ELECTRON-CAPTURE DETECTOR WITH AN ION SIGNAL

JANUSZ ROSIEK*

Institute of Nuclear Physics and Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Krakow (Poland)

and

JAN LASA

Institute of Nuclear Physics, ul.Radzikowskiego 152, 31-342 Krakow (Poland)

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SUMMARY

A design of an electron capture detector equipped with two anodes is introduced. The conditions of the detector supply which result in a signal at the first anode of electron nature and a signal at the second anode of ion nature were defined. This construction enables one to design an electronic system which limits the influence of fluctuations in temperature and pressure on the value of the basic current of the detector.

INTRODUCTION

The detection of electronegative compounds in gas chromatography is based on the utilization of the electron capture phenomenon in the ionization chamber, *i.e.*, in the electron capture detector. The process of electron capture leads both to a decrease in the number of free electrons and an increase in the number of negative ions in the volume of the detector. The quantitative detection of the electronegative component reacting with electrons in the process of capture can be carried out by means of measurements of the current of negative ions, the current of electrons or the sum of both these currents.

At present, the second method of the detection is generally applied because it has the highest sensitivity. The duration of the voltage pulse creating an electric field between the detector electrodes is chosen such that only electrons reach the anode.

A dependence of the detector ionization current on the duration of the voltage pulse, t_p, supplying the detector shows whether we are dealing with measurements of the electron current only or of the electron and ion currents. If the ionization current is constant above a certain pulse width, t_p, then only electrons are collected by the anode in this region. If this characteristic has a certain inclination, then the measured detector ionization current has both electron and ion components. The first case can easily be fulfilled in a detector supplied with an argon–methane mixture. Due to the high mobility of electrons, the voltage pulse of duration from 0.1 to 1 μs helps to collect the

electrons in the detector and the characteristic described above has a range of saturation. In the case of a detector supplied with nitrogen in which electrons have a decisively lower mobility, the curve describing the dependence of the ionization current on the pulse duration, t_p, does not have a distinct refraction that would indicate a flow of two kinds of electric charges having different mobilities, *i.e.*, electrons and negative ions to the anode. This fact is not of great significance as regards the detection sensitivity which is still high even when the voltage pulses supplying the detector are between 1 and 100 μs. The improbability of accurate determination of the detector supply conditions where only the electron current is measured makes difficult an interpretation of the measurements especially when using mathematical models of the detector as a chemical reactor.

In this paper a new constructional type of electron-capture detector and its supply with a pulse voltage helping to measure the electron and ion components of the detector ionization current are presented. The possibility of the measurement of both components of the detector ionization current is of assistance when investigating the participation of the ion current in the measured detector signal, and the observation of changes in the electron and negative ion charges caused by the presence of molecules of the sample in the detector. It has been observed that changes in the pressure of the carrier gas and detector temperature cause opposite changes in the ion and electron currents, which has enabled the construction of a system of improved stability.

DESCRIPTION OF THE DETECTOR AND SUPPLY SYSTEM

Fig. 1 shows the construction of the electron-capture detector. The detector consists of a body (4) in which a radioactive source (3) (22 mm × 10 mm I.D., activity of ^{63}Ni up to 5 mCi) is situated. Two anodes (1 and 2) connected with generators of rectangular pulses by the capacitors are placed concentrically inside the radioactive source.

Fig. 2a presents the system of supplying the detector with pulse voltages and the method of measurement of the ionization current of both anodes. Fig. 2b shows the shape and time course of the voltage pulses from the pulse generators (1 and 2). The pulse amplitude is 50 V while the duration of the pulse supplying anode 1 is t_1 and that
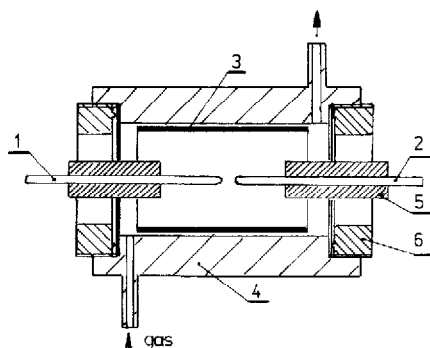

Fig. 1. The design of the electron-capture detector with two anodes (1 and 2), radioactive source (3), detector body (4), ceramic insulator (5) and nut (6).
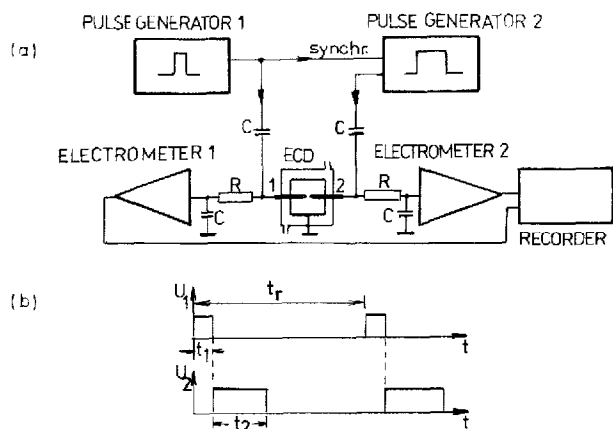
Fig. 2. (a) System of supply and measurement of the detector signal. (b) Time courses of the voltage pulses supplying anode 1, of amplitude U_1 and duration t_1, and supplying anode 2, of amplitude U_2 and duration t_2. ECD = Electron-capture detector; C = capacitor; R = resistor.

of anode 2 is t_2. These durations can be regulated independently within the range from 1 to several hundred μs. The generators of pulses 1 and 2 are synchronized such that the trailing edge of the pulse t_1 initiates the pulse t_2 supplying electrode 2. Generator 1 operates as described[1] and helps to measure automatically the dependence of the ionization current of anode 1 on the repetition time of the pulse, t_r. Since generator 2 is synchronized with generator 1, the measurement of the ionization current of anode 2 can also be made automatic as a function of the repetition time of the pulses supplying this electrode.

In the course of measurements the detector was supplied with nitrogen as the carrier gas (contamination level of ca. 1 ppm). The detector signal for strongly negative halogenated hydrocarbons separated on a chromatographic column of length 1 m packed with 10% DC-200 on 100–200 mesh Chromosorb W has been investigated.

RESULTS

The measurement of the electron component of the detector ionization current by one anode and the ion component by the other anode was the objective of the construction of the detector with two anodes supplied with voltage pulses of different durations. It was assumed then that the first pulse will collect a rapidly moving electron charge. The other pulse ought to collect the slower negative ions that were not collected during the short first pulse. It seems that all the electrons will not be collected by the first pulse, but their participation in the current of the second electrode will be less than that of the anions.

The collection properties of the two electrodes was compared in such a way that both electrodes were supplied with a pulse voltage of the same duration, i.e., $t_1 = t_2$ and with subsequent pulses of duration $2t_1$, or they were combined in parallel and treated in this way as one electrode. Fig. 3 presents current characteristics corresponding to different variations of supplying the detector with pulses of duration $t_1 =$
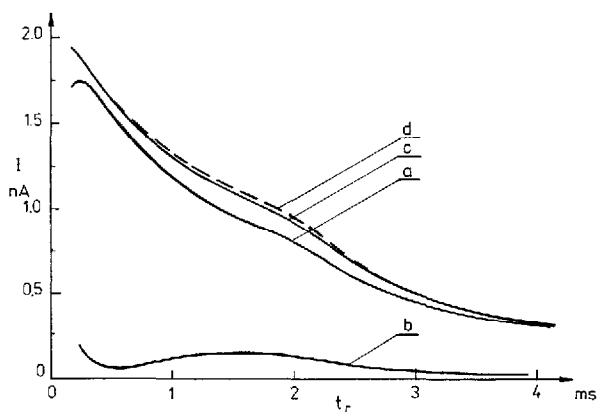
Fig. 3. The dependence of the ionization current of the detector on the pulse repetition for different ways of detector supply. See the text.

$t_2 = 20$ μs. Curve a represents the detector current characteristic of anode 1 which is supplied with the first voltage pulse and curve b is the ionization current of anode 2 supplied with a second pulse immediately after the collection of charge by anode 1. It is seen that a decisively greater charge is collected by anode 1. Anode 2 collects a considerably smaller charge which is evidence of the charge exhaustion, i.e., of the nature of the source from which it arises. The detector is completely symmetrical, i.e., inversion of the sequence of supplying the anodes does not influence the courses of the current characteristics a and b in Fig. 3. The fact that the sum of the currents measured by both anodes supplied successively by pulses of duration 20 μs equals the current collected by one anode supplied with a voltage pulse of duration 40 μs by (see curve c in Fig. 3) is evidence for the equivalence of the performances of the two anodes. When the two electrodes were connected together and supplied with voltage pulses of 40 μs, the ionization current collected was as shown by curve d in Fig. 3.

From the characteristics presented in Fig. 3 it follows that electrodes 1 and 2 supplied successively with voltage pulses of 20 μs collect practically the whole of the available electric charge in the detector.

The influence of the pulse duration on the value of the charge collected is presented in Fig. 4. During the measurements both detector anodes were connected together. The pulses supplied were repeated every 320 μs (Fig. 4b) or 4000 μs (Fig. 4a) at the temperatures shown. An increase in the detector temperature resulted in an increase in the charge collected. This can be accounted for by the process of detachment of electrons from molecules of oxygen which is a contaminant of the carrier gas[2]. When the repetition time, t_r, is 320 μs the charge collected reaches saturation for pulse durations greater than 20 μs. For long repetitions (Fig. 4a) the saturation state is not obtained within the range of durations of the pulses, t_1, applied. This makes the determination of t_1 at least difficult. From Fig. 4a it follows that the collection of charges occurs more slowly for long repetition times, what can be accounted for by the origin of the plasma and by a decrease in the electron mobility[3,4] in the long voltageless state in the detector.

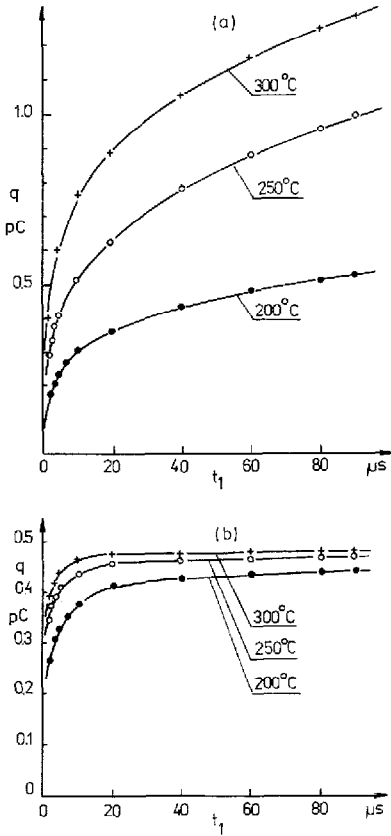The influence of different times t_1 at a constant value of t_2 on the course of the

Fig. 4. The dependence of the charge collected by two detector electrodes joined together on the duration of the pulses supplied. Repetition times, t_r: 4000 (a) and 320 μs (b). The detector temperatures are given.

detector current characteristics is presented in Fig. 5. The characteristics I_1 and I_2 are the ionization currents measured by anodes 1 and 2 respectively. The dashed curves represent the ratio I_2/I_1. Analyzing the course of the characteristics in Fig. 5, the following effect can be observed. A pulse of duration $t_1 = 3$ μs collects only the electron component. On the other hand, a pulse applied to the other anode and lasting 120 μs collects negative ions and electrons, and the maximum current occurs for a repetition time of about 1200 μs (Fig. 5a). An increase in t_2 up to 9 μs results in an increase in the current collected by the first anode and the second anode collects the remaining electrons and negative ions, and the maximum current occurs at a repetition time of 1000 μs. A pulse of duration 90 μs at the first electrode collects practically all the electric charges in the detector, while the curve I_2 in Fig. 5c represents, most probably, the falling parts of the curves I_2 of Fig. 5a and b. The ratio I_2/I_1 is almost constant for repetition times over 2000 μs. For shorter repetition times this ratio is not uniquely determined because of the complex character of the factors influencing the values of the currents collected by both anodes.

The measurements the results of which are presented in Figs. 4 and 5 do not
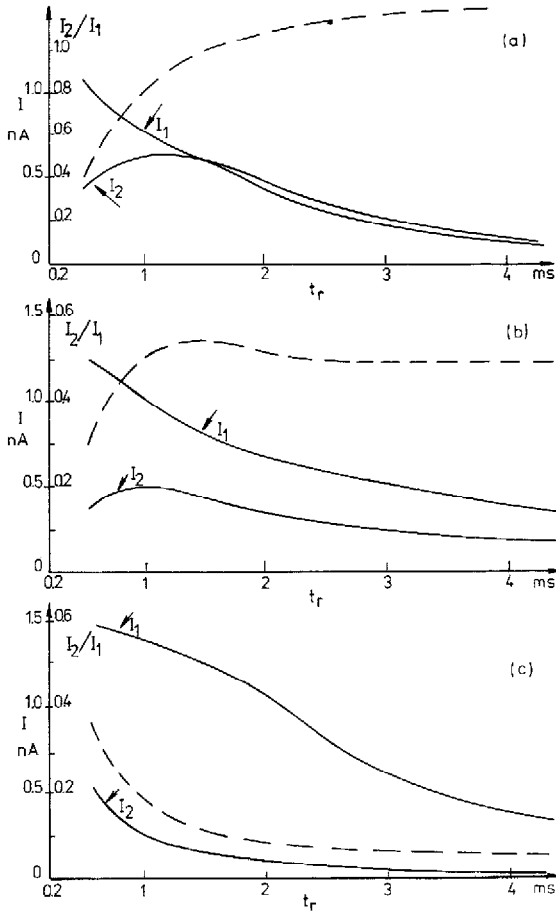
Fig. 5. Dependence of the ionization currents at anodes 1 and 2 on the repetition time, $t_1 = 3$ (a), 9 (b) and 90 μs (c); $t_2 = 120$ μs. $---$, I_2/I_1.

allow an unique determination of the parameters of the pulse supplying anodes 1 and 2 which would collect the electron and ion components of the detector ionization current. We tried to determine these conditions by measuring the polarity of the observed signal in the measurement circuit of anodes 1 and 2 caused by the sample introduced in the detector. If anode 1 collects electrons, then the sample introduced in the detector ought to cause a decrease in the current in its measuring circuit, *i.e.*, a signal of negative polarity. On the other hand, the signal ought to be of positive polarity in the measurement circuit of the second anode if it collects the anions. A small concentration of oxygen was introduced in the detector. It caused several percentage decrease in the ionization current. The signals of both anodes for different pulse durations, t_1 and t_2, were observed. The charges collected in the measurement configurations of both anodes are denoted by Δq_1 and Δq_2 respectively. Exemplary results are shown in Fig. 6. It was observed that the signal Δq_1 is always of negative polarity. The polarity of the signal Δq_2 depends on the configuration of the parameters
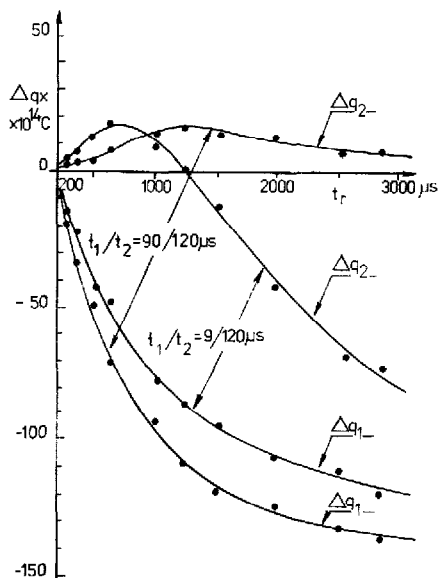
Fig. 6. The dependence of the signal at anode 1, Δq_1, and at anode 2, Δq_2, for the given pulse durations t_1 and t_2 on the pulse repetition for a constant oxygen concentration in the detector.

t_1 and t_2 and the repetition time, t_r. For $t_1/t_2 = 9/120 \ \mu s$, Δq_2 is of positive polarity for repetition periods from 200 to 1200 μs, *i.e.*, in the period for which the current I_2 of Fig. 5b has a bulge. For $t_1/t_2 = 90/120 \ \mu s$ and the whole range of repetition time (from 200 to 3000 μs), Δq_2 has a positive polarity. Thus the curve I_2 in Fig. 5c refers to the ion current.

In order to determine optimum detection conditions, the times t_1 and t_2 were changed so that the signals of both anodes were of the opposite polarity and their ratio, $p = |\Delta q_2/\Delta q_1|$, was maximized. Fig. 7 shows the dependence of the absolute values of
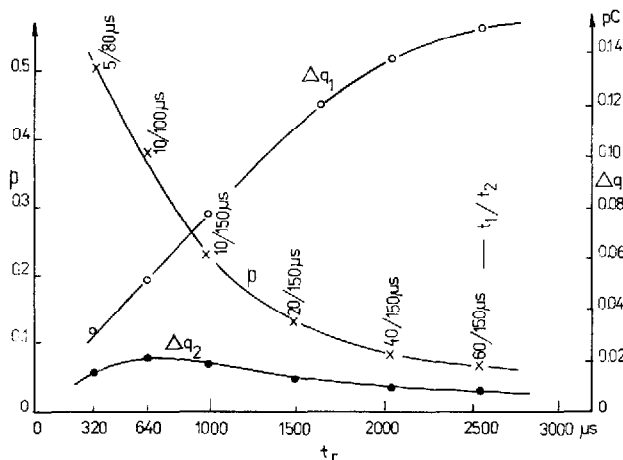

Fig. 7. The dependence of the electron signal, Δq_1, and of the ion signal, Δq_2, and the ratio, $P = |\Delta q_2/\Delta q_1|$ on the pulse repetition time for an oxygen sample. The values of t_1 and t_2 for which p was defined are marked on curve p.

Δq_1 and Δq_2 as well as their ratio, p, on the repetition time, t_r. The values t_1 and t_2 for which p was defined are marked on the curve p. It is seen that for short repetition times, t_r, the ion signal may reach 50% of the electron signal, and as t_r increases this proportion diminishes in favour of the electron signal. It was stated that for $t_1 < 3~\mu s$ the signal Δq_2 is of negative polarity, which means that anode 2 collects a lot of electrons and their loss connected with the presence of the sample molecules in the detector is bigger than the increase in the negative ions collected by this anode. It can also be stated that the proportion of the signals of both anodes decreases simultaneously with the filling factor of the pulsed voltage, defined as $k = (t_1 + t_2)/t_r$.

DISCUSSION

The results of the measurements presented in Fig. 7 prompt the question: can we treat the signals measured by anodes 1 and 2 as the electron and ion signal. Is it possible to measure the negative ion current in the detector supplied by a pulsed voltage if these ions move at least 1000 times more slowly than the electrons in the electric field of the detector. Maybe both signals are of electron character and the change of the signal polarity at anode 2 is connected with the change in the electron drift velocity, caused by the space charge that occurs in the detector.

The problem of the collection of anions was studied by Wells[5] in order to explain the limitation of the linearity range in the constant-current system of the detector. He stated that the high concentration of the sample tested that accompanied the high frequency of pulses at the end of the measurement range caused the collection, by the anode, also of the negative ions.

The attempt to estimate the probability of the collection of the anions by the detector electrodes introduced below will allow us to conclude that the signal observed in the measurement system at anode 2 is the ion signal.

The conversion of the electron in the capture process into anions means the loss of the free charge observed in the detector where only the electrons would constitute the measured current. The pulsed electric field that occurs in cycles between the detector electrodes will cause a step drift of the ion in the direction of the anode and if recombination does not take place then the amount of electrons collected will not change in spite of the capture process that occurs in the detector.

It can be assumed that at the time $t = 0$ a certain number of anions, A_0, occurs in the detector which has a plate-parallel geometry. Moreover, it can be assumed that for the correspondingly low anion concentration, there will be no change in the positive ion concentration, p. If we disregard the ion diffusion in the time between the pulses of uniform electric field, the number of ion jumps necessary to reach the anode, if at time $t = 0$ the distance between this ion and the anode is x, will be

$$n(x) = xL/U\mu_j t_p \tag{1}$$

where U is the amplitude of the voltage pulse in V, μ_j is the mobility of the negative ion in $m^2/V \cdot s$, t_p is the duration of the voltage pulse in s and L is the distance between the anode and cathode in m. The total residence time of the anion in the detector equals $n(x)t_r$, where t_r is the repetition time of the pulses supplied. The rate of loss of the anion in the ion–ion recombination process is represented by

$$da/dt = -\alpha_c ap \tag{2}$$

where α_e is the rate constant for the recombination of negative ions with positive ones in m^3/s, a and p are the concentrations of negative and positive ions respectively, in ions/m^3. After integrating the dependence 2 in the range from $t = 0$ to $t = n(x)t_r$ we obtain the anion concentration in the layer of thickness dx drifting from the distance x to the anode

$$a_x = A_0/V \cdot \exp[-\alpha_e pn(x)t_r]$$ (3)

where V is the detector volume.

The layer considered contained initially $dA_0 = A_0 dx/L$ of the anions, of which

$$dA_x = (A_0/L) \cdot \exp[-\alpha_e pn(x)t_r]dx$$ (4)

reach the anode. From the whole detector volume the anode will be reached by

$$A_F = \int_0^L dA_x dx$$ anions, and after integration of eqn. 4 the fraction of their initial

amount in the detector is:

$$\frac{A_F}{A_0} = \frac{U\mu_j t_p}{\alpha_e pL^2 t_r}\left[1 - \exp(-\alpha_e t_r L^2/U\mu_j t_p)\right]$$ (5)

A similar treatment carried out for a detector of cylindrical electrode geometry, where the anode and cathode have radii a and b respectively, leads to the following dependence defining the number of the negative ion jumps from the location r to the anode

$$n(r) = \frac{(r^2 - a^2)}{2U\mu_j t_p}\ln(b/a)$$ (6)

and the relative number of negative ions collected is

$$\frac{A_F}{A_0} = \frac{2\{1 - \exp[-z(b - a)^2] \cdot \exp(za^2)\}}{z(b^2 - a^2)}$$ (7)

where:

$$z = \frac{\alpha_e pt_r \cdot \ln(b/a)}{2U\mu_j t_p}$$

Calculations of A_F/A_0 were done for the following values of the parameters that occur in eqns. 5 and 7: $\mu_1 = 3.3 \cdot 10^{-4}$ $m^2/V \cdot s$, $\alpha_e = 3 \cdot 10^{-12}$ m^3/s; ref. 6, $t_r = 1.5 \cdot 10^{-3}$ s, $t_p = t_1 + t_2 = 20$ $\mu s + 150$ $\mu s = 1.7 \cdot 10^{-4}$ s (which gives the filling factor $k = t_p/t_r = 0.11$); $U = 50$ V. For plane geometry, $L = 4.5 \cdot 10^{-3}$ m; for cylindrical geometry, $a = 0.5 \cdot 10^{-3}$ m, $b = 5 \cdot 10^{-3}$ m. For the detector saturation current $I_0 = 3 \cdot 10^{-9}$ A, the rate of generation of positive ions equals $1.78 \cdot 10^{10}$/s and

their concentration in the detector volume, $V = 10^{-6}$ m^3, is $p = 0.78 \cdot 10^{14}$/m^3. The proportion A_F/A_0 calculated is 0.37 for plane geometry and 0.56 for cylindrical geometry, and is a measure of the probability of collection of the anions formed in the electron capture process. This probability depends to a great extent on the residence time of the ion in the detector which depends in turn on the filling factor of the pulsed voltage and the drift length. Both for the plane and cylindrical geometries the calculated probability of the negative ion collection is estimated to be large.

The initial number of anions, A_0, equals the decrease in the number of free electrons in the detector as a result of their capture by the sample molecules. It can be assumed that the specifically defined ratio A_F/A_0 represents the ratio of the signals of both electrodes if one of them collects the electrons only and the other the anions.

The experimental values of the ratio of the electrode signals are lower than the ones calculated as above. For example, for the repetition time, $t_r = 1500$ μs the value $p = 0.13$ while the calculated ratio $A_F/A_0 = 0.56$. This discrepancy may result from the longer distance and by the same token greater number of jumps required in the direction of the collecting electrodes under the influence of the electric field effected by the pulse applied to both anodes. In consequence, the ion's path is not along the detector radius but is more complex. The field of the space charge entails deceleration of the ion in the direction of the anodes.

Influence of the pressure and temperature changes on the signals of both electrodes

Fig. 8 represents an example of the analysis of halogenated hydrocarbons. The chromatograms designated Si and S2 were obtained in the measuring circuit of anodes 1 and 2, respectively. Fig. 8a presents the chromatograms of the liquid sample of halogenated hydrocarbons into which 2 cm^3 of air were injected in order to obtain the
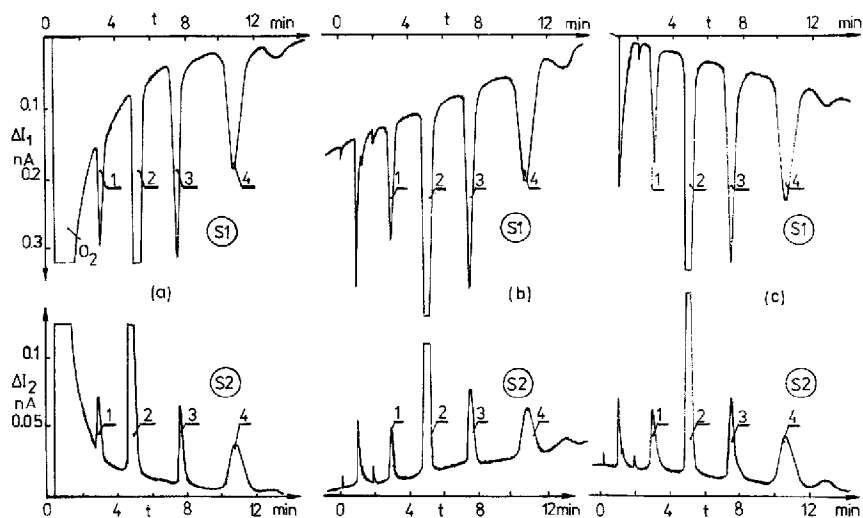

Fig. 8. Chromatograms obtained in the measurement of the signal of electrode 1, S1, and electrode 2, S2. Peaks: 1 = CHCl$_3$; 2 = CH$_3$CCl$_3$; 3 = CCl$_4$; 4 = C$_2$HCl$_3$. The drift of zero line was caused by: (a) contamination of the carrier gas by oxygen; (b) change in carrier gas pressure in the detector; (c) change in the detector temperature.

drift of the zero line. It is seen that at both anodes the contamination of the signal of the carrier gas by oxygen decreases with time. Fig. 8b presents chromatograms where the zero line drift is caused by a change in gas pressure in the detector obtained by connecting its outlet to a closed vessel. It is seen that an increase in gas pressure results in a change in the ionization current at both anodes in the same directions. Fig. 8c presents chromatograms where the drift of the zero line is caused by a change in the temperature of the detector obtained by switching on the thermostat. In this case the changes in the current at both electrodes are of opposite sign.

The influence of the temperature and pressure on the direction of the changes in the ionization currents at anodes 1 and 2 introduced above may be used for constructing a system that demonstrates the stability of the detector operation. Fig. 9 presents an example of the operation of such a system. In Fig. 9a the signal of anode 1 for a vestigial quantity of CCl_4 and C_2HCl_3 is shown, while Fig. 9b represents the signal at anode 2 for the same sample. Fig. 9c shows the signal at anode 2 when it is five times amplified, while Fig. 9d represents the difference between the signals in 9a and c. In consequence, a readable and stable detector signal was obtained.

The utilization of the two signals of the detector equipped with two collecting electrodes stabilizing its operation is possible for pulse parameters such that the signal polarities of the electrodes have opposite signs.

The chromatograms in Fig. 8 are very similar to bipolar chromatograms presented by McMahon and Aue[7]. The possibility of obtaining a positive signal from an electron-capture detector was suggested by Aue et al.[8]. These authors used a three-chamber detector with a bifurcated current flow to two anodes. One anode was exposed to the gas chromatographic effluent and gave a negative signal. The second anode, not exposed to the effluent, produced a positive signal. Signals of opposite polarity from the two electrodes were generated owing to the space charge effect.
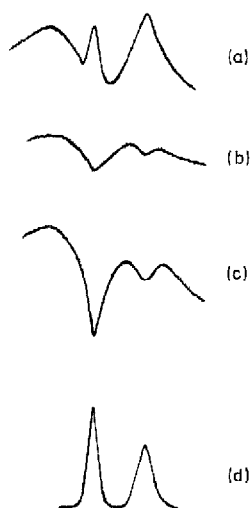

Fig. 9. Illustration of the stability of the basic current of the detector. (a) Electron signal of electrode 1 for vestigial concentration of CCl_4 and C_2HCl_3. (b) Ion signal of electrode 2 for the same sample. (c) Ion signal amplified. (d) Difference between signals a and c.

Our chromatograms were obtained in a different way to the method described above. We used an one-chamber detector in which both anodes were identically exposed to the column effluent and placed close to each other. Signals of opposite polarity are generated owing to a properly selected sequence and width of the pulses. Theoretical relationships for the detector signal are based on the assumed homogeneity of the detector (reactor model). We expect that charge effects described in many works, *e.g.* refs. 8–11, may influence the signals. A quantitative description of space charge effects is difficult owing to the lack of exact spatial solutions of the Poisson equation for a detector cell working in the pulse mode.

CONCLUSIONS

Providing an electron-capture detector with two anodes and the application of a suitable system for supplying these anodes with pulsed voltages enables us to obtain two signals, one having the character of an electron signal, the other of an ion signal.

In spite of its research purpose, the detector described makes possible the construction of a system eliminating the influence of the pressure fluctuation on the detector basic current, and by the same token the improvement of the stability of its operation.

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