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THE ELECTRON CAPTURE DETECTOR

THEORY AND PRACTICE

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SUMMARY

A theoretical model is presented which accurately describes the performance characteristics of the electron capture detector under practical conditions. The signal and ionization efficiency are related, by a simple numerical method, to the detector saturation current and ion recombination rate and to the rate constant of the forward reaction of electrons and sample molecules and to the flow-rate of the carrier gas. Some practical examples and a new coulometric detector are also described.

INTRODUCTION

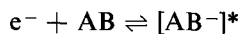
The electron capture detector has been used in gas chromatography for 17 years. It is still probably the most sensitive method of chemical analysis and through its use Wentworth and his colleagues¹⁻³ have made significant contributions to the chemistry of the gaseous free electron. Perhaps because of the pressure to use the detector in the solution of practical and theoretical problems it has barely changed since its inception. It is still a simple two-electrode ion chamber with an internal radiation source and there is no comprehensive theory of its response which explains numerically the signals it generates.

This lack of understanding has led to frustrations and to disappointments as well as to successful applications. An eloquent account of the controversial nature of this analytical method is given by Aue and Kapila⁴ in a review paper.

This paper presents a working theory of the detector which so far seems to account numerically for its responses over a wide range of applications. The practical features of analysis by electron capture are discussed in the light of this new theory. Details are also given of a new detector specifically designed to function as a gas phase coulometer and also the use of this new detector as an electronic vapour switch.

PHYSICAL BASIS

The first step in the reaction between gaseous free electrons and molecules is the formation of an excited negative ion:



The subsequent reactions of this excited negative molecular ion are complex and have been the subject of detailed investigation^{2,5}. Without denying their scientific importance and analytical significance^{3,5}, these reactions nevertheless rarely determine the practical response of the detector, because practical analysis by electron attachment is usually limited to those substances which are sensitively detected. With these substances, the equilibrium of the reaction is far to the right-hand side and heavily weighted in favour of the formation of negative molecular ions. Furthermore, the negative ions produced are rapidly scavenged by their reaction with the positive ions that are always present in vast excess within the detector. In these circumstances, it is justifiable to describe the processes causing the removal of electrons and molecules from the detector as follows:



Reaction 1 is a simple phenomenological irreversible second-order reaction with a rate constant k_1 . Reaction 2 includes all processes for removing electrons by recombination with positive ions or reaction with free radicals. Reactions 3 and 4 concern the removal of sample molecules by processes other than in reaction in the gas phase with electrons. The most important is reaction 4, the removal of sample molecules by ventilation during the flow of carrier gas.

Let us assume that the gas and electrons within the detector are uniformly mixed and that the reaction proceeds as in a stirred reactor. Fig. 1 illustrates the model. The detector volume is V , the gas flow-rate U , the rate of injection of electrons A and of sample molecules B . The sample flow-rate is assumed to be negligible compared with the gas flow-rate U . Inside the detector, the steady-state concentrations are e^- for electrons and c for molecules. The outflow of molecules from the detector is cU , and this is usually considerably less than the influx B . The residence time of electrons within the detector is too short for a sensible proportion of them to leave the detector in the carrier gas stream. It is assumed that the detector is operated in the pulse sampling mode and that the intervals between the sampling pulses are T . The units are molecules, cubic centimetres and seconds.

The rates of removal of electrons and molecules from the detector can now be specified:

$$\frac{de^-}{dt} = A - e^-(k_1c + k_d) \quad (5)$$

$$\frac{dc}{dt} = B - c\left(k_1e^- + k_x + \frac{U}{V}\right) \quad (6)$$

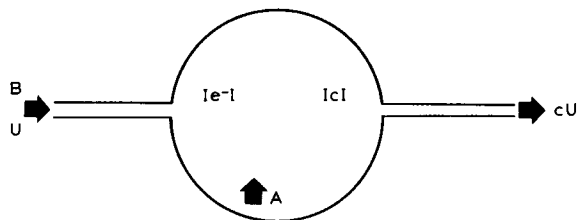


Fig. 1. Model of the detector as a stirred reactor. Carrier gas input, U ml·sec⁻¹; sample input, B molecules·sec⁻¹; electron input, A electrons·sec⁻¹; sample and electron concentrations, c and e^- particles·cm⁻³, respectively.

The free-electron concentration within the detector for a known internal sample concentration (c) can be found from eqn. 5 as follows. Let all of the electrons be removed, say by a sampling pulse. Their concentration will then increase from zero according to the equation

$$e^- = A\{1 - \exp[-(k_1c + k_a)T]\}/(k_1c + k_a) \quad (7)$$

until reduced to zero by the next sampling pulse. The interval between sampling pulses is always less than 1 msec, so that the fluctuations of the electron concentration are rapid and their time average can reasonably be used in eqn. 6 to calculate the expected sample concentration (c) from a known e^- .

The average is obtained by integrating eqn. 7 over the time period of a single sampling pulse and dividing by the pulse period:

$$e^-_{av} = A[(k_1c + k_a)T - \{1 - \exp[-(k_1c + k_a)T]\}]/(k_1c + k_a)^2T \quad (8)$$

Finally, the concentration of sample molecules within the detector is determined by substituting the average electron concentration into eqn. 9:

$$c = B\{1 - \exp[-(k_1e^- + k_x + U/V)T]\}/(k_1e^- + k_x + U/V) \quad (9)$$

In gas chromatography the sample input rate (B) changes at a rate that is very slow compared with the reaction rate time constant, so that the concentration c can be taken simply as

$$c = B/(k_1e^- + k_x + U/V) \quad (10)$$

and the exponential part of eqn. 9 will be effectively zero for these long time intervals.

Eqns. 8 and 10 can be solved numerically using a simple programmable calculator and the interesting quantities relating to detector performance are then directly available. All of the initial quantities are known, excepting only k_a and k_x . k_a is found for a given detector by observing the current at different pulse intervals when clean carrier gas is flowing. k_a is simply the pulse frequency (Hz) at which the current is $1/e$ of the current for zero pulse period. The latter is obtained by extrapolating to zero the currents at short pulse intervals. In most instances, k_x can be neglected but it can be determined by observing the response of two detectors in series.

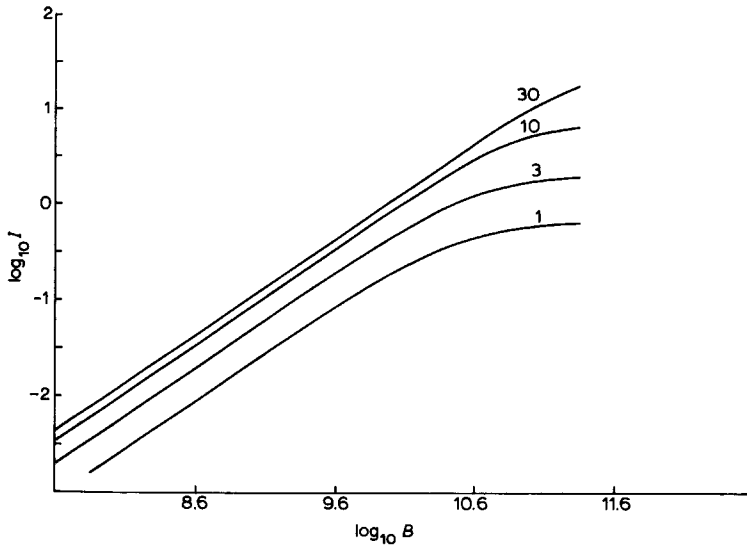


Fig. 2. Variation of detector signal current in amperes (I) with rate of sample input (B) in molecules per second. Parameter identifying lines: detector saturation current in nanoamperes.

PREDICTIONS OF THE MODEL AND COMPARISON WITH EXPERIMENTAL RESULTS

The predictions of the model can be applied to either the fixed pulse period⁶ or to the pulse frequency feedback⁷ methods of detector operation. Fig. 2 illustrates the change of detector signal current in amperes for different rates of sample input in molecules per second. The parameter varied between sets of curves is the rate of input of electrons (A) to the detector. This corresponds to the use of radioactive sources of different strengths. The figures against the curves indicate the ion current in clean carrier gas for each of the electron inputs. The sample molecule is assumed to be one with a high rate constant for reaction with free electrons and the value chosen for k_1 is $2.5 \cdot 10^{-7} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{sec}^{-1}$. With large ion currents, the electron concentration within the detector will be much greater than the sample molecule concentration over a very considerable range, and consequently the rate of ionization of the sample will be pseudo-first order with respect to sample concentration. The response in these circumstances is linear with concentration and this indeed is found in practice. The well-known Wentworth equation¹ for the response of the electron capture detector, which served so well in early days when less efficient ionization sources were used, does not apply when nearly all of the sample input is ionized. For lesser electron inputs or for less strongly electron-attaching compounds, the curvilinear response of the Wentworth relationship is again valid. Fig. 3 shows for the same conditions the variation of ionization efficiency with flow-rate of carrier gas for a constant rate of sample input which is assumed to be small. Also shown are experimental measurements using sulphur hexafluoride as the test compound for comparison. This agreement between theory and practice has been shown to hold with a wide range of test substances.

The response of the detector in the pulse frequency feedback mode⁷ of operation can also be obtained from eqns. 8 and 10 by observing the change in pulse period

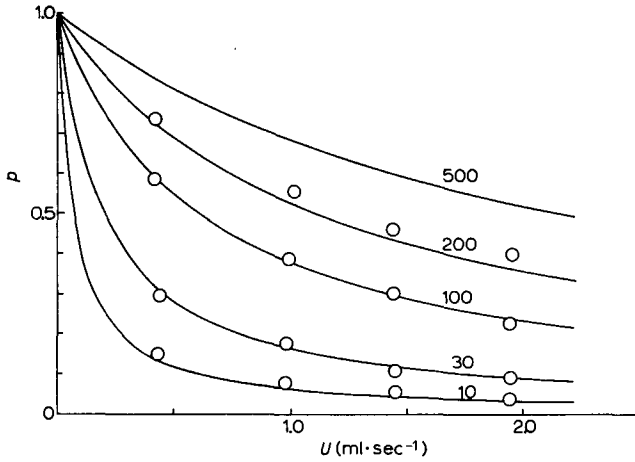


Fig. 3. Variation of ionization efficiency (p) with flow-rate of carrier gas (U). Parameter identifying lines: pulse period in microseconds. \circ , Experimental measurements with sulphur hexafluoride.

for differing sample inputs when the detector current is held constant. Fig. 4 illustrates the change in pulse frequency with variation of the rate of sample input. In Fig. 4, the rate of electron input to the detector (A) is assumed to be high, corresponding to a d.c. saturation ion current of 10^{-8} A. Also, the sample is assumed to be one with a high rate constant reaction. The parameter varied to produce the set of curves on the diagram is flow-rate of carrier gas through the detector and these different flow-rates are marked on the curves.

Fig. 4 illustrates the conditions where the pulse feedback method of operation

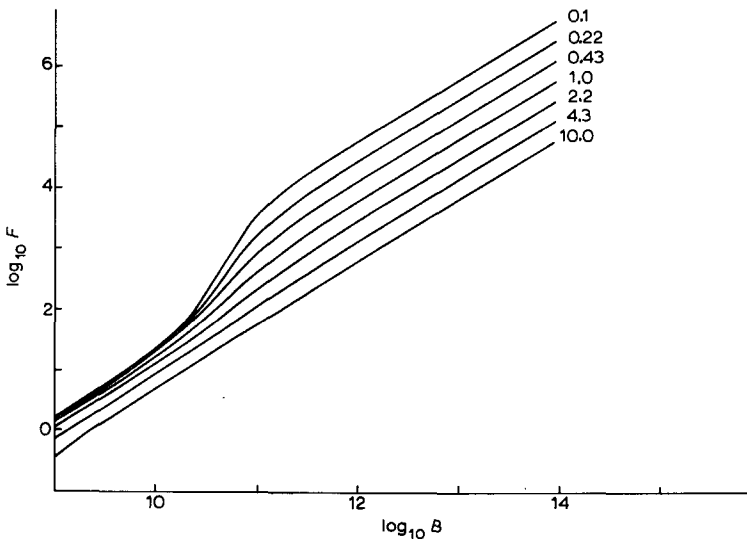


Fig. 4. Variation of pulse frequency (F Hz) with rate of sample input (B molecules \cdot sec $^{-1}$). Parameter identifying lines: flow-rate of carrier gas (U ml \cdot sec $^{-1}$). Detector saturation current: 10 nA.

fails. These are a high ionization intensity from the radioactive source, an intensely electron-attaching sample substance and a slow flow-rate of carrier gas. When all of these three conditions are present, as in the upper curves of Fig. 4, the frequency is no longer linearly related to sample concentration. However, even under these unfavourable conditions, the use of a high flow-rate of carrier gas almost restores a linear response (lower curve of Fig. 4). Fig. 5 shows as a set of lines the relationship between the pulse frequency and rate of sample input when the ion current of the detector is reduced to 10^{-9} A. The response is now linear with sample input for all but the lowest flow-rates.

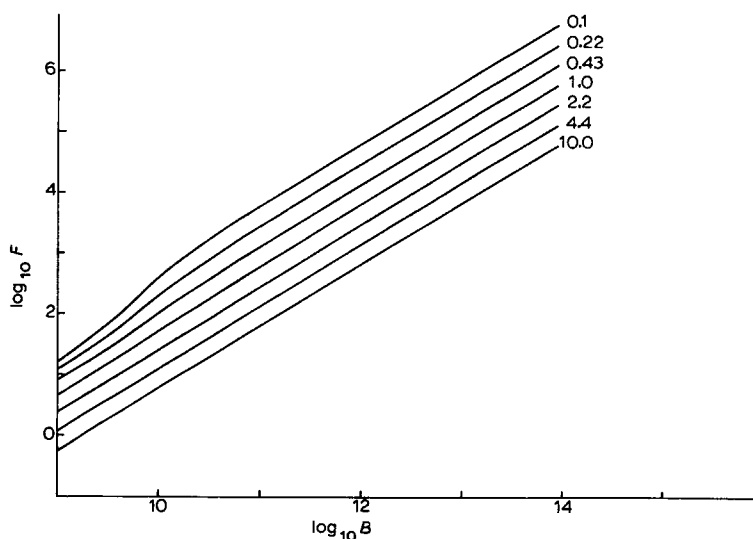


Fig. 5. Variation of pulse frequency (F Hz) with rate of sample input (B molecules \cdot sec $^{-1}$). Parameter identifying lines: flow-rate of carrier gas (U ml \cdot sec $^{-1}$). Detector saturation current: 1 nA.

RESPONSE FACTORS

The equilibrium constants for the reaction between electrons and electron-attaching compounds varies with temperature, electron energy and with the presence of other molecular species (see, for example, ref. 5). A brief examination of published detector responses reveals that, even when the above conditions are constant, large variations in detector response are still to be found. The most frequent source of these discrepancies is the failure to take account of the fact that the electron-molecule reaction is second order. Whenever the forward rate constant is large, conditions are such that the electron concentration is greater than that of the molecules being detected. Under these circumstances, the response tends towards coulometry; response factors then approach an asymptote corresponding to the complete reaction of the molecules. Figs. 2-5 indicate that small changes in either the flow-rate of carrier gas or the ionization current can significantly affect the proportion of molecules ionized and hence the detector response factor. These problems can be overcome by choosing conditions of operation such that the detector functions in the pseudo-first order reaction region.

This is usually true for weakly electron-attaching compounds when their concentration greatly exceeds that of the electrons. Also, as described in the next section, conditions where the electron concentration is in excess of sample concentration can provide consistent responses.

It is, of course, possible from a knowledge of the reaction kinetics to calculate the detector response under any conditions of operation, for example, by using eqns. 8 and 10. The comparison of experimental results with such calculations is illustrated in Fig. 3. Usually, however, this approach is less convenient than is the choice of more favourable operating conditions. Sullivan⁸ introduced a simple procedure whereby approximate rate constants for the forward reaction can be deduced from the molecular properties of candidate compounds. He also introduced a simple relationship which accurately predicts detector response in the pulse feedback mode of operation, provided that the restrictions of the pseudo-first order reaction are not violated.

Some electron reactions involve third molecular bodies. For example, the attachment of electrons to N_2O is facilitated by the simultaneous presence of CO_2 and the end-product negative ion is CO_3^- (ref. 9). This effect is not unique to either N_2O or CO_2 and can sometimes be used to improve sensitivity in analysis. But when an electron-attaching trace compound is sought in a great excess of otherwise apparently inert material, care is needed in order to check that this phenomenon is not the source of error.

COULOMETRY

The possibility of practical gas-phase coulometry has been reported¹⁰ and examples of its possible advantages and disadvantages discussed⁴. Since then, it has been found practical to design detectors in which this desirable property is enhanced. This design simulates an assembly of detectors connected in series for gas flow, but with their electrical outputs connected in parallel. If the proportion ionized in each of these detectors is p and is identical then for n detectors, the total proportion ionized is

$$p_{total} = 1 - (1 - p)^n$$

If n is greater than 5 and p greater than 0.7, ionization efficiencies for the assembly will exceed 99.8%. It is not necessary to connect five detectors in series physically; it is sufficient to construct a detector, as shown in Fig. 6, which is a long tube. The introduction of baffles to define a series of mixing zones might be a useful addition,

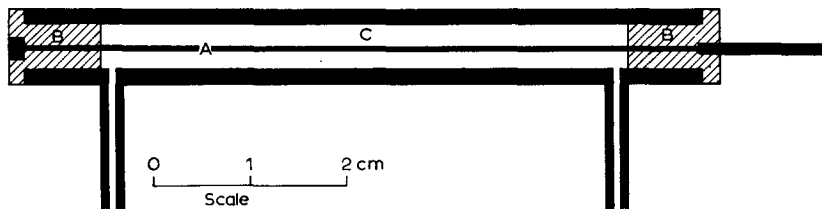


Fig. 6. Design for a coulometric detector. Body, metal; insulation, PTFE; anode wire, 0.05 cm in diameter. Radioactive source, tritium, to give a d.c. saturation current of between 30 and 50 nA.

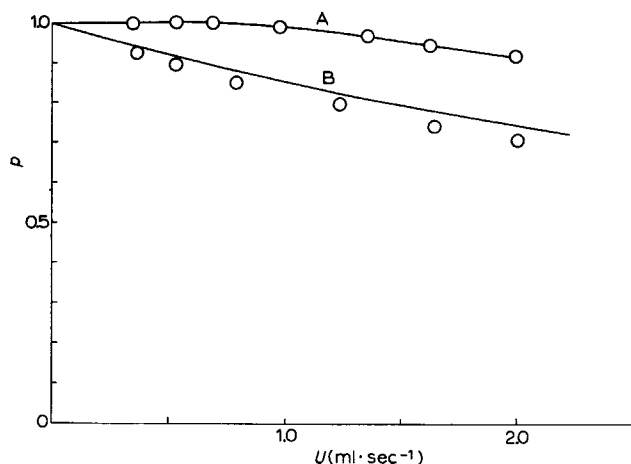


Fig. 7. Variation of ion efficiency (p) with flow-rate of carrier gas (U ml·sec⁻¹) for a coulometric detector and a square detector. Both detectors employed the same radioactive source, which was on foil 5 cm long and 1.5 cm wide. The test substance was dibromodifluoromethane.

but the performance of an open tube without baffles appears to be satisfactory for most purposes in the analysis of strong electron absorbers. Fig. 7 compares the performance of the detector shown in Fig. 6 with a detector of the same volume but of square construction and in which the gas was mixed. The test substance was dibromodifluoromethane and the long detector can be seen to be a practical coulometer for flow-rates up to as great as 60 ml·min⁻¹. In contrast, the conventional detector is only close to coulometric in response for very low flow-rates. The intriguing concept of the plate height of a theoretical detector can be applied to the long detector and it would appear to be in the region of 2 cm in the example illustrated, which is not very efficient when compared with columns but provides a good starting point.

With coulometry, the peak area (X) in ampere·seconds is related to the mass of substance (m) in grams as follows:

$$m = MX/9.65 \cdot 10^4$$

where M is the molecular weight of the substance. When coulometric the response of the detector is absolute and independent of the ambient variables of temperature and pressure.

GAS SWITCHING WITH COULOMETRIC DETECTORS

When a stream of carrier gas bearing an electron-absorbing substance passes through a coulometric detector, almost all of the substance is removed by ionization. If now a high d.c. potential is applied to the detector anode, the electrons are removed so rapidly that there is no opportunity for reaction and the electron-attaching substance flows through unaffected. The flow of substance through the detector can therefore be switched on as desired simply by applying a potential across the detector. Fig.

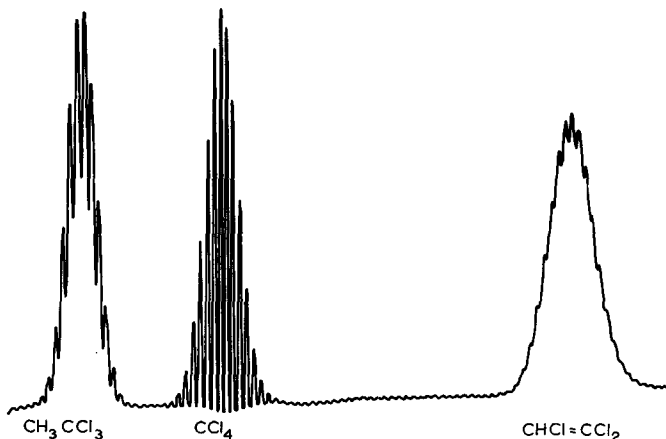


Fig. 8. The electronic switching of vapour concentration. A coulometric detector ahead of the chromatographic detector was switched on and off at 3-sec intervals. Note the complete switching of carbon tetrachloride, the partial switching of 1,1,1-trichloroethane and the slight effect only with the weak electron attacher trichloroethylene.

8 shows a chromatogram obtained by interposing such a switched detector between the column outlet and a conventional detector connected to an amplifier and a recorder. The switching phenomenon is seen to be virtually complete for the strong electron absorber carbon tetrachloride and the effect decreases with the rate of electron attachment.

This switching procedure has considerable practical interest. It provides the means of improving both sensitivity and selectivity of analysis by electron capture. Sensitivity can be improved by the selective amplification of the a.c. signal of the switching frequency followed by synchronous detection. Selectivity can be improved in that only strong absorbers give rise to the a.c. signal and the presence of a considerable excess of weakly electron-absorbing material is not seen. The existence of a precise electronic gas switch has many other applications and uses in gas chromatography and will be described in a subsequent paper.

CONCLUSIONS

The electron capture detector depends for its operation upon predictable reactions in the gas phase. If the kinetic conditions of the reaction within the detector are known, it is possible, at least in the pulse sampling mode of operation, to calculate the response to a known input of test substance. These same considerations may be true with a d.c. mode of operation but are likely to be more difficult to interpret.

In practice, provided that care is taken to avoid the second-order reaction zone, either the pulse feedback or the fixed frequency modes of operation can give consistent and reliable analysis. For strongly electron-attaching compounds, coulometric detection seems to be the method of choice. Here the detector is absolute and response factors need no longer be known. The detector is also to a considerable extent unaffected by changes in temperature, pressure or flow-rate of carrier gas.

Even at this late stage it is still worth listing the following rules for good performance:

- (1) the use of metal diaphragm diffusion-resistant pressure regulators;
- (2) the use of cleaned and baked metal tubing for all gas connections to the chromatograph;
- (3) the avoidance of flow regulators at the head of the chromatograph column as these usually employ plastic diaphragms which contaminate the gas stream;
- (4) care to insure that the injection septa have been thoroughly baked or boiled to remove electron-absorbing vapours;
- (5) the use of a quartz crystal oscillator to stabilize the pulse frequency.

This simple set of precautions was applied to the design of an automatic chromatograph for the analysis of background concentration of fluorocarbons in the air of a remote region. This apparatus has operated with a full-scale chart deflection of $5 \cdot 10^{-10}$ A, taking four samples daily for 3 months, entirely without attention. It did not include any provision for the automatic adjustment of the baseline.

It would be premature to claim that the detector is now domesticated. There are still phenomena such as negative excursions below the baseline after the emergence of a peak which require a full explanation. There is also considerable scope for the further improvement of detector sensitivity through, for example, the separate collection of the negative ions after their formation. The outstanding development of the drift tube detector by Karasek and Kane¹¹ has shown one way by which this might be achieved and some of the added advantages of so doing.

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