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DESTRUCTIVE AND NON-DESTRUCTIVE MODELS OF THE COULOMETRIC ELECTRON-CAPTURE DETECTOR

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SUMMARY

A description of the operation of the electron-capture detector is proposed, based on destructive and non-destructive models for molecules of investigated compounds which either undergo or do not undergo destruction in the capture process. The equations derived enable one to define conditions that must be fulfilled for the capture efficiency and detection efficiency to reach their maximum values. Using the plots provided, it is possible to determine the source activity, the carrier gas flow-rate, the repetition time of supply pulses and the concentration of investigated molecules that are necessary to achieve coulometric detection. Using the non-destructive model of the electron-capture detector, it is also possible to explain the occurrence of the hypercoulometric effect.

INTRODUCTION

Despite the wide application of the electron-capture detector in chromatography, there are conflicting ideas concerning the basic physical principles of its operation in the literature. A review of up-to-date theoretical descriptions of the electron-capture detector, illustrated with practical effects occurring during the operation of such a detector, was published by Aue and Kapila¹ in 1973.

Theoretical considerations relating the detector signal with the process of electron capture by electronegative molecules, basing on a kinetic model of the detector, were given by Wentworth and co-workers²⁻³; Lovelock⁴ used the model of a flow chemical reactor. The main objects of theoretical studies, apart from seeking a complete description of the physical processes that take place during the operation of the detector, are to lower the detection limit and to increase the dynamic range. As a result of such studies, new methods of using the electron-capture detector were developed, namely the constant ionization current method, described by Maggs *et al.*⁵, which increases the dynamic range of the detector to 10^4 , and the coulometric method,

described by Lovelock *et al.*⁶, with which detection with maximum sensitivity can be achieved.

The coulometric method of detecting electronegative compounds enables one to decrease the detection limit and also eliminates the necessity for calibrating the detector for trace amounts, which is always difficult and sometimes impossible for technical reasons. Operation of the electron-capture detector in the coulometric regime demands that certain conditions be fulfilled, which may not be possible for certain compounds.

The aim of this work was to specify conditions for the appearance of the coulometric effect for the two possible processes of electron capture by the molecule of the investigated compound, namely the destructive process, after which the molecule loses its electronegative properties, and the non-destructive process, in which the molecule, after a certain "lifetime" in the state of a negative ion, remains an electronegative molecule.

BASIC CONDITIONS FOR THE APPEARANCE OF THE COULOMETRIC EFFECT

The following differential equations describe the balance of charge and mass in the electron-capture detector, given by Lovelock⁴ for the model of a flow chemical reactor:

$$\frac{dc}{dt} = \frac{B}{V} - k_1 e c - c \frac{U}{V} \quad (1)$$

$$\frac{de}{dt} = \frac{A}{V} - k_1 e c - e k_d \quad (2)$$

where

- B (molecules/sec) = number of molecules introduced into the detector in unit time;
- A (electrons/sec) = number of electrons generated in the detector in unit time;
- c and e (cm^{-3}) = concentrations of molecules and electrons in the detector, respectively;
- V (cm^3) = detector volume;
- U (cm^3/sec) = carrier gas flow-rate through the detector;
- k_1 (cm^3/sec) = rate constant for the reaction $\text{AB} + e \xrightarrow{k_1} \text{AB}^-$;
- k_d (sec^{-1}) = rate constant for the removal of electrons in processes other than the above.

Coulometric detection is effected when the detector signal, measured in elementary charge units in a given time interval, is equivalent to the number of molecules introduced into the detector during the same period. The detector signal arises as a result of the formation of negative ions in the process of electron capture that takes place between the free electrons and molecules of the investigated compound, of ion recombination and of collection of charges in the pulsed electric field provided by the elec-

trodes. The detector signal is thus determined by the efficiency of the process of electron capture, defined as

$$W = \frac{\text{No. of electrons participating in capture}}{B} = \frac{k_1 e c V}{B} \quad (3)$$

and the detection efficiency, defined as

$$S = \frac{\Delta Q}{N} \quad \text{or} \quad S = \frac{\Delta Q}{BT} \quad (4)$$

where ΔQ is the change of electron charge inside the detector caused by introducing a sample containing $N = BT$ molecules, and T is the repetition time for pulses feeding the detector.

The efficiency of electron capture, W , depends on the correlation between the average energy of electrons in the detector and the energy of resonance capture for the given compound. The detection efficiency takes into account the manner of supplying the detector and of measuring its signal.

Under stationary conditions, when U , A and B remain constant, *i.e.*, $dc/dt = 0$ and $de/dt = 0$, the following dependence can be obtained from eqns. 1 and 2:

$$W = \frac{k_1 e V}{k_1 e V + U} = \frac{1}{1 + \frac{U}{k_1 Q}} \quad (5)$$

The value of W approaches unity if the term $U/(k_1 Q)$ with respect to unity is neglected. This condition is fulfilled for compounds with large k_1 in a detector of large internal charge, $Q = e V$, and for low gas flow-rates, U .

THE DESTRUCTIVE MODEL OF THE ELECTRON-CAPTURE DETECTOR

The assumptions that the investigated molecule takes part in the capture process only once and that the created negative ion on recombination changes the charge inside the detector by one unit are based on the fact that the following processes occur in the detector:



In the above scheme, it is assumed that products of the possible dissociation of the AB^- ion are not electronegative and do not take part in the process of capture in the detector for a second time. Using the definition stated by eqns. 1-3, it is possible

to express the efficiency of an electron-capture detector as a function of several variables in the following form:

$$W = \frac{(A + B) + \frac{k_d}{k_1} \cdot U - \sqrt{(A + B + \frac{k_d}{k_1} \cdot U)^2 - 4AB}}{2B} \quad (9)$$

If we adopt the notation

$$\xi = A/B \quad (10)$$

and

$$\eta = \frac{k_d}{k_1} \cdot \frac{U}{B} \quad (11)$$

eqn. 9 becomes

$$W = \frac{1}{2} [1 + \xi + \eta - \sqrt{(1 + \xi + \eta)^2 - 4\xi}] \quad (12)$$

Eqn. 12 defines the dependence of the electron-capture efficiency, W , as a function of the following variables: $W = f(A, B, k_1, k_d, U)$. It is interesting that W does not depend on the detector volume, V .

RANGE OF VARIABILITY OF PARAMETERS ξ AND η

Table I gives the range of ξ , determined on the basis of assumed values of the ionization current used in modern electron-capture detectors and based on the mass of sample introduced, where the molecular mass of pesticides is assumed to be of the order of 400.

TABLE I
RANGE OF VARIABILITY OF ξ

Current (A)	A (electrons/sec)	Mass of sample (g)	B (molecules/sec)	$\xi = \frac{A}{B}$
10^{-8} – 10^{-9}	$0.625 \cdot 10^{10}$ – $6.25 \cdot 10^{10}$	10^{-9} – 10^{-13}	$5 \cdot 10^{12}$ – $5 \cdot 10^8$	$1.25 \cdot 10^{-2}$ – $1.25 \cdot 10^3$

In order to determine the range of η , k_1 was assumed to lie between 10^{-7} cm³/sec·molecules for pesticides (after Sullivan⁷) and 10^{-12} for oxygen (after Christophorou *et al.*⁸). The values of k_d were taken from Lovelock *et al.*⁶, Van de Wiel and Tommassen⁹ and Lasa *et al.*¹⁰, within the range 10^3 – 10^4 sec⁻¹.

Table II presents the assumed values of the constants k_1 , k_d and U (B taken from Table I) and the calculated range of variability for η .

TABLE II

VALUES OF k_1 , k_d , U AND B AND RANGE OF VARIABILITY OF η

k_1 ($\text{cm}^3/\text{sec. molecules}$)	k_d (sec^{-1})	U (cm^2/sec)	B ($\text{molecules}/\text{sec}$)	η
10^{-7} - 10^{-12}	10^3 - 10^4	0.1-10	$5 \cdot 10^{12}$ - $5 \cdot 10^8$	$2 \cdot 10^{-2}$ - 10^8

RESULTS OF CALCULATIONS OF CAPTURE EFFICIENCY

The theoretically calculated dependence of the capture efficiency, W , on ξ and η for the ranges given in Tables I and II are illustrated in Figs. 1-4. Figs. 2 and 4 concern values of W smaller than unity. Using these plots, it is possible to determine the value of B (and consequently the mass of sample introduced) of a compound with known k_1 for which the capture efficiency is either unity or close to unity, the value of A (detector ionization current) necessary for this purpose and the necessary carrier gas flow-rate, U .

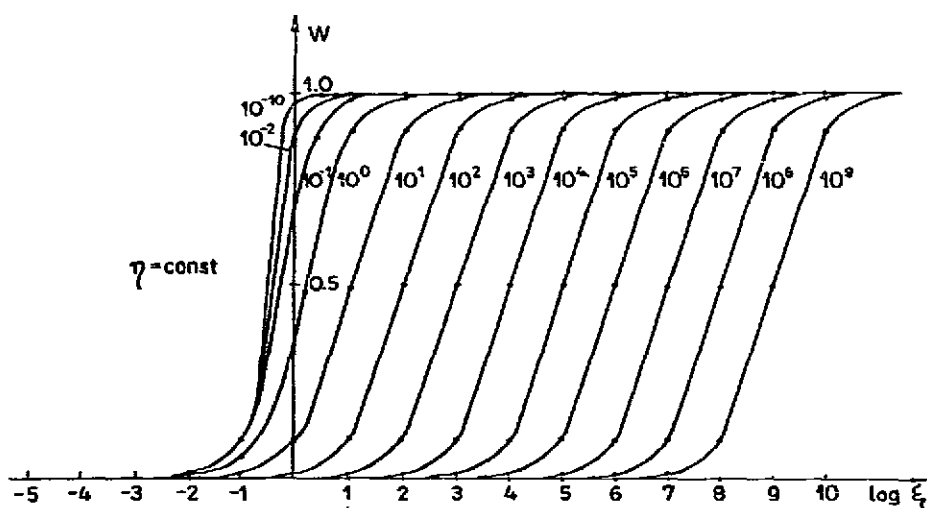


Fig. 1. Dependence of electron-capture efficiency, W , on ξ for constant values of η for the destructive model.

It is also seen from these plots that a compound which undergoes degradation into weakly electronegative fragments in the capture process cannot form ions with an efficiency greater than unity, and even for such a case it is necessary for special conditions with respect to the values of B , A , k_1 , k_d and U to be fulfilled.

DETECTION EFFICIENCY UNDER CONDITIONS OF PULSED VOLTAGE SUPPLY

When the detector is supplied with a pulsed voltage, changes in concentrations of electrons, e , and of electronegative molecules, c , connected with capture occurring

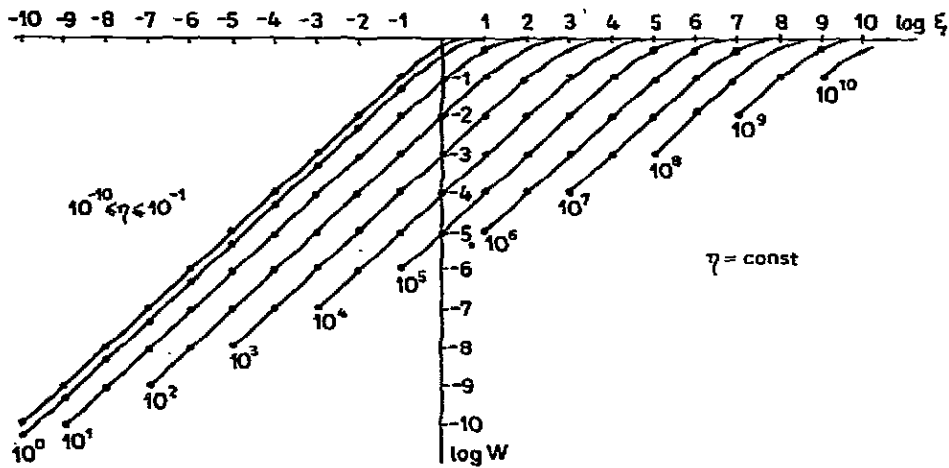


Fig. 2. Dependence of electron-capture efficiency, W , on ξ for constant values of η for the destructive model.

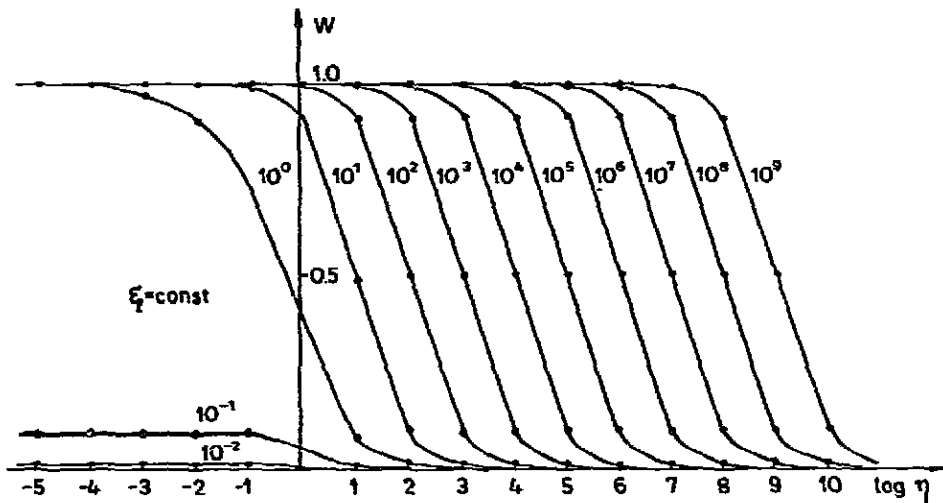


Fig. 3. Dependence of electron-capture efficiency, W , on η for constant values of ξ for the destructive model.

between consecutive pulses are observed, even though A and B remain constant. Assuming that during the voltage pulse all electrons are collected between the electrodes and that a voltage pulse does not change the mean energy of electrons in the detectors, i.e., that k_1 and k_d remain constant, the detection efficiency is given by

$$S = \frac{Q_0(T) - Q_c(T)}{BT} \quad (13)$$

where $Q_0(T)$ is the charge collected without a sample, $Q_c(T)$ is the charge collected with the sample present in the detector and T is the repetition time for pulses feeding the detector.

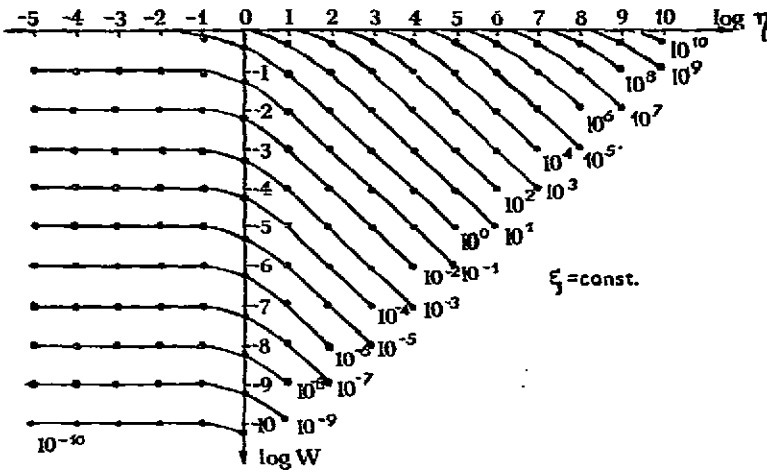


Fig. 4. Dependence of electron-capture efficiency, W , on η for constant values of ξ for the destructive model.

The non-linear eqns. 1 and 2 can be solved numerically, and show that c does not change much within a time period T of the order of several hundred microseconds. Therefore, in order to find an approximate analytical solution of the set of eqns. 1 and 2, the following relationships were used:

$$\bar{e} = \frac{A}{V(k_1 \bar{c} + k_d)} \left\{ 1 - \frac{1}{k_1 \bar{c} + k_d} \left[1 - e^{-(k_1 \bar{c} + k_d)T} \right] \right\} \tag{14}$$

$$e = \frac{A}{V(k_1 \bar{c} + k_d)} \left[1 - e^{-(k_1 \bar{c} + k_d)T} \right] \tag{15}$$

$$\bar{e} = \frac{B - U\bar{c}}{k_1 \bar{c}V} \tag{16}$$

where \bar{e} and \bar{c} are the mean values of e and c over the period T . Solution of the above set of equations leads to

$$S = \xi \left[\frac{1}{k_d T} (1 - e^{-k_d T}) - \frac{1}{x k_d T} (1 - e^{-x k_d T}) \right] \tag{17}$$

and

$$\frac{1}{x k_d T} (1 - e^{-x k_d T}) - 1 - \frac{x}{\xi} \left(\eta - \frac{1}{x-1} \right) = 0 \tag{18}$$

where x is the solution of eqn. 18.

After expanding the exponential term into a power series, eqn. 18 can be solved approximately and the final equation for detection efficiency is then

$$S = \frac{(\xi m - \xi - \eta + 1) + \sqrt{(\xi m - \xi - \eta + 1)^2 + 4 \left(\xi \cdot \frac{k_d T}{2} + \eta \right)}}{2 \left[\xi \cdot \frac{k_d T}{2} + \eta \right]} \tag{19}$$

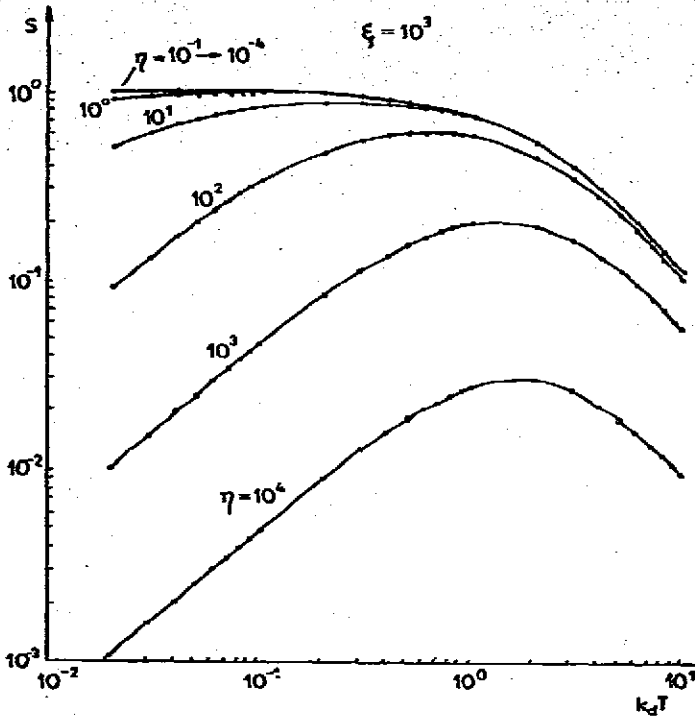


Fig. 5. Dependence of detection efficiency, S , on the supply parameter $k_d T$ for $\xi = 10^3$.

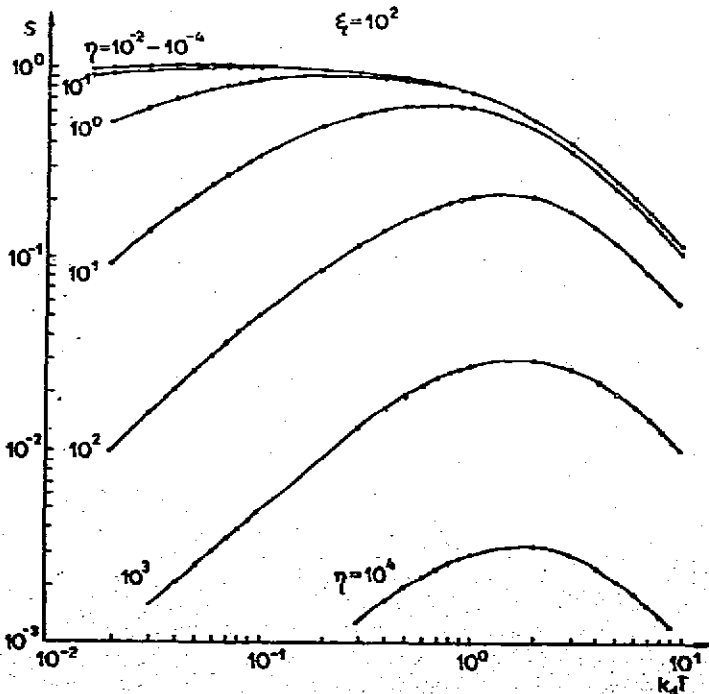


Fig. 6. Dependence of detection efficiency, S , on the supply parameter $k_d T$ for $\xi = 10^2$.

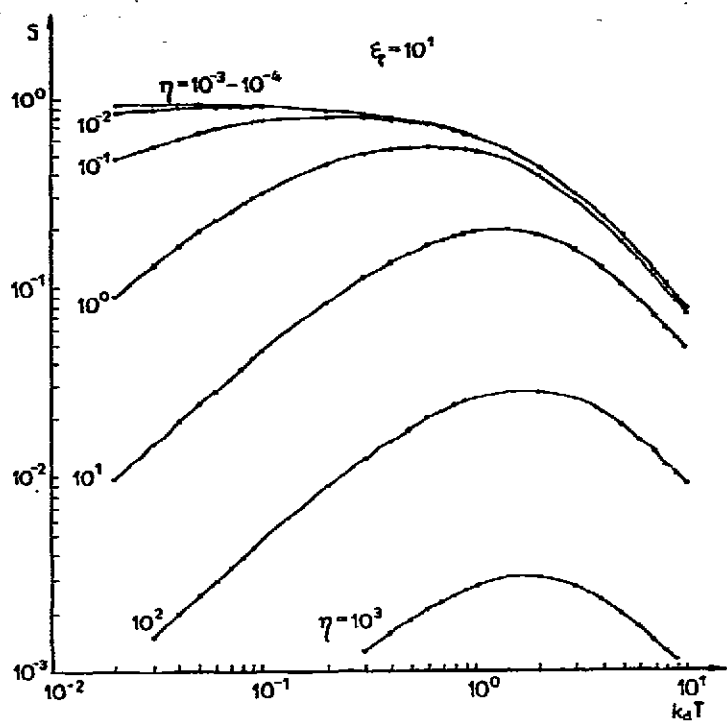


Fig. 7. Dependence of detection efficiency, S , on the supply parameter $k_d T$ for $\xi = 10$.

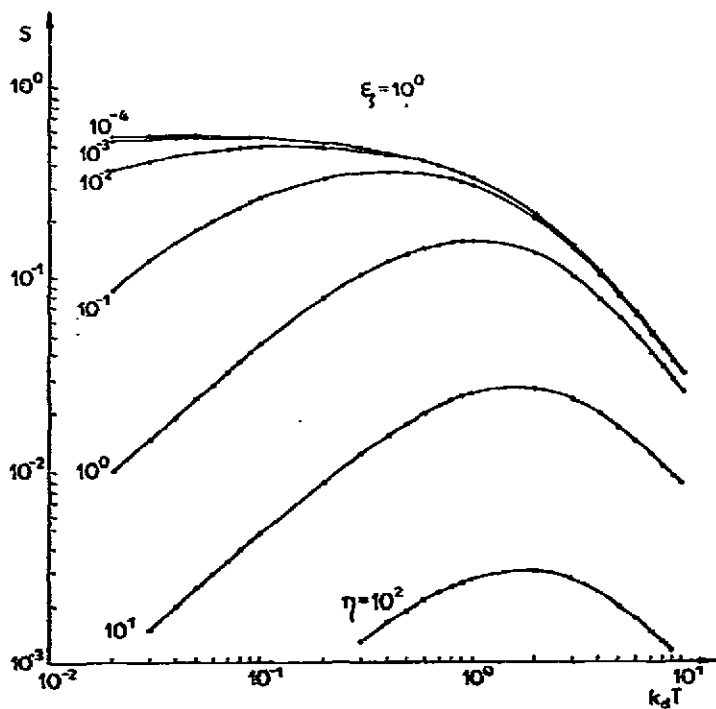


Fig. 8. Dependence of detection efficiency, S , on the supply parameter $k_d T$ for $\xi = 1$.

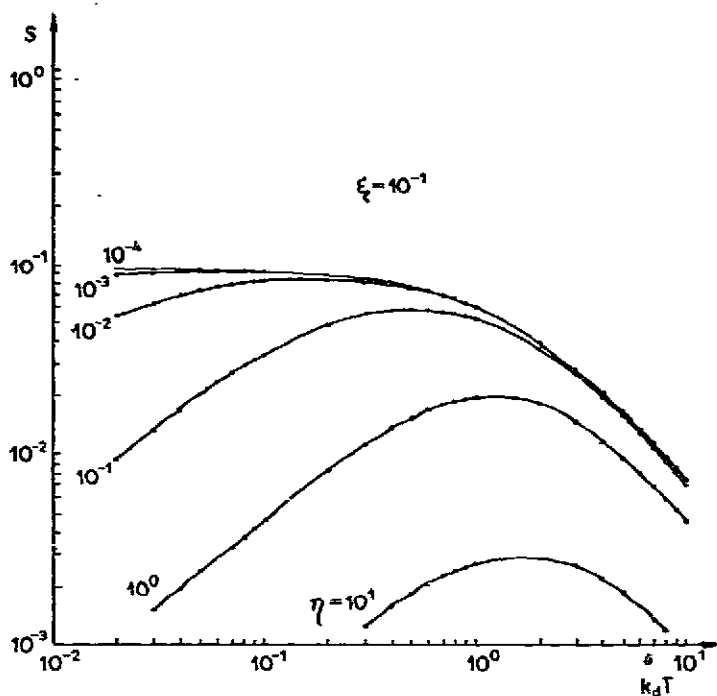


Fig. 9. Dependence of detection efficiency, S , on the supply parameter $k_d T$ for $\xi = 0.1$.

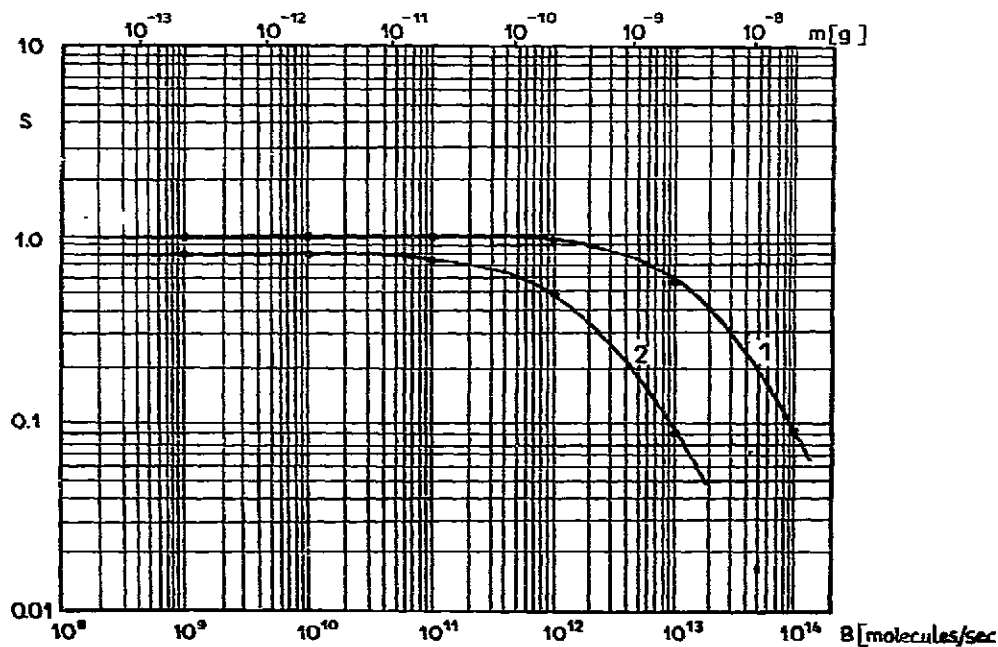


Fig. 10. Dependence of detection efficiency, S , on the number of introduced molecules, B (molecules/sec), or mass of sample, m (g). The following constants were chosen: $k_d T = 0.1$, $k_1 = 5 \cdot 10^{-7}$ (cm³/sec), $U/V = 1$ sec⁻¹. Curve 1, $A = 10^{13}$ electrons/sec, basic detector current = $1.6 \cdot 10^{-8}$ A; curve 2, $A = 10^{12}$ electrons/sec, basic detector current = $1.6 \cdot 10^{-9}$ A.

where $m = (1 - e^{-k_d T}/k_d T)$. S values were calculated for various η , ξ and $k_d T$ values and are presented in Figs. 5-9. Fig. 10 illustrates the dependence of S on the number of molecules introduced, B , (or the corresponding sample mass) for the destructive model of the electron-capture detector.

THE NON-DESTRUCTIVE MODEL OF THE ELECTRON-CAPTURE DETECTOR

Reactions that occur in the detector can be assumed as follows:

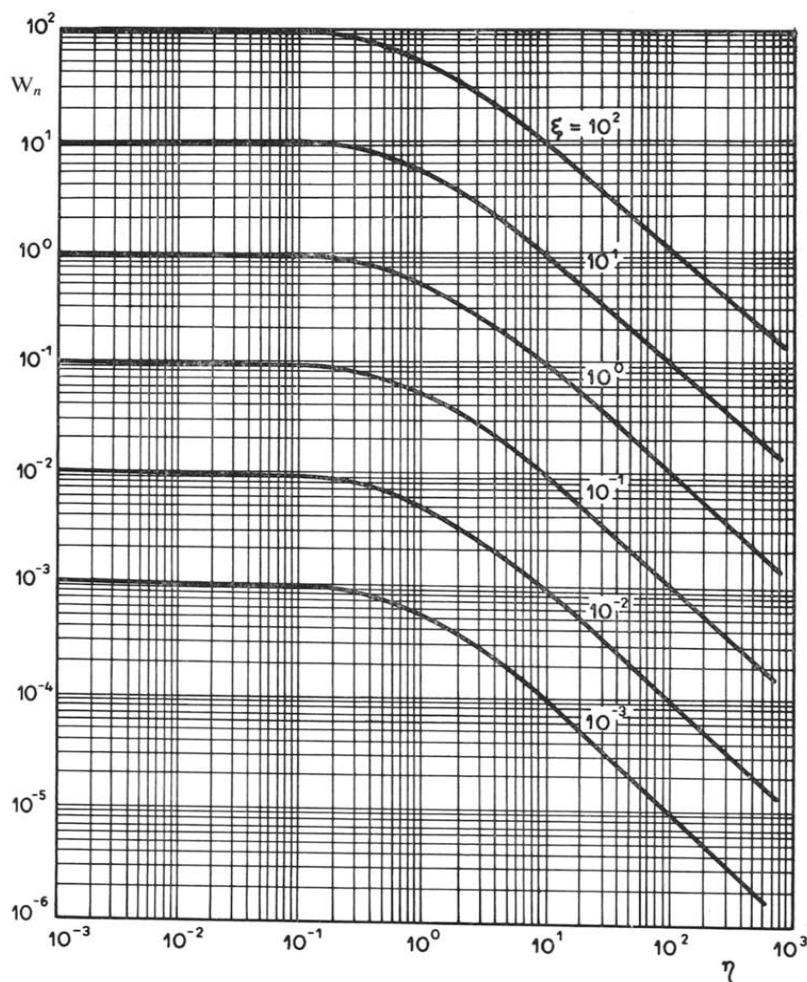
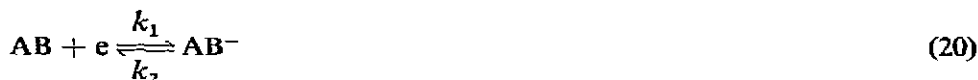


Fig. 11. Dependence of electron-capture efficiency, W_n , on η for constant values of ξ for the non-destructive model.

where X^+ denotes the positive ion. For low concentrations of AB molecules, it can be assumed that $k_1 \gg k_2$, and the process defined by k_2 can therefore be neglected. Assuming moreover that the recombination process in reaction 21 takes place very rapidly, one can postulate that the molecule participates in the capture process during the whole period of its presence in the detector.

With the above assumptions, eqns. 1 and 2 become

$$\frac{dc}{dt} = \frac{B}{V} - c \cdot \frac{U}{V} \quad (22)$$

$$\frac{de}{dt} = \frac{A}{V} - k_1 ec - k_d e \quad (23)$$

For the quiescent state, using the definition contained in eqn. 3 (denotations as before), the capture efficiency of the detector for compounds not undergoing destruction is given by the following equation, which follows from solving eqns. 22 and 23:

$$W_n = \frac{\xi}{1 + \eta} \quad (24)$$

The behaviour of the above dependence for wide ranges of ξ and η is shown in Fig. 11. Fig. 12 illustrates the dependence of the capture efficiency, W_n , on the number of molecules introduced, B .

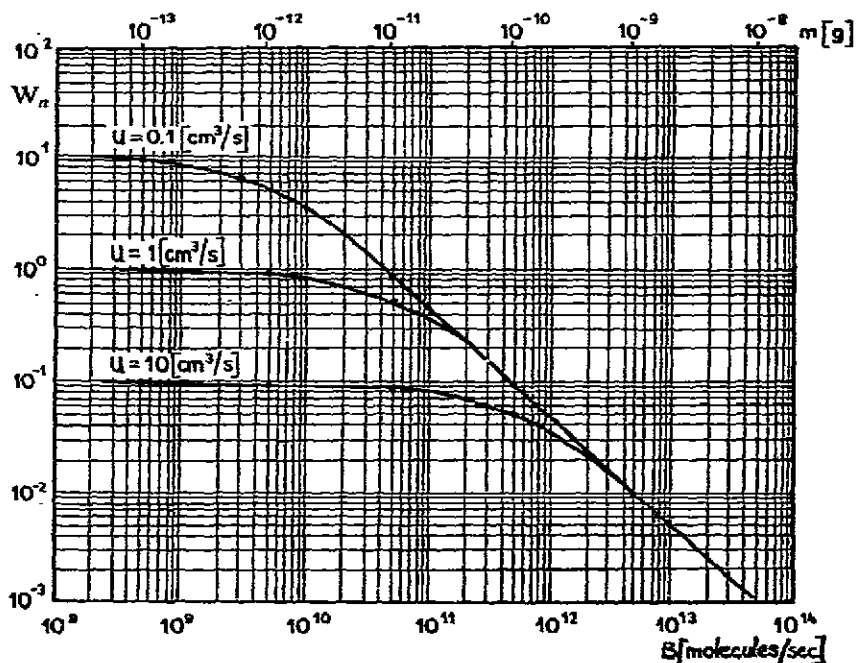


Fig. 12. Dependence of electron-capture efficiency, W_n , on the number of molecules, B (molecules/sec), introduced into the detector, or on the mass of sample, m (g), for constant flow-rates of carrier gas.

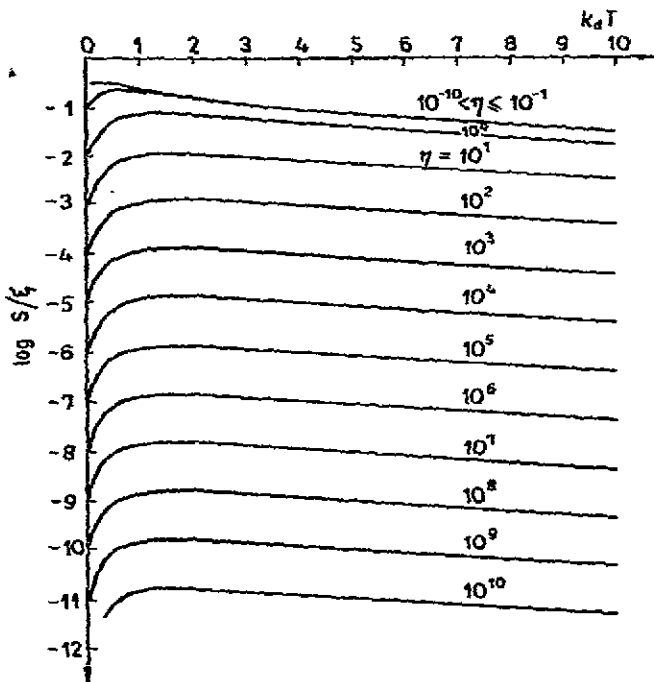


Fig. 13. Dependence of $\log S/\xi$ on the supply parameter $k_d T$ and constant values of η for the non-destructive model.

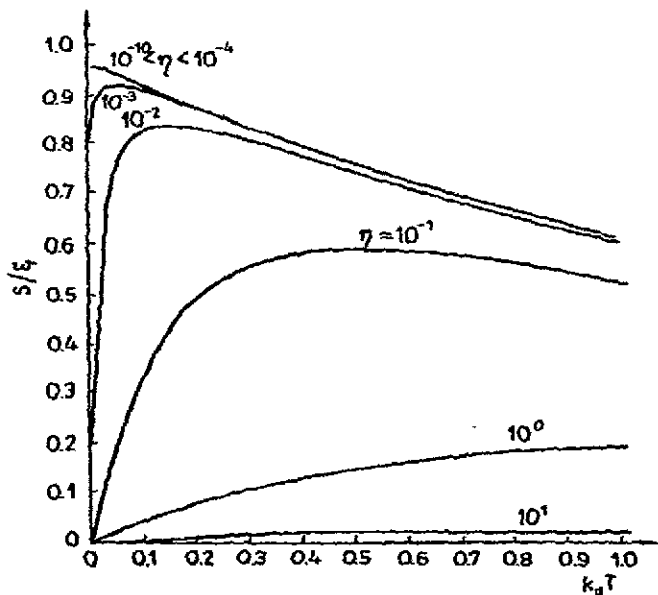


Fig. 14. Dependence of the ratio S/ξ on the supply parameter $k_d T$ and constant values of η for the non-destructive model.

The detection efficiency in the analysis of compounds that do not undergo destruction, taking into account the definition contained in eqn. 4 and using a pulsed voltage supply, is

$$S = \xi \left\{ \frac{1}{k_d T} \left(1 - e^{-k_d T} \right) - \frac{1}{\frac{1 + \eta}{\eta} \cdot k_d T} \left[1 - e^{-\frac{k_d T(1 + \eta)}{\eta}} \right] \right\} \quad (25)$$

Graphical representations of the ratio S/ξ for such a type of detection, as functions of the voltage supply parameter, $k_d T$, and several values of η are presented in Figs. 13 and 14.

CONCLUSIONS

(1) The models of the electron-capture detector presented provide conditions that must be fulfilled for the detection to be of a coulometric character.

(2) When k_d is known for the measuring system and k_1 is known for the investigated compound, it is possible to determine the parameters of pulses supplying the detector and to determine the range of concentrations of the investigated compound for which detection is of a coulometric character.

(3) The model of the non-destructive detector explains the hypercoulometric effect that occurs in electron-capture detectors.

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