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## PHYSICAL PARAMETERS AFFECTING THE QUANTITATIVE RESPONSE OF THE CONSTANT CURRENT ELECTRON-CAPTURE DETECTOR

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### SUMMARY

While the response of the constant current pulsed (CCP) electron-capture detector reflects the extent of reaction between electrons and analyte molecules, it can also be dependent upon other non-analyte electron loss processes. These might include electron losses by reaction with carrier gas impurities, by recombination with positive ions, by diffusion to walls, by ventilation with carrier gas flow, and by migration through small fields generated by contact potentials. These physical factors are examined in detail here with regard to their potential affect on the quantitative response of the CCP electron-capture detector. Experiments indicate that as long as the base frequency of pulsing is moderate to fast, non-analyte electron loss processes within the CCP electron-capture detector will be well-behaved and in harmony with the expectations of simple and idealized theory, and a constant molar response to well-behaved analytes can be expected over the entire dynamic range of the instrument. With the use of slower base frequencies of pulsing, however, non-analyte electron losses are more complicated and non-ideal behavior in the form of non-linear calibration curves is observed. An attempt is made to identify the specific causes of the non-ideal behavior which accompanies the use of the slower pulse frequencies.

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### INTRODUCTION

Because of its great sensitivity, the electron-capture detector is widely used in the gas chromatographic (GC) analysis of numerous environmentally important compounds. Unfortunately, quantitation with this detector has often been difficult because of non-linear and unpredictable relationships between the measured response and analytical concentration. During its early use<sup>1</sup> the electron capture detector was operated in the direct current or fixed frequency pulsed (FFP) modes where a change in measured cell current ( $\Delta I$ ) was taken as the response to sample. With either of these two modes, linear calibration curves were generally obtained only over the initial 10% of the entire response range. In 1967, Wentworth and Chen<sup>2</sup> showed that if the response in the FFP mode was taken as  $\Delta I/I$ , where  $I$  is the instantaneous cell current, that linear calibration curves could be obtained over the initial 90% of the entire response range. In 1971 Maggs *et al.*<sup>3</sup> described another mode for the pulsed

electron-capture detector where the cell current is held constant by a feedback network which alters the frequency of pulsing. The increase in pulse frequency ( $\Delta f$ ) is then taken as the response to sample. This mode, known as the constant current pulsed (CCP) mode, has been shown to provide linear responses to many compounds over the entire dynamic range. While the CCP mode is now generally acknowledged as the preferred means of controlling an electron-capture detector, for very strongly responding compounds even the CCP mode is still non-linear. This is because for these compounds the electron capture process, itself, alters the concentration of analyte in the detector and thereby complicates the observed response. In order to eliminate this problem, Knighton and Grimsrud<sup>4</sup> recently demonstrated that the response of a CCP electron-capture detector to strongly responding compounds should be taken according to the function  $(f - f_0)(H + f)/f$ , where  $f$  is the instantaneous frequency of pulsing,  $f_0$  is the baseline (or analyte-free) frequency and  $H$  is an experimentally determined constant. With this response function, linear calibration curves for tetrachloromethane and trichlorofluoromethane were obtained over the entire response range.

The above improvements in the quantitative response of the electron-capture detector have been inspired largely by consideration of the chemical factors associated with the primary reaction between the electron and the analyte molecule. That is, certain simplifying assumptions concerning the physical aspects of the electron-capture detector plasma are generally made and then attention is focused on details of the electron capture reaction. This approach has led to improved analytical configurations in spite of its omission of details concerning relatively complex physical-dynamic aspects of the electron-capture detector plasma. Nevertheless, it seems quite possible that these physical aspects of the electron-capture detector may have measurable effects on calibration curves.

In this paper we have attempted to characterize some of the physical factors which may affect the quantitative response of a <sup>63</sup>Ni CCP electron-capture detector. We will describe here the experimental conditions under which ideal or linear responses can be obtained. We will also describe experimental conditions under which non-linear responses are observed which appear to be caused by physical rather than chemical effects. We will then consider several possible causes of these anomalous observations. A moderately responding compound, dichlorodifluoromethane and a strongly responding compound, trichlorofluoromethane, will be used as test analytes. The electron capture chemistry of these two molecules is well known and, therefore, will allow anomalous observations to be attributed to physical rather than chemical effects. Each of these volatile compounds is introduced to an electron-capture detector from an exponential dilution volume which produces an accurate and continuous variation in analyte concentration through the upper 99% of the response range of the detector.

## EXPERIMENTAL

The arrangement of the apparatus used in this study is shown in Fig. 1. The electron-capture detector, exponential diluter and electronics package used to control the detector were all home built. The detector was machined from stainless steel and is of concentric coaxial design where the cylindrical cell walls are formed by a 15 mCi

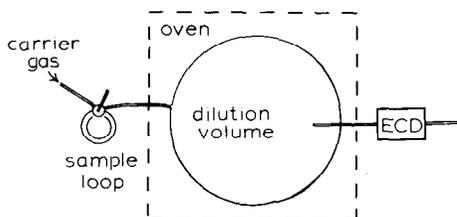


Fig. 1. General schematic of the experimental apparatus used for the wide range calibration of the electron-capture detector response to volatile halogenated methanes.

$^{63}\text{Ni}$  on platinum foil. The internal diameter of the cylindrical cell is 1.4 cm, and its internal length is 1.4 cm. Pulses of positive polarity are applied to a 1/16-in. stainless-steel rod which serves as the central anode. The detector temperature was  $150^\circ\text{C}$ . The electronics package used to control the detector has been previously described<sup>5</sup> and allows the detector to be operated in either the FFP or the CCP mode of operation. The FFP circuit allows for the pulses to be applied to the anode at intervals from  $40\ \mu\text{sec}$  to 10 msec and the resulting current was measured using an operational amplifier electrometer. In both the FFP and CCP modes of operation the pulses are of  $1\ \mu\text{sec}$  duration and 50 V in amplitude. With argon-methane carrier gas, these pulse parameters provided complete collection of electrons with each pulse. When operated in the CCP mode, the reference current is continuously variable up to 15 nA allowing for the selection of any desired baseline frequency. A maximum pulse frequency of 100 kHz is imposed by our pulse generator<sup>5</sup>.

Samples of trichlorofluoromethane and dichlorodifluoromethane were prepared by dilution of the neat gases into nitrogen by use of gas-tight syringes and airtight containers which were maintained above atmospheric pressure. The final dilution and transfer of the sample to the exponential diluter was accomplished using a 30-ml gas-tight syringe and the 5-ml gas-sampling loop (Carle 8030) shown in Fig. 1. The exponential diluter was constructed from a 1.0-l pyrex round-bottomed flask and was connected to the sample loop and the detector by 1/4-in. (O.D.) glass tubing. The volume of the exponential diluter was determined to be 1.093 l by weighing the volume of water contained by the diluter. The diluter was housed in an oven which was maintained at  $38^\circ\text{C}$ . The carrier gas was argon-methane (9:1) which was passed through both oxygen- and water-removing traps before entering the diluter. The volume flow-rate of the carrier gas through the exponential diluter,  $F_D$ , was obtained using the expression  $F_D = F_B(T_D/T_B)$ , where  $F_B$  is the measured volume flow using a bubbler and  $T_D$  and  $T_B$  are the temperatures of the diluter ( $311^\circ\text{K}$ ) and the bubbler ( $298^\circ\text{K}$ ), respectively. The measured volume flow exiting the detector was determined to be  $0.926 \pm 0.020\ \text{ml/sec}$  from the average of ten individual determinations. This yields a volume flow through the exponential diluter of  $0.97 \pm 0.02\ \text{ml/sec}$ .

The output signal from the CCP electron-capture detector is a voltage proportional to frequency and is monitored simultaneously by a strip chart recorder and by an Apple II-plus computer equipped with a Cyborg Isaacs model 91A interface. The strip chart record of a typical experiment is shown in Fig. 2. The computer enabled the total 0–10 V signal of the detector to be monitored without further alteration of the signal over the entire course of each experiment. The computer

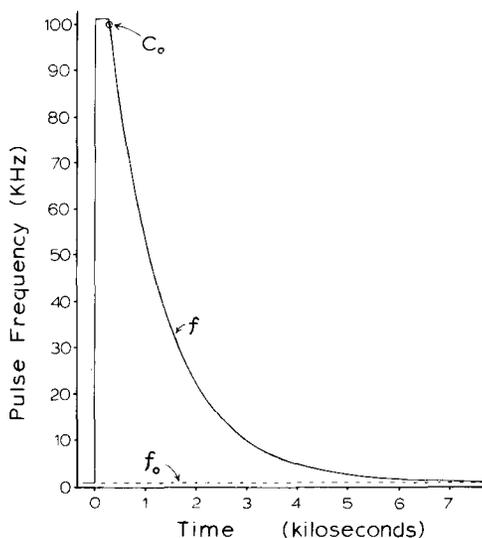


Fig. 2. Strip chart record of a typical experimental run showing exponential decay of the detector frequency response with time. Analyte concentration can be determined at any elapsed time using eqn. 1 where  $C_0$  is the concentration at which  $f = 100$  kHz. Baseline frequency,  $f_0$ , is the observed frequency prior to sample injection.

retains one data point and a real time clock measurement every 10 sec. This one data point, however, represents the average of 100 individual measurements taken at 10-msec intervals over a 1-sec period. Each experiment was allowed to run for 10,000 sec, and at the conclusion the raw data was transferred to disk.

In the experiments described here the instantaneous frequency,  $f$ , was measured as a function of time as shown in Fig. 2. However, it is the change in frequency,  $f - f_0$  (where  $f_0$  is the measured frequency in the absence of sample), caused by analyte presence which is of primary interest. The baseline frequency,  $f_0$ , was determined immediately before the injection of a sample and was then assumed to remain constant over the duration of the experiment (the validity of this assumption is discussed below). Sample concentration at any point in time,  $C$ , was calculated by substituting the appropriate values of flow-rate,  $F_D$ , diluter volume,  $V$ , and elapsed time,  $t$ , into eqn. 1. The initial concentration,  $C_0$ , is the concentration at the moment when the measured frequency is 100 kHz.

$$C = C_0 e^{-(F_D t/V)} \quad (1)$$

The molar responses reported here were obtained by dividing the instantaneous change in frequency response by the corresponding concentration entering the cell as determined by eqn. 1.

The response to the strongly responding compound, trichlorofluoromethane, will be reported in two forms,  $(f - f_0)$  and  $(f - f_0)(H + f)/f$ . The value of  $H$  in the latter response function was determined from pairs of high- and low-concentration data points by the procedure described in detail in the original description of this response function<sup>4</sup>. The values for  $H$  used here were determined for each experiment by taking the average of ten selected pairs of high- and low-concentration data points.

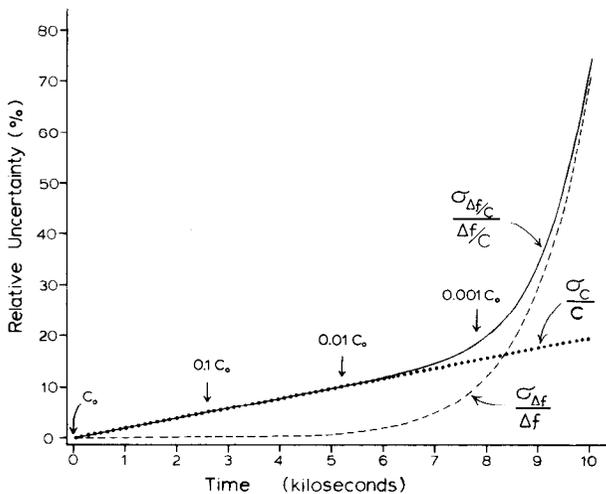


Fig. 3. Relative uncertainty in the determination of the relative molar response,  $\sigma_{\Delta f/C}/\Delta f/C$  (solid line), and its individual components calculated concentration,  $\sigma_c/C$  (dotted line), and measured frequency response  $\sigma_{\Delta f}/\Delta f$  (dashed line), as a function of dilution time. Decadic decreases in concentration from  $C_0$  are marked at their corresponding elapsed time intervals.

### Errors

The relative molar responses reported in this study are determined by dividing the instantaneous change in frequency response by the corresponding instantaneous analyte concentration eluting from the exponential diluter. The error in the measurement of the molar responses by this method will be expected to increase with time because the uncertainty in both the measurement of  $f-f_0$  and the calculation of analyte concentration will increase as the experiment progressed. For a typical experiment, the expected relative uncertainty in the measurement of frequency response ( $\sigma_{\Delta f}/\Delta f$ ), instantaneous concentration ( $\sigma_c/C$ ), and the overall molar response, ( $\sigma_{\Delta f/C}/\Delta f/C$ ), have been plotted in Fig. 3. The curves for the relative uncertainties are obtained as follows: the greatest contribution to uncertainty in the measurement of  $\Delta f$  is variation in the selected baseline frequency,  $f_0$ , over the time of the experiment. By monitoring  $f_0$  (without added sample) over extended periods the variations of  $f_0$  were found to be equal to  $\sigma_{f_0} = 0.01 f_0$  for all frequencies examined. The standard deviation for the change in frequency response is taken to be the same, as that for the baseline frequency  $\sigma_{\Delta f} = \sigma_{f_0}$ . Thus, the relative uncertainty of the  $\Delta f$  response is given by  $\pm 0.01 f_0/\Delta f$  and has been plotted as the dashed line in Fig. 3. At any point during the experiment the greatest contributions to uncertainty in the analyte concentration as calculated by eqn. 1 are due to the uncertainties in the preparation of the original concentration,  $C_0$ , and in the measured flow-rate,  $F_D$ . For this study, only relative molar responses over the dynamic range of the instrument will be reported. Therefore, the uncertainty in  $C_0$  is unimportant since any error in the magnitude of  $C_0$  will cancel in the calculation of relative molar responses. The critical source of uncertainty in concentration is related to the measured carrier gas flow-rate. After numerous measurements, the relative uncertainty in measurement of  $F_D$  was determined to be  $\pm 2.0\%$ . The effect of this uncertainty in flow-rate on the

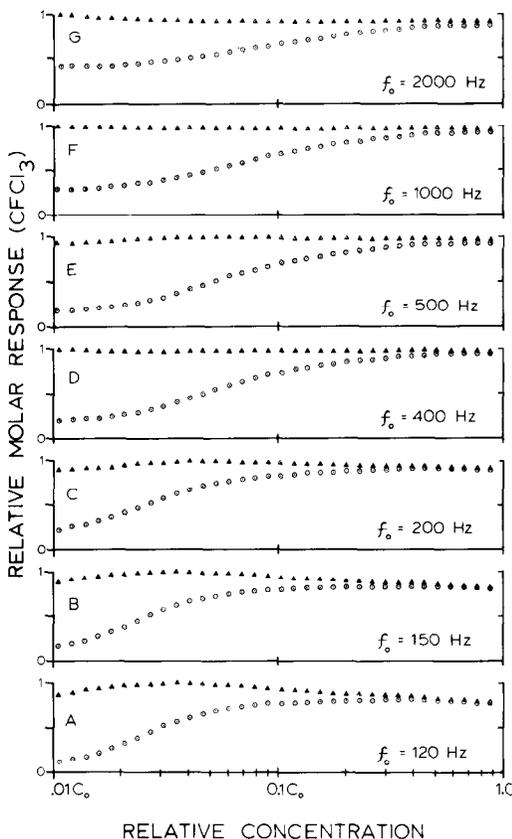
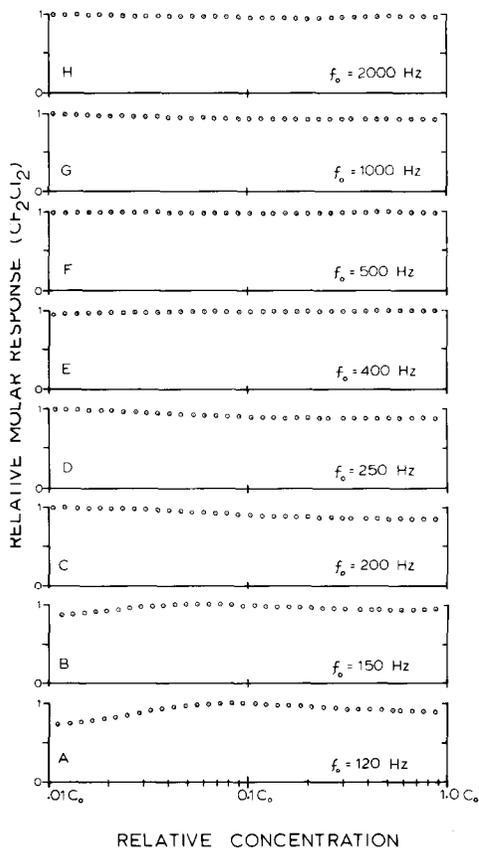


Fig. 4. Relative molar responses,  $\Delta f/\text{conc}$ , for dichlorodifluoromethane versus concentration at different baseline frequencies of pulsing. Maximum response of the instrument,  $f = 100$  kHz, occurred at concentration  $C_0$ . The values of  $C_0$  and the maximum molar responses for each case are listed in Table I.

Fig. 5. Relative molar responses,  $\Delta f/\text{conc}$  (circles) and  $\frac{(H+f)}{f}/\text{conc}$  (triangles), for trichlorofluoromethane versus concentration at different baseline frequencies of pulsing. Maximum response of the instrument,  $f = 100$  kHz, occurred at concentration  $C_0$ . The values of  $C_0$  and the maximum molar responses for each case are listed in Table II.

uncertainty in the concentration of analyte being delivered by the diluter is shown as the dotted line in Fig. 3. The net relative uncertainty in the final determination of relative molar response is then provided by the square root of the sum of the squares of the individual uncertainties in response and calculated concentration. This result is shown as the solid line in Fig. 3.

Fig. 3 shows that the major contribution to the uncertainty in the relative molar response during the early portion of the experiment is due to the uncertainty in calculated concentration, while at later times the uncertainty in the  $\Delta f$  response measurement becomes dominant. Placing an acceptable limit of uncertainty in the relative molar response at  $\pm 10\%$ , only data collected over the first 5000 sec should be used. This corresponds to approximately a hundred-fold dilution in original sam-

TABLE I

PARAMETERS ASSOCIATED WITH THE RELATIVE MOLAR RESPONSES REPORTED IN FIG. 4

	$C_0$ (ppb)	Maximum molar response (Hz ppb <sup>-1</sup> )	$I$ (nAmp)
A	$1.3 \cdot 10^4$	8.0	1.5
B	$1.1 \cdot 10^4$	9.3	1.9
C	$8.1 \cdot 10^3$	$1.4 \cdot 10^1$	2.7
D	$6.1 \cdot 10^3$	$1.7 \cdot 10^1$	3.4
E	$2.9 \cdot 10^3$	$3.0 \cdot 10^1$	5.7
F	$1.9 \cdot 10^3$	$5.1 \cdot 10^1$	7.0
G	$8.2 \cdot 10^2$	$1.3 \cdot 10^1$	8.6
H	$3.3 \cdot 10^2$	$3.0 \cdot 10^2$	9.4

ple concentration,  $C_0$ . For this reason the molar responses of trichlorofluoromethane and dichlorodifluoromethane shown in Fig. 4 and 5 are only reported over the first two decades of relative concentration, where the measurements of relative molar response are expected to be accurate to within  $\pm 10\%$ .

## RESULTS

The relative molar responses of a CCP electron-capture detector to dichlorodifluoromethane over the upper 99% of the response range is shown in Fig. 4 where eight different selections of baseline frequencies,  $f_0$ , have been used. For all choices of  $f_0$  the frequency responses ( $\Delta f$ ) shown are from the range, 1 kHz to 100 kHz. The concentration of dichlorodifluoromethane which causes saturation at 100 kHz differs with choice of  $f_0$  and is indicated for each case in Tables I and II. Fig. 4 clearly indicates that the most uniform molar responses to dichlorodifluoromethane occur with use of the fastest baseline pulse frequencies. For the four cases where  $f_0$  is 2000,

TABLE II

PARAMETERS ASSOCIATED WITH THE RELATIVE MOLAR RESPONSES REPORTED IN FIG. 5

	$C_0$ (ppb)	Maximum molar response (Hz ppb <sup>-1</sup> )	$I$ (nA)	$H$ (Hz)
A	$2.1 \cdot 10^2$	$6.0 \cdot 10^2$	1.8	$1960 \pm 500$
B	$1.8 \cdot 10^2$	$6.6 \cdot 10^2$	2.1	$1740 \pm 640$
C	$1.4 \cdot 10^2$	$7.5 \cdot 10^2$	2.7	$1500 \pm 150$
D	$6.9 \cdot 10^1$	$1.5 \cdot 10^3$	5.1	$2720 \pm 60$
E	$4.6 \cdot 10^1$	$2.2 \cdot 10^3$	6.3	$3140 \pm 100$
F	$1.8 \cdot 10^1$	$5.5 \cdot 10^3$	8.2	$3390 \pm 100$
G	8.1	$1.3 \cdot 10^4$	9.2	$3540 \pm 200$

1000, 500 or 400 Hz, the  $\Delta f$  molar responses vary by less than 10% over the entire range. On the other hand, when the chosen  $f_0$  is slower than 400 Hz significant variations are then observed. With baseline frequencies of 250 and 200 Hz, a significant decrease in molar response is observed with increasing sample concentration. With  $f_0$  equal to 150 or 120 Hz, the molar responses first increase measurably and then decrease with increased concentration. These results clearly recommend the use of the faster baseline frequencies for easy calibration of a CCP electron-capture detector to dichlorodifluoromethane.

In Fig. 5 the corresponding results for the case of trichlorofluoromethane are shown. For each experiment, however, two forms of molar responses are now shown. One is the usual  $\Delta f$  response (circles) as was used above for the case of dichlorodifluoromethane. It is seen that for all choices of  $f_0$ , the  $\Delta f$  molar responses are extremely variant, increasing in magnitude throughout most of dynamic range. This result is to be expected for trichlorofluoromethane and has been previously explained in detail<sup>4</sup>. Briefly, the  $\Delta f$  molar response to trichlorofluoromethane increases with increased concentration because the rate of electron capture by trichlorofluoromethane is so fast that the process of measurement also destroys a large fraction of the trichlorofluoromethane population when the electron population is high (low analyte concentration). As the trichlorofluoromethane concentration is increased, a lower population of electrons destroys a continuously smaller fraction of the trichlorofluoromethane molecules. Since the  $\Delta f$  response is proportional to the instantaneous concentration of analyte molecules in the cell, the observed  $\Delta f$  molar response to trichlorofluoromethane increases as the electron population is decreased by greater analyte input rate.

If the recently proposed<sup>4</sup> response function,  $(f-f_0)(H+f)/f$ , is used for the trichlorofluoromethane data, the dependence of molar response on the chemical effect just described can be removed. This response function, which we have named the extended response function of the CCP electron-capture detector incorporates the alteration of instantaneous analyte concentration by the electron-capture reaction and will be proportional to the analyte concentration which enters the detector. The molar responses in Fig. 5 obtained with the extended definition of response (triangles) clearly provide a more constant molar sensitivity to trichlorofluoromethane over the entire concentration ranges for all choices of baseline frequency. Again, however, only for the four fastest baseline frequencies are the molar responses constant to within  $\pm 10\%$  over the entire response range. With choices of baseline frequencies less than 400 Hz, significant variations in molar response are again observed. While the major cause of non-linearity of the CCP electron-capture detector to trichlorofluoromethane has been removed by use of the extended response function, a residual and significant degree of non-linearity still exists with the slower baseline frequencies. It may be significant to note that the trends observed for the extended molar responses to trichlorofluoromethane shown in Fig. 5 closely resemble those of the normal molar responses to dichlorodifluoromethane shown in Fig. 4. This observation suggests that the source of residual non-linearity observed with slow pulsing may be due to a physical effect of the electron-capture detector which is common to both calibrations, rather than a chemical one, which might have been expected to be unique and different for each compound.

An inherent assumption in the development of the response functions for the

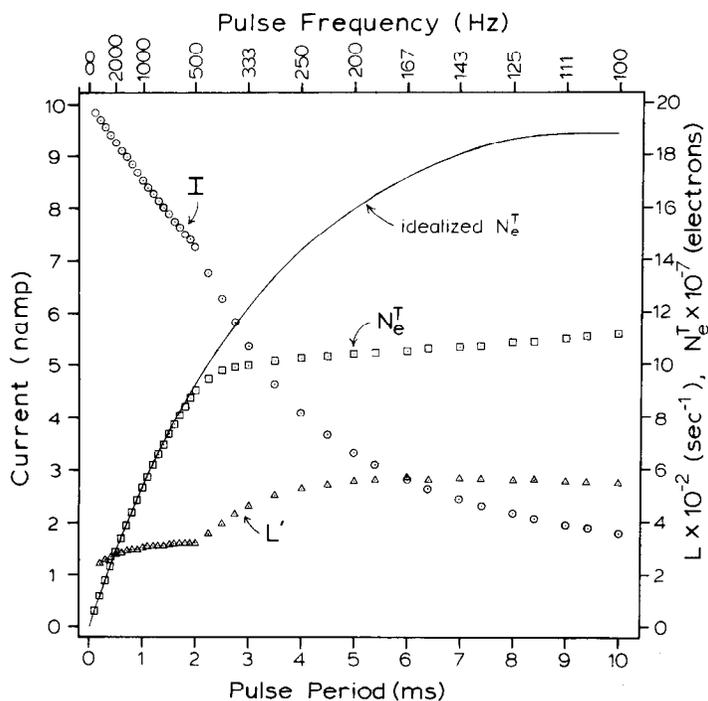


Fig. 6. Standing current,  $I$  (circles), measured at the anode as a function of pulse period. Electron population in the cell at the instant of pulsing,  $N_e^T$  (squares), was obtained from the product of standing current and pulse period. Predicted electron population (solid line) determined from eqn. 2 and an assumed constant value of  $L' = 300 \text{ sec}^{-1}$ . First order electron loss rate constant,  $L'$  (triangles), evaluated from the standing current measurements and eqn. 2.

CCP electron-capture detector has been that electron losses by pathways other than electron capture have reaction rates which are either insignificant or invariant to changes in analyte concentration and pulsing frequency. Non-ideal behavior in the form of non-linear calibration curves might be taken to indicate that this above assumption is not valid whenever a slow baseline frequencies are employed. A potential probe for assessing the dependency of non-analyte electron losses on pulsing frequency is available in the measurement of standing current,  $I$ , as a function of applied pulse frequency in the absence of sample. This measurement is shown in Fig. 6 where the reciprocal of frequency, pulse period,  $T$ , is also shown as the abscissa. The measured current primarily reflects the rate of electron collection at the central electrode by repeated electrostatic pulses. The attenuation of measured current by the arrival of positive ions at the anode between pulses will be quite small (5%) for this cell of truncated cylindrical design<sup>6</sup> and will be ignored here. Therefore,  $N_e^T$ , the electron population which exists in the cell at the end of each period immediately prior to the pulse, is obtained from the product of  $I$  and  $T$  and is shown in Fig. 6 at all values of  $T$ . If the rate constant for non-analyte loss,  $L'$ , is constant for all pulse frequencies, the magnitude of  $N_e^T$  as a function of pulse period,  $T$ , would be expressible by eqn. 2<sup>4</sup>:

$$N_e^T = \frac{S}{L'} (1 - e^{-L'/T}) \quad (2)$$

where  $S$  is the ion-pair production rate caused by the  $^{63}\text{Ni}$  beta radiation. According to this expression  $N_e^T$  should rise rapidly with increasing  $T$  near  $T = 0$  and should gradually level off and approach a constant equilibrium value at long  $T$  as shown by the solid line in Fig. 6 where values for  $S$  and  $L'$  of  $6.2 \cdot 10^{10}$  and  $300 \text{ sec}^{-1}$ , respectively, have been used. It is seen that the experimental values for  $N_e^T$  conform reasonably well to the early portion of this curve for constant  $L'$ , but beginning at *ca.*  $T = 2.0$  msec, the experimental points begin to markedly deviate from the predicted curve so that an equilibrium value of  $N_e^T$  is observed sooner and at a lower magnitude than predicted by the solid curve. In the original characterization of a  $^{63}\text{Ni}$  electron-capture detector by Simmonds *et al.*<sup>7</sup> a similar discontinuity of  $N_e^T$  measured as a function of  $T$  was reported. Also, Wentworth *et al.*<sup>8</sup> have shown that similar discontinuities are observed in the measurement of the standing currents of electron-capture detectors having tritium sources. Also shown in Fig. 6 is the value of  $L'$  calculated by eqn. 2 from the experimental values of  $N_e^T$  at each  $T$  and by assuming that  $S$  remains constant. The result is that at the faster frequencies, the value of  $L'$  is reasonably constant at *ca.*  $L' = 300 \text{ sec}^{-1}$  but starting at a period of *ca.*  $T = 2.0$  msec ( $f = 500 \text{ Hz}$ ) begins to increase with slower pulsing. Again, between  $T = 4.0$  msec and 10 msec the value of  $L'$  has stabilized somewhat at *ca.*  $L' = 500 \text{ sec}^{-1}$ . These measurements of standing currents suggest that the rate constant for non-analyte loss is constant and independent of pulse frequency in this cell only as long as the frequencies allowed are 500 Hz or greater.

The standing current measurements in Fig. 6 and the molar response data in Figs. 4 and 5 clearly display a common trend. That is, the molar response and the measured value of  $L'$  are constant only if as the slower pulse frequencies are avoided. When frequencies of less than 500 Hz are used, variations in the molar responses as well as variations in the directly measured value of  $L'$  are observed. As was mentioned above and will be described in more detail below, a variation in  $L'$  with pulse frequency is considered a probable cause of molar response variations. Therefore, the coincidence of breakdown in idealized behavior in the measurement of molar responses and standing currents whenever the slower pulse frequencies are used may indicate a common origin. In the next section the possible causes of the idealized and anomalous behavior described above will be systematically considered.

#### THEORY AND SPECULATIONS

We have recently presented a theoretical justification for the conventional and the extended responses of the CCP electron-capture detector<sup>4</sup>. The continued discussion here will focus on physical rather than chemical details and the equations developed in the earlier treatment will provide a convenient starting point for the factors to be highlighted here. In the previous treatment a differential equation (eqn. 2, ref. 4) described the rate of change of electron population during the period between pulses. For our discussion here this equation will be rewritten in the following manner:

$$\frac{dN_e}{dt} = S - (k_a n_a + L') N_e \quad (3)$$

where  $S$  is the ion-pair production rate of the  $^{63}\text{Ni}$  source,  $k_a$  is the electron capture

rate constant for the analyte molecule,  $n_a$  is the instantaneous analyte concentration,  $N_e$  is the instantaneous electron population and the constant,  $L'$ , is the rate constant for all electron losses other than by reaction with sample. From this beginning, the normal response function of the CCP mode was derived to yield eqn. 4

$$f - f_0 = G n_a \quad (4)$$

where  $f$  is the instantaneous pulse frequency and  $f_0$  is the pulse frequency in the absence of analyte, and  $G$  is a constant composed of fundamental and experimental factors. For strongly responding compounds, where the instantaneous concentration,  $n_a$ , of analyte would be significantly altered by the electron capture reaction, the extended response function of the CCP electron-capture detector was derived:

$$(f - f_0) \frac{(H + f)}{f} = G n_a^0 \quad (5)$$

where  $H$  is a second constant composed of fundamental and experimental factors and  $n_a^0$  is the concentration of analyte in the carrier gas entering the detector. This response function was shown to provide a linear response to tetrachloromethane and trichlorofluoromethane whereas the conventional response function did not.

The successful development of eqns. 4 and 5 requires that the nonanalyte electron loss constant,  $L'$ , in eqn. 3 must remain constant under all conditions of the cell. In other words, if eqn. 4 and 5 are to provide a basis for linear responses by the CCP electron-capture detector, the net rate constant for the sum of all electron loss processes other than by reaction with analyte must remain constant as analyte enters the cell with increasing concentration (thereby causing both an increase in the negative ion concentration within the cell and an increase in the frequency of pulsing). If these rather drastic alterations of conditions cause a significant change in  $L'$ , non-linear responses using either the conventional or extended definitions of response might be expected.

We will now turn our attention to a detailed assessment of all the possible non-analyte loss processes. At first inspection, the electron-capture detector might appear to be an impossibly complex reactor in which many factors combine to complicate its response in a manner which might defy precise description. In recent years, however, significant advances in our understanding of the dynamics of the pulsed electron-capture detector have been made and, fortunately, several of these lead to almost surprising simplicity. It is useful at this point to recall a few of these simplifying factors. The ion pair production rate within the typical  $^{63}\text{Ni}$  electron-capture detector is reasonably constant throughout its active volume<sup>9,10</sup> (The precise nature of any residual unevenness in ionization by  $^{63}\text{Ni}$  for any given cell geometry can be calculated<sup>10</sup>.) There will be a strong tendency for the maintenance of charge balance within the pulsed electro-capture detector. In fact, for a detector that has no external fields applied, charge balance between positive ions, electrons and negative ions will be strictly maintained<sup>11</sup>. With the typical pulsed cell, all electrons are removed to the anode, thereby creating the negative component of the measured detector current. On the other hand, positive ions are not measurably affected by the pulsed fields, themselves, even when relative fast pulsing is used<sup>6</sup>. However, in an effort to maintain charge balance (which is grossly perturbed following the removal of all electrons),

the excess positive ions are transported to and neutralized on the various cell surfaces by the slower process of space-charge driven migration through the electric field which their excess has created<sup>12</sup>. Two convenient consequences of this dynamic system has direct bearing on our discussion here. The first is that all of the cell's electrons which are being continuously produced by <sup>63</sup>Ni radiation will be contained within the positive ion space-charge field for a period of time following each pulse until charge balance is achieved. Furthermore, if a relatively fast pulse frequency is used, a positive ion space-charge field will be continuously maintained and all electrons will be "held" within the plasma by this field. Therefore, certain electron loss processes (such as diffusion to the walls) will not be possible when relatively fast pulsing is used. With slower frequencies sufficient time is allowed between successive pulses so that the electron population increases to the point where the positive space-charge is neutralized. From that point of time in the period between pulses, other electron loss processes (such as diffusion to walls) becomes possible. Another important and simplifying consequence of the space-charge view of the pulsed <sup>63</sup>Ni electron-capture detector is that the steady-state positive ion concentration will be expected to be reasonably constant throughout the entire pulsed detector volume. This is because throughout this pulsed cell, positive ions are being destroyed either by recombination with electrons and negative ions or by space-charge driven migration to the cell boundaries, and all of these processes have approximately the same rate coefficients at atmospheric pressure<sup>12</sup>. Since the positive ions are also being formed at a relatively constant rate in all regions of space by <sup>63</sup>Ni radiation, the steady-state concentration of positive ions should be relatively uniform throughout the active volume of the pulsed cell. Previous measurements by atmospheric pressure ionization mass spectrometry (APIMS) have strongly supported this view of positive ion behavior in a pulsed electron-capture detector<sup>12</sup>.

Within this review of the pulsed electron-capture detector, the following general expression might be written for  $L'$  which includes contributions from reaction with carrier gas impurities, recombination with positive ions, diffusion to cell boundaries, and ventilation by carrier gas flow:

$$L' = k_B n_B + R n_+ + m \left( \frac{D_a}{\Lambda^2} + \frac{F}{V} \right) \quad (6)$$

where  $k_B$  is the second order rate constant for reaction with carrier gas impurities,  $n_B$  is the concentration of electron capturing impurities,  $R$  is the second order rate constant for the recombination of electrons with positive ions,  $n_+$  is the concentration of positive ions,  $D_a$  is the ambipolar diffusion coefficient of the electron<sup>11,13</sup>,  $\Lambda$  is the cell size parameter determined by the dimensions of the cell<sup>14</sup>,  $V$  is the cell volume,  $F$  is the flow-rate of gas through the cell, and  $m$  is a value between zero and one which is equal to the fraction of the time between pulses during which the electron population has grown sufficiently great as to have neutralized the excess positive charge created by the prior pulse. With fast to moderate frequencies of pulsing, the value of  $m$  is zero since the electrons will never reach a population sufficient to neutralize the excess positive ion charge. Therefore, the last two contributions to eqn. 6, diffusion to walls and ventilation, are not allowed with fast pulsing and only reactions with either impurities or positive ions can then contribute to  $L'$ . As the rate of pulsing is decreased a frequency will eventually be reached where the value of  $m$

will begin to assume a non-zero value. From this frequency to lower frequencies the contributions to  $L'$  from diffusion and ventilation might become continuously more probable. After viewing the experimental data shown in Figs. 4–6, it is tempting to conclude that something such as described by eqn. 6 is operative where the value of  $L'$  suddenly changes ( $m$  suddenly becomes non-zero) at some particular frequency of pulsing. However, while the general form of this equation seems consistent with the experiments, it can be shown that diffusion and ventilation should not contribute significantly to the total magnitude of  $L'$  even with very slow pulsing. (In a theoretical consideration of a completely field-free,  $^{63}\text{Ni}$  source, Siegel and McKeown<sup>11</sup> have previously concluded that the contributions of ventilation and diffusion to electron loss were of negligible magnitude relative to that of recombination.) Since this point is crucial to an assessment of our experimental results, the expected magnitude of each term in eqn. 6 for four experimental system will be considered in detail. First, electron loss by reaction with column bleed is given by the product,  $k_{\text{B}}n_{\text{B}}$ . If the carrier gas is free of impurities, this term will equal zero. If impurities are present, their concentration will be constant over the period of time between pulses and, therefore, will not cause a variation in  $L'$ . (Since our chromatographic system appeared to be essentially free of impurities, as can be determined by measurements of direct current and pulsed mode standing currents<sup>6</sup> it was concluded that the contribution of impurities to  $L'$  was small and probably negligible in our experiments.) For the predicted contribution from recombination, values for  $R^{11}$  and  $n_{+}$  of  $ca. 3 \cdot 10^{-6} \text{ sec}^{-1}$  and  $1 \cdot 10^8 \text{ ml}^{-1}$ , respectively, provide reasonable approximations. (The value for  $n_{+}$  is obtained from the measured standing current of 3.3 nA at a pulse period of 5 msec. At this frequency, a charge-neutral plasma is probably achieved during the latter portion of the period and the electron current measurement at this frequency indirectly provides a measure of the positive ion population.) These estimates provide a predicted  $Rn_{+}$  product of  $300 \text{ sec}^{-1}$ . Taking values for  $A$ ,  $D_{\text{a}}$ , and  $V$  of  $0.25 \text{ cm}^{14}$ ,  $0.25 \text{ cm}^2 \text{ sec}^{-1}$  (ref. 13) and 2 ml, respectively, the diffusion contribution,  $D_{\text{a}}/A^2$  is predicted to be only  $ca. 4.0 \text{ sec}^{-1}$ , or 1.3% as large as the recombination contribution. The last term due to ventilation,  $F/V$ , becomes equal to  $0.5 \text{ sec}^{-1}$  with a flow-rate of  $1.0 \text{ ml sec}^{-1}$  and, therefore, seems even less likely to contribute significantly to  $L'$ .

To summarize the above consideration of the individual terms in eqn. 6, the recombination term  $Rn_{+}$  is by far the predominate electron loss term. At this point, it might be tempting to conclude that the non-idealized behavior observed in Figs. 4–6 whenever slow pulsing frequencies were used is due to changes in the positive ion density,  $n_{+}$ . The change in  $L'$  deduced from the current measurements in Fig. 6 would then be interpreted as resulting from a change in  $n_{+}$ , alone. Thus, with a change in pulse period from 2.0 msec to 4.0 msec, this interpretation would suggest that the positive ion density increases about 60%. This interpretation, however, is not supported by previous mass spectrometry measurements of positive ion density within a pulsed electron-capture detector<sup>12</sup> by APIMS, where it was shown that positive ion density does not vary measurably with changes in frequency from 1000 to 150 Hz. The only dependence of positive ion density on frequency observed in that study was a small one (less than 25%) and this change occurred between 2.0 and 5.0 kHz. In addition to those earlier APIMS measurements we have since repeatedly looked for positive ion variations with changes in pulsing frequency using several other APIMS

source designs and have never observed any measurable dependence on frequency from zero to 2 kHz. These APIMS measurements provide strong evidence that the change in  $L'$  shown in Fig. 6 between the frequencies of 250 Hz to 500 Hz. is probably not in fact due to a change in positive ion density. Therefore, it may be appropriate to consider an additional possibility which has not yet been discussed here and, to the best of our knowledge, has not been previously described in the published literature as source of error in analysis by the electron-capture detector.

The additional factor to be considered is the effect of contact potentials which have been previously recognized primarily for their effects on the operation of the direct current electron-capture detector<sup>1</sup>. With the original discovery of the pulsed mode<sup>1</sup>, it was hoped that the effects of contact potentials might be eliminated. However, it seems entirely likely that with slow pulse frequencies, they may not be. So far in this discussion the assumption has been made that the surfaces of the cell are perfect conductors on which ions and electrons are instantly neutralized upon arrival. This allows us to assume that the electrical potentials at all surfaces are determined solely by the externally connected circuit, and are, therefore, at ground potential during the period between pulses. However, after a few years' experience with several commercial and home-made <sup>63</sup>Ni electron-capture detectors and with several <sup>63</sup>Ni APIMS sources, we have noted that contact potentials can be established on even new and thoroughly cleaned cells, and that these can have significant effects on current and ion intensity measurements. For example, several of our home-made and commercial detectors have exhibited significantly high standing currents without the application of any external fields, pulsed or direct current. Our most spectacular example of this is a 9 mCi <sup>63</sup>Ni cell of conventional pin-cup design which displays a current of *ca.* +2 nA with no fields applied. This one is an exceptional case, however, as most cells exhibit a pulse-free current of a few tenths of a nanoampere. We have observed apparently identical cells with field-free currents of opposite polarities. This effect can not be attributed to the arrival at the anode of long-range beta particles since this effect would be much smaller in magnitude and always would be of negative polarity. While the magnitude of the field-free current of a given cell has been unpredictable, it can be affected by the immediate history of the cell. For example, if a direct current field is applied for 1 h to a cell which exhibits a field-free current and is suddenly removed, a new field-free current is then observed which slowly drifts back to its previous equilibrium value. The time required for this drift can be minutes or hours. As indicated above we believe these anomalous observations may be due to the effects of contact potentials which can exist on surfaces which are not perfectly conducting. That is, if a film of semiconducting material separates the metallic conducting surface from the ions and electrons which are arriving at the cell boundary, the ions and electrons may not be instantaneously neutralized by contact with this surface. Therefore, a surface can acquire small, but significant steady-state charges which depend on the arrival and neutralization rates of charged particles on it. These potentials could conceivably increase the rates of electron and ion losses in the adjacent gas by causing an additional means for their migration through weak contact potential fields provided these fields are the dominating ones for some portion of the period. In our use of many <sup>63</sup>Ni cells we have noted that with reasonably fast pulsing, little or no effect of the contact potentials on standing currents and responses are observed with cells which exhibit a field-free current of only a few tenths of a

nanoampere. Only with slower pulsing are these unpredictable effects of the contact potentials observed. Presumably, with more rapid pulsing the electric field then continuously provided by the positive ion space charge "holds" electrons with the ionized gas and away from surfaces and the smaller contact potentials. With slow pulsing the effects of the contact potentials increasingly influence the measured current because the positive ion excess is then matched by electron population during the latter portion of pulse periods. During this time the contact potentials can provide the most significant electric fields in existence and can then influence the motion of electrons and ions.

While we feel that events such as just described are occurring under certain conditions of an electron-capture detector, a precise understanding and quantitative description of the effects of contact potentials does not yet seem possible. The most significant characterization of it is that its affect on standing currents and responses to sample is in accordance with the form of eqn. 6, where a factor,  $m$  provides a weighting factor for its importance and assumes a value of zero with reasonably fast pulsing. The cell used for the measurements presented in this paper had a field-free current equal to +0.1 to +0.2 nA (positive current at the central electrode). While the magnitude of this current is small, it does not necessarily mean that contact potentials are weaker in this cell than in one with a larger field-free current. A small magnitude of current may reflect a fortuitous cancellation of net charge to the central electrode while contact potentials actually do exist at points along the cell boundaries and are, in fact, causing increased migration of electrons and ions in the plasma. While the point has clearly not been resolved, the effects of contact potentials appear to be a plausible cause of the variations in molar responses in Figs. 4 and 5 and the variation in  $L'$  shown in Fig. 6 whenever slow pulse frequencies are used.

## CONCLUSIONS

The experimental results provided in the paper clearly support the use of baseline frequencies which are at least moderately fast if the most linear response to a compound over the entire dynamic range of a CCP electron-capture detector is desired. In choosing a moderately fast baseline frequency (*e.g.* 1000 Hz) instead of a slow one (*e.g.* 120 Hz) the sacrifice which accompanies this choice is that the total dynamic range of response will be reduced. However, at the low concentration end of the response range the detection limit to dichlorodifluoromethane was observed to be about the same for all frequencies. The dynamic response range is reduced with a choice of a faster baseline frequency, because the instrumental saturation point is then reached with a lower concentration of analyte. Considering that our linear response range with  $f_0 = 1$  kHz is *ca.* four orders of magnitude, the loss of approximately one additional order of response range at the high-concentration end would seem to be worth trading for linearity of response throughout the dynamic range.

The possible causes of the non-idealized behavior of a pulsed electron-capture detector when low pulse frequencies are used have been considered. It is concluded that this behavior can not be attributed to complications associated with electron loss by simply diffusion to walls, by ventilation, or by reaction with carrier gas impurities. The possibility that changes in positive ion density cause non-idealized behavior can not be ruled out. However, our observation that idealized behavior occurs

with the use of frequencies of 500 Hz and greater suggests that positive ion concentration remains relatively constant over this frequency range. In addition, previous APIMS measurements indicate that positive ion density also remains constant with slower pulse frequencies. These considerations argue against the assignment of positive ion variation as the cause of non-idealized behavior. The remaining explanation for the anomalous results reported here with slow pulsing is that uncontrolled contact potentials exist on the surfaces of an electron-capture detector and these significantly affect the dynamics of the detector plasma if the positive ion space-charge is allowed to be neutralized by use of long periods between pulses. Within this view the effects of contact potentials are not observed with sufficiently fast pulsing because a positive ion space-charge field is the dominant electric field present during the time between pulses and this force does not allow electrons to reside in regions near the cell boundaries. Therefore, the only non-analyte loss processes possible with faster pulsing are recombination with positive ions and retention with carrier gas impurities. These non-analyte loss processes appear to be well-behaved at least within this frequency range and allow an idealized view of the physical aspects of the pulsed electron-capture detector to be assumed.

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