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## THE ELECTRON-CAPTURE DETECTOR

### II. DESIGN AND PERFORMANCE

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#### SUMMARY

The model developed in Part I is used to estimate the performance of electron-capture detectors operating in coulometric, constant-current and constant-frequency modes. Coulometric operation is difficult to achieve directly but coulometric responses can be estimated by extrapolation. Detection limits can be substantially less than 1 pg and this mode of operation is preferred where practicable. Where coulometry cannot be attained either directly or by extrapolation, the constant-frequency mode should be utilised with calibration standards for quantitative analysis. The constant-current mode offers a wide dynamic range but responses are non-linear for strongly electron-capturing materials.

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#### INTRODUCTION

The electron-capture detector (ECD) has been widely used for the analysis of trace amounts of strongly electron-capturing materials such as, for example, some explosives or pesticide residues. Detection limits of better than parts per  $10^9$  (v/v) have been achieved but at these low levels quantitative analysis is difficult, not least because ECD responses under practical working conditions are themselves difficult to predict. In Part I<sup>1</sup> a theoretical model of the operation of the ECD under certain limiting conditions was developed and the extrapolation of results from this model to practical conditions was discussed. The object here is to examine detector design and performance in the light of this model and to make recommendations concerning the optimum operational modes for quantitative analysis with the ECD.

#### ECD DESIGN

The most important decision facing the ECD designer is the specification of the electron source. For compatibility with gas chromatographic (GC) columns and to ensure that the resolution of chromatographic separations is not affected by dead volumes, detector volume should be small, typically not more than a few millilitres; source size is therefore limited. In addition, since the detector will be required for

routine work, the source should have the minimum possible requirements for operational controls and for maintenance. The range of choice is thus severely restricted and almost every ECD described to date has relied on a radioactive  $\beta$  particle emitter as the electron source.

Thermal electrons, designated  $\varepsilon$ , are produced from  $\beta$  particles by interactions with carrier gas molecules



Typically each  $\beta$  particle has an initial energy  $\approx 10$  keV and around 30 eV are expended in forming an electron/positive ion pair in normal carrier gases (argon/methane or nitrogen), (see, for example ref. 2, p. 35). Each  $\beta$  particle will thus produce  $10^2$ – $10^3$  thermal electrons so that a 1-mCi or  $4 \cdot 10^7$   $\beta$  particles per sec source will give  $\approx 10^{10}$  electrons per sec and a maximum current of *ca.* 1 nA.

Direct ionisation of the carrier gas as shown in eqn. 1 is the most probable process when nitrogen is the carrier but in argon metastable atoms may be formed.



These metastable argon atoms have a relatively long lifetime and would be lost from the detector by ventilation unless deactivated. The deactivation process normally involves production of an electron/ion pair by reaction with any polyatomic molecule



Thus with pure argon as carrier the presence of sample increases the electron concentration and thus the detector current, the reverse of the desired electron-capturing effect, leading to anomalous responses. Addition of  $\approx 5\%$  methane to the carrier results in all metastables being deactivated by methane and prevents this type of response.

The rate of thermal electron production by eqn. 1 (or by eqns. 2 and 3) is subject to fluctuations due to the stochastic nature of radioactive decay. Noise produced in the ECD system as a result of these fluctuations is a major factor in determining the limits of detection of the system. The noise may be minimised by selecting sources with the maximum possible activity compatible with safety and with the minimum possible  $\beta$  particle energy.

Some relevant properties of currently available  $\beta$  particle sources are given in Table I<sup>3,4</sup>. The maximum current and noise levels are typical values and are taken from Dwight *et al.*<sup>4</sup>; the  $\beta$  particle energy is the value at the maximum of the number/energy distribution. The rate of electron production is calculated directly from the maximum current assuming that at this maximum all the electrons produced are collected. In a clean system the current is independent of temperature (see, *e.g.*, ref. 5).

Most commercially produced detectors employ <sup>63</sup>Ni sources since they are readily available and operate to reasonably high temperatures. Tritium sources seem attractive in that they offer high activity combined with low  $\beta$  particle energy but their performance in practice often falls below expectation, perhaps because of surface contamination effects. The <sup>55</sup>Fe source has only recently been described<sup>4</sup>. It has a

TABLE I  
SOME PROPERTIES OF ELECTRON SOURCES FOR THE ECD

<i>Properties</i>	<i>Sources</i>			
	<sup>63</sup> Ni foil	<sup>3</sup> H titanium foil	<sup>3</sup> H in scandium foil	<sup>55</sup> Fe on nickel alloy foil
$\beta$ particle energy (keV)	66	18	18	5.387–5.640
$\beta$ particle range (mm)	$\approx 10$	$\approx 2.5$	$\approx 2.5$	$\approx 0.5$
Maximum activity (mCi cm <sup>-2</sup> )	10	170		3
Upper temperature limit (°C)	350	220	325	400
Maximum current (pA)	9	30		0.5
	(15-mCi source)	(500-mCi source)		(5-mCi source)
Rate of electron production, $R\nu$ (sec <sup>-1</sup> )	$6 \cdot 10^{10}$	$2 \cdot 10^{11}$		$3 \cdot 10^9$
Noise level* (pA)	1.5	3		0.1

\* Measured at ambient pressure in nitrogen at 21°C.

relatively low activity and rate of electron production but this is compensated for by its low noise level and, as will be seen below, this source appears to have attractive properties for some applications. However, it should be stressed that published information on GC-ECD work with <sup>55</sup>Fe sources is extremely limited and the practical value of the source remains to be proven.

A variety of detector geometries have been employed in the past, some important examples of which are shown in Fig. 1. The plane parallel designs tend to have larger volumes than the cylindrical and for this reason the latter are preferred. In the coaxial design the distance from source to anode should be greater than the  $\beta$  particle range to ensure that all  $\beta$  particles are fully deactivated, maximising electron production, and to prevent collisions of energetic  $\beta$  particles with the anode which may cause surface corrosion and increase adsorption rates. The distance should not however be so great as to make efficient electron collection impossible when a narrow ( $\approx 1 \mu\text{sec}$ ), low-voltage (50 V) pulse is applied to the anode. This condition is easily met for low-diameter tritium or <sup>55</sup>Fe detectors, particularly when argon-methane is the carrier gas but it is less readily met with <sup>63</sup>Ni sources and nitrogen carrier. Nitrogen will deactivate energetic electrons to thermal levels only inefficiently, methane is very much more effective. Electrons in nitrogen therefore tend to be at somewhat higher energies than in argon-methane and are thus less affected by electric fields and less easily collected. Van de Wiel and Tommassen<sup>5</sup> have clearly demonstrated this effect using a detector with a 10-mCi <sup>63</sup>Ni source. They found that a 40-V pulse of  $< 4 \mu\text{sec}$  duration was sufficient to collect all the electrons in the detector when argon-methane was the carrier gas but a pulse duration  $> 20 \mu\text{sec}$  was required with nitrogen.

In displaced coaxial cylinder designs, the cell geometry is such that direct collisions of  $\beta$  particles with the anode are unlikely and smaller diameters are possible within the limitation that collisions of  $\beta$  particles with the radioactive source itself should be minimised. Again the distance from the reaction volume to the anode

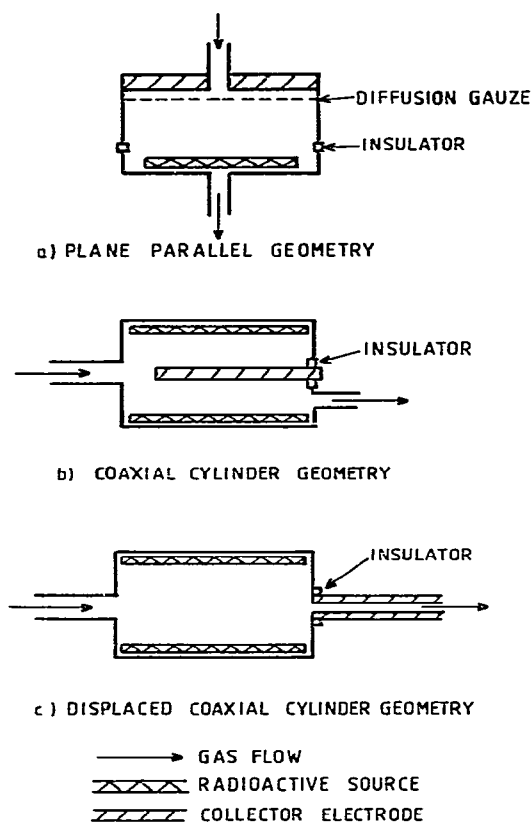


Fig. 1. Schematic diagram of alternative ECD geometries.

should not be great enough to prevent all of the electrons in the cell being collected at each pulse.

Coaxial cylinder cells with  $^{63}\text{Ni}$  sources typically have volumes of up to 5 ml and a diameter of 1–2 cm. Displaced coaxial cylinder designs can be rather smaller. Patterson<sup>6</sup> has described such a cell with a total volume of 0.3 ml employing a 7.5-mCi  $^{63}\text{Ni}$  source. Even with nitrogen as carrier a 50-V pulse of 0.64  $\mu\text{sec}$  duration was sufficient to collect all electrons present. It is unlikely that other commercially available ECD systems will achieve this performance, but since most manufacturers do not provide a variable pulse width facility it is difficult to check this.

The remaining feature of ECD design which warrants consideration is the need for adequate temperature control. Since the ECD should always be operated at a temperature above that of the GC column in order to minimise contamination by condensation of column effluents, it requires its own temperature control system separate from the GC oven. In addition, since detector response is for many materials a function of temperature, this control system should provide a detector temperature which is well defined throughout the volume and closely controlled. In some commercial designs ECD temperature is controlled only by placing the base of the detector body in contact with a thermostatically controlled metal block. This is likely to produce a temperature gradient within the detector and as such is unsatisfactory.

Devaux and Guiochon<sup>7</sup> argue that in the worst case temperature fluctuations of  $\pm 0.01^\circ\text{C}$  can give a noise level in the ECD of 1 pA. Their detector current increased strongly with temperature however, suggesting that the system was contaminated, possibly with oxygen in the carrier gas<sup>5</sup>. Probably a more realistic estimate for a reasonably clean system is that by Pellizzari<sup>8</sup> who argues that a fluctuation of  $\pm 0.3^\circ\text{C}$  will produce an error of 1% in the determined concentration of sample. Likewise, a fluctuation of  $\pm 3^\circ\text{C}$  will produce an error of 10%. In the absence of impurity, temperature control to  $\pm 1^\circ\text{C}$  is adequate but oxygen impurity in the carrier gas will severely increase the system noise level unless temperatures are controlled to  $\pm 0.1^\circ\text{C}$  or better.

## DETECTOR PERFORMANCE

### *Definitions and numerical values*

The major concern of this part of the report is to produce numerical estimates of ECD performance for different modes of operation and for materials with different electron capture rate coefficients. The aspects of performance of most interest are the limit of detection (the smallest detectable sample input concentration) and the linear response range (the range of sample input concentrations over which detector response is linear with concentration). Estimates will be based on the assumption that the detector and the carrier gas are clinically clean.

The ECD operating conditions giving optimum detection of a particular material are a function of the ability of that material to capture electrons as measured by the rate constant,  $k_1$ , of the electron-capture reaction.



For the present purpose, and quite arbitrarily, materials for which  $k_1 \rightarrow 5 \cdot 10^{-7} \text{ ml sec}^{-1}$ , the collision theory limiting rate constant<sup>9</sup>, will be described as being strongly electron capturing and materials for which  $k_1 \approx 10^{-10} \text{ ml sec}^{-1}$  as weakly electron capturing. Materials for which  $k_1 < 10^{-10} \text{ ml sec}^{-1}$  are likely to be more efficiently detected by techniques other than electron capture and are not considered here.

The electron/positive ion recombination rate constant,  $k_2$ , and the negative ion/positive ion recombination rate constant,  $k_3$ , have comparable values<sup>1</sup>, normally in the range  $10^{-6}$  to  $10^{-7} \text{ ml sec}^{-1}$  (refs. 10 and 11). For these calculations it will be assumed that  $k_2$  and  $k_3$  are equal and a value of  $5 \cdot 10^{-7} \text{ ml sec}^{-1}$  will be adopted.



The notation adopted is that defined previously<sup>1</sup>; a glossary of symbols employed is given on pp. 208 and 209. The identities

$$\lambda = k_1 c + k_2 \eta_+ + u/v \quad (7)$$

and

$$\alpha = k_2 \eta_+ + u/v \quad (8)$$

will be employed for convenience.

### Coulometric operation

It follows<sup>1</sup> that, when the conditions

$$k_1 \bar{\eta}_e \gg u/v \quad (9)$$

and

$$t_p \ll \alpha^{-1} \quad (10)$$

are met the response of an ECD is given by

$$\Delta I_{\text{coul}} = I_0 - I = vQB \quad (11)$$

This type of response, where the change in the number of electrons collected per unit time exactly equals the number of sample molecules input in that time, is described as being coulometric. With the possible exception of cases where electrons react with products of the original electron-capturing reaction (eqn. 4), it represents the largest possible response.

In a GC system the gas flow,  $u$ , cannot be much less than  $0.1 \text{ ml sec}^{-1}$ . If it is assumed that eqn. 9 is met at this flow-rate and that positive ion losses by diffusion can be ignored then the pulse periods at which eqn. 10 holds can be evaluated. When  $t_p \ll \alpha^{-1}$  and if positive ions are lost only by ventilation then from ref. 1,

$$\eta_+ = Rv/u \quad (12)$$

Using values of  $Rv$  from Table I,  $\eta_+$  and  $k_2 \eta_+$  can be estimated and hence the maximum value of  $t_p$  estimated as one tenth of the value of  $(k_2 \eta_+)^{-1}$ ; it is assumed that  $k_2 \eta_+ \gg u/v$  so that  $k_2 \eta_+ = \alpha$ , this is true in any practical system. Results are given in Table II.

TABLE II

### POSITIVE ION CONCENTRATION AND MAXIMUM PULSE PERIODS FOR COULOMETRIC RESPONSE

Gas flow-rate,  $u = 0.1 \text{ ml sec}^{-1}$ . It is assumed that  $k_1 \bar{\eta}_e \gg u/v$  and that positive ions are lost only by ventilation.  $k_2 = 5 \times 10^{-7} \text{ ml sec}^{-1}$ ,  $t_p(\text{max}) = 0.1 (k_2 \eta_+)^{-1}$ .

	$Rv$ ( $\text{sec}^{-1}$ )	$\eta_+$ ( $\text{ml}^{-1}$ )	$k_2 \eta_+$ ( $\text{sec}^{-1}$ )	$t_p(\text{max})$ ( $\mu\text{sec}$ )
<sup>55</sup> Fe (5 mCi)	$3 \cdot 10^9$	$3 \cdot 10^{10}$	$1.5 \cdot 10^4$	7.0
<sup>63</sup> Ni (15 mCi)	$6 \cdot 10^{10}$	$6 \cdot 10^{11}$	$3 \cdot 10^5$	0.3
<sup>3</sup> H (500 mCi)	$2 \cdot 10^{11}$	$2 \cdot 10^{12}$	$1 \cdot 10^6$	0.1

In real systems positive ion diffusion losses cannot be ignored and positive ion concentrations will be less than and maximum pulse periods greater than those estimated in Table II. Nevertheless Table II does illustrate that very short pulse periods are required for true coulometry and, under these conditions, electron concentrations are very low leading to low dynamic range and a rapid fall-off in sensitivity with increasing sample input. Lovelock and Watson<sup>12</sup> have pointed out that improved performance is achieved by operating at longer pulse periods, typically 100–300  $\mu\text{sec}$ , and making allowance for electron loss by recombination. Provided that the change in detector current  $\Delta I$  is relatively small, say less than 10% of the detector standing current, then electron recombination is little affected by the presence of sample. The fraction,  $p$ , of the electrons produced which are collected by the pulse can be estimated from

$$p = \frac{\eta_e^0(t_p)}{Rvt_p} = I_0/\varphi \quad (13)$$

where  $I_0$  is the observed current in the absence of sample and  $\varphi$  the maximum possible (zero pulse period) current. The observed sample response  $\Delta I$  is then converted to the coulometric response  $\Delta I_{\text{coul}}$  by

$$\Delta I_{\text{coul}} = \Delta I/p \quad (14)$$

The sample response  $\Delta I$  should of course be determined under conditions where the condition (eqn. 9), which implies complete sample ionisation, is met. Data from Lovelock *et al.*<sup>13</sup> and calculations by Lovelock and Watson<sup>12</sup> indicate that this is hardly possible at gas flow-rates compatible with chromatographic applications (except perhaps in large-volume detectors) but that complete ionisation is approached as the flow-rate is reduced. Under these conditions the extent of sample ionisation was shown in Part I to be given by

$$x = \frac{k_1 \bar{\eta}_e}{k_1 \bar{\eta}_e + u/v} \quad (15)$$

so that

$$\frac{1}{x} = 1 + \frac{u}{k_1 \bar{\eta}_e v} \quad (16)$$

Hence  $x \rightarrow 1$  as  $u \rightarrow 0$  and, provided  $\bar{\eta}_e$  is not a function of carrier gas flow-rate, the sample response at complete ionisation can be determined from a plot of the reciprocal response against flow-rate by extrapolating to zero flow<sup>12</sup>. It needs to be stressed that, for this method to be applicable,  $\bar{\eta}_e$  must not vary significantly with carrier gas flow-rate so that reactions with impurities such as GC column bleed, which might be expected to vary in concentration with flow, must not be a significant electron loss mechanism. The coulometric response can only be estimated in a clean ECD system.

Limits of detection in the coulometric mode can be calculated from eqn. 11

with  $\Delta I = 2 \times$  system noise and  $v_{\frac{1}{2}} = 1$  ml. This gives the limit in terms of rate of sample input and conversion to the corresponding sample concentration at the limit depends on the shape of the input chromatographic peak. Very crudely, the peak can be regarded as triangular with widths at half peak height,  $t_{\frac{1}{2}}$ , of between 5 sec and 30 sec covering the range likely to be encountered in practice. It follows then that the limit of detection in terms of concentration is

$$c_{\min} = B_{\min} t_{\frac{1}{2}} \quad (17)$$

Values of  $B_{\min}$  and  $c_{\min}$  have been calculated for  $^{55}\text{Fe}$ -,  $^{63}\text{Ni}$ - and  $^3\text{H}$ -based detectors. An estimate of the minimum mass which can be detected has also been made on the assumption of a sample molecular weight of 150. The results are given in Table III.

TABLE III

## LIMITS OF DETECTION IN THE COULOMETRIC MODE

Calculated from  $B_{\min} = 2 \times \text{Noise}/vQ$ . Limiting concentrations are based on GC peak half-widths of 5 and 30 sec and limiting masses on the basis of a molecular weight of 150.

	Noise (pA)	$B_{\min}$ ( $\text{ml}^{-1} \text{sec}^{-1}$ )	$t_{\frac{1}{2}} = 5 \text{ sec}$		$t_{\frac{1}{2}} = 30 \text{ sec}$	
			$c_{\min}$ ( $\text{ml}^{-1}$ )	$m_{\min}$ (fg)	$c_{\min}$ ( $\text{ml}^{-1}$ )	$m_{\min}$ (fg)
$^{55}\text{Fe}$ (5 mCi)	0.1	$1.25 \cdot 10^6$	$6 \cdot 10^6$	1.5	$3.75 \cdot 10^7$	9.3
$^{63}\text{Ni}$ (15 mCi)	1.5	$1.875 \cdot 10^7$	$9 \cdot 10^7$	22	$5.6 \cdot 10^8$	140
$^3\text{H}$ (500 mCi)	3	$3.75 \cdot 10^7$	$1.9 \cdot 10^8$	47	$1.1 \cdot 10^9$	275

The limits shown in Table III represent the best possible ECD performance. It is unlikely that these limits can be attained directly in a single observation; multiple injections to estimate zero flow responses and correction for electron recombination are required, complicating the method. Nevertheless this mode of operation is attractive for quantitative studies where, for one reason or another, calibration standards are not available<sup>12</sup>. It should be noted that the method employs constant frequency ECD operation and not the constant-current mode now so often supplied in commercial equipments.

The upper limit to the linear range in coulometric mode is reached when sample input,  $B$ , approaches the rate of electron production,  $Rv$ , of the source so that  $\bar{n}_e$  falls and eqn. 9 cannot be met. The range is therefore certainly less than  $Rv/B_{\min}$  and for all three sources is unlikely to exceed  $\approx 5 \cdot 10^2$ .

An alternative approach to coulometry is to employ a d.c. mode detector so that  $t_p = 0$  and eqn. 10 is met under all conditions. In the d.c. mode the electron concentration is determined by the rate of electron production and the electron drift velocity between source and collector under the influence of the permanently applied collection voltage. Charge separation effects and the short residence time of electrons in the ECD minimise electron/ion recombination. Typically the field in the detector may be  $100 \text{ V cm}^{-1}$  and under these conditions at atmospheric pressure the electron



drift velocity is  $4 \cdot 10^5$  cm sec<sup>-1</sup> (ref. 10, p. 545). Assuming a cross sectional area in the drift region of 1 cm<sup>2</sup>, the electron densities,  $\bar{\eta}_e^0$ , in <sup>55</sup>Fe-, <sup>63</sup>Ni- and <sup>3</sup>H-based detectors can therefore be estimated as  $7.5 \cdot 10^3$  ml<sup>-1</sup>,  $1.5 \cdot 10^5$  ml<sup>-1</sup> and  $5 \cdot 10^5$  ml<sup>-1</sup> respectively. Taking  $k_1$  to have its largest possible value of  $5 \cdot 10^{-7}$  ml sec<sup>-1</sup>, eqn. 10 can therefore be met in a d.c. ECD for values of  $u$  less than about  $4 \cdot 10^{-4}$  ml sec<sup>-1</sup>,  $7.5 \cdot 10^{-3}$  ml sec<sup>-1</sup> and  $2.5 \cdot 10^{-2}$  ml sec<sup>-1</sup> for <sup>55</sup>Fe-, <sup>63</sup>Ni- and <sup>3</sup>H-based detectors, respectively. Such low values are difficult, if not impossible, to reconcile with chromatographic requirements and extrapolation to zero flow of responses determined at a series of flow-rates is still required. In addition d.c. mode ECD operation is problematic because of space charge and contact potential effects<sup>14</sup> which can lead to distortion of peak shapes and, in extreme cases, to spurious peaks. For these reasons the d.c. mode is rarely used.

*Operation at constant frequency, long pulse periods*

At long pulse periods,

$$t_p \gg \lambda^{-1} \quad (18)$$

and with

$$k_1 \bar{\eta}_e \ll u/v \quad (19)$$

the detector response is given by

$$\frac{I_0 - I}{I} = \frac{\bar{\eta}_e^0 k_1 v}{Ru} B \quad (20)$$

and is linear in sample concentration.

For small samples  $I \approx I_0$  and, since

$$I_0 = \eta_e^0 vQ/t_p \text{ and } \eta_e^0 = \bar{\eta}_e^0 \text{ at long times.}$$

eqn. 18 can be written as

$$\Delta I = I_0 - I = \frac{\bar{\eta}_e^0{}^2 v^2 Qk_1}{Rut_p} B \quad (21)$$

As was shown previously<sup>1</sup> with  $t_p \gg \alpha^{-1}$  then

$$\eta_+ = \bar{\eta}_e^0 = \frac{R}{\alpha} \quad (22)$$

In practice  $\alpha = k_2 \eta_+$  since  $k_2 \eta_+ \gg u/v$  so that

$$\eta_+ = \bar{\eta}_e^0 = \left( \frac{R}{k_2} \right)^{\frac{1}{2}} \quad (23)$$

and substituting in eqn. 21 gives

$$\Delta I = \frac{v^2 Q k_1}{k_2 u t_p} B \quad (24)$$

The best possible limits of detection in this mode are obtained with  $k_1$  as large and  $t_p$  as small as is possible consistent with eqns. 18 and 19 which, for the purposes of these calculations, can be assumed to be when

$$t_p (\text{min}) = \frac{10}{k_2 \eta_+} \quad (25)$$

and

$$k_1 (\text{max}) = 0.1 (u/v) \overline{\eta_e^0} \quad (26)$$

Substituting these expressions in eqn. 24 and substituting from eqn. 23 for  $\overline{\eta_e^0}$  and  $\eta_+$  gives

$$\Delta I = \frac{vQB}{100} \quad (27)$$

Thus the greatest possible response in this mode is two orders of magnitude less than the coulometric response.

The upper limit to the range of the detector in this mode is reached when the detector current falls to a level approaching the system noise level  $I_n$ . At this limit, eqn. 18 can be written

$$\frac{I_0}{2I_n} = \frac{\overline{\eta_e^0} k_1 v}{Ru} B_{\text{max}} \quad (28)$$

Also from eqn. 18 we have

$$\frac{2I_n}{I_0} = \frac{\overline{\eta_e^0} k_1 v}{Ru} B_{\text{min}} \quad (29)$$

so that the linear range of the system is

$$\frac{B_{\text{max}}}{B_{\text{min}}} = \left( \frac{I_0}{2I_n} \right)^2 \quad (30)$$

The optimum limits of detection for linear responses in the long pulse period mode for three types of detector are listed in Table IV. Also listed are the electron and positive ion concentrations, the linear range and the values of  $k_1$  and  $t_p$  calculated from eqns. 25 and 26 with  $v = 1$  ml and  $u = 1$  ml sec<sup>-1</sup>. It should be noted that this mode is applicable only to weakly electron capturing materials. For materials with

TABLE IV  
LIMITS OF DETECTION IN LONG PULSE PERIOD MODE

Optimum detection limits,  $B_{\min}$ , in long pulse period constant-frequency mode and the corresponding values of  $k_1$  and  $t_p$  ( $v = 1 \text{ ml}$ ,  $u = 1 \text{ ml sec}^{-1}$ ). For lower values of  $k_1$  or greater values of  $t_p$ ,  $B_{\min}$  will rise while for higher values of  $k_1$  or lower values of  $t_p$ ,  $B_{\min}$  will decrease but the response will be non-linear.

	$R$ ( $\text{ml}^{-1} \text{ sec}^{-1}$ )	$\bar{\eta}_e^0 = \eta_+$ ( $\text{ml}^{-1}$ )	$k_1$ (max) ( $\text{ml sec}^{-1}$ )	$t_p$ (min) (ms)	Noise (pA)	$B_{\min}$ ( $\text{ml}^{-1} \text{ sec}^{-1}$ )	Linear range
$^{55}\text{Fe}$ (5 mCi)	$3 \cdot 10^9$	$7.7 \cdot 10^7$	$1.2 \cdot 10^{-9}$	260	0.1	$1.25 \cdot 10^8$	$6 \cdot 10^6$
$^{63}\text{Ni}$ (15 mCi)	$6 \cdot 10^{10}$	$3.5 \cdot 10^8$	$2.8 \cdot 10^{-10}$	60	1.5	$1.9 \cdot 10^9$	$9 \cdot 10^6$
$^3\text{H}$ (500 mCi)	$2 \cdot 10^{11}$	$6.3 \cdot 10^8$	$1.6 \cdot 10^{-10}$	30	3	$3.8 \cdot 10^9$	$2.5 \cdot 10^7$

higher electron-capture rate constants,  $k_1$ , improved (*i.e.*, lower) limits of detection may be obtained but, for small samples, the response is non-linear in sample concentration. Sensitivity will in fact decrease as sample concentration is increased until  $\bar{n}_e$  falls to a value where the condition in eqn. 19 can be met. The best possible response at long pulse periods is obtained with  $k_1$  sufficiently large to ensure that every sample molecule captures an electron. Under this condition the limit is determined from the fraction of the electrons produced in the detector which are actually collected rather than being lost by recombination or ventilation. For small samples and at long pulse periods this fraction is  $\bar{n}_e^0/Rt_p$  and for the sources of interest is  $\approx 8\%$  or less, at least one order of magnitude less than the coulometric mode.

Materials with lower values of  $k_1$  than those tabulated will give a correspondingly worse (*i.e.*, higher) limit of detection but the linear range will be unaltered.

#### Operation at constant frequency, intermediate and short pulse periods

The long pulse period mode just described provides excellent linear range for weakly electron capturing materials but it does not provide the optimum lower detection limit. The condition for optimum detection of such materials derived in Part I can be written as

$$\alpha t_p \approx 1.79 \quad (31)$$

The approximation results from the variation in  $\bar{\eta}_+$  with  $t_p$ . The weakly electron capturing condition is met if  $k_1 \bar{\eta}_e \ll u/v$ . It was further shown that the sensitivity,  $S$ , of the ECD for weakly electron capturing materials is given by

$$S = \frac{dI}{dB} = \frac{k_1 v}{u} \frac{dI}{d\lambda} \quad (32)$$

while

$$I = \frac{\varphi}{\lambda t_p} [1 - \exp(-\lambda t_p)] \quad (33)$$

where  $\varphi = RvQ$ . Substituting  $\lambda t_p = 1.79$  into eqn. 33 gives

$$I = 0.47\varphi \quad (34)$$

$\varphi$  is the maximum (*i.e.*, d.c.) current available from the detector.

To the extent that  $\eta_+$  can be regarded as constant, optimum detection of weakly electron-capturing materials is achieved at the pulse period giving a standing current of about half the maximum available (d.c.) current. With  $\lambda t_p = 1.79$  it follows that

$$S = -0.3 \frac{k_1 v \varphi}{u \lambda} \quad (35)$$

For small samples,  $\lambda$  can be replaced by  $\alpha$  and, under normal operating conditions  $\alpha = k_2 \eta_+$  so that both  $\alpha$  and  $\varphi$  vary with source strength. At short pulse periods  $\alpha$  is linear in source strength  $R$  (eqn. 12) and at long pulse periods it is linear in  $R^{\frac{1}{2}}$  (eqn. 23). At these intermediate pulse periods an intermediate dependence is expected so that  $S$  should increase with source strength but the increase should not be large.

The lower limit of detection can be derived from the expression

$$B_{\min} = \frac{2I_n}{S} \quad (36)$$

provided that  $S$  can be estimated. However  $S$  is a function of  $\alpha$  and hence of  $\eta_+$  and at these intermediate pulse periods the value of  $\eta_+$  is a function of pulse period. It is therefore not possible to produce a general expression for  $B_{\min}$  in this mode and optimum detection limits need to be determined experimentally. The model can be used only to make the qualitative statements that (a) optimum detection of weakly electron-capturing materials is achieved at a pulse period such that the detector standing current is about half of its maximum (zero pulse period) value, and (b) that for more strongly electron-capturing materials optimum detection is obtained at shorter pulse periods with the limit of detection for strongly electron-capturing materials approaching, but not attaining, the coulometric limit. Since detector responses in this mode cannot be theoretically predicted, quantitative work demands the use of accurately calibrated standard solutions of samples of interest in the relevant concentration ranges. For low-level trace analysis, preparation of such standards may be a major problem in itself<sup>12</sup>.

The linear range in this pulse mode is also difficult to estimate from first principles. The condition for linearity of response is that  $S$  does not change significantly with sample input which, from eqn. 35, implies that  $\lambda$  is constant. This condition is met for small samples,  $k_1 c \ll k_2 \eta_+$ , when  $\lambda = \alpha$  but this small sample condition requires knowledge of the positive ion concentration if it is to be used quantitatively and this information is not available. In practical ECD systems a linear response (within 5%) is obtained in this mode for samples which remove up to 30% of the available standing current of the detector, corresponding to a range of about  $10^2$ – $10^3$  in input concentration.

One final point is worth making: at short pulse periods, detection of strongly electron-capturing materials is optimised while more weakly capturing materials are more efficiently detected at longer periods. Short pulse period operation increases the selectivity of the detector for strongly electron-capturing materials. Since these are the materials most likely to be selected for detection by electron capture the short pulse period mode is widely used in practice.

*Constant-current operation*

The response of an ECD operating in constant current mode was given in Part I as

$$f - f_0 = \frac{f_0 k_1}{\alpha} c \quad (37)$$

and for samples for which  $k_1 \bar{\eta}_e \ll u/v$ , so that the extent of ionisation is small, this becomes

$$f - f_0 = \frac{f_0 k_1 v}{\alpha u} B \quad (38)$$

At the limit of detection  $B$  approaches zero and  $f \approx f_0$ . The base frequency  $f_0$  giving the optimum limit of detection for a particular sample in this mode is therefore identical with the frequency of operation which gives the optimum limit in the constant-frequency mode. As in the constant-frequency mode, the optimum base frequency  $f_0$  varies from material to material with electron-capturing ability and, for weakly electron-capturing materials, is defined by  $\alpha = 1.79 f_0$ . The difficulty in calculating values for  $\alpha$  from first principles means that the optimum detection condition must be determined experimentally.

Eqn. 38 is the equivalent of eqn. 21 in the constant-frequency mode with the important difference that eqn. 38 is valid for all values of  $f_0$  (or  $t_p$ ) while eqn. 21 is valid only for small values of  $f_0$ . For materials and detector designs for which eqn. 38 holds the linear range is given by

$$\frac{B_{\max}}{B_{\min}} = \frac{f_{\max} - f_0}{2f_n} \quad (39)$$

where  $f_{\max}$  is the maximum possible frequency (*i.e.*, the reciprocal of the pulse width and  $f_n$  the noise level. Typically  $f_{\max}$  is  $\approx 10^6$  Hz,  $f_0 \approx 10^3$  Hz and  $f_n \approx 5$  Hz so that the linear range is  $10^5$ . In practice since  $\alpha$  varies with  $f_0$  the linear range is perhaps an order of magnitude less. For weakly electron-capturing materials therefore, constant-current operation combines optimum detection limits with a wide linear range.

For strongly electron-capturing materials the constant-current detector response is given by eqn. 37 and, in the limit where  $k_1 \bar{\eta}_e \gg u/v$  so that  $B = k_1 \bar{\eta}_e c$ ,

$$f - f_0 = \frac{f_0}{\alpha \bar{\eta}_e} B \quad (40)$$

If  $\eta_+$  and therefore  $\alpha$  can be regarded as constant, it follows from eqn. 40 that the response to strongly electron-capturing materials in this constant current mode is linear only for small sample inputs where  $\bar{\eta}_e = \bar{\eta}_e^0$ . As the sample input increases  $\bar{\eta}_e$  and, with it, the extent of sample ionisation fall until, for high enough inputs, eqn. 38 holds. Thus for a strongly electron-capturing material in a detector for which  $k_1 \bar{\eta}_e^0 \gg u/v$ , the detector response will be large and constant for small sample inputs but will

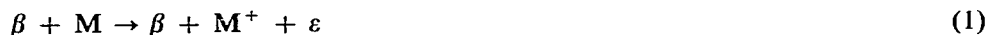
fall away to a lower level as sample input is increased, subsequently remaining constant at this level up to high inputs. This non-linearity in constant current ECD response is often ignored but it needs to be stressed that optimum linearity is only obtained if the degree of sample ionisation is small and is thus not compatible with optimum detection. As in the constant-frequency mode, optimum detection limits for strongly electron-capturing materials approach but do not attain the coulometric limit. Quantitative work in this mode again demands the use of accurately calibrated samples and is, of course, complicated by the non-linear response.

## DISCUSSION

### *Detector design*

The lack of any alternative to  $\beta$  particle emitters as ECD electron sources imposes severe limitations on detector design and application. Such sources are inadequate in two respects which have important practical consequences; they produce a population of electrons at energies which are above thermal energies and at the same time they produce an equal number of positive ions.

The energy distribution of electrons in the ECD is a function of both the carrier gas and time. The initial electron energy is governed by the dynamics of the  $\beta$  particle quenching reaction.



Typically each electron will have an excess energy of  $\approx 1$  eV, this energy is lost by collisions with the carrier gas at a rate which depends on the nature of the carrier gas. At short ECD pulse periods, the average electron energy is likely to be higher than at long pulse periods since in the latter case more time is available for thermalisation. Nitrogen is less efficient than argon-methane mixtures in quenching excited electrons and electron energies will therefore be higher in nitrogen. In general electron-capture reactions are resonance processes, proceeding most rapidly for electrons with a particular energy but at much reduced rates for electrons with only slightly more or less energy (see, *e.g.*, ref. 2, Ch. 6). Variations in electron energy can therefore have profound effects on ECD responses and, since electron-energy distributions in the ECD are not easily estimated, these effects are not readily quantified.

Positive ion effects are also of importance since they directly affect ECD electron concentrations in a way which changes with pulse period and because they may drift to the collector electrode between pulses thus changing the measured detector current<sup>10</sup>. Only under limiting conditions of very short or very long pulse periods can the positive ion concentration and therefore the electron concentration be estimated directly. These conditions are of little practical significance.

Ideally, a source for an ECD should produce electrons at thermal energies with no positive ions. Such a source would provide a detector in which electrons were lost only by ventilation or by collection at the electrode. Higher electron concentrations could be achieved and the time for the electron concentration to reach its maximum value would be increased from milliseconds to seconds. Coulometric detection would then be available in pulsed mode for a wide range of substances and, by varying the pulse period, the selectivity of the detector could be adjusted as desired.

### *ECD performance*

Because of the positive ion concentration effects, quantitative descriptions of ECD performance are not possible in the intermediate pulse period mode which is of most practical interest in GC systems. For a limited range of very strongly electron capturing materials d.c. or short pulse period mode operation will give optimum response, approaching coulometry as the carrier gas flow-rate is reduced. Linear response range will be limited. For other materials optimum responses for small samples are obtained at longer pulse periods with, for weakly electron-capturing materials, the optimum being that period at which the standing current is reduced to half of its d.c. value. At this standing current responses for strongly electron-capturing materials will be about half the coulometric response. For general purpose operation this half maximum current criterion defines the optimum condition for ECD operation in either constant-frequency or constant-current mode. Where interest is primarily in more strongly electron-capturing compounds however, shorter pulse periods will tend to improve responses to these substances while reducing responses to weakly electron-capturing materials, thus increasing the specificity of the detector.

Provided that the optimum pulse frequency for detection of a particular sample is selected, there is no difference in detection limits between constant-current and constant-frequency mode devices. In modern equipments the constant-current mode is often preferred because of its claimed superior linear response range. However, as was shown above, responses in constant-current mode detectors are linear only if  $k_1 \bar{\eta}_e \ll u/v$  so that the extent of sample ionisation is negligible, say  $< 10\%$ . In general this condition is met only for low values of  $k_1$ , *i.e.*, for weakly electron-capturing samples, or for very high zero sample pulse frequencies  $f_0$ . At such high frequencies  $\bar{\eta}_e = R/2f_0$  so that the linearity condition becomes  $f_0 \gg k_1 Rv/2u$ . For  $k_1 \rightarrow 5 \cdot 10^{-7}$  ml  $\text{sec}^{-1}$  and  $u = 1$  ml  $\text{sec}^{-1}$  this implies that  $f_0 > 150$  kHz for a 15-mCi  $^{63}\text{Ni}$  source and  $f_0 > 7.5$  kHz for a 5-mCi  $^{55}\text{Fe}$  source. The required base pulse frequency for the  $^{63}\text{Ni}$  source is too high to be practical and neither this source nor  $^3\text{H}$  can be used in a constant-current mode detector if linearity of response to strongly electron-capturing materials is required. It should be possible to obtain linear responses from a  $^{55}\text{Fe}$  source ECD and the low noise level of this source should compensate for the lower sensitivity, giving limits of detection at least comparable to those obtained with  $^{63}\text{Ni}$  and  $^3\text{H}$  sources in the same mode. This limit will be at least one order of magnitude below the coulometric limit, however, and unless a very wide dynamic range is essential, operation at a lower constant frequency where sample ionisation is more nearly complete is preferred. Under such conditions, detection limits may approach the coulometric limit and the linear range is likely to cover at least a factor of  $10^2$  in sample input concentration.

Although an ECD for GC applications which gives a genuinely coulometric response is difficult, if not impossible, to produce, the coulometric response can be calculated from data obtained under conditions where coulometry is approached. Some uncertainty is introduced by the extrapolation which is required but for strongly electron-capturing materials and in clean ECD systems this uncertainty may be negligible. In view of the great difficulty involved in the preparation of accurate calibration standards at trace levels, say parts per  $10^{10}$  (v/v), this quasi-coulometric approach to the absolute calibration of ECD responses is particularly attractive.

## CONCLUSIONS

The constant-current mode ECD now widely used provides a wide dynamic range but responses to small samples of strongly electron-capturing materials are non-linear in sample concentration. This mode of operation is suitable for qualitative work but at best is highly inconvenient when quantitative results are required. Theoretical considerations and limited experimental evidence<sup>4</sup> suggest that, in constant-current mode, a <sup>55</sup>Fe electron source will provide optimum range and limits of detection.

Responses in the constant-frequency mode are linear in sample concentration for

(a) Weakly electron-capturing samples at long pulse periods (typically > 5 msec): Such samples are probably better detected using other systems.

(b) Strongly electron-capturing samples at intermediate pulse periods (0.1–1 msec) provided that the sample size is small so that the detector current is not reduced by more than  $\approx 20\%$ .

(c) Strongly electron-capturing samples under conditions where a coulometric response can be obtained either directly or by extrapolation.

Coulometric detection, whether direct or indirect, requires extremely clean ECD systems and factors such as column bleed present very real problems. On the other hand this mode offers the optimum detection limits, being capable of detecting samples of substantially less than 1 pg of strongly electron-capturing materials in systems where electronic rather than chemical noise predominates. Additionally, responses in this mode are quantitative and calibration using standard solutions is not necessary; this can be a substantial advantage since accurate standard preparation at trace levels is fraught with difficulties.

Exact quantitative descriptions of the ECD operating at intermediate pulse periods are not possible because of lack of information on processes involving positive ions. Quantitative work in this mode therefore requires the use of accurate calibration standards. Limits of detection can approach the coulometric limit but may fall short of this by an order of magnitude or more in systems where impurities such as column bleed provide an important electron loss mechanism.

Future improvements in the performance of the ECD may stem from the development of electron sources which do not at the same time produce positive ions or from techniques which involve the determination of product ions as well as reactant electrons. Some progress in this direction has been made with the plasma chromatograph<sup>17</sup>, a drift tube device, but considerable effort is still required to make this type of instrument compatible with GC.

## GLOSSARY OF SYMBOLS

$v$	Detector volume (ml)
$B$	Rate of sample input to detector ( $\text{ml}^{-1} \text{sec}^{-1}$ )
$B_{\text{max}}$	Maximum rate of sample input for which detector response is linear ( $\text{ml}^{-1} \text{sec}^{-1}$ )
$B_{\text{min}}$	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 ( $\text{ml sec}^{-1}$ )
$Q$	Electronic charge (C)
$I_0$	Detector current with no sample present (A)
$I$	Detector current, sample present (A)
$\Delta I$	Change in detector current with sample present (A)
$\Delta I_{\text{count}}$	Change in detector current at coulometric limit (A)
$I_n$	Detector noise level expressed as fluctuation in detector current (A)
$\varphi$	Detector current in DC mode ( $= RvQ$ ) (A)
$p$	Fraction of electrons produced which is collected ( $= I_0/\varphi$ )
$S$	Detector sensitivity expressed as the change in detector current with the rate of sample input ( $\text{A ml sec}$ )
AB	Any sample molecule
$\text{AB}^-$	Product of reaction between sample molecules and electrons
A	Neutral product(s) of $\text{AB}^-$ decomposition
M	Any carrier gas molecule
$\text{M}^+$	Positive ion(s) formed by collision of $\beta$ particles with carrier gas molecules
X	Any impurity molecule
$\beta$	Highly energetic electrons
$\varepsilon$	Electrons at (or close to) thermal energies
$\eta_e^0$	Number density of thermal electrons in the detector in the absence of sample ( $\text{ml}^{-1}$ )
$\eta_e$	Number density of thermal electrons in the detector in the presence of sample ( $\text{ml}^{-1}$ )
$\bar{\eta}_e^0, \bar{\eta}_e$	Time averaged values of $\eta_e^0, \eta_e$ ( $\text{ml}^{-1}$ )
$\eta_+$	Number density of positive ions in the detector ( $\text{ml}^{-1}$ )
$\bar{\eta}_+$	Time averaged value of $\eta_+$ ( $\text{ml}^{-1}$ )
$\eta_-$	Number density of negative ions in the detector ( $\text{ml}^{-1}$ )
$c$	Number density of sample molecules in the detector ( $\text{ml}^{-1}$ )
$c_{\text{min}}$	Minimum detectable number density of sample molecules ( $\text{ml}^{-1}$ )
$m_{\text{min}}$	Minimum detectable mass of sample molecules (g)
$t_p$	Interval between electron collection pulses in 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 ( $\text{ml sec}^{-1}$ )
$k_2$	Electron/positive ion recombination rate constant ( $\text{ml sec}^{-1}$ )
$k_3$	Positive ion/negative ion recombination rate constant ( $\text{ml sec}^{-1}$ )
$t_{\frac{1}{2}}$	Width of gas chromatographic peak at half peak height (sec)

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