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DESIGN AND PERFORMANCE OF A SOLUTE-MODULATED ELECTRON-CAPTURE DETECTOR

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SUMMARY

The design criteria for a solute-modulated electron capture detector are discussed. The factors affecting the linear range and degree of modulation are examined and shown to be related to the response time of the detector. The factors investigated are modulator and detector cell volumes, carrier gas flow-rates, modulation frequency, sample concentration and attachment rate constant. The relationships between these factors have been examined using a numerical model and the results are shown to be in good agreement with measured values. The limitations of the detector for packed and capillary column gas chromatography are discussed.

INTRODUCTION

It is a common practice to reduce the noise and drift from a transducer by modulating the signal that enters the device. Subsequent narrow band amplification followed by synchronous demodulation can result in a significant reduction in noise; often several orders of magnitude. The noise reduction is best obtained if only the signal of interest is modulated and not the noise.

This principle of modulation was first applied to chromatography by Lovelock[1] who used an electron-capture detector as the transducer. The detector signal was modulated by means of a solute switch located between the column and the electron-capture detector in which the concentration of sample entering the detector was modulated between two levels. The use of the solute switch in conjunction with synchronous detection of the output signal from the electron-capture detector was shown to provide a significant enhancement of the signal-to-noise ratio for several practical analyses[2,3]. Boshoff and Hopkins[4] utilized a solute-switched electron-capture detector for the determination of chlorinated pesticides and demonstrated a significant improvement in selectivity for them when in the presence of a complex matrix. A brief review of the technique has recently been given by Poole[5].

The key component in the detector is the modulator cell or solute switch. It is similar to an electron-capture detector, but having a much higher density of thermal electrons available to attach to compounds. It functions by periodically destroying compounds that respond strongly in an electron-capture detector (the "signal") while

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not destroying weakly responding compounds that may be interferences (the "noise"). The mechanism by which the sample is destroyed is electron attachment[6–8]. Compounds that attach electrons are subsequently destroyed by recombination with the positive ions in the cell and thus are unable to be detected in the electron-capture detector that follows. The attachment process can be stopped by removing the electrons from the cell by means of an electric field. The periodic application of the field modulates the electron concentration and hence the concentration of sample leaving the modulator cell. The degree of modulation is detected by using a conventional electron-capture detector following the modulator cell.

While several papers have appeared demonstrating the utility of a modulated electron-capture detector, none have dealt specifically with the design parameters that affect the operation of the device. This paper investigates the relationships between the signal bandwidth, modulation frequency, cell volume and gas flow-rates, and their effects on the linear range and selectivity of a solute-modulated electron-capture detector.

THEORETICAL

Modulator cell requirements

In order to optimize the modulator cell parameters it is first necessary to know the frequency bandwidth of the chromatographic peaks to be investigated. For convenience the peaks of interest are divided into packed and capillary column types. Packed column peaks are those with width at half height, $W_{1/2}$, greater than 5 sec. Capillary column peaks are defined as those with $W_{1/2}$ less than 5 sec but greater than 0.5 sec. In order to maintain a peak height fidelity of 0.98 the response time of the detector, τ, should be approximately $\tau = 0.1\ W_{1/2}$[10]. The time constant for capillary should therefore be 0.050 sec and for packed 0.500 sec. These time constants correspond to signal, or "information", frequency bandwidths of 6.5 and 0.65 Hz respectively[11]. When using synchronous demodulation detection it is necessary for the modulation frequency to be at least twice the information bandwidth[12] in order to maintain the fidelity of the waveform. Thus the minimum modulation frequency that is required to handle capillary peaks is approximately 13 Hz and for packed column peaks it is 1.3 Hz. In general the minimum modulation frequency, f_m, to maintain a 0.95 peak fidelity is given by:

$$f_m > 20/3\ W_{1/2} \tag{1}$$

The modulation frequency can be related to the electronic time constant, τ_e, detector cell time constant, τ_d, and modulator cell time constant, τ_m, by

$$f_m = 1/T \tag{2}$$

where T is the modulation period and is given by

$$T = 2(\tau_e + \tau_d + \tau_m + \tau_x) \tag{3}$$

where τ_x is the time constant for the volume between the cells. Here it is assumed that the modulator cell operates at a 50% duty cycle, hence the factor of two. That is to say, the time during which electrons are present to destroy the sample (electric

field off) is equal to the time that electrons are absent from the cell (electric field on). In the case of finite volume cells the time constant is given by

$$\tau_i = \frac{\zeta_i V_i}{F} \quad i = \text{d, m, x} \tag{4}$$

where V_i is the cell volume, F is the gas flow-rate and ζ_i is a parameter that depends on the degree of mixing in the cell. For plug-like flow $\zeta = 1$, for fully mixed flow $\zeta \approx 3$.

It is generally possible to make the electronic time constant negligible by comparison to τ_d, τ_m and τ_x and thereby exclude it from eqn. 3. The 0.100-ml detector cell used in this study has been shown previously[9] to provide a nearly plug-like flow profile. It was also shown that the flow in the 0.200-ml and 0.300-ml concentric cylinder modulator cells was more plug-like than fully mixed. The volume between the active regions of the two cells is approximately 0.080 ml and can be treated as a mixing volume. The minimum modulation period as given by eqn. 3, is thus:

$$T = \frac{2}{F}(\zeta_d V_d + \zeta_m V_m + \zeta_x V_x) \tag{5a}$$

Assuming $\zeta_d = 1$, $\zeta_m \approx 1$, $\zeta_x \approx 3$, and using the volumes $V_d = 0.100$ ml, $V_m = 0.200$ ml:

$$T = \frac{2}{F}[0.100 + 0.200 + 3(0.080)] = \frac{1.08}{F} \tag{5b}$$

The maximum modulation frequency is therefore:

$$f_{max} = F/1.08 \tag{6}$$

For a flow-rate of 2 ml/sec the maximum modulation frequency that can be used is approximately 1.85, which is sufficient for packed column use, but excludes the use of capillary columns.

Modulator cell kinetic model

In the preceding section a relationship was developed between the maximum modulation frequency and the gas flow-rate, modulator and detector cell volumes, and the degree of mixing that occurs in them. This relationship is summarized in eqn. 5a. Modulation periods less than that given in eqn. 5a are possible, but will result in less than the maximum obtainable modulation amplitude. What is often not appreciated when using synchronous demodulation techniques is that for the same amplifier gain the demodulated output signal is at best half of the unmodulated signal; often it is much less. The increase in signal-to-noise ratio that can be obtained with this technique comes from noise reduction and not increased sensitivity as has sometimes been stated[5]. Since only the a.c. portion of the waveform is amplified, and none of the d.c., it is important to maintain the maximum modulation amplitude that is possible. Any reduction in amplitude will result in a similar reduction in the final signal.

In the system described here the modulation period is determined by the time

required to purge the modulator cell and the response time of the detector. The amplitude of modulation is determined by the amount of sample destroyed as it flows thru the modulator cell. To investigate the parameters affecting the modulation amplitude a simple model was used. Consider a differential length of the annular region of the cell cross-section located at the entrance of the cell. Prior to entering the β-radiation field the initial conditions at time $t = 0$, are:

$$[e^-]_0 = [+]_0 = [AB^-]_0 = 0 \tag{7a}$$

$$[AB^-]_0 = \text{initial solute concentration} \tag{7b}$$

The reactions occurring within the annulus are

$$\beta + N_2 \xrightarrow{k_p} e^- + [+] + \beta^* \tag{8a}$$

$$e^- + [+] \xrightarrow{k_r} N_2 \tag{8b}$$

$$e^- + AB \underset{k_{-1}}{\overset{k}{\rightleftarrows}} AB^- \tag{8c}$$

$$AB^- + [+] \xrightarrow{k_n} \text{neutral species} \tag{8d}$$

$$e^- \xrightarrow{\alpha_-(t)} \text{removal by electric field} \tag{8e}$$

$$[+] \xrightarrow{\alpha_+(t)} \text{removal by electric field} \tag{8f}$$

where N_2 is the carrier gas and $[+]$ is the positive ion species formed by the β collisions, *i.e.*, $[N_2^+]$, $[N_4^+]$, etc. Here it is assumed that only non-dissociative attachment occurs. If diffusion and turbulent mixing between adjacent differential segments is neglected it is reasonable to regard the species present in the reactions given by eqn. 8a–f as all moving together in a reference frame traveling down the axis of the cell. Therefore the maximum amount of solute that can be destroyed by electron attachment is at the end of the transit time of the annulus thru the cell, which is given by:

$$\tau_m = V_m/F \tag{9}$$

The neglect of diffusion processes and ventilation of the reacting species out of the cell has been shown by Grimsrud and co-workers[13,14] to be reasonable in the absence of an applied field where space charge forces dominate. In Grimsrud's model of the electron capture detector the negative electron charge is held in place by the positive ion space charge. As anions are formed charge is conserved so that the positive ion density remains constant. This latter point has recently been explored in greater detail[15] and has been shown to be valid. The assumption of a constant positive ion density considerably reduces the complexity of the coupled rate equations that need

to be solved in order to find the solute concentration as a function of time, since the effects of space charge-driven diffusion can be neglected. A further simplification occurs if it is recognized that eqns. 8e and 8f are not required during the first half of the modulation period. This is the sample destruction (field off) portion of the cycle. If the applied field is strong enough during the next half period, then no electrons will be attached and the only process of importance during this time is the movement of the sample thru the cell with no sample destruction occurring. It is further assumed that the production of thermal electrons is uniform throughout the cell, which is reasonable for a cell of the dimensions used in this work[17]. The coupled equations to be solved are therefore reduced to:

$$\frac{d[e^-]}{dt} = k_p - k_r[+][e^-] - k[AB][e^-] + k_{-1}[AB^-] \tag{10a}$$

$$\frac{d[+]}{dt} = k_p - k_r[+][e^-] - k_n[+][AB^-] \tag{10b}$$

$$\frac{d[AB]}{dt} = k_{-1}[AB^-] - k[AB][e^-] \tag{10c}$$

$$\frac{d[AB^-]}{dt} = k[AB][e^-] - k_n[+][AB^-] - k_{-1}[AB^-] \tag{10d}$$

The important quantity to be determined from the solution of eqn. 10 is the switch efficiency, S, defined as

$$S \equiv \frac{[AB]_0 - [AB]_{\tau_m}}{[AB]_0} \tag{11}$$

where τ_m is given by eqn. 9. The quantity $[AB]_m$ will be the minimum sample concentration leaving the modulator cell when the field is off, and S will be the fraction of sample destroyed.

EXPERIMENTAL

The modulated electron-capture detector used in this study is shown in Fig. 1 and comprised of modulator cell and a detector cell. The detector cell has an effective volume of 100 μl and had been described in detail previously[9]. The detector cell has an inner diameter of 0.4.75 cm with 2.5 mCi of nickel-63. The modulator cell has an inner diameter of 0.475 cm, length of 1.97 cm and contains 250 mCi of tritium foil. A modulator pin is located down the center of the cell and has a diameter such that the volume of the modulator cell is either 300 or 200 μl. Both cells are maintained at a temperature of 250°C.

A Varian 3700 gas chromatograph was used and the standard constant current electron-capture detector electronics were used to detect the modulated signal from the detector cell. The electronics had a time constant of 30 msec. The modulated output signal from the electron-capture detector electronics was then amplified and

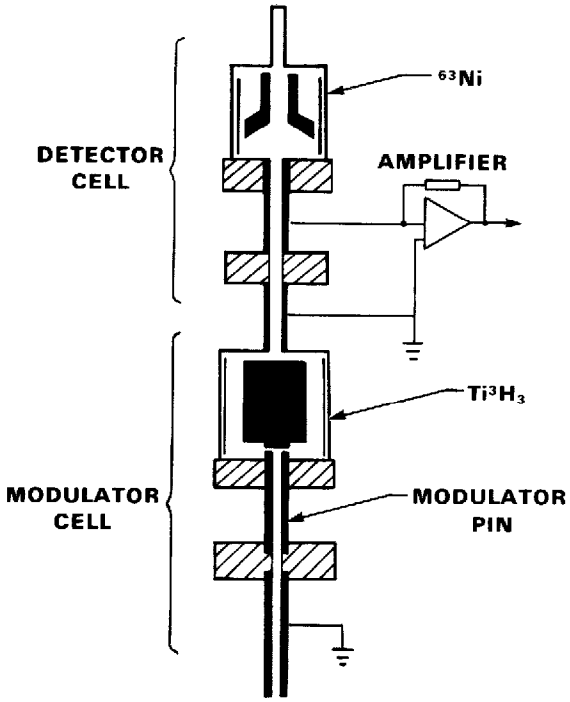

Fig. 1. Modulated electron-capture detector.

demodulated using an Ithaco Model 391A lock-in amplifier. A Nicolet 1170 signal averager was used to digitize some of the modulated waveforms prior to amplification by the lock-in. This allowed measurements to be made of the shape of the waveform and the degree of modulation.

A 2-m, 3% OV-101, column was used for sample introduction. A carrier gas flow-rate of 0.5 ml/sec of nitrogen was used throughout this work, with nitrogen make-up gas added at the end of the column in order to vary the total flow of gas thru the modulator and detector cells.

RESULTS

Experimental results

The fraction of the sample transmitted thru the modulator cell was measured as a function of voltage applied to the center pin. For all samples tested, the amount transmitted as measured by the detector cell reached a plateau at 40 V, independent of the polarity of the applied field, and was the same as that measured without foil in the modulator cell. A modulating voltage of 50 V was therefore used throughout this work. The low plateau voltage and the lack of dependence on polarity is in sharp contrast with the findings of Kapila and Aue[18]. However their cell had a larger volume and was of the asymmetric design. The concentric cylinder cell used in this work would produce a much stronger field for the same potential difference[9] and therefore the results of this work are not inconsistent with their observations.

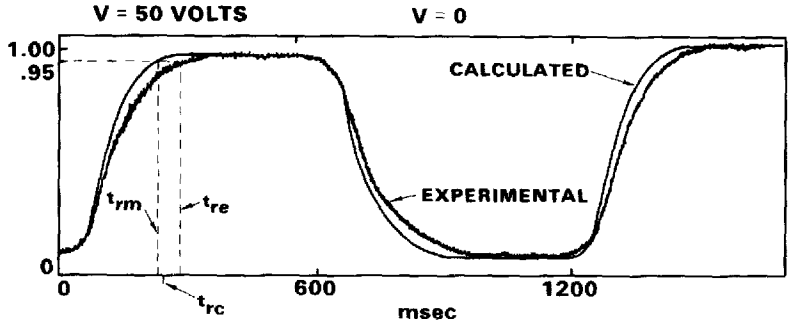

Fig. 2. Electron-capture detector response to modulated sample concentration for one period. Solid line calculated. Calculated time constant, t_{rm} = 265 msec; experimental, t_{re} = 298 msec; calculated from eqn. 5, t_{rc} = 270 msec.

The rise time, t_r, and fall time, t_f, of the modulated waveform, prior to lock-in amplification, were measured using SF_6. The times were taken to be the time required to reach 0.95 of the maximum or minimum (plateau) response. Measurements were made for the 0.200-ml modulator cell at flow-rates of 0.67, 1.0 and 2.0 ml/sec, and for the 0.300-ml cell at 1.0, 1.5 and 3.0 ml/sec. The concentration ranged between 5 and 200 ppb. The measured times were generally found to be in good agreement with those predicted by eqn. 3, within ±10%.

In an attempt to fit the measured shape of the waveform to the simple model presented here, the coupled eqns. 10a–d were solved using a third order predictor–corrector method[16] with variable step size. A more complete description of the calculation will be given later in this section. The quantity [AB] was determined as a function of time from 0 to τ_m. The resultant concentration profile was then convoluted with the mixing volume between the cells, followed by a convolution with the detector cell assuming plug flow and lastly by the electronic time constant[10]. The convolutions were then repeated on the concentration distribution assuming the reaction to be instantly shut off by the application of a strong electric field. The resulting waveform was then compared to the experimental data for V_m = 0.200 ml and flow-rates of 0.67, 1.0 and 2.0 ml/sec.

Fig. 2 shows the calculated and experimental results for SF_6 with V_m = 0.200

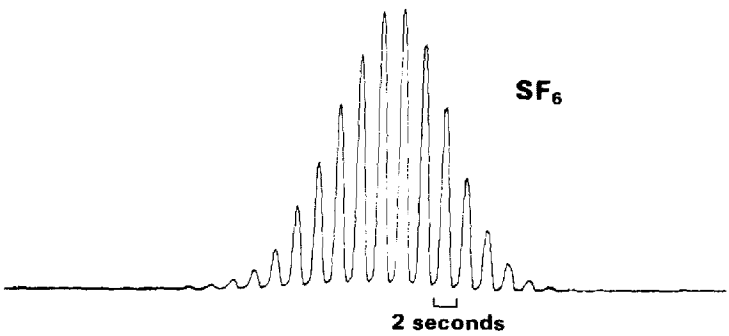

Fig. 3. Electron-capture detector response to modulated sample peak. F = 0.5 ml/sec, V_m = 0.200 ml, f = 0.5 Hz.

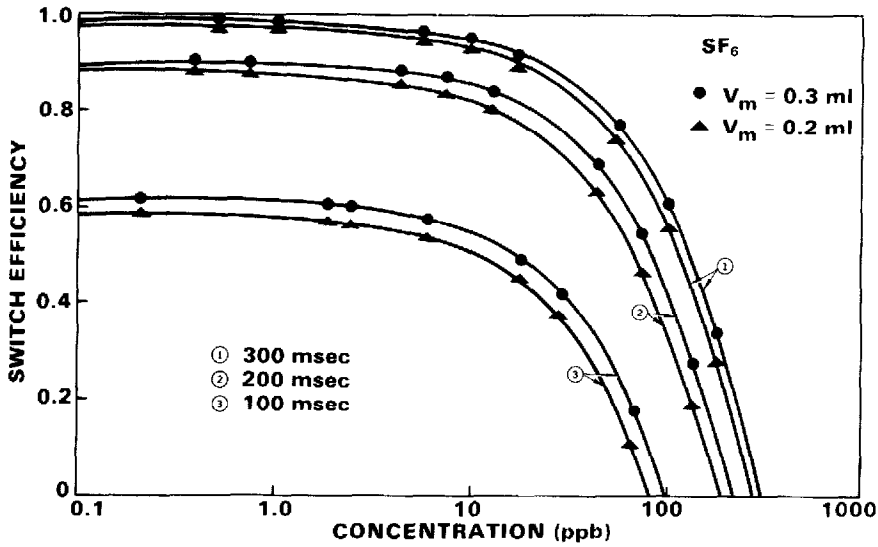

Fig. 4. Switch efficiency for SF_6. (▲) V_m = 0.2 ml, F = 0.667, 1.0 and 2.0 ml/sec; (●) V_m = 0.3 ml, F = 1.0, 1.5 and 3.0 ml/sec. Transit times: 300 (1), 200 (2) and 100 msec (3).

ml and F = 2.0 ml/sec. Here the calculated response time, t_{rc}, is assumed to be equal to one half of the minimum modulation period, T, as given in eqn. 5. Because of the uncertainty in the sample concentration and the rate constants, the two sets of data were both normalized to unit amplitude to compare their shapes. The important observation to be made is that the simple model used here adequately predicts the time required to reach the maximum and minimum concentrations. Fig. 3 shows a peak modulated at 0.5 Hz, which is slightly less than the maximum that should be used according to eqn. 3.

The switch efficiency was measured as a function of sample concentration for SF_6 and lindane. The values in the graphs shown in Figs. 4 and 5 were determined by measuring the peak heights of the signals with and without a constant 50 V applied to the modulator. These values should faithfully reflect the degree of modulation, *i.e.*, switch efficiency, for any frequencies used that are less than or equal to those given by eqn. 3. The switch efficiencies were measured for V_m = 0.200 ml with F = 0.67, 1.0 and 2.0 ml/sec; and V_m = 0.300 with F = 1.0, 1.5 and 3.0 ml/sec. The flow-rates were chosen so that the transit time thru the modulator cell would be the same for both volumes; 300, 200 and 100 msec were used. It can be seen that for two different volumes if the flow-rates are such that the transit times are the same, the switch efficiencies are nearly the same. This is in agreement with the assumptions of the model in which the efficiency, in the absence of mixing, is determined by the residence time of the annular plug in the modulator cell. In general the efficiency of the 0.300-ml cell is greater than of the 0.200-ml cell, which may indicate that more mixing and hence a longer residence time may occur. Noise measurements were made with the lock-in amplifier using a 400-msec output time constant. The minimum detectable quantities (MDQs) are indicated in Fig. 5 for lindane by the horizontal bars at the end of the solid lines, which were determined by extrapolating to a 2:1

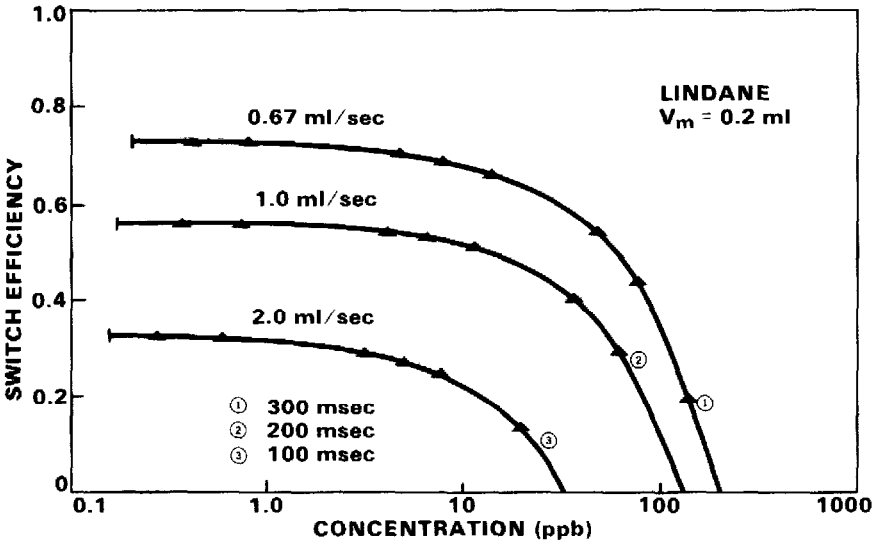

Fig. 5. Switch efficiency for lindane. V_m = 0.2 ml, F = 0.67 (1), 1.0 (2), 2.0 ml/sec (3). Transit times for curves 1–3 as in Fig. 4.

signal-to-noise ratio. The concentrations indicated along the axis of the figure are those at the detector. However, the MDQs have been corrected for the dilution effect of the make-up gas and thus better represent the true detection limits of the system in terms of the amount leaving the end of the column.

Fig. 6A shows a chromatogram obtained with 50 V d.c. applied to the modulator and with the output taken from the constant current electronics with an output time constant of 330 msec. Fig. 6B shows the same chromatogram modulated at a

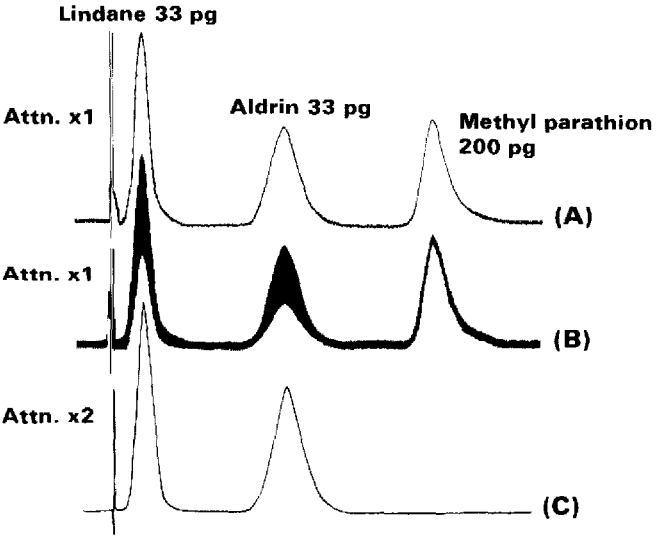

Fig. 6. A, Unmodulated chromatogram; B, modulated chromatogram, f = 1 Hz, F = 1.0 ml/sec; C, synchronously demodulated chromatogram.

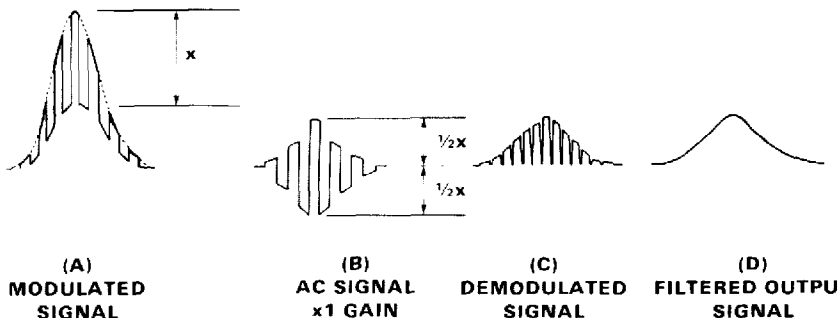

Fig. 7. A, Modulated signal; B, a.c. signal from amplifier, × 1 gain; C, synchronously demodulated signal; D, filtered output signal.

frequency of 1 Hz and a time constant of 30 msec. The increase in noise is due to the increased bandwidth, *i.e.*, smaller time constant, as well as the 1-Hz modulation of the baseline. Fig. 6C shows the output from the lock-in amplifier with a gain of 10 and an output time constant of 400 msec. Although the amplifier had a gain of 10, the output of the amplifier is only approximately a factor of 2 greater. This is because only the a.c. part of the signal is amplified, which is only about half of the original peak height. In addition over a factor of 2 is lost in the a.c. amplifier when the d.c. component is removed. This is illustrated in Fig. 7. The noise in Fig. 6C is approximately half of that in 6A, resulting in a signal-to-noise improvement of almost four.

The modest increase in signal-to-noise as seen in Fig. 6C by comparison to that in Fig. 6A can be better understood by examining the noise spectrum. Fig. 8 shows the noise power spectrum obtained by Fourier transforming the background signal of the detector without modulation. Since the bulk of the noise power exists below 3 Hz, a significant reduction in noise can not be realized unless modulation frequencies much greater than this are used. The modulation frequency used in Fig. 6 was only 1 Hz, which is the maximum that is allowed given the volume and flow-rates used. The high flow-rates used in Fig. 6A are not really needed if no modulation is performed, and in fact causes a loss in sensitivity due to solute dilution. Thus, if the only noise source is from the detector itself, such as from a constant level of

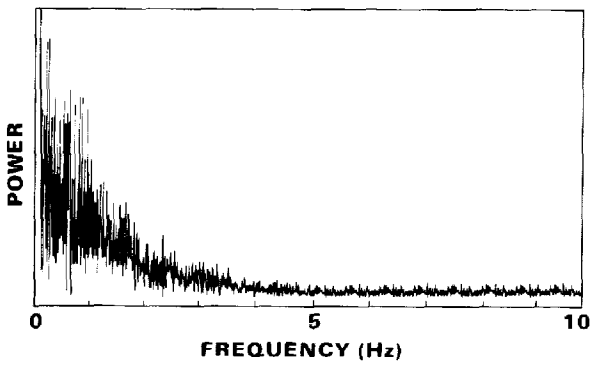

Fig. 8. Noise power spectrum.

TABLE I

KINETIC PARAMETERS

	A	*Refs.*	*B*	*Refs.*	*Units*
k_p	$3 \cdot 10^{10}$	20	$3 \cdot 10^{11}$	6	molecule ml^{-1} sec^{-1}
k_r	$3 \cdot 10^{-6}$	14, 15, 19	$3 \cdot 10^{-6}$		ml $molecule^{-1}$ sec^{-1}
k_n	$3 \cdot 10^{-6}$	14, 15, 19	$3 \cdot 10^{-6}$		ml $molecule^{-1}$ sec^{-1}
k	$1.1 \cdot 10^{-7}$	19, 22	$1.1 \cdot 10^{-7}$		ml $molecule^{-1}$ sec^{-1}
k_{-1}	$1.5 \cdot 10^{-12}$	20, 21, 23	$1.5 \cdot 10^{-12}$		sec^{-1}

contamination, then very little improvement in signal-to-noise can be obtained. However, if the "noise" is caused by interferences such as the methylparathion peak in Fig. 6 then a significant improvement can be realized.

Calculation results

The numerical solutions to eqns. 10a–d were obtained using the parameters listed in Table I. The parameters listed in column A of the table were used to calculate the concentration profile of the modulated waveform that was discussed at the beginning of the previous section. The value, k, in Table I (A) was varied until the calculated switch efficiency was equal to the experimental value at low concentrations for $V_m = 0.200$ ml and $F = 1.0$ ml/sec. The value of $1.1 \cdot 10^{-7}$ ml $molecule^{-1}$ sec^{-1} is in reasonable agreement with the value of $2.41 \cdot 10^{-7}$ (ref. 21) and $3.1 \cdot 10^{-7}$ (ref. 22) found in the literature for SF_6. Values of k_{-1} between 10^{-12} and 10^{-8} sec^{-1} were found to have no effect on the results. This is presumably due to the large value of the recombination rate constant, k_n, which dominates the reaction of AB^-. Fig.

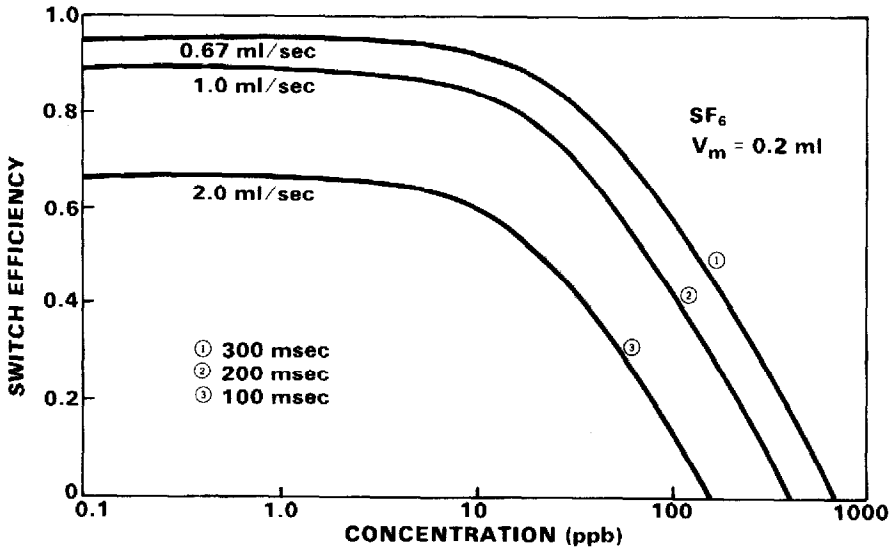

Fig. 9. Calculated switch efficiency for SF_6. $V_m = 0.2$ ml, $F = 0.67$ (1), 1.0 (2) and 2.0 ml/sec (3). Transit times: 300 (1), 200 (2) and 100 msec (3).

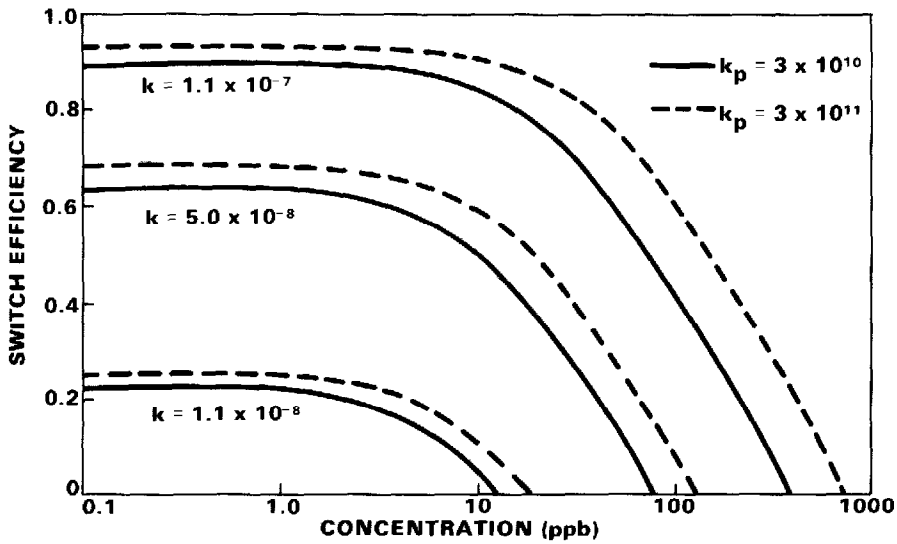

Fig. 10. Calculated switch efficiency. $k_p = 3 \cdot 10^{10}$ (———) or $3 \cdot 10^{11}$ molecule ml^{-1} sec^{-1} (– – –); F = 1.0 ml/sec; V_m = 0.2 ml.

9 shows the calculated switch efficiencies for SF_6 and are in close agreement with the experimental data of Fig. 4. The data in Fig. 10 are for the thermal electron production rates of $3 \cdot 10^{10}$ and $3 \cdot 10^{11}$ molecule ml^{-1} sec^{-1}, and for various attachment rate constants, k. Increasing the production rate by a factor of 10 does not significantly increase the switch efficiency or the linear range. This is due to the simultaneous increase in the recombination rate which tends to prevent the electron concentration from increasing in proportion to the production rate. The dependence of the efficiency on the attachment rate constant, however, is much stronger. Decreasing k by a factor of ten reduces the switch efficiency from 0.90 to 0.22. This strong dependence on k is the basis for the selectivity of strongly responding compounds over weakly responding compounds. The switch efficiency is a measure of selectivity only if the sample concentrations are the same. For example, the a.c. amplifier cannot distinguish between 100% modulation of a strongly attaching compound and a 1% modulation of a weakly attaching compound whose concentration is 100 times greater; the magnitude of the a.c. signal is the same. Selectivity therefore should be determined as usual by comparing the ratio of the response to the concentration of each compound. Some increase in efficiency and linear range may occur if argon–methane were used, due to the smaller recombination rate constant[8]; however this aspect was not investigated in this work.

CONCLUSIONS

The results presented here show that a solute-modulated electron capture detector can be useful if the operating limits of the device are understood. The design requirements for maintaining a reasonable peak fidelity exclude the use of capillary columns. Even the less stringent requirements of packed column peaks require high

flow-rates which reduce the absolute sensitivity of the detector due to sample dilution. This loss of sensitivity offsets the reduced noise that results from the synchronous detection of the modulated signal. Thus, the lower limit of detection will not be substantially different than that of a normal electron-capture detector. In those analyses where very low frequency noise (drift) is a significant problem, the modulated electron-capture detector could be quite useful.

The sample destruction portion of the modulation cycle requires that the thermal electrons be in great excess of the sample. Due to this restriction the dynamic range is extremely limited, thereby confining the use of the detector to trace analyses. It is for these applications that the increased selectivity offered by the solute modulation technique provides the greatest potential advantage. The identification of trace components in a complex matrix is often limited by the "chemical noise" of the matrix and not by the detector noise. The ability to suppress the background chemical interferences would result in lower practical detection limits, as well as improve the quantitative precision of an analysis.

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