CHROMSYMP. 704

EFFECTS OF CONTACT POTENTIALS ON THE PULSED ELECTRON-CAPTURE DETECTOR

P. ROTOCKI* and B. DROZDOWICZ

Institute of Nuclear Physics, Radzikowskiego 152, 31–342 Cracow (Poland)

SUMMARY

Studies of the effect of the contact potential difference on the standing current and the response of the constant-frequency electron-capture detector are reported. The effect of temperature and carrier gas flow-rate on the contact potential difference is also shown. The space charge [P. L. Gobby, E. P. Grimsrud and S. W. Warden, *Anal. Chem.*, 52 (1980) 473] model proved useful in the interpretation of the experimental results.

INTRODUCTION

In most commercial electron-capture detectors the anode and the cathode are made of different materials. The cathode is usually a radioactive source (^{3}H or ^{63}Ni) and the anode is usually made of stainless steel. The difference in the work functions of the electrodes materials constitutes the contact potential difference. The contact potential difference can range from fractions of a volt up to several volts, and such a potential difference can cause a detector current of in the nanoampere range, which, depending on the polarity of the potential difference, either opposes or enhances the current normally measured by an electrometer. The contact potential difference between the two clean metals does not depend significantly on the temperature, assuming that the metals are at the same temperature. However, the temperature can affect the adsorption–desorption phenomena of the charges on the metal surface, hence modifying the detector pulse-free current. The influence of the adsorbed material on the contact potential difference was described by Loeb[1]. He considered three different layers: adsorbed layers of ions, adsorbed layers of dipoles and adsorption by the Van der Waal's forces. These were said to create dipole layers at the metal surface, lowering or raising the contact potential difference, depending on the polarity.

Lovelock[2] pointed out that the contact potentials can cause an anomalous detector response in d.c. operation. He found that when the contact potential difference opposed the applied potential, the gas chromatographic (GC) peak had an unexpectedly large area, whereas if the potential difference enhanced the applied potential, a diminished response was observed. Lovelock, who proposed the pulse sampling mode of electron-capture detector operation, suggested that with this mode of operation the effects of the contact potentials are rarely, if ever, encountered.

In 1980, Grimsrud and Warden[3] found that the effects of the contact potentials on the constant-frequency detector response were insignificant for short pulse periods (t_p < 500 μs). Grimsrud and Warden proposed a modification of the circuit for measuring the detector current, which consisted of the addition of a small potential, E_{bias}, to compensate for the effects of contact potential. The value of E_{bias} was set so as to achieve zero-detector current when there was no pulse applied to the cell. Grimsrud and Connolly[4] believe that additional small but significant potentials can be created at the cell boundaries owing to the unequal rates at which the charges of opposite sign arrive at the electrodes, which is in accordance with Loeb's findings mentioned above.

In more recent work, Knighton and Grimsrud[5] considered the effects of the contact potential on detector operation. Their electron-capture detectors exhibited high standing currents without the application of any external field. They observed field-free currents of opposite polarities, ranging from a few tenths up to several nanoamperes. They also introduced a parameter L', the rate constant for all electron losses other than those which are caused by a reaction with a sample, in which the effects of the contact potentials were taken into account.

Recently, Simon and Wells[6] thoroughly evaluated the effect of contact potentials on the detector standing current in a constant-current mode for two geometries of the detector, *viz.*, cylindrical and coaxial displaced cylinders. They used four different cell configurations, pulsing the pin or the outer cylinder with pulses of different polarity. They pointed out that there are two effects to be considered in the pulse-free period of detector operation: contact potential and space charge effects. Simon and Wells showed that when the field generated by the contact potential difference is in opposition to that generated by the applied pulses, it could overcome the field generated by the space charge for sufficiently long pulse periods. For small pulse periods, the space charge effects dominate, and for t_p approaching zero the d.c. mode is approached. They also showed that for a contact potential difference opposing the potential applied to the cell, a local minimum in the current *versus* pulse frequency plot was observed. They attributed this phenomenon to the averaging of the electric fields generated by the space charge and the contact potential difference. If, on the other hand, the contact potential difference enhanced the potential applied to the cell, no local minimum in the plot was observed. They attributed this to the minimization of the space charge field in such a cell configuration. They discussed in a similar way the question of the displaced coaxial geometry.

In this work, the effects of contact potential on the standing current and on the response of the constant-frequency electron-capture detector were examined for various values and for two possible polarities of the contact potential difference.

EXPERIMENTAL

A GCHF 18.3 gas chromatograph (G.D.R.) was used. A pin-cup electron-capture detector with a ^{63}Ni ionization source of 10-mCi activity was built in our laboratory. The volume of the electron-capture detector was 1 cm³. A 1/16-in. stainless-steel pin protruded up to half of the height of the cell, and the ionization source formed the outer cylinder. The pulse voltage generator was also built in our laboratory, with the following parameters: pulse amplitude, 50 V; pulse period range, 10–30 000 μs; and pulse duration range, 1–100 μs.
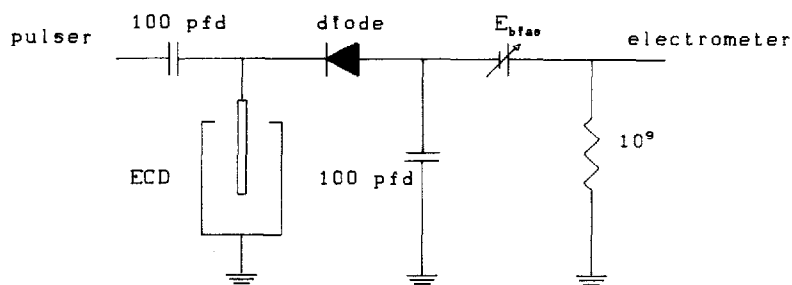
Fig. 1. Circuit for measuring the constant-frequency electron-capture detector current.

The circuit for measuring the detector current, which is depicted in Fig. 1, was similar to that proposed by Grimsrud and Warden[3], where a small potential, E_{bias}, was added to compensate for the effects of the contact potential. The detector was maintained at 200°C. A stainless-steel 1.5 m × 4 mm I.D. silica gel column, operating at ambient temperature, was used. The carrier gas was nitrogen, purified by passage through a two-stage filter packed with activated charcoal and 5 Å molecular sieve. The carrier gas flow-rate was maintained at 75 cm³/min. The detector current was measured by an RFT 6350 electrometer (G.D.R.) and the chromatograms were plotted on a TZ-4100 recorder (Laboratorní Přístroje, Prague, Czechoslovakia). SF_6 with a specified purity of 99.7% was obtained from Merck-Schuchard. A mixture of 2.4 ppb (v/v) of SF_6 in nitrogen was prepared in 2-l stainless-steel bottles by the successive dilution method. This concentration was chosen so as to give a detector response of less than 10% of the standing current. On-column injections were made with help of a six-port valve, made by Valco (U.S.A.). Approximately 1 cm³ of sample was injected several times in order to minimize the standard deviation of the detector response. A pulse duration of 9 μs was sufficient for the collection of all the thermal electrons during the pulse.

A small potential, E_{bias}, was used not only to compensate for the effects of the contact potential but also to set a desired value of the pulse-free current. The value of the pulse-free current measured without adding E_{bias} to the measuring circuit was of the order of + 108 pA in our detector, *i.e.*, with a polarity opposing that of the standing current. This value constituted 12% of the maximum detector current. The maximum detector current, I_0, was of the order of − 830 pA, and the pseudo-recombination rate constant, k_D, was of the order of 540 s^{-1}.

RESULTS AND DISCUSSION

The results indicating the effects of the contact potential on both the detector standing current, I_b, and the detector response to a sample, R, will be discussed in relation to the Gobby et al.[7] space charge model. Other possible electron-capture detector models were also considered, such as the modified Wentworth et al.[8] kinetic model, or the space charge model developed by Aue and Kapila[9], but neither of them provided a satisfactory explanation of the experimental data. The reason is obvious: those models were developed with different assumptions and for cell configuration other than that used in this study. The space charge model of Aue and Kapila, which

considers that the electron capture and negative ion migration cause the detector response, works successfully under the condition that the "centre of charge" is situated close to the cathode and far from the anode. This is not the case here. We found the Wentworth *et al.* kinetic model helpful when considering the effects of the contact potential under the condition that the electric field generated by the contact potentials enhanced the potential applied by the pulser, whereas for the opposite configuration of these fields the experimental data were difficult to reconcile with the kinetic model predictions.

Some important attributes of the Gobby *et al.* space charge model should be mentioned. The model is applied to an electron-capture detector in which ionization produces a uniform distribution of the ion–electron pairs throughout the cell. The pulse amplitude and the pulse width are chosen so that all the thermal electrons can be collected. In the pulse-free portion of the pulse period, the positive ions that are in excess after the removal of the electrons dissipate to all the grounded surfaces of the cell. The ions are driven by the space charge field which they themselves have generated. The thermal electrons produced between pulses form, together with the surrounding positive ions, a plasma region in which the charge neutrality is maintained. The plasma is surrounded by the positive-ion sheath, which separates it from the cell boundaries. The sizes of both the plasma and the ion sheath are subject to changes during the time after the pulse. The size of the plasma increases with time after the pulse, whereas for the size of the ion sheath the reverse is expected. It is believed that there is no gradient of the positive ion density throughout the cell, because the positive ions are lost at nearly the same rate by the recombination within the plasma and by the space-charge-driven migration in the positive-ion sheath zone.

Battery current

An electric field, generated by the contact potential difference, causes a mea-
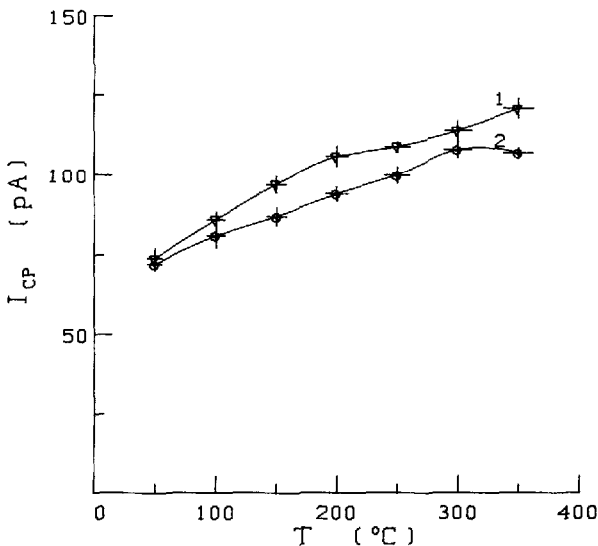

Fig. 2. Battery current, I_{CP}, *versus* detector temperature, T. Curve 1, decreasing T; curve 2, increasing T. The error bars shown are equal to 2 standard deviations.
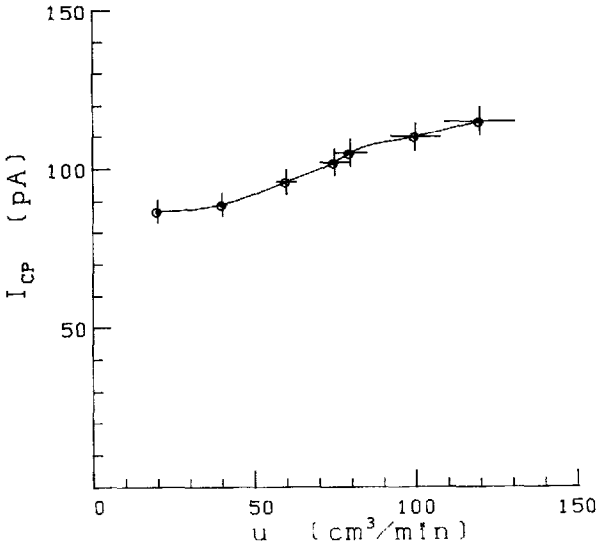
Fig. 3. Battery current, I_{CP}, *versus* carrier gas flow-rate, u. Error bars as in Fig. 2.

surable detector current, I_{CP}, with a polarity and size that vary with the experimental conditions. This current will be referred to as the battery current. It is measured with no pulse applied to the cell. Fig. 2 shows the relationship between I_{CP} and the detector temperature, T. The results obtained varied with the way in which the detector temperature was changed. Increasing T from 50 to 350°C resulted in curve 1, and when T was decreased the next day from 350 to 50°C curve 2 was obtained. The plots show that I_{CP} is strongly temperature dependent.

Fig. 3 shows the relationship between I_{CP} and carrier gas flow-rate, u. When u was increased from 20 to 120 cm³/min I_{CP} increased by 30%. With the electric field generated solely by the contact potential difference, we can consider that our detector is working in the d.c. mode. An increase in carrier gas flow-rate can result in slightly higher values of the gas pressure in the detector and hence in a higher value of the current, as is shown in Fig. 3. It is more difficult to interpret the relationship between I_{CP} and the detector temperature, as the picture is more complex. All the physical phenomena that determine the detector current are strongly temperature dependent. The detector temperature affects the ionization, recombination and electron-capture rate constants and also the electron mobility. Also, adsorption/desorption phenomena, which affect the contact potential difference, are sensitive to changes in temperature. All this makes it difficult to predict and interpret the I_{CP} *vs.* detector temperature relationship.

Standing current and electron concentration

Fig. 4 shows the relationship between the detector standing current, I_b, and the pulse period, t_p, measured for three values of I_{CP}. The results obtained are in agreement with those of Simon and Wells[6]. A local minimum in the plot is observed if the I_{CP} polarity is opposite to the I_b polarity (curve 3). This phenomenon was found to occur in the coaxial cylinders geometry, as recently reported by Simon and Wells.
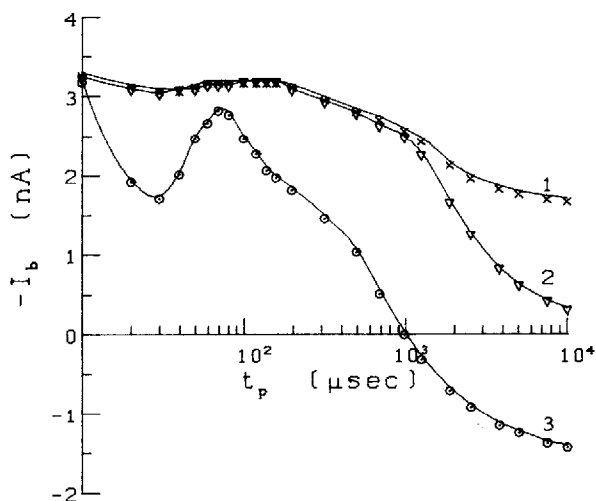
Fig. 4. Detector standing current, $-I_b$, *versus* pulse period, t_p, for three values of the battery current, I_{CP}:
(1) -1.6 nA; (2) 0 nA; (3) $+1.6$ nA.

They attributed this effect to the pulse period-dependent competition between the electric fields generated by the space charge (positive ions) and by the contact potential. A ^{63}Ni foil of greater activity was used in our measurements, which resulted in a higher value of the maximum detector standing current, I_0. Higher values of the standing current allow a more distinctive presentation of the "local minimum" effect, such as that depicted in Fig. 4.

The detector characteristics are often illustrated by the relationship between the electron concentration, b, and the pulse period, t_p, as presented in Fig. 5. The plots have different shapes, depending on the I_{CP} value. For $I_{CP} = 0$ (curve 2), this relationship can be accurately described by the Wentworth *et al.*(or similarly Gobby *et al.*) equation for b in the following form:

$$b = k_p R_\beta \, [1 - \exp{(-k_D t_p)}]/k_D \tag{1}$$

where $k_p R_\beta$ (mol l^{-1} s^{-1}) is the rate of production of ion–electron pairs in the detector and k_D (s^{-1}) is the pseudo-recombination rate constant, reflecting the loss of electrons by reactions other than electron capture by the sample molecules.

However, the other plots cannot be described by eqn. 1. The conclusion is that neither $k_p R_\beta$ nor k_D can be determined if the effects of the contact potential are not compensated for. A knowledge of these rate constants is necessary for the evaluation of the electron-capture rate constant for the sample molecules and for optimization of the detector[10].

Detector response

The small potential, E_{bias}, which is used to compensate for the effects of the contact potential can be varied to cover the desired range of the battery current, I_{CP}. To illustrate the correlations between the detector response and the size of the battery current, I_{CP}/I_0 (I_0 = maximum detector current) rather than I_{CP} was taken as the

independent variable. The ratio of I_{CP} to I_0 is not so sensitive to changes in the detector geometry, the activity of the ionization source, temperature and pressure, which similarly affect either of two currents. The variability of I_{CP}/I_0 was chosen so as to reflect the real conditions of the detector operation.

The detector response was measured as the difference between the standing currents corresponding to the absence and the presence of a sample, at the maximum of a chromatographic peak. The ratio of two detector responses, R_{CP}/R_0, was chosen to reflect the effect of the contact potential difference on the detector response, where R_{CP} is the detector response corresponding to a set value of the battery current, I_{CP}, and R_0 is the detector response at $I_{CP} = 0$. The correlations between detector response and battery current were measured at three different values of the supply parameter, $k_D t_p$. At $I_{CP} = 0$, the detector response approaches the maximum value at $k_D t_p = 1.7$. In addition to this value, also two others, the preceding ($k_D t_p = 1$) and the following ($k_D t_p = 3$) ones, were used.

Fig. 6 shows the effect of the contact potential on the detector response for the contact potential difference which generates the electric field enhancing that generated by the applied pulse. The relationship between the detector standing current, I_b, and battery current, I_{CP}/I_0, for three values of $k_D t_p$ is also shown. For $k_D t_p = 1$ and 1.7 the battery current, I_{CP}, only slightly affects the detector standing current. At $k_D t_p = 3$, an increase in I_{CP}/I_0 from 0 to 50% results in a 50% increase in the standing current. For all three $k_D t_p$ values, the detector response, expressed as the ratio R_{CP}/R_0, decreases nearly proportionally to the increase in the battery current, I_{CP}. An E_{bias} of about 0.5 V is needed to achieve an I_{CP}/I_0 ratio of 50% in this configuration. Such a low value certainly could not influence the collection of the thermal electrons during the pulse, as it constitutes only a small fraction of the pulse amplitude (50 V). However, even such a low potential can significantly alter the
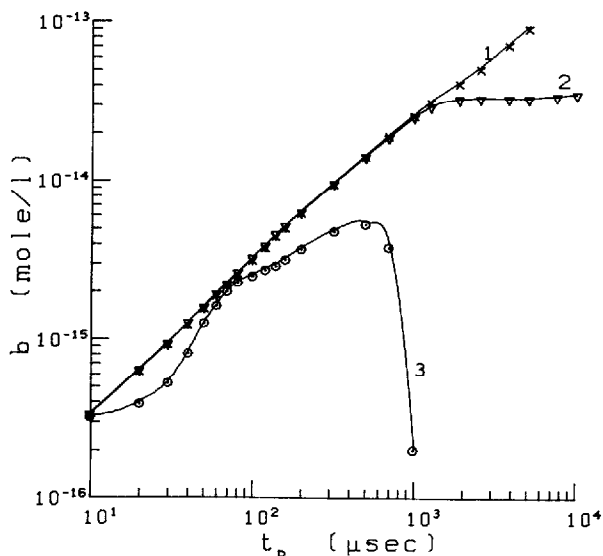

Fig. 5. Electron concentration, b, *versus* pulse period, t_p, for three values of the battery current, I_{CP}, as in Fig. 4.
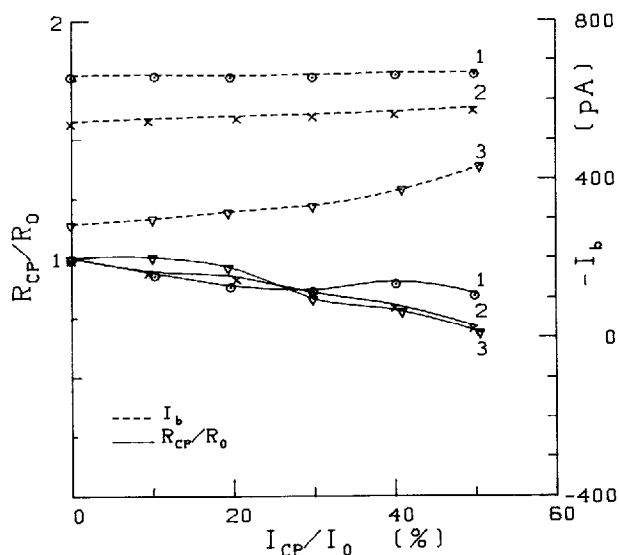
Fig. 6. Effect of contact potential on the detector standing current and the response for the contact potential difference, generating the electric field that enhances that applied to the cell. Supply parameter, $k_D t_p = $ (1) 1, (2) 1.7 and (3) 3.

detector kinetics in the remaining pulse-free portion of the pulse period, especially for higher values of the pulse period. There seem to be at least two reasons for the increase in the detector standing current with an increase in battery current. The first is that even low fields, created by the contact potential difference, will act to prevent the migration of the positive ions to the anode, an effect that undoubtedly leads to an increase in standing current. The second reason is that, for sufficiently long pulse-free periods, the positive ions that are in excess after the pulse can dissipate, driven by a space charge field to such on extent that the field generated by the contact potential difference can overcome the space charge field, resulting in the collection of some fraction of the electrons created by ionization. This effect is also more significant for higher values of $k_D t_p$ and I_{CP} and has a similar influence on the standing current to the previous one. The collection of the thermal electrons in the periods between pulses results in a diminished time-averaged electron concentration in the detector. This, in turn, will be responsible for the smaller than normal (*i.e.*, at $I_{CP} = 0$) extent of the electron-capture reaction with the sample molecules, and hence a decrease in the detector response. The effect is less pronounced at lower values of $k_D t_p$, owing to non-linearity in the correlation between the electron concentration in the detector and the pulse period, t_p. For $k_D t_p$ values of 1, 1.7 and 3, the corresponding values of the electron concentration constitute 63, 82 and 95% of the maximum electron concentration, respectively. It is obvious that higher values of $k_D t_p$ create greater possibilities for the space charge dissipation.

The results become considerably more difficult to interpret when the electric field generated by the contact potential opposes that generated by the external pulse. Fig. 7 shows the influence of the contact potential on the detector standing current and on the corresponding response for three values of the supply parameter, $k_D t_p$.

As shown. the range over which the standing current and the response change is much greater than in the previous detector configuration. The detector standing current decreases as the battery current increases. The standing current changes sign, going through zero at a value of the battery current that is inversely proportional to the $k_D t_p$ value. This effect is due to the fact that the detector, in the pulse-free portion of the pulse, is operated in a "reversed field" mode, with the central pin becoming the cathode and the ionization source serving as the anode. We can no longer neglect the influence of the contact potential difference on the amplitude of the pulse, as in this instance the values of the E_{bias} applied to cause some battery current are much higher than in the previous instance. About 35 V is needed to achieve an I_{CP}/I_0 of 50%. Such an E_{bias} value becomes comparable to the amplitude of the pulse and can certainly reduce the collection of thermal electrons during the pulse.

In the periods between pulses, the migration of the excess of positive ions is favoured in the central pin direction, thus causing a reduction in the standing current. These two effects, becoming stronger with an increase in the battery current, combine to cause a strong decrease in the standing current following the increase in I_{CP}/I_0. At certain values of I_{CP}/I_0, the positive component of the standing current arising from the collection of the positive ions at the central pin becomes equal to the negative component arising from the collection of the thermal electrons. With sufficiently long periods between pulses, lower I_{CP} values are required to achieve this balance, as greater densities of the positive ions and longer collection periods make the balance between these two current components easier. If the battery current is increased any further, the positive component of the standing current dominates over the negative component.

Whereas the explanation of the effect of the contact potential on the standing
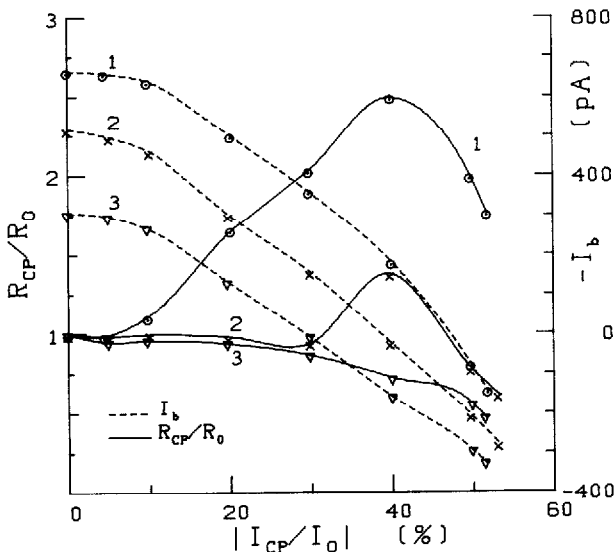

Fig. 7. Effect of contact potentials on the detector standing current and the response for the contact potential difference generating the electric field that opposes that applied to the cell. Supply parameter values as in Fig. 6.

current seems to be obvious, the picture becomes considerably more complicated if the influence of the contact potential difference on the response is considered. As shown in Fig. 7, at $k_D t_p = 1$, the plot of the correlation between detector response (R_{CP}/R_0) and battery current (I_{CP}/I_0) reaches a maximum. At $k_D t_p = 1$, the detector response at its maximum is 2.5 times greater than the response measured at $I_{CP} = 0$. It should be noted, however, that this value is still lower than the response measured at the optimum value of $k_D t_p$ and at $I_{CP} = 0$. At higher $k_D t_p$ values, the maximum disappears and, at $k_D t_p = 2$, the relationship between response and battery current becomes a monotonically decreasing function. Let us consider why the effect of the contact potential on the detector response changes its character depending on $k_D t_p$. As was said earlier, we can no longer neglect the influence of the battery current on the amplitude of the pulse. As the contact potential difference and, hence, the battery current increase, the net result is a decrease in the pulse amplitude. Therefore, fewer electrons are collected during the pulse leaving more electrons to be captured by the sample molecules, which results in an increased response. The picture changes if the excess of the positive ions can dissipate in the period between pulses to such an extent that some fraction of the thermal electrons can be collected. As a result, the concentration of the electrons and, hence, the response decrease. At higher values of $k_D t_p$, this effect becomes more pronounced, because even at low values of I_{CP}/I_0 the space charge can dissipate between pulses and in the remaining portion of this period a substantial collection of electrons takes place, and thus only a decrease in the response is observed.

CONCLUSIONS

The results indicate that the effects of the contact potential cannot be neglected in the constant-frequency mode of operation of the electron-capture detector. These effects introduce significant changes in the shapes of the detector characteristics such as the relationship between electron concentration and pulse period. As the important detector parameters, such as pseudo-recombination rate constant, ionization rate constant or electron capture rate coefficient, can be evaluated by using the relationship between the concentration of electrons and the pulse period, it is essential that the effects of the contact potential be compensated for.

The contact potential difference affects the detector response in a polarity-dependent manner. Generally, the response decreases with increasing battery current (and contact potential difference). The exception is that, if the battery current polarity is opposite to that of the standing current, the maximum in the relationship between response and battery current is observed at $k_D t_p$ less than 1.7, a phenomenon that can be explained by using the space charge model of Gobby et al.[7].

If the effects of the contact potential are compensated for, our electron-capture detector becomes more reliable as its response to a given sample concentration becomes more reproducible, assuming that repeatable injections are made. Such a compensation should also facilitate interlaboratory comparisons.

REFERENCES

1 L. B. Loeb, *Static Electrification*, Springer Verlag, Berlin, 1958.
2 J. E. Lovelock, *Anal. Chem.*, 35 (1963) 474.
3 E. P. Grimsrud and S. W. Warden, *Anal. Chem.*, 52 (1980) 1842.
4 E. P. Grimsrud and M. J. Connolly, *J. Chromatogr.*, 239 (1982) 397.
5 W. B. Knighton and E. P. Grimsrud, *J. Chromatogr.*, 288 (1984) 237.
6 R. Simon and G. Wells, *J. Chromatogr.*, 302 (1984) 221.
7 P. L. Gobby, E. P. Grimsrud and S. W. Warden, *Anal. Chem.*, 52 (1980) 473.
8 W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, 70 (1966) 445.
9 W. A. Aue and S. Kapila, *J. Chromatogr.*, 188 (1980) 1.
10 P. Rotocki and J. Lasa, *J. Chromatogr.*, 294 (1984) 51.