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THE ELECTRON-CAPTURE DETECTOR

I. THEORETICAL MODEL

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SUMMARY

The role of positive ions in the electron-capture detector is reviewed in the light of recent evidence. Variations in positive ion concentration cannot be ignored except under limiting conditions not generally employed in practice. Solutions to the equations describing the electron concentrations in the detector are derived and their validity and that of the underlying assumptions is discussed. Comparison is made with results from numerical models. The widely used constant current mode of operation is shown to give non-linear responses to strongly electron-capturing samples and therefore to be inappropriate for quantitative studies.

INTRODUCTION

Since it was first described by Lovelock and Lipsky¹ the electron-capture detector (ECD) has become a major tool of the environmental scientist. It has high sensitivity for the detection of certain classes of compounds, including such important materials as the halocarbons, and has been used to provide the basic data on which such problems as the effects of aerosol propellants on the upper atmosphere and the persistence of insecticides in the environment are assessed. These matters can have far-reaching economic implications and it was, for example, evidence from gas chromatographic (GC)-ECD studies that was very largely responsible for the world-wide discontinuation of the use of DDT. The ECD also finds major applications in civil and military explosives vapour detection equipment and provides forensic scientists with their most sensitive method of detecting traces of explosives following chromatographic separation of field-collected samples.

It is not surprising then to find that there is a voluminous and rapidly growing literature describing the operation and applications of the ECD, but unfortunately this literature is characterised by its confusion. As Aue and Kapila have observed in a recent review² there are many contradictory statements concerning the variation of ECD responses with such basic system parameters as temperature and gas flow-rates. They note that "research on ECD characteristics is largely divided into two areas, one analytical, mundane and of public importance and the other physico-chemical,

esoteric and of special interest. There is little communication between the two —". Little has changed since this statement was made. Too often, theoretical descriptions of the ECD leave unclear the conditions under which they are applicable and thus confuse rather than clarify the issue. Practising chromatographers, finding the theory unhelpful, tend to settle for ECD operating conditions as recommended by manufacturers and fail to optimise performance against the materials of interest to them.

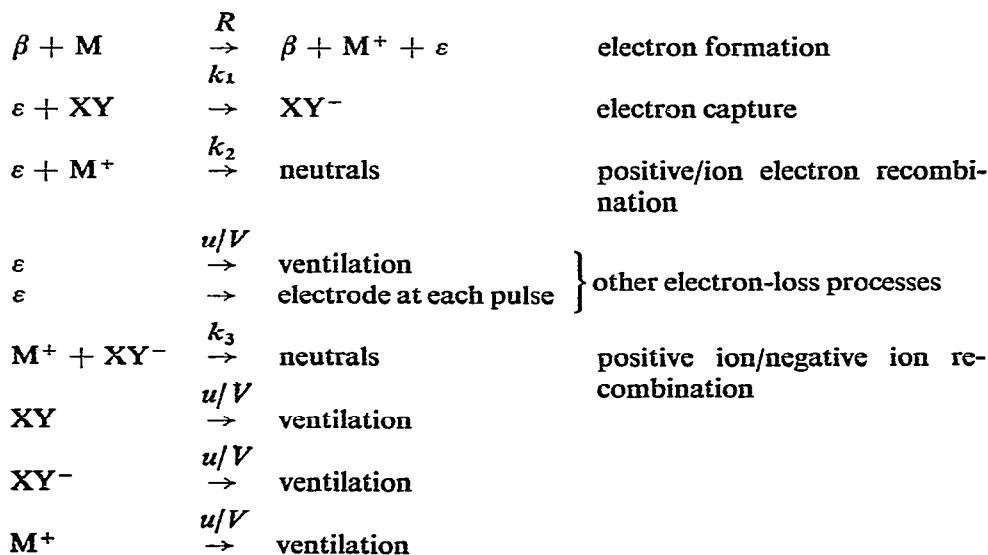
In this report the stirred reactor model of the ECD, and in particular the role of positive ions in that model, will be critically examined. In the light of this examination, solutions to the differential equations describing electron concentration in the ECD will be obtained for certain well defined limiting conditions. The applicability of these solutions to quantitative descriptions of the ECD will be discussed. A subsequent report will discuss detector design and performance.

STIRRED REACTOR MODEL OF THE ECD

The basic model

The ECD can be regarded as a volume, V , into which sample XY flows at a rate BV in a carrier gas of flow-rate u . A radioactive source produces energetic electrons, β , which interact with the carrier gas, M , producing 10^2 – 10^3 thermal electron (ϵ)/positive ion pairs per β particle. The overall rate of electron and positive ion production is RV . The electron, positive ion, negative ion and sample concentrations in the cell are denoted η_e , η_+ , η_- and c , respectively, and at any given time each of these concentrations is assumed to be uniform throughout the detector volume. Periodically a voltage pulse applied to an electrode causes the electrons to be collected but, because of the low mobility of ions relative to electrons, has no effect on the ion populations. The pulse period is denoted t_p , and the pulse width is negligible in comparison.

The current produced by this repetitive collection of electrons is measured and constitutes the detector output. The system can be described by the following set of equations



A glossary of the symbols employed in this report and their definitions is given in Appendix A. The rate constants k_2 and k_3 are controlled largely by coulombic interactions and only to a small extent by details of ionic structure, so that a single value independent of the nature of the ions involved can be assumed for each.

Following Wentworth *et al.*³ the conventional description of the ECD proceeds with the assertion that the positive ion concentration in the detector cell greatly exceeds that of the electrons and can be regarded as a constant. This follows, it is argued, since electrons are being continually removed by the pulse, a loss mechanism which is not available for positive ions. This argument can hold only under conditions where the electrons lost during the pulse represent a significant fraction of the number produced between pulses and it thus breaks down as the pulse period t_p becomes large. It is precisely this long pulse period condition which is assumed in order to solve the differential equations defined by Wentworth *et al.* The argument they present is inconsistent.

An alternative justification for the assertion that positive ions are present in excess argues that electrons are lost more rapidly by diffusion to the walls of the cell than are the much more massive positive ions. Such a mechanism will not be available at short pulse periods, however, since after the pulse the cell contains an excess of positive ions and the space charge field will prevent loss of electrons, encouraging rather the preferential loss of positive ions (see below). At longer pulse periods the positive ion and electron concentrations become more nearly equal in value and, at the concentrations concerned, ions and electrons no longer diffuse independently. As Siegel and McKeown⁴ have shown, under these conditions ambipolar diffusion (ref. 5, p. 512*ff*) prevails and there is no preferential loss mechanism for electrons. The space charge fields associated with ambipolar diffusion are weak and are easily overcome by applied fields, causing ions and electrons to diffuse independently. Ambipolar diffusion between pulses does not therefore affect electron collection by the pulse.

The conventional description of the ECD based on the assumption of the presence in the detector cell under all conditions of a large excess of positive ions is clearly untenable. The results obtained by Wentworth *et al.*, however, and expanded in a number of reports since then have been found to be useful in describing ECD behaviour. A more careful consideration of the ECD and, in particular, of positive ion concentration variations in the ECD, is required to show why this is so and to demonstrate the conditions under which the results are valid.

Positive ions in the ECD

Any model of the ECD has to be tested against experimental observations of ECD behaviour and particularly against two important observations made in the absence of any added sample in clean ECD systems. These observations are that

(1) The electron concentration in a typical ECD system reaches a steady state value in a time period of *ca.* 5 msec after the application of an electron collecting pulse (*e.g.* ref. 6);

(2) In this steady state the electron and positive ion densities are approximately equal⁴.

The second of these observations is worth some amplification as it does not seem to have been generally accepted. First, it must be emphasised that it is based on experiment and, unless the experiment can be invalidated, must be regarded as an

empirical fact. Secondly, the steady state condition being considered is the state approached as $t_p \rightarrow \infty$. In this state the electrons lost in the pulse are an insignificant fraction of the total number produced between pulses and, as no mechanism exists for charge formation in the ECD between pulses, charge neutrality must prevail. That this is so can be seen by considering an alternative. Suppose that, in the steady state, the positive ion concentration exceeded the electron concentration. As a consequence (see below) positive ions must be lost by diffusion to the walls under the influence of the space charge and, as there is no compensating loss mechanism for electrons, the rate of the positive ion/electron recombination must decrease, causing the electron concentration to increase and thus showing that a steady state did not in fact exist.

It has been argued⁷ that positive ion/electron recombination is not a significant process in the ECD and that its rate is low compared with positive ion/negative ion recombination. That this view is in error is strongly suggested by data from Wentworth *et al.*³ which they have recently re-emphasised⁸, by Siegel and McKeown's results⁴ which, they show, have strong support from the literature (see, *e.g.* refs. 5 and 9) and by recent results from Grimsrud *et al.*¹⁰. All this evidence suggests that positive ion/electron and positive ion/negative ion recombination rates are comparable. In this report positive ion/electron recombination will be treated as a significant process linking positive ion and electron concentrations and contributing to the existence of charge neutrality at long pulse periods.

The time scale required for a steady state to be achieved within the ECD is of importance for the information it gives on the processes involved in setting up the steady state. The volume V of a typical ECD cell is 1 ml, and the gas flow-rate u is 1 ml sec⁻¹. The time constant for ventilation from the cell is therefore *ca.* 1 sec, much longer than the time taken to establish the steady state. Some other, more rapid, process must therefore be implicated. All the available evidence suggests that, in the case of the electrons, this process is positive ion/electron recombination. For the positive ions it appears that the process must also include diffusion of positive ions to the cell walls under the influence of the positive space charge existing after the electron collection pulse. The importance of space charge effects in the ECD was first alluded to by Lovelock⁷, and more recently Bros *et al.*¹¹ and Wentworth and Chen⁸ have made attempts to allow for these effects in descriptions of pulsed ECD systems. Recent and important work by Grimsrud *et al.*¹⁰ provides clear experimental evidence that loss of positive ions by diffusion is of importance in the ECD. This loss mechanism must be added to the basic model outlined above.



The significance of this space charge controlled positive ion loss mechanism will vary with time after the electron collection pulse since, as the electron concentration builds up, the space charge field is diminished, eventually falling to zero in the steady state. This time variation greatly complicates exact solutions for the equations describing ECD behaviour. Further complications arise because diffusion losses will depend on the geometry and physical dimensions of the ECD cell. Any solutions will thus apply only to the cell design considered. The nature of the positive ion loss mechanism is such that general and exact descriptions of the ECD are not possible except under limiting conditions. The conditions under which solutions can be

obtained and the general applicability of these solutions will be examined in the next sections.

Exact solutions for ECD behaviour: general validity

The time variations of η_e , η_+ , η_- and c are given by eqns. 1-4:

$$\frac{d\eta_e}{dt} = R - \eta_e(k_1c + k_2\eta_+ + u/V) \quad (1)$$

$\eta_e \rightarrow 0$ at each pulse.

$$\frac{d\eta_+}{dt} = R - \eta_+(k_2\eta_e + k_3\eta_- + k_D(t) + u/V) \quad (2)$$

$$\frac{d\eta_-}{dt} = k_1\eta_e c - \eta_-(k_3\eta_+ + u/V) \quad (3)$$

$$\frac{dc}{dt} = B - c(k_1\eta_e + u/V) \quad (4)$$

The electron concentration averaged over the pulse period is defined by eqn. 5:

$$\bar{\eta}_e = \frac{1}{t_p} \int_0^{t_p} \eta_e dt \quad (5)$$

Similar time-averaged values of the other ion and neutral concentrations can also be defined. In the absence of sample the electron concentration will be written η_e^0 , while the symbols $\eta_e(t_p)$, $\eta_+(t_p)$, etc., will be used to designate concentrations immediately before application of the collecting pulse.

In the absence of sample and for a fixed pulse period t_p , a pseudo-steady state will be established with $\eta_+(t_p)$, $\eta_e^0(t_p)$, $\bar{\eta}_+$ and $\bar{\eta}_e^0$ constant after a sufficient number of pulses. If a small sample is now admitted to the ECD such that $\eta_e^0(t_p)$ is changed by $\Delta\eta_e$, where $\Delta\eta_e \ll \eta_e^0(t_p)$, then $\eta_+(t_p)$ will not appreciably change in value. Thus for any given pulse period, $\eta_+(t_p)$ and $\bar{\eta}_+$ can be regarded as constant in the small sample limit. This limit is of course of great interest to chromatographers and, from eqn. 1, can be defined by the inequality $k_1c \ll \alpha$, where $\alpha = k_2\bar{\eta}_+ + u/V$.

In the absence of sample, eqn. 1 can be integrated over the pulse period to give an expression for $\eta_e^0(t_p)$ provided that η_+ can be replaced by a function $\bar{\eta}_+$ which is, for a given pulse period, constant.

$$\eta_e^0(t_p) = \frac{R}{\alpha} [1 - \exp(-\alpha t_p)] \quad (6)$$

For very short pulse periods ($t_p \ll \alpha^{-1}$), $\eta_e^0(t_p)$ is small and positive ion losses by recombination are negligible, so that η_+ will, in the pseudo-steady state, rise to its limiting value of $R/(k_D + u/V)$ and remain constant. Hence $\eta_+(t_p) \gg \eta_e^0$ and $\eta_+(t_p) = \bar{\eta}_+$ so that eqn. 6 is valid and, with t_p replaced by t , can be used to express the variation in electron concentration with time.

For long pulse periods ($t_p \gg \alpha^{-1}$), eqn. 6 becomes

$$\eta_e^0(t_p) = \frac{R}{\alpha} \quad (7)$$

Under these conditions the effect of the pulse on electron concentration can be ignored and a steady state is established with $d\eta_e/dt = 0$ and $\eta_e^0(t_p) = \bar{\eta}_e^0 = \bar{\eta}_+ = \eta_+(t_p)$. Again η_+ is effectively constant with time and eqn. 6 is valid.

Continuing with this long pulse period case, addition of sample provides no new charge formation mechanism so charge neutrality must be retained and

$$\eta_+ = \eta_e + \eta_- \quad (8)$$

From eqn. 2, remembering that at long pulse periods diffusion losses can be ignored relative to total ion formation,

$$\eta_+ = \frac{R}{k_2\eta_e + k_3\eta_- + u/V} \quad (9)$$

and hence, from eqn. 8,

$$\eta_+ = \frac{R}{k_2\eta_+ + (k_3 - k_2)\eta_- + u/V} \quad (10)$$

It was shown above that, to a good approximation, $k_3 = k_2$ so that

$$\eta_+ = \frac{R}{k_2\eta_+ + u/V} \quad (11)$$

Hence, by comparison with eqn. 7,

$$\eta_+ = \eta_e^0$$

Thus the presence of sample does not, in the long pulse period case, cause any variation in the positive ion concentration.

At very long and very short pulse periods therefore the assumption can be made that the positive ion concentration does not vary with time and the conventional model of the ECD can be applied. At intermediate pulse periods, which are in fact of the greatest practical significance, this is not the case and the temporal variation of the positive ion concentration will change both with pulse period and added sample concentration. Lovelock and Watson¹² have recently provided evidence, however, that the contribution of positive ion/electron recombination to electron loss at a constant sample input but varying carrier gas flow-rate does not change, within experimental error, over a range of pulse periods from *ca.* 150 to 250 μ sec, implying that $k_2\bar{\eta}_+$ is constant over this range. In what follows it will be assumed that η_+ can be replaced by an averaged value $\bar{\eta}_+$, which can be regarded as a constant. This value will be selected, through eqn. 6, to lead to an exact solution of eqn. 1 for the pseudo-steady state electron concentration immediately before the collection pulse at a constant pulse period, t_p . It will not, except in limiting cases, reproduce the temporal variation of the electron concentration between pulses and, even within this limitation, the validity of the assumption will be increasingly questionable as the pulse period and/or the sample concentration varies. Nevertheless the assumption is of value because it facilitates comparison between different modes of ECD operation provided that its inherent limitations are remembered.

Constant-frequency mode operation

If sample is entering an ECD at a constant rate and electrons are being sampled at a constant pulse period, t_p , then a pseudo-steady state will be established such that $d\bar{c}/dt = 0$ and, from eqn. 4,

$$\bar{c} = \frac{B}{k_1 \bar{\eta}_e + u/V} \quad (13)$$

In practice it is not likely that c will vary significantly with time between pulses so that \bar{c} can be replaced by c . Providing then that η_+ can be replaced by $\bar{\eta}_+$ which is constant, eqn. 6 becomes

$$\eta_c(t_p) = \frac{R}{\lambda} [1 - \exp(-\lambda t_p)] \quad (14)$$

where $\lambda = k_1 c + k_2 \bar{\eta}_+ + u/V$.

The problem then is to find conditions under which eqn. 14 is valid and can be solved to give a relationship between $\eta_c(t_p)$ and c and, through eqn. 13, between $\eta_c(t_p)$ and B . One such condition is that t_p is large and constant, $t_p \gg \lambda^{-1}$. It then follows from eqn. 14 that

$$\eta_c(t_p) = \frac{R}{\lambda} = \frac{R}{k_1 c + k_2 \bar{\eta}_+ + u/V} \quad (15)$$

and

$$\frac{1}{\eta_c(t_p)} = \frac{k_1 c}{R} + \frac{(k_2 \bar{\eta}_+ + u/V)}{R} = \frac{k_1 c}{R} + \frac{1}{\eta_c^0(t_p)} \quad (16)$$

Hence

$$\frac{\eta_c^0(t_p) - \eta_c(t_p)}{\eta_c(t_p)} = \eta_c^0(t_p) \frac{k_1 c}{R} \quad (17)$$

Assuming the electron collection pulse width is such that all the electrons present are collected, then the detector current $I = [\eta_c(t_p) V Q] / t_p$, where Q is the charge on an electron. At a fixed value of t_p , therefore, eqn. 17 becomes

$$\frac{I_0 - I}{I} = \eta_c^0(t_p) \frac{k_1 c}{R} \quad (18)$$

If the sample is only weakly electron capturing, *i.e.* k_1 is small, then $k_1 \bar{\eta}_e \ll u/V$ and, from eqn. 13, $c = BV/u$ so that eqn. 18 becomes

$$\frac{I_0 - I}{I} = \frac{\eta_c^0(t_p) k_1 V}{Ru} B = K_1 B \quad (19)$$

This expression is equivalent to that of Wentworth *et al.*³ for the constant-frequency mode detector, but the derivation differs in the justification for the assumption that the positive ion concentration is constant. The expression applies only for

weakly electron-capturing material. The upper limit of the linear range in this mode is approached when I falls to a value approaching the system noise, implying that $k_1c \gg \alpha$ at this limit.

For small samples ($k_1c \ll \alpha$), $I \approx I_0$ and $\lambda \approx \alpha$. From eqn. 15 $R = \eta_c(t_p)\alpha$ and eqn. 19 can be written

$$I_0 - I = \frac{\eta_c^0(t_p) Q k_1 V^2 B}{t_p \alpha u} \quad (20)$$

In practical systems at long pulse periods $k_2 \bar{\eta}_+ \gg u/V$, so that $\alpha = k_2 \bar{\eta}_+ = k_2 \eta_c^0(t_p)$; eqn. 20 then becomes

$$I_0 - I = \frac{k_1 Q V^2 B}{k_2 t_p u} \quad (21)$$

Thus, for small samples of weakly electron-capturing materials the change in detector current is linear in sample input and independent of the source strength in this long pulse period mode.

Although eqn. 19 gives a method of obtaining a linear relationship between detector current and sample input over a wide range of sample inputs, it is in practice not much used. A good deal of constant pulse frequency ECD analysis in fact employs pulse periods of *ca.* 100 μ sec or less because this condition, although sacrificing linear range, does allow improved limits of detection. If a fraction, x , of the sample input to the ECD reacts to form negative ions then eqn. 1 can be written as

$$\frac{d\eta_c}{dt} = R - xB - \eta_c \alpha \quad (22)$$

Generally x is a function of time so that eqn. 22 cannot be integrated but in the special case where $x \rightarrow 1$ over the entire pulse period the integration can be made over the pulse period to give

$$\eta_c(t_p) = \frac{R - xB}{\alpha} [1 - \exp(-\alpha t_p)] \quad (23)$$

When $B = 0$, *i.e.* for pure carrier gas,

$$\eta_c^0(t_p) = \frac{R}{\alpha} [1 - \exp(-\alpha t_p)] \quad (24)$$

Hence

$$\eta_c^0(t_p) - \eta_c(t_p) = \frac{xB}{\alpha} [1 - \exp(-\alpha t_p)] \quad (25)$$

For short pulse periods, $t_p \ll \alpha^{-1}$, eqn. 25 becomes

$$\eta_c^0(t_p) - \eta_c(t_p) = xB t_p \quad (26)$$

and the detector response, which is proportional to $[\eta_c^0(t_p) - \eta_c(t_p)]/t_p$, is linear in xB .

Following the argument developed by Rosiek *et al.*¹³, the fraction of sample molecules ionised can be written

$$x = \frac{\int_0^{t_p} k_1 \bar{\eta}_e c \, dt}{B t_p} \quad (27)$$

Given that B and c do not change with time, eqn. 27 becomes

$$x = \frac{k_1 \bar{\eta}_e c}{B} \quad (28)$$

But from eqn. 13 $B = c(k_1 \bar{\eta}_e + u/V)$ so that

$$x = \frac{k_1 \bar{\eta}_e}{k_1 \bar{\eta}_e + u/V} \quad (29)$$

Hence $x \rightarrow 1$ if $k_1 \bar{\eta}_e V \gg u$.

Lovelock *et al.*¹⁴ have described an ECD operating in this mode, pointing out that the so-called coulometric response depends only on input sample concentration. It is worth stressing that the coulometric response is obtained not just by ensuring that every sample molecule entering the ECD captures an electron ($k_1 \bar{\eta}_e V \gg u$); with k_1 sufficiently large this can be achieved provided t_p and, therefore, $\bar{\eta}_e$ is sufficiently large. It is also necessary that every electron produced is collected so that one fewer electron is collected for every sample molecule entering the ECD. This means that pulse periods must be short ($t_p \ll \alpha^{-1}$). Under this condition $\bar{\eta}_e$ is also small so that the other condition for coulometry is difficult to achieve.

For low values of t_p and ignoring diffusion losses, $\bar{\eta}_+$ is given by the ventilation controlled limit VR/u . For a detector of volume 1 ml with a maximum current of 30 nA, RV is $2 \cdot 10^{11} \text{ sec}^{-1}$ and, giving u the lowest value consistent with efficient chromatography, *ca.* 0.1 ml sec^{-1} , and adopting a typical value for k_2 of $5 \cdot 10^{-7} \text{ ml sec}^{-1}$, then $\bar{\eta}_+$ is $2 \cdot 10^{12} \text{ ml}^{-1}$ and $\alpha (k_2 \bar{\eta}_+)$ is *ca.* 10^6 sec^{-1} . It follows that t_p must be substantially less than $1 \mu\text{sec}$ for a coulometric response; this pulse period is comparable with the pulse width and it follows that the electron collection voltage must be applied continuously if coulometry is to be achieved. The detector is then operating in d.c. mode. Diffusion losses will tend to reduce the positive ion concentration below the ventilation controlled limit, but even so very short pulse periods, approximating to d.c. operation, are required for true coulometry.

In d.c. mode, gas-phase charge separation will tend to occur and electrons will drift with a velocity imposed by the electric field to the collector electrode. In a field strength of 100 V cm^{-1} at atmospheric pressure in air, the electron drift velocity is *ca.* $4 \cdot 10^5 \text{ cm sec}^{-1}$ (ref. 5, p. 546) so that, for a detector volume of 1 ml with a cross-section of 1 cm^2 in which electrons are produced at a rate of $2 \cdot 10^{11} \text{ sec}^{-1}$, the electron concentration in the absence of sample will be *ca.* 10^6 ml^{-1} . Losses by reaction with positive ions can be ignored because of the charge separation effect. For a strongly electron-capturing sample k_1 may be $5 \cdot 10^{-7} \text{ ml sec}^{-1}$, so that $k_1 \bar{\eta}_e V$ is 0.5 ml sec^{-1} and u must be less than 0.1 ml sec^{-1} for a coulometric response. Lower values of k_1 require a proportional reduction in u for coulometry but, as was stated above, substantially lower values of u are not consistent with the requirement for efficient chro-

matographic separation. Coulometric mode ECD operation is therefore only possible for strongly electron-capturing compounds and even then only with sources producing a high electron concentration.

Even for materials for which a coulometric response is possible the linear range will be limited because $\bar{\eta}_e$ falls as B increases. Rates of sample input approaching the rate of electron production will result in a drop in detector response and, for optimum range, the rate of electron production should be as high as possible.

Returning to the description of the pulsed or a.c. mode ECD, it is clear that the fraction of sample ionised, x , does not in general approach unity under conditions where eqn. 26 is valid. Detector response is a product of two terms; the number of electrons reacting, which increases with t_p , and the fraction of the total number of electrons produced between successive pulses which is collected; this falls with t_p . The maximum response and therefore the optimum limit of detection condition will appear at higher values of t_p as k_1 , or the electron-capturing ability of the sample, decreases until a limit is reached where $k_1\bar{\eta}_e \ll u/V$ for all values of t_p and the fraction of the total sample input which is ionised is negligible compared with the total sample input.

Under this negligible sample ionisation condition the sample concentration within the detector is, from eqn. 13, $c = BV/u$ and, provided $\bar{\eta}_+$ is constant, the detector current can, from eqn. 1, be written as

$$I = \frac{\varphi}{\lambda t_p} [1 - \exp(-\lambda t_p)] \quad (30)$$

where $\varphi = RVQ$ and $\lambda = (k_1c + k_2\bar{\eta}_+ + u/V)$. The sensitivity of the detector, S , is then given by

$$S = \frac{dI}{dB} = \frac{k_1V}{u} \frac{dI}{d\lambda} \quad (31)$$

again provided that $\bar{\eta}_+$ is constant. The maximum detector response is obtained when S is at a maximum with respect to pulse period, *i.e.* when $dS/dt_p = 0$. It can be shown that this condition obtains when $\lambda t_p = 1.79$.

For small samples when $k_1c \ll \alpha$ this condition becomes $\alpha t_p = 1.79$ and defines the pulse period for the optimum limit of detection of weakly electron-capturing materials. Since k_1 is low the small sample condition may be met for such materials over a considerable range of sample concentration so that S remains constant and a useful linear range may be available. Linearity for more strongly electron-capturing materials will be limited.

At this stage it should be remembered that $\bar{\eta}_+$ and therefore α are functions of t_p , so that the analysis above is not exact. In fact for values of $t_p \approx \lambda^{-1}$, $\bar{\eta}_+$ is decreasing as t_p increases so that $\bar{\eta}_e^0$ increases more rapidly than would be the case if $\bar{\eta}_+$ were constant. At a given pulse period in this range, therefore, the degree of input sample ionisation is greater than it would be if $\bar{\eta}_+$ were constant and, as a consequence, the maximum response is obtained at a shorter pulse period than would otherwise be the case.

Constant-current mode operation

Maggs *et al.*¹⁵, in an important advance, noted that eqn. 30 indicated an alternative mode of ECD operation. Instead of I being allowed to vary with c while t_p was held constant, they suggested that t_p should be varied so that I remained constant. It follows from eqn. 30 that if I is constant and $\bar{\eta}_+$ does not vary with t_p then

$$\lambda t_p = (k_1 c + k_2 \bar{\eta}_+ + u/V) t_p = \text{constant} = K_2 \quad (32)$$

The pulse period when $c = 0$ is designated t_p^0 and, from eqn. 32, $K_2 = (k_2 \bar{\eta}_+ + u/V) t_p^0 = \alpha t_p^0$. Putting $f = 1/t_p$ and $f_0 = 1/t_p^0$, eqn. 32 can be rearranged to give

$$f - f_0 = \frac{k_1}{K_2} c = \frac{f_0 k_1}{\alpha} c \quad (33)$$

If $k_1 \bar{\eta}_+ \ll u/V$ so that the fraction of the sample input which is ionised is negligible in comparison with the total input, then $c = BV/u$ and eqn. 33 becomes

$$f - f_0 = \frac{k_1 V}{K_2 u} B = \frac{f_0 k_1 V}{\alpha u} B \quad (34)$$

Thus the change in frequency required to maintain the detector current constant is linear in sample input concentration provided $\bar{\eta}_+$ (and hence α) is constant. Eqn. 34 is equivalent to eqn. 19 in constant-frequency mode in that both apply only to weakly ionised samples, but eqn. 34 is not restricted to long pulse periods.

From eqn. 34 the detector response ($f - f_0$) increases as f_0 increases but, since the maximum frequency attainable is limited by the pulse width, the detector range decreases. Bros and Page¹⁶ have suggested that the optimum value of f_0 is that which gives the most precise determination of sample concentration. From eqn. 30 the current in the ECD can be written as

$$I = f(\lambda t_p) \quad (35)$$

Fluctuations in I can therefore be written as

$$\delta I = f'(\lambda t_p) \delta(\lambda t_p) \quad (36)$$

From eqn. 32 it follows that the error in c and therefore in B (when the fraction of the sample which is ionised is small) is at least as great as the error in (λt_p) . This error is given by

$$\frac{d(\lambda t_p)}{(\lambda t_p)} = \frac{1}{(\lambda t_p) f'(\lambda t_p)} \delta I \quad (37)$$

and is minimised for a given δI by maximising $(\lambda t_p) f'(\lambda t_p)$. The value of δI is fixed by fluctuations in the radioactive source decay rate and by the electronics of the system. It can be shown that the minimum error condition is met when $\lambda t_p = 1.79$ and thus when

$$f_0 = \frac{\alpha}{1.79} \quad (38)$$

It will be noted that this optimum base frequency is precisely the frequency that gives maximum response for small sample inputs into a constant-frequency mode ECD when the fraction of the sample that is ionised is small. Constant-frequency mode operation therefore combines for weakly electron-capturing samples the optimum detection limit with the maximum linear range. From eqn. 30, putting $\lambda t_p = 1.79$, the optimum current for constant-current mode operation with negligible sample ionisation is 0.46φ , where φ is the current under d.c. electron collection conditions.

The condition $\lambda t_p = 1.79$ defines the optimum condition for determination of the sample concentration c within the detector. The parameter of greater interest is, however, the sample input concentration, Bu/V , and only when $k_1 \bar{\eta}_c \ll u/V$ so that $c = Bu/V$, are the optimum conditions for determination of c and B identical.

For more strongly electron-capturing materials the optimum detection limit will be obtained at higher base frequencies (lower pulse periods) until the limit is reached where the sample is entirely ionised, $k_1 \bar{\eta}_c V \gg u$. Under this condition $c = B/k_1 \bar{\eta}_c$ so that, from eqn. 33,

$$f - f_0 = \frac{f_0}{\alpha \bar{\eta}_c} B \quad (39)$$

As $\bar{\eta}_c$ is a function of B , this response is linear only for small samples ($k_1 c \ll \alpha$) where $\bar{\eta}_c \approx \bar{\eta}_c^0$. This result is of particular significance because it clearly shows that responses to strongly electron-capturing materials in the constant current ECD are non-linear, imposing a severe limitation on the analytical applications of this operating mode. By analogy with the constant-frequency mode, the optimum response would be obtained with $f_0 \gg \alpha$ but, as the discussion above showed, this condition is unattainable. In practice the maximum value of f_0 is likely to be $ca. 10^4 \text{ sec}^{-1}$; higher frequencies would severely limit the detector range. For less strongly electron-capturing materials the optimum value of f_0 will decrease to the limit $\lambda/1.79$.

This analysis of the constant-current detector has ignored the variation of $\bar{\eta}_+$ and therefore α and λ with f . This variation is probably the limiting factor on the dynamic range of the system in the negligible sample ionisation regime and, as was shown above, will tend to move the optimum detection limit to higher base frequencies than the above discussion predicts.

Impurity effects

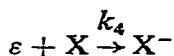
The discussion so far has assumed that, in the absence of sample, the negative charge in the ECD is entirely contained in the free electron population. In practice this condition rarely applies. Siegel and McKeown⁴ found that it took several days of high-temperature baking of their atmospheric pressure ionisation-mass spectrometry system to reduce negative ion concentrations to negligible levels. This degree of cleanliness is hardly possible in GC systems where column bleed is a perpetual problem.

Gross contamination of the carrier gas in a GC-ECD system may cause serious problems in the chromatographic separation. Depending on the nature of the contaminant, retention times and resolution may vary with time. Impurities introduced at the sample injection stage can also cause problems, particularly if they are retained for long times on the column. In the ECD itself, adsorption of contaminants onto the

radioactive source or the electrode can markedly reduce the free electron concentration and increase system noise, reducing the detection limit and the linear range. For these reasons samples in high concentrations should never be directly injected into GC-ECD systems. Clean-up procedures should be established for highly contaminated samples.

In the present context, trace impurity effects are of more importance. Because of the great sensitivity of the ECD, even minute traces of impurity can markedly affect ECD performance. Van de Wiel and Tommassen⁶ have shown that the presence in nitrogen carrier gas of 10 ppm of oxygen can reduce the electron concentration in an ECD at long pulse periods by a factor of two.

In the simplest approximation, trace impurity effects can be allowed for by adding a single reaction to the model



The analysis given above still applies except that $k_2\bar{\eta}_+$ becomes $(k_2\bar{\eta}_+ + k_4\eta_x)$ and the definitions of α and λ are changed accordingly. In the small sample limit, $k_1c \ll \alpha$, the trace impurity concentration η_x will not vary with sample input and, from eqn. 24 the major effect of the impurity will be to reduce $\eta_e^0(t)$, the electron concentration in the detector at a time t , and to reduce the time taken for $\eta_e^0(t)$ to reach its plateau value.

Impurities may be introduced into the ECD in the carrier gas supply, as a result of column or septum bleed, by leaks in the gas lines, with the sample or by other means. The concentration of impurity may or may not vary with carrier gas flow-rate depending on the source. If the concentration should decrease with flow-rate then at high flow-rates and short pulse periods, where the time for reaction between electrons and impurities is limited, impurity effects will be less important than at low flow-rates and long pulse periods. Variations in ECD standing current with carrier gas flow-rate at long pulse periods are therefore indicative of impurity effects.

The effect of a reduction in the electron density, $\eta_e^0(t)$, in a constant-frequency mode ECD with a sample which is ionised only to a small extent is a proportionate reduction in detector response both in the long pulse period optimum linearity condition (eqn. 19) and in the optimum detection limit condition (eqn. 31). Strongly electron-capturing materials may still be detected coulometrically but this mode of operation becomes increasingly difficult to attain as $\eta_e^0(t)$ falls. If the fraction of the input sample ionised in the detector is large but still less than unity, detector response will be reduced by the presence of impurity. The extent of the reduction in response for small samples will increase to the limit where it is equal to the fractional reduction in $\eta_e^0(t)$ as the extent of sample ionisation falls. The pulse period for optimum detection of such materials will increase as impurity concentration increases to the limit where $\lambda t_p = 1.79$.

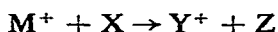
In constant-current mode with samples which are ionised only to a small extent, detector response is independent of η_e^0 so that impurities will have no effect on the response at a fixed value of λt_p . As impurity and therefore λ increase the base frequency for optimum operation must however be increased to maintain the equality $f_0 = \lambda/1.79$.

The largest responses for samples which are significantly but not completely

ionised will be obtained at base frequencies which are reduced as impurity concentration increases. The absolute response in these circumstances will also be reduced until, at high enough impurity levels, it approaches the response expected for materials for which the fraction of the sample input ionised is small (eqn. 34).

There is one further important consequence of the presence of impurity in the carrier gas which arises from this model. For both the constant-frequency and constant-current mode ECD, operating under optimum detection limit conditions, response is linear only in the small sample limit where $\bar{\eta}_e \approx \bar{\eta}_e^0$. The small sample condition can be written $k_1c \ll (k_2\bar{\eta}_+ + k_4\eta_x + u/V)$ and hence is more easily met for higher impurity concentrations. As Sullivan and Burgett have pointed out¹⁷, linearity of response may be improved by impurities such as column bleed.

Impurities may in addition have more subtle effects in that they can change the nature of the positive ions within the ECD by reactions with the primary positive charge carrier:

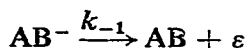


The new positive ion may recombine with electrons and/or negative ions at rates different from those with which the primary ion recombines, and it may also drift in the positive space charge field at a different rate. These effects will produce variations in the quantitative ECD response depending on the nature and amount of the impurity.

Clearly impurities must play an important role in determining quantitatively the ECD response. Because, by their very nature, impurities will vary in type and in concentration from laboratory to laboratory, it is scarcely surprising that contradictory results have been obtained in apparently similar experiments². An exact description of the ECD requires either that impurity levels are insignificant, which is unlikely to be true in GC systems where, for example, column bleed is likely to occur, or that the nature, the concentrations and the reaction rates of impurities and species derived from them are known so that allowance can be made for their presence. This is equally unlikely.

Secondary reactions and temperature dependence of responses

So far, secondary reactions have been ignored but this is no longer possible if a model for the temperature dependence of ECD response is to be constructed. The simplest secondary process is the reverse of the original electron-capturing reaction:



If this reaction is significant then, for example, eqn. 17 must be rewritten as

$$\frac{\eta_e^0(t_p) - \eta_e(t_p)}{\eta_e(t_p)} = \frac{\eta_e(t_p) (k_3\eta_+ + u/V)}{(k_3\eta_+ + u/V + k_{-1})} \frac{k_1c}{R} \quad (40)$$

In general, k_1 will not vary much with temperature but k_{-1} will increase with temperature. It follows therefore that detector response will decrease as the temperature increases. This type of response is typical of strongly electron-capturing materials.

If the electron-capture process does not produce a stable negative ion, *i.e.* if a dissociative capture mechanism is involved, a different temperature dependence may be observed:



If AB is weakly electron capturing it is possible that, at low temperatures, AB⁻ will dissociate, reforming an electron. At higher temperatures, however, dissociation to A + B⁻ will become increasingly important, effectively increasing the efficiency of the electron-capture process provided that B⁻ is stable. The detector response will thus increase with temperature in a case of this type.

Even on the basis of this rather simplified model, it is clear that detector responses may vary with temperature and that the sense of this variation may differ with different materials. Detector optimisation must include detector temperature optimisation. It should also be noted that responses to carrier gas impurities may be temperature dependent. Thus electron capture by impurity oxygen begins to become reversible at temperatures above 150°C, and the electron concentration in a detector thus contaminated will increase in this temperature range. This effect, which is an excellent test for the presence of oxygen, may mask variations in sample response.

It is worth noting that the differing temperature dependencies of detector responses can be used to enhance the response of one material relative to another which is potentially interfering. A more detailed description of the temperature dependence of ECD response has been given by Wentworth *et al.*¹⁸.

DISCUSSION

The model of the ECD which has been developed is in many respects an amalgam of previous studies, but it differs from them in that the positive ion concentration has not been assumed to be large and constant under all operating conditions. Direct experimental confirmation of this is not easy to obtain. Siegel and McKeown⁴ quote data from their mass spectrometric study which suggest that the electron and positive ion concentrations are identical for long pulse periods, but sampling ions from atmospheric pressure into the low-pressure region of a mass spectrometer is problematic and could distort the ion populations. Careful measurements of the electron concentration in an ECD as a function of pulse period should in principle be capable of resolving this matter, and it is interesting to note that the data of Van de Wiel and Tommassen⁶ on the variation of electron density with pulse period fit only poorly to an expression of the $[1 - \exp(-\lambda t_p)]$ form, which the constant positive ion concentration model predicts. In fact the rate of increase of electron density is higher than this simple model predicts, consistent with a reduction in positive ion concentration as pulse period increases. Wentworth and Chen⁸ have shown that their numerical model of the ECD, which allows for positive ion losses at short pulse periods, gives a better fit to this data than does the conventional model.

The variation in the positive ion concentration with pulse period and, except at long pulse periods, with sample concentration, imposes restrictions on the extent that the descriptions of the ECD derived above can be quantitatively applied. Perhaps equally important in this respect is the observation by Grimsrud *et al.*¹⁰ that positive

ions will drift to the ECD electrode under the influence of the positive space charge in the ECD after the electron-collecting pulse. The measured current is not therefore due solely to collection of electrons but is modified by the positive ion current. The importance of this effect will be greatest at short pulse periods and will vary with detector geometry, carrier gas and very probably the impurities in the carrier gas. An accurate quantitative description of the ECD is therefore difficult, if not impossible. Any ECD system, even systems designed to give coulometric operation, should be calibrated where possible by injection of standard solutions of materials of interest if a quantitative chemical analysis is to be carried out.

The controversy over the positive ion concentration illustrates a major weakness of the ECD. The parameter which is of over-riding practical interest is the concentration of molecular species entering the detector, yet this is monitored only indirectly by the change in electron concentration. It is not surprising to find that there is considerable interest in techniques such as plasma chromatography¹⁹ and atmospheric pressure ionisation-mass spectrometry^{20,21} where at least some of the ion concentrations are monitored directly. These techniques are not without both fundamental²² and practical (size and expense) problems themselves and the day that they will replace the ECD is still some way away.

Numerical methods

Rigorous solutions of the differential equations describing the electron concentration in the ECD require that the positive ion concentration be regarded as a variable. Provided that positive ion loss modes can be specified and modelled, numerical solutions to the differential equations may be obtained. As ion losses are dependent on the geometry of the detector, such solutions may only apply to the geometry specified.

Wentworth and Chen⁸ have recently provided such a numerical model. They assume that the positive ions lost due to the space charge field represent a constant fraction, f , of the positive ions remaining at the end of the pulse period and that f is independent of pulse period. They find then that in the steady state the ratio of the electron and positive ion concentrations becomes constant and also equal to f . Bros *et al.*¹¹ have reached a similar conclusion. In general, f is small so that this model assumes in effect that the positive ion concentration is, under all conditions, much greater than the electron concentration. This is precisely the condition earlier assumed by Wentworth *et al.*³ and shown above to be invalid. The validity of this revised model is therefore worth examination.

The ratio of the positive ions lost to the positive ions remaining at the end of the pulse period is given in terms of the model developed above by

$$f = \frac{\int_0^{t_p} (k_2 \eta_e + k_D + u/V) \eta_+(t) dt}{\eta_+(t_p)} \quad (41)$$

In general this fraction can be evaluated only if η_e and η_+ are constant or their variations known. If however t_p is small, then η_e can be neglected and eqn. 40 becomes

$$f = \frac{(k_D + u/V) \eta_+(t_p) t_p}{\eta_+(t_p)} \quad (42)$$

The steady-state value of $\eta_+(t_p)$ is given, however, by

$$\eta_+(t_p) = \frac{R}{k_D + u/V} \quad (43)$$

so that

$$f = \frac{Rt_p}{\eta_+(t_p)} = \frac{\eta_c(t_p)}{\eta_+(t_p)} \quad (44)$$

Thus at short pulse periods the ratio of the electron and positive ion concentrations at the end of the pulse period is equal to the fraction of positive ions lost. This equality breaks down, however, as the pulse period increases because recombination can then no longer be ignored. As was argued above, at long pulse periods the electron and positive ion concentrations must become equal because

- (1) Positive ions and electrons are produced at the same rate;
- (2) Recombination losses are the same for both;
- (3) As the electron concentration increases, preferential loss of positive ions by diffusion under the influence of the space charge becomes less favoured.

Effectively then, the assumption that a constant fraction of the positive ion population is lost each pulse period is exactly equivalent to the assumption that the positive ion concentration under all operating conditions is greatly in excess of the electron concentration. This assumption is invalid except at short pulse periods, and a more sophisticated model for the variation of the positive ion concentration with time is required if any general and rigorous solutions are to be produced.

Lovelock²³ and Lovelock and Watson¹² have also produced numerical solutions to the equations describing the ECD. They assume that the positive ion concentration does not vary with time, restricting the general applicability of their solutions, but they produce experimental evidence supporting this assumption over narrow ranges of pulse period. Two conclusions from their study are of particular significance in the light of the present model. The first is their clear demonstration of the non-linearity of response of the constant-current ECD to strongly electron-capturing samples. This non-linearity of response, as was pointed out above, severely limits the applicability of the constant-current mode ECD for quantitative analysis. Linear responses are obtained for weakly electron-capturing materials but other detectors may be equally as sensitive to these materials. For qualitative analyses the superior dynamic range of the constant-current ECD may be advantageous but this alone scarcely justifies the emphasis in modern GC-ECD equipments on constant-current mode applications.

The second significant feature of their calculations is the illustration that a truly coulometric response cannot be obtained from an ECD operating under conditions compatible with GC work. With argon-methane as carrier gas and a 250- μ sec pulse period, 10% of electrons are lost by recombination, whereas in nitrogen this proportion rises to 30%, giving upper limits of 90 and 70% ionisation of sample in these carriers. Even these limits are approached only at very low carrier flow-rates and for low impurity levels in the carrier. The zero carrier gas flow response can be estimated from experimental values by plotting the reciprocal of the response (coulombs⁻¹) of an ECD to a constant concentration of test substance against flow-rate and extrapolating to zero flow-rate.

It is clear from the model developed here and from the numerical model produced by Lovelock that there is no single best operating mode for the ECD. Optimisation of linear range or limit of detection may require quite different conditions and these conditions will vary depending on the electron-capturing ability of the sample of interest. Constant-current mode detectors, much favoured by manufacturers, provide a wide dynamic range of response but this response is non-linear for the strongly electron-capturing materials for which the ECD is most likely to be used. Truly coulometric detection probably cannot be achieved except perhaps in d.c. mode with near-zero flow-rates. The ionisation efficiencies of constant-frequency mode ECDs at zero carrier gas flow-rate can, however, be estimated from responses at several different flow-rates with allowance being made numerically for electron/ion recombination. This approach can give an accuracy of 5% or better¹². Alternatively, ECDs can be designed so that virtually all the sample input is ionised²³ by increasing the detector volume and the pulse period (reaction time). Losses of electrons by recombination are not much affected for small sample inputs, and the output signal from such a detector, after allowance for recombination, closely approximates to the sample input.

Such "quasi-coulometric" detection modes offer probably the best method for the quantitative estimation of strongly electron-capturing materials where standard solutions for calibration are not, for whatever reason, available. Where such standards are available, however, they should be employed as the lack of precise data on the variation in positive ion concentrations in the ECD with operation conditions renders exact theoretical descriptions of the ECD impossible.

The role of impurities in determining ECD responses has already been stressed. One further aspect of this role is worth consideration, however. In the model developed here impurities can be regarded as competing with positive ions and with sample for electrons. At high impurity levels when $k_2\eta_+ \ll k_4\eta_x$ the variations of η_+ with time cease to be significant. The electron concentration under these circumstances is low and, at all pulse periods, is much less than the positive ion concentration; additionally the steady-state electron concentration is attained rapidly, perhaps in 1 msec or less. Sample responses in these circumstances are much reduced from levels in clean systems but variations in response are accurately predicted by eqn. 19 even for quite short pulse periods. In effect, the model of Wentworth *et al.*³ applies under these circumstances. It may be that failure to appreciate the role impurities play has led to ECD work being carried out under far from optimum conditions where, however, positive ion effects are insignificant, and has delayed the development of an accurate and comprehensive model of performance.

CONCLUSIONS

Exact theoretical descriptions of the operation of the ECD cannot be produced because of lack of information on the rates by which positive ions are lost by diffusion in the positive space charge field existing immediately after the electron-collection pulse. An approximate model can be developed, however, and used to compare different operating modes providing that the underlying assumptions are understood and the limiting conditions clearly defined. Consideration of such a model shows that constant-frequency rather than constant-current mode operation gives optimum

linearity of response. Because of the difficulty in exactly describing the ECD theoretically, quantitative chemical analysis requires where possible that the system be calibrated using known standards. Where standards are not available, operation in a "quasi-coulometric" mode is recommended.

GLOSSARY OF SYMBOLS

V	Detector volume (ml)
B	Rate of sample input to detector ($\text{ml}^{-1} \text{sec}^{-1}$)
B_{max}	Maximum rate of sample input for which detector response is linear ($\text{ml}^{-1} \text{sec}^{-1}$)
B_{min}	Minimum detectable rate of sample input (limit of detection) ($\text{ml}^{-1} \text{sec}^{-1}$)
R	Rate of production of thermal electrons in the detector ($\text{ml}^{-1} \text{sec}^{-1}$)
u	Carrier gas flow-rate ($\text{ml} \text{sec}^{-1}$)
Q	Electronic charge (C)
I_0	Detector current with no sample present (A)
I	Detector current, sample present (A)
ΔI	Change in detector current with sample present (A)
I_n	Detector noise level expressed as fluctuation in detector current (A)
φ	Detector current in d.c. mode ($= RVQ$) (A)
S	Detector sensitivity expressed as the change in detector current with the rate of sample input (A ml sec)
AB	Any sample molecule
AB^-	Product of reaction between sample molecules and electrons
A	Neutral product(s) of AB^- decomposition
B^-	Charged product(s) of AB^- decomposition
M	Any carrier gas molecule
M^+	Positive ion(s) formed by collision of β particles with carrier gas molecules
X	Any impurity molecule
X^-	Product(s) of reaction between impurity molecules and electrons
β	Highly energetic electrons
ϵ	Electrons at (or close to) thermal energies
η_0^0	Number density of thermal electrons in the detector in the absence of sample (ml^{-1})
η_e	Number density of thermal electrons in the detector in the presence of sample (ml^{-1})
$\bar{\eta}_e^0, \bar{\eta}_e$	Time-averaged values of η_0^0, η_e (ml^{-1})
η_+	Number density of positive ions in the detector (ml^{-1})
$\bar{\eta}_+$	Time-averaged value of η_+ (ml^{-1})
η_-	Number density of negative ions in the detector (ml^{-1})
c	Number density of sample molecules in the detector (ml^{-1})
c_{min}	Minimum detectable number density of sample molecules (ml^{-1})
m_{min}	Minimum detectable mass of sample molecules (g)
t_p	Interval between electron collection pulses in pulsed mode ECD (sec)
t_p^0	Interval between electron-collection pulses in the absence of sample in constant-current pulsed mode ECD (sec)
f	Electron-collection pulse frequency (Hz)
f^0	Electron-collection pulse frequency in absence of sample (Hz)

- f_n Detector noise level expressed as fluctuation in detector pulse frequency required to maintain constant detector current (Hz)
- k_1 Rate constant for attachment of electrons to sample molecules (ml sec^{-1})
- k_2 Electron/positive ion recombination rate constant (ml sec^{-1})
- k_3 Positive ion/negative ion recombination rate constant (ml sec^{-1})
- k_4 Rate constant for attachment of electrons to impurity molecules (ml sec^{-1})
- k_D Rate constant for loss of positive ions by diffusion (ml sec^{-1})
- k_{-1} Rate constant for the reverse of the electron-attachment reaction (sec^{-1})
- α Composite pseudo-unimolecular rate constant for electron loss from ECD in the absence of sample ($= k_2\eta_+ + u/V$) (sec^{-1})
- λ Composite pseudo-unimolecular rate constant for electron loss from ECD in the presence of sample ($= k_1c + k_2\eta_+ + u/V$) (sec^{-1})
- $t_{\frac{1}{2}}$ Width of gas chromatographic peak at half peak height (sec)
- K_1 Proportionality constant between $-\Delta I/I$ and B in long-pulse-period mode ECD (ml sec)
- K_2 Value of λt_p (or αt_p^0) which is held constant in constant-current mode ECD

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