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DETECTION BY SOLUTE SWITCHING AND SYNCHRONOUS DEMODULATION OF THE ELECTRON-CAPTURE DETECTOR SIGNAL

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SUMMARY

Factors influencing the performance of the electron-capture detector as a solute switch are discussed. The possibility of improving the detection limit of the solute-switched detector for $CFCl_3$ (F-11) and CCl_4 (F-10) is examined. An improvement is reached for broad peaks lasting for many modulation periods but it is not good enough to justify the implementation of the technique to the trace analysis of these compounds.

INTRODUCTION

It was first shown by Lovelock in 1975[1] that a coulometric electron-capture detector, when inserted between the chromatographic column and the detector, may operate as a chopper and modulate the concentration of a solute in the carrier gas at some chosen frequency. The detector, which usually is a second coulometric detector, will sense the changes and yield a signal with an alternating current component at a switching frequency. The amplitude of this component may then be selectively amplified in a narrow-band alternating-current amplifier and later synchronously demodulated, *i.e.* converted into a steady direct-current level. This may be done with a low-pass filter and an electronic phase-sensitive detector switched to the same frequency as the solute chopper, but at a phase shifted by a special delay circuit to match the time lost during the flow of the gas between the switch and detector. The basics of this signal processing procedure are shown in Fig. 1. The technique permits us to amplify the signal under the condition where noise and drift are largly rejected and thus may increase the sensitivity of detection. An improvement in the signal-to-noise ratio by a factor of *ca.* 30 was reported[2] and the potential of raising it further to 100 was suggested[1]. As this is quite challenging, a study was undertaken to establish, both theoretically and experimentally, the influence which the frequency of the solute switching exerts on the modulation efficiency of the signal under various operational conditions for the modulator and the detector.
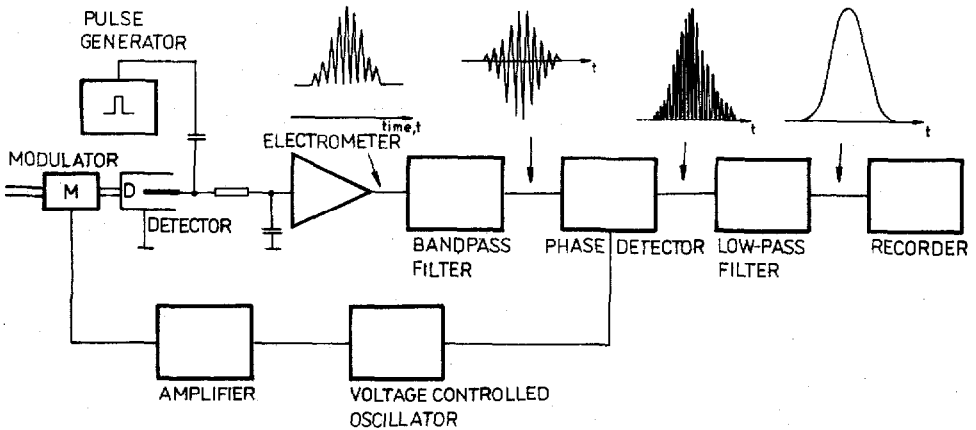
Fig. 1. Block diagram of an electronic device for solute switching and synchronous detection of chromatographic peaks.

MODULATION OF THE ELECTRON-CAPTURE DETECTOR SIGNAL WITH SOLUTE SWITCHING

Theoretical analysis

An ideal solute switch when turned on should instantly remove all of the solute and when turned off should instantly allow the carrier to flow unimpeded. The coulometric electron-capture detector will operate as a solute chopper when the applied potential is changed from 0 to about 20 V positive. However, the changes of the free passage and the destruction of the solute are not instantaneous, as illustrated in Fig. 2. At positive potential, electrons are rapidly removed by the anode, thus reducing their concentration to zero. Then, they participate hardly at all in the removal of the solute molecules from the detector cell. However, a certain amount of time is required
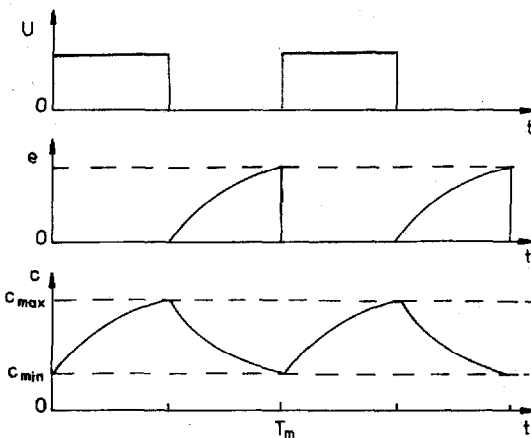

Fig. 2. Periodical changes of the concentration of electrons (e) and capturing molecules (c) inside the modulator at a steady state of the modulation process.

before the molecules accumulate in the detector, according to the differential equation

$$\frac{dc}{dt} = \frac{b}{V_s} - \frac{u}{V_s} \cdot c \tag{1}$$

where c is the concentration of the sample molecules in the solute switch cell (molecules/cm^3), V_s is the volume of the solute switch cell (cm^3), u is the flow rate of the carrier gas (cm^3/sec) and b is the rate of injection of the sample molecules into the switch (molecules/sec). The concentration of the sample molecules in the carrier gas at the outlet of the switch will reach approximately the same level as that at the inlet, after at least three times constants for ventilation of the switch, i.e. $3V_s/u$.

At zero potential, electrons are not removed and they accumulate within the detector, according to the equation

$$\frac{de}{dt} = \frac{a}{V_s} - k_1 ec - k_d e \tag{2}$$

where e is the concentration of electrons inside the switch (electrons/cm^3), a is the rate of injection of electrons inside the switch (electrons/sec), k_d is the pseudorecombination rate constant (sec^{-1}) and k_1 is the rate constant for dissociative electron attachment of sample molecules (cm^3/sec). The concentration of electrons may reach a level sufficient for reacting and for removing solute molecules AB in the dissociative electron-capture process

$$AB + e \xrightarrow{k_1} A + B^-$$
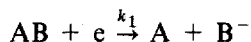
but again, some time is needed, as the decrease in concentration of the molecules follows the equation

$$\frac{dc}{dt} = \frac{b}{V_s} - k_1 ec - \frac{u}{V_s} \cdot c \tag{3}$$

Providing that the applied potential is switched on and off at a constant frequency $1/T_m$, where T_m is the time period of switching, in sec, and that constant values of maximal and minimal concentrations of electrons (e) and molecules (c) over the period T_m (steady state of modulation process) have been reached, eqns. 1–3 can be solved for the following boundary conditions: $e(0) = e(T_m) = 0$; $c(0) = c(T_m) = c_{min}$; and $c(T_m/2) = c_{max}$, which leads to the relationships

$$c_{max} = \frac{b}{u} - \left(\frac{b}{u} - c_{min}\right) \exp\left(-uT_m/2V_s\right) \tag{4}$$

$$e_{max} = \frac{a}{V_s (k_1 c_{min} + k_d)} \cdot \{1 - \exp[-(k_1 c_{min} + k_d)T_m/2]\} \tag{5}$$

$$c_{min} = \frac{1}{k_1\,e_{max} + u/V_s} \cdot \left\{ \frac{b}{V_s} - \left[\frac{b}{V_s} - c_{max}\left(k_1\,e_{max} + u/V_s\right) \right] \right. \cdot$$

$$\left. \exp\left[-(k_1 e_{max} + u/V_s)\,T_m/2 \right] \right\}$$

Relationships 5 and 6 were obtained under the additional assumption that first the maximum value for e is reached rather quickly and then the slower process of decrease of the solute concentration takes place. If we define modulation depth as

$$M = \frac{c_{max} - c_{min}}{c_{max}} \tag{7}$$

then it can be proved that

$$M = 1 - \frac{w}{1 - (1 - w)\exp\left(\dfrac{-uT_m}{2V_s}\right)} \tag{8}$$

where w is determined by the non-linear equation

$$\frac{1 + w - w\,[\xi(w + \eta) + 2]}{1 - w} = \exp\left\{ -\frac{uT_m}{2V_s}\,[\xi(w + \eta) + 2] \right\} \tag{9}$$

where $\xi = a/b$ and $\eta = k_d u/k_1 b$.

The set of eqns. 8 and 9 have been solved numerically for the parameter ξ, η and $\dfrac{uT_m}{V_s}$ ranging from 0.01 to 100 (ref. 3). The results are shown in Figs. 3–5.

For practical applications it is important to know the dependence of the modulation depth on the rate of sample molecules, b, and the rate constant for the dissociative electron attachment, k_1. From Figs. 6 and 7 it may be seen that for low values of b, i.e. less than $1 \cdot 10^{-11}$ molecules/sec, and relatively long periods of modulation T_m, i.e. lasting a few seconds, the modulation depth practically does not depend on b, but is roughly proportional to the value of k_1.

The fluctuations of the solute concentration in the carrier gas generated by the solute switch are dampened before detection because of the finite volume of the connections between the modulator and the detector, and because of the volume of the detector itself. In order to assess the dampening, it is convenient to assume that the generated modulation of the solute has the form of a sinusoidal function

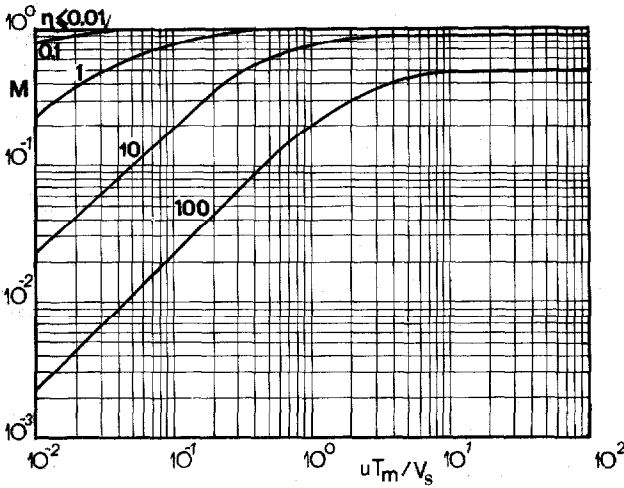$$c_g = c_g^0 + c_g^1 \sin\left(\frac{2\pi}{T_m} \cdot t \right) \tag{10}$$

Fig. 3. Dependence of modulation depth M on the parameter uT_m/V_s and on η for $\xi = 100$.
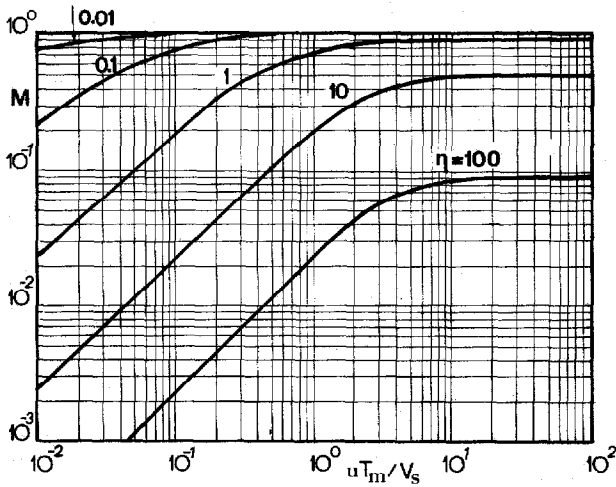
Fig. 4. Dependence of modulation depth M on the parameter uT_m/V_s and on η for $\xi = 10$.

where c_g^0 and c_g^1 are the average value and the amplitude of fluctuations of the solute concentrations, respectively. The changes in the solute concentration inside the detector, c_d, can be described by the equation

$$\frac{dc_d}{dt} = \frac{u}{V_d} \cdot c_g - \frac{u}{V_d} \cdot c_d - k_1 e_d c_d \tag{11}$$

where V_d is the detector volume (cm^3).

As a result, one obtains

$$c_d = c_g^0 + c_g^1 \frac{1}{\left[1 + \left(2\pi \cdot \frac{\tau_d}{T_m}\right)^2\right]^{1/2}} \cdot \sin\left(\frac{2\pi}{T_m} \cdot t + \varphi\right) \tag{12}$$

where

$$\varphi = \text{arc tg}\left(-\frac{2\pi}{T_m}\tau_d\right) \tag{13}$$
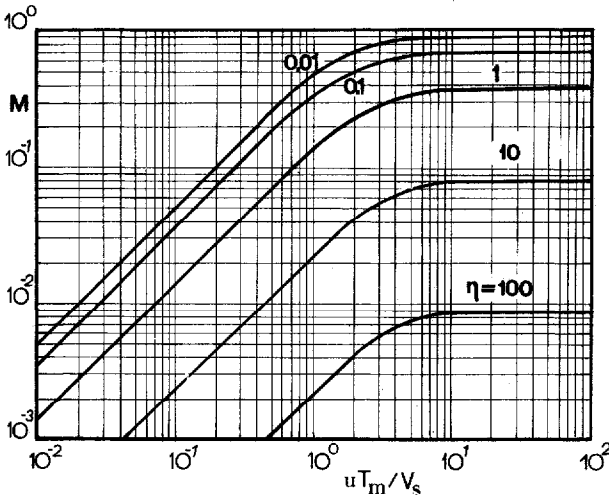
$$\tau_d = \frac{1}{k_1 e_d + u/V_d} \tag{14}$$

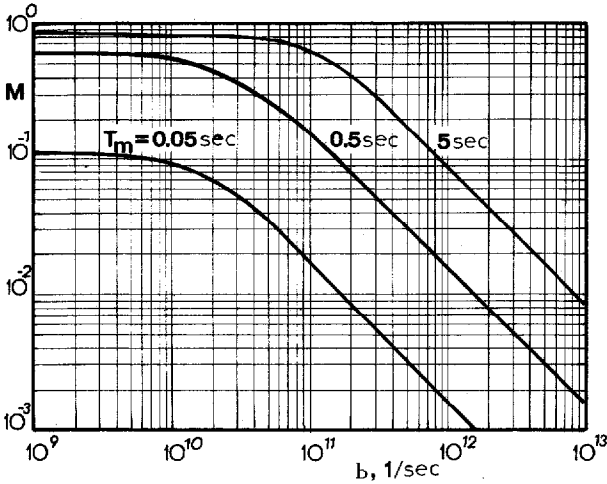Fig. 5. Dependence of modulation depth M on the parameter uT_m/V_s and on η for $\xi = 1$.

Fig. 6. Theoretical relationship between rate of the sample molecule injection (molecules/sec), b, and the depth of modulation for different T_m values.
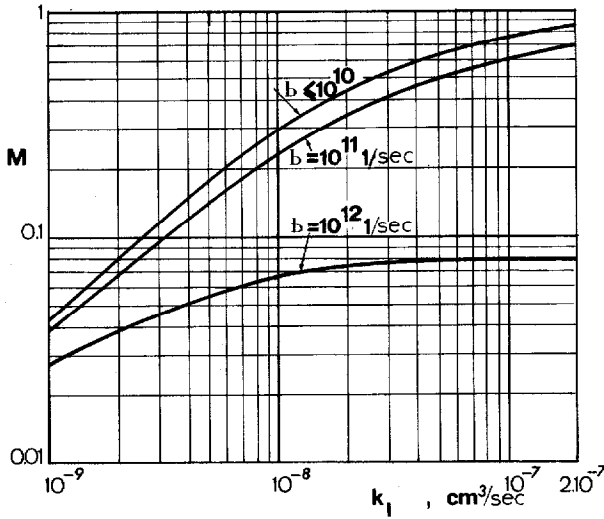
Fig. 7. Theoretical relationship between the depth of modulation and the rate constant for dissociative electron attachment, k_1, for different b (in molecules/sec) values.

and e_d = the mean concentration of electrons inside the detector (electrons/cm^3). This means that the fluctuations of the sample concentration in the detector decrease by a factor of $\left[1 + \left(2\pi \cdot \dfrac{\tau_d}{T_m}\right)^2\right]^{1/2}$ and are shifted in phase.

If we define the modulation depth for the solute in the detector as

$$M_d = \frac{c_{d\ max} - c_{d\ min}}{c_{d\ max}} \tag{15}$$

then it can be derived that

$$M_d = \frac{2M}{M + (2 - M)\left[1 + \left(2\pi \cdot \dfrac{\tau_d}{T_m}\right)^2\right]^{1/2}} \tag{16}$$

The modulations measured at the output of the detector are dampened even further, owing to the time constant of the electrometer and recorder, τ_{el}. It can be shown that the modulation depth for the recorded signal, S, defined as

$$M_e = \frac{S_{max} - S_{min}}{S_{max}} \tag{17}$$

is related to M_d by the following equation:

$$M_e = \frac{2\ M_d}{M_d + (2 - M_d)\left[1 + \left(2\pi \cdot \dfrac{\tau_{el}}{T_m}\right)^2\right]^{1/2}} \tag{18}$$

Relationships 16 and 18 between M, M_d and M_e create an important link between the theoretical efficiency, M, of the solute switching by the coulometric electron-capture detector and the actually measured modulated electrical signal. Therefore, those relationships form the basis for an experimental verification of the theory developed here.

Measurements of the modulation depth

Fig. 8 shows a diagram of the apparatus used for the measurement of the electron-capture detector signal with the alternating-current component due to the solute switching. Two coulometric electron-capture detectors[4], designated M and D, were connected in series just after the chromatographic column C. The first one, M, operated as a solute switch with an applied potential of 25 V turned on and off for equal amounts of time at constant intervals ranging from 0.5 to 5 sec. The second detector was used as a sensor and supplied with pulses of 60 V amplitude and 160 μsec period. Both detectors were equipped with tritium radioactive foils yielding saturation currents of 29.1 and 32.0 nA for the modulator and the detector, respectively. The overall time constant for the electrometer E and the recorder R was 0.15 sec. The carrier gas used was purified nitrogen. It was run through the modulator and the detector at a fixed volumetric flow-rate which varied from 0.2 to 40 cm^3/sec. To obtain flow-rates higher than 2 cm^3/sec, an additional stream of nitrogen was directed straight to the modulator to avoid the column.
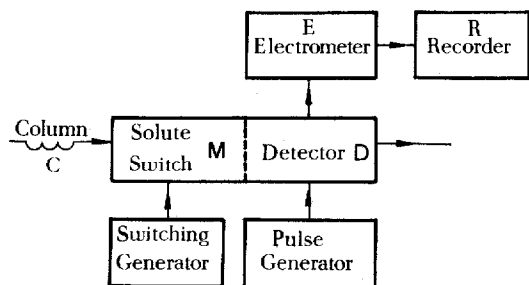
Fig. 8. Diagram of the apparatus for measurements of modulated signals.

The results of measurements of the depth of modulation of the signal for F-11 and CCl$_4$ are illustrated in Fig. 9a and b. They are compared with the results of calculations obtained for the value of the parameter b corresponding to the apex of the chromatographic peak. The expression used for an evaluation of this value is based on the triangular approximation of the peak shape; it runs as follows:

$$b_{max} = \frac{m_d}{\mu t_h} \cdot A_v \tag{19}$$

where b_{max} is the rate of introduction of the sample molecules into the detector at the peak apex, m_d is the mass of the analysed sample molecules (g), μ is the mass number of the sample molecule (g), A_V is Avogadro's number and t_h is the peak width at half height expressed in time units.
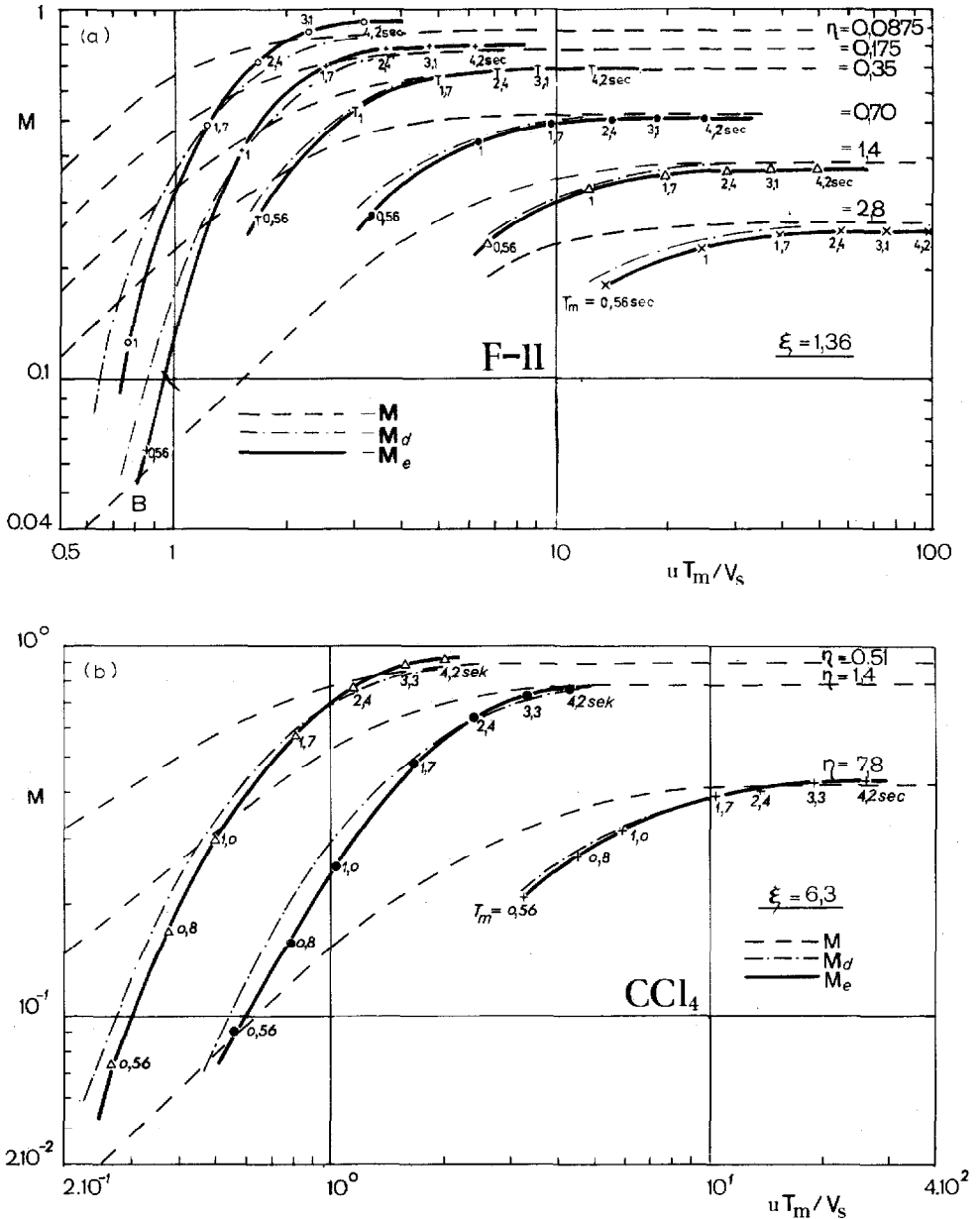
Fig. 9. Comparison of measured and calculated values of modulation depth for (a) Freon F-11 and (b) CCl_4, for different η parameters and T_m values.

The calculations were performed with the help of formulae 8, 9, 16 and 18 for the following data: $a = 2 \cdot 10^{11}$ electrons/sec, $k_d = 2.85 \cdot 10^3$ s^{-1}, $V_s = 1.2$ cm^3 (the modulator volume), $m_d = 1.13 \cdot 10^{-9}$ g for CCl_4 and $2.2 \cdot 10^{-10}$ g for F-11 and $t_h = 30$ sec for CCl_4 and 20 sec for F-11. The values calculated agree with those measured within an error of a dozen or so per cent.
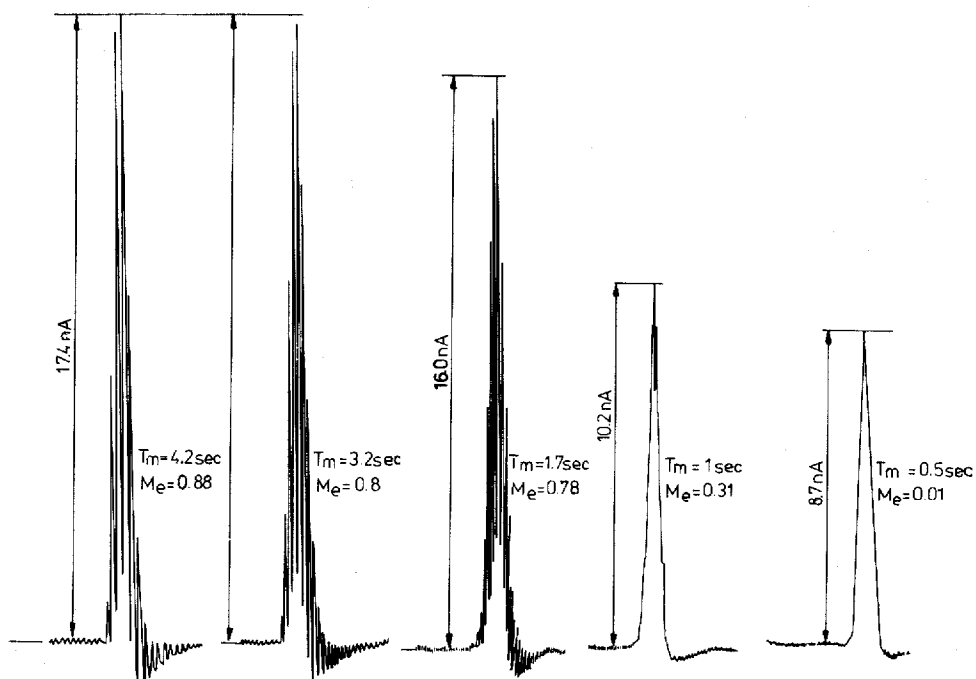
Fig. 10. Influence of the modulation period T_m on modulation depth for Freon F-11.

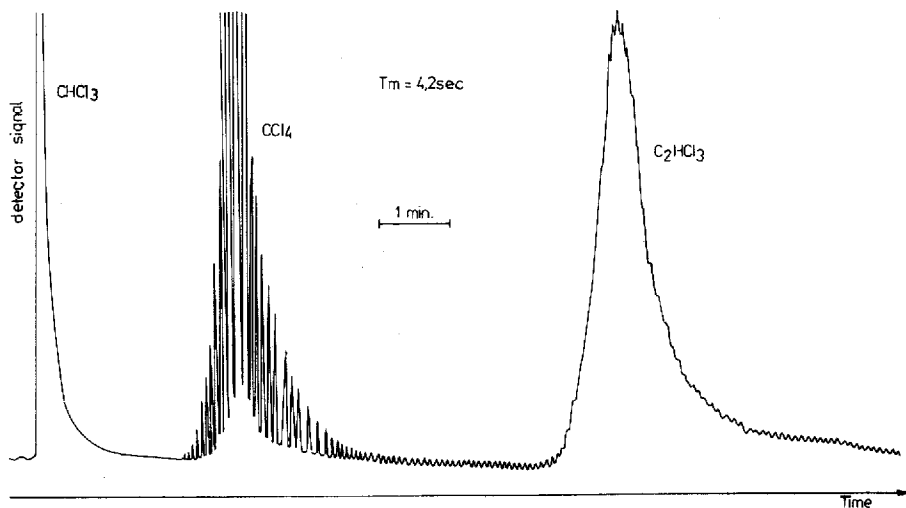
Fig. 11. Comparison of modulation depth for three halocarbons.

The chromatograms shown in Fig. 10 illustrate the influence of the modulation period, T_m, on the modulation depth for F-11. The shorter the period the smaller the modulation of the detector signal.

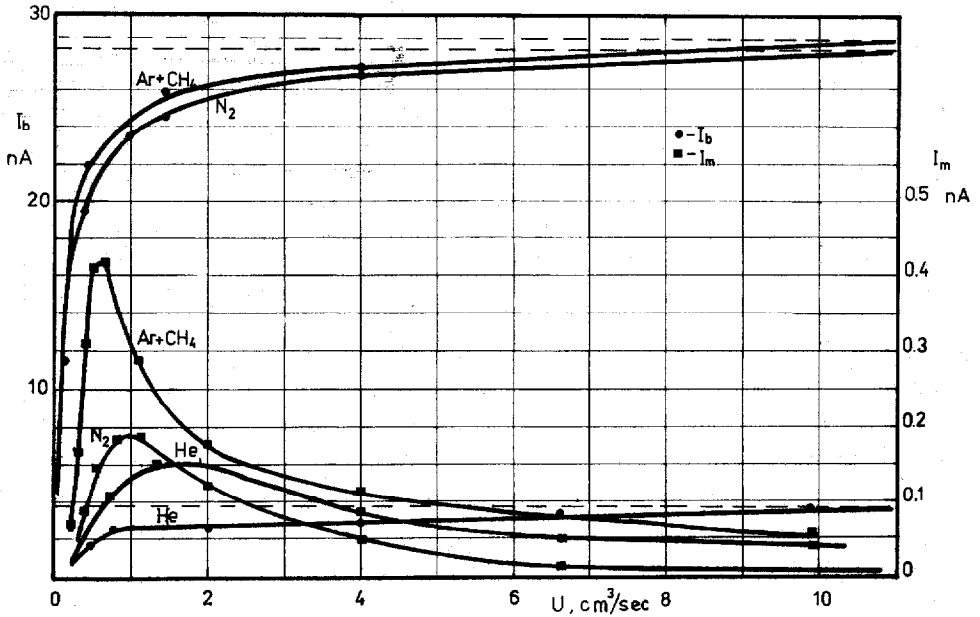The chromatogram shown in Fig. 11 is an example of the selectivity of solute

Fig. 12. Influence of carrier gas flow-rate on the basic detector current I_b and the magnitude of the amplitude of the residual modulation I_m obtained for three different gases.
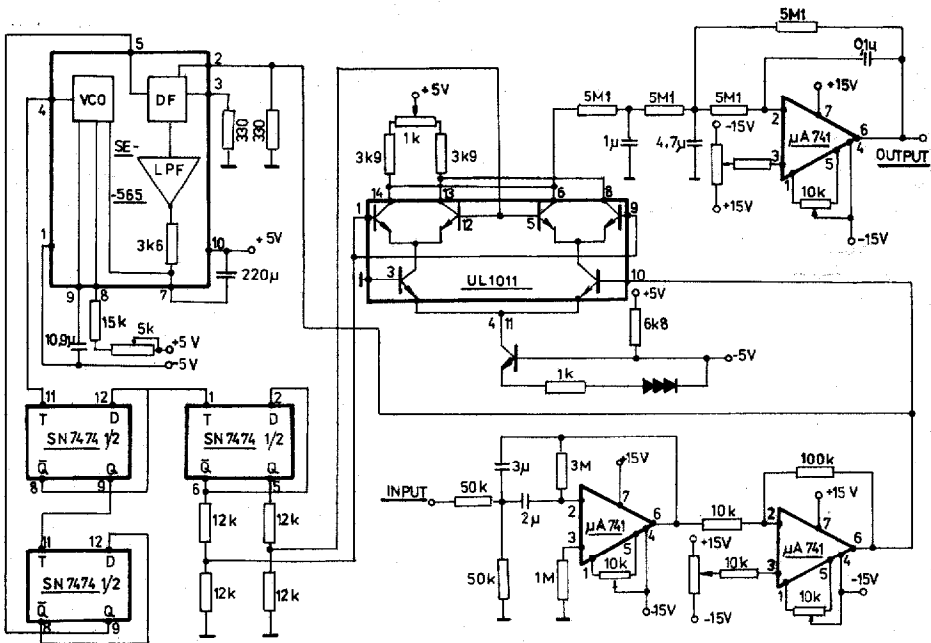

Fig. 13. The electronic circuit for synchronous demodulation.

switching. Only the CCl_4 peak is modulated while the other two, for $CHCl_3$ and C_2HCl_3, are nearly instant. This is in agreement with Fig. 7, which links the modulation depth with the k_1 rate constant for the electron-capture process. The gain observed in the selectivity of the method is of some practical importance for the routine determination of chlorinated pesticides[5]. In Fig. 11 one may also notice residual modulation of the base line. We have so far found it impossible to eliminate it, even when extremely pure gases, such as 99.9995% pure helium, were used. The amplitude I_m of the residual modulation can amount to anything from a fraction to a few per cent of the saturation current, I_b, depending on the kind of carrier gas and its flow-rate. This situation is shown by the plots in Fig. 12 obtained for He, N_2 and Ar + 10% CH_4.

It seems that the modulation of the basic current is caused by strongly electronegative impurities in the carrier gases used. Singh and Lillian[6] reported that even in well purified gases a remnant F-11 concentration of ca. 10 ppt can be found.

The residual modulation of the base line is a highly undesirable phenomenon because it leads to a deterioration of the signal-to-noise ratio in the detection by synchronous demodulation.

SYNCHRONOUS DEMODULATION

A block diagram of the equipment used for solute switching and detection by synchronous demodulation is shown in Fig. 1. Two different synchronous demodu-
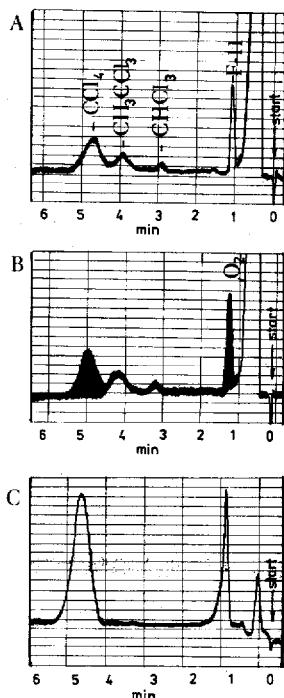

Fig. 14. Comparison of the chromatograms obtained in the case of (A) an electron-capture detector operating in the pulsed mode with constant frequency, (B) solute switching and (C) synchronous demodulation.
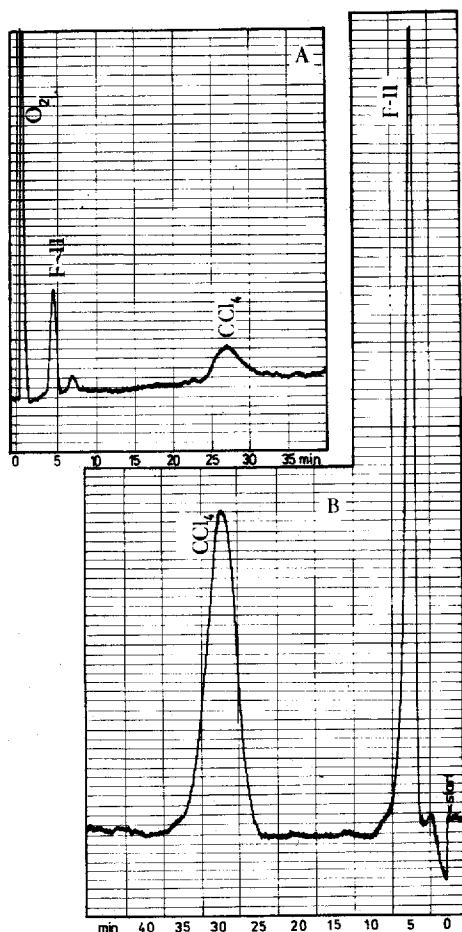
Fig. 15. Effect of the enhancement of the signal-to-noise ratio for relatively long peaks. Chromatograms of air sample: A, pulsed mode; B, detection with modulation.

lators were tried. They both shared a common switching supply which was a square-wave generator operated at a frequency of 0.5 Hz with an output amplitude of 25 V. The first system employed was a Model 232 professional lock-in amplifier (Unipan, Warsaw, Poland), the other was specially built in our laboratory. Its circuit is shown in Fig. 13. Fig. 14 shows three chromatograms obtained during the analysis of an air sample containing 1.7 pg of F-11 and 4.8 pg of CCl_4. The upper chromatogram shows a direct display of the signal of the electron-capture detector run in the fixed pulse mode. The middle one shows a display of the signal generated by the solute-switched electron-capture detector. The lower chromatogram is obtained after solute switching and synchronous demodulation. An increase in the signal-to-noise ratio may be seen only for the CCl_4 peak but not for F-11. This lack of improvement for F-11 triggered investigations that led to the conclusions that the signal-processing procedures described here enhances the signal-to-noise ratio only for relatively long peaks, lasting several modulation periods at least. A more detailed theoretical justi-

fication of this fact, together with the analysis of conditions which must be set for the modulator and the electronic system to obtain the best performance of the method is in preparation. Fig. 15 demonstrates that the method improves the signal-to-noise ratio for F-11 if the peak lasts sufficiently long. The analysis was performed on a longer column filled with 20% DC-200 on 100–200 Chromosorb W. However, in practice it seems much better to use shorter columns and deal with sharp peaks than to employ long, heavily coated columns and then apply sophisticated signal-processing procedures to obtain the same or only slightly better signal-to-noise ratio.

An improvement in the sensitivity for broad peaks is not the only benefit of the technique. There are other advantages which include the improvement in selectivity and the abolition of baseline drift.

CONCLUSIONS

Factors influencing the performance of the electron-capture detector as a solute switch were examined in order to improve the detection limit. An improvement was obtained only for broad peaks lasting many modulation periods, but it is not good enough to justify implementation of the technique to trace analyses.

ACKNOWLEDGEMENTS

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