ion–electron pairs in a detector: $k_p R_\beta = (1.05 \pm 0.45)$ · 10^{-11} mole/l · sec;

(ii) maximum detector current: $I_0 = (1.0 \pm 0.1) \cdot 10^{-9}$ A;

(iii) noise current: $I_n = (1.20 \pm 0.17) \cdot 10^{-12}$ A;

(iv) pseudo-recombination rate constant: $k_D = (2813 \pm 291)sec^{-1}$;

(v) maximum concentration of the electrons: $b_{max} = (3.76 \pm 0.37) \cdot 10^{-15}$ mole/l;

(vi) carrier gas flow-rate: $u_{N_2} = (37.85 \pm 2.20)$ ml/min.

The dependence of the standardized detector response, R', for SF_6 on the supply parameter, $k_D t_p$, for three chosen concentration values is shown in Fig. 10. When comparing Figs. 10 and 2, one can observe that the optimum values of $k_D t_{p(opt)}$ for given value of the sample concentration are in the range 1–2, which corresponds well with earlier findings, except for curve 3 for the smallest sample concentration, which is probably due to the very high standard deviation of the detector response at low concentrations. The dependence of the optimum supply parameter on the ratio of the sample concentration to the pseudo-recombination rate constant, c/k_D, is plotted in Fig. 11. The course of the curve in Fig. 11 is slightly different from the calculated curve presented in Fig. 3, but it is still possible to notice that when c/k_D decreases the optimum supply parameter $k_D t_p$ approaches the predicted value of 1.79.
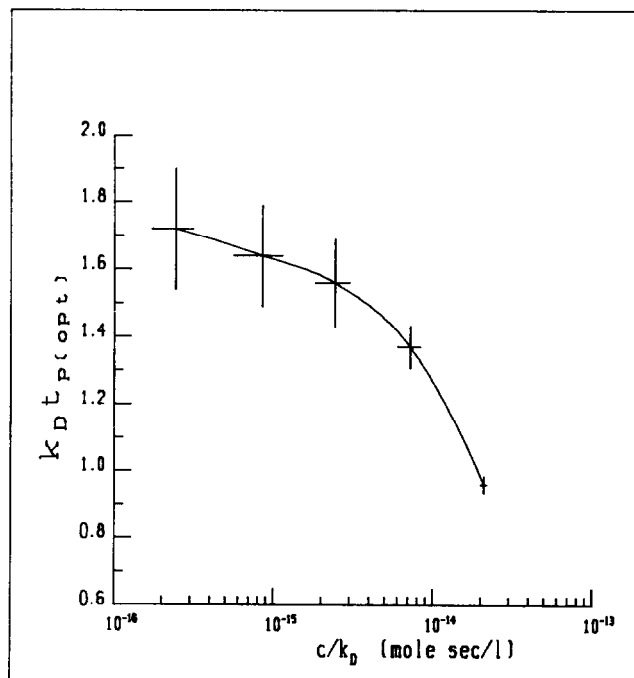
Fig. 11. Optimum supply parameter, $k_D t_{p(opt)}$, *versus* sample concentration standardized to k_D value, *i.e.*, c/k_D. Error bars as in Fig. 10.

Standardized response values, R', for different c/k_D values and three arbitrarily chosen values of $k_D t_p$ are presented in Table I. These values served as a basis for Fig. 12, which shows graphically the function $R' = f(c/k_D)$. It may be interesting to have an estimate of the electron-capture rate constant k_1, as one can draw a comparison between the predicted and obtained values for either the optimum supply parameter

TABLE I

STANDARDIZED ECD RESPONSE, R', AND PRINCIPLE CHARACTERISTICS OF THE ECD FOR SF_6

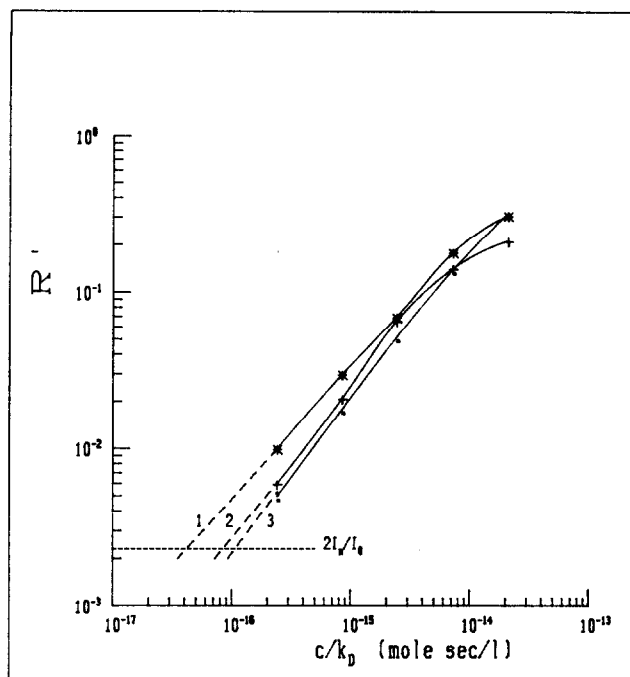| c/k_D (mole · sec/l)	Parameter	$k_D t_p$		
		0.5	1.8	3.0
$2.09 \cdot 10^{-14}$	R'	0.320	0.310	0.212
$7.20 \cdot 10^{-15}$	R'	0.140	0.180	0.142
$2.42 \cdot 10^{-15}$	R'	0.052	0.070	0.066
$8.50 \cdot 10^{-16}$	R'	0.018	0.030	0.021
$2.43 \cdot 10^{-16}$	R'	0.005	0.010	0.006
—	$(c/k_D)_{min}$ (mole · sec/l)	$1.21 \cdot 10^{-16}$	$4.52 \cdot 10^{-17}$	$8.47 \cdot 10^{-17}$
—	$(c/k_D)_{max}$ (mole · sec/l)	$2.53 \cdot 10^{-15}$	$6.50 \cdot 10^{-16}$	$6.93 \cdot 10^{-16}$
—	LR	21.0	14.4	8.2

Fig. 12. Standardized ECD response, R', for SF_6 *versus* c/k_D for different values of supply parameter $k_D t_p$: (1) 1.8; (2) 3.0; (3) 0.5.

$k_D t_p$, or the standardized response of the ECD. An appropriate fitting procedure gives for SF_6 a value of $k_1 = (1.87 \pm 0.53) \cdot 10^{14}$ l/mole · sec or $(3.10 \pm 0.98) \cdot 10^{-7}$ cm^3/sec · molecule, which seems to be in reasonable agreement with the value given by Christophorou *et al.*[11] of $k_1 = 2.7 \cdot 10^{-7}$ cm^3/sec, obtained by the electron swarm method ($T = 300°K$).

Table I also contains the experimentally determined values of the standardized minimum and maximum sample concentrations, $(c/k_D)_{min}$ and $(c/k_D)_{max}$, and the linearity range, LR.

CONCLUSIONS

The theoretical characteristics of the electron-capture detector calculated on the basis of the Wentworth equation were found to be in good agreement with the experimental results for SF_6. The procedure presented enables us to choose the optimum pulse period of the pulses supplying the ECD, with the k_D value determined as proposed by Wentworth *et al.* The optimum pulse period, $t_{p(opt)}$, depends on the pseudo-recombination rate, k_D on the sample concentration, c, and on the electronegative properties of the sample molecules characterized by k_1. These parameters also influence the minimum detectable concentration, x_{min}, and as the linear range, LR, of the ECD. The detector sensitivity, S, is proportional to the electron-capture rate constant and to the radioactive source activity, expressed by $k_p R_\beta$. The plots of the calculated dependences join all the parameters together and should prove helpful in the application of the ECD in analytical practice.

REFERENCES

1 J. Lasa and A. Korus, Report No. PL/880/74, Institute of Nuclear Physics, Cracow, 1974.
2 R. A. Landowne, *Anal. Chem.*, 42 (1970) 1468.
3 M. E. Morrison and W. H. Corcoran, *Anal. Chem.*, 39 (1967) 255.
4 M. Takeuchi, *Nippon Kagaku Kaishi*, 10 (1976) 1565.
5 J. Rosiek, I. Śliwka and J. Lasa, *J. Chromatogr.*, 137 (1977) 245.
6 I. Śliwka, J. Lasa and J. Rosiek, *J. Chromatogr.*, 172 (1979) 1.
7 J. Connor, *J. Chromatogr.*, 200 (1980) 15.
8 W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, 70 (1966) 445.
9 E. D. Pellizzari, *J. Chromatogr.*, 98 (1974) 323.
10 W. E. Wentworth and E. C. Chen, *J. Chromatogr.*, 186 (1978) 99.
11 L. G. Christophorou, D. L. McCorkle and J. G. Carter, *J. Chem. Phys.*, 54 (1971) 253.