Journal of Chromatography, 210 (1981) 389–399
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,710

STUDY OF SPACE CHARGE PHENOMENA IN d.c. ELECTRON-CAPTURE DETECTORS

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(Received December 30th, 1980)

SUMMARY

The influence of space charge phenomena on the field and the potential in a d.c. electron-capture detector (ECD) under simplified conditions was studied. The results make it possible to explain the shape of the current–voltage characteristics of a d.c. ECD and the dependence of the sensitivity of such a detector on the electrode distance with positively and negatively polarized sources. All of these dependences were studied using an ECD with variable geometry (electrode distances between 0.25 and 30 mm) and a changeable radioactive source (^{3}H, ^{63}Ni, ^{241}Am).

INTRODUCTION

The theoretical description of the properties of the d.c. electron-capture detector (ECD) by Scolnick[1] and also the investigations of the processes in the pulse ECD by Wentworth and co-workers[2–4] and Lovelock[5] did not take into account space charge phenomena, but Lovelock[6] had already pointed out in 1963 that in an ion chamber with a low potential and a high density of ions the current flow is strongly affected by the presence of space charges. Bros *et al.*[7] presented a theoretical model of the pulse ECD taking into consideration a positive ion space charge.

The question of the influence of space charges on the processes in the d.c. ECD became very important in connection with the so-called "hypercoulometric response" first observed by Aue and Kapila[8]. Hypercoulometric response means that the sensitivity of the d.c. ECD exceeds the theoretical maximum value of 96,500 C/mole given by Faraday's number and named the coulometric response. Aue and Kapila explain this behaviour, which causes the theoretical detection limit of $3.3 \cdot 10^{-16}$ mole (ref. 9) to be decreased by one order of magnitude with the occurrence of space charges[10]. Such space charges were considered in more detail in this work. After a theoretical consideration of the influence of space charges on potential and field in a d.c. ECD, experimental results obtained with a specially designed ECD with variable geometry and changeable source are presented.

0021-9673/81/0000–0000/$02.50

THEORETICAL

Fig. 1 shows schematically an ECD with an electrode distance d greater than the range a of the radiation of the source used. Within space I charged particles of both sign are present. Within space II a unipolar current of positive ions or electrons, depending on the polarization of the electrodes, flows in the pure carrier gas while in a carrier gas with electronegative compounds added a unipolar current of positive ions or electrons and negative ions flows. In each electropositive carrier gas electrons with mobilities of about 10^4 cm^2/V sec and positive ions with mobillities of about 2 cm^2/V sec are present, so that independent of the polarization space charges occur which decelerate the motion of the electrons and accelerate the motion of the positive ions.

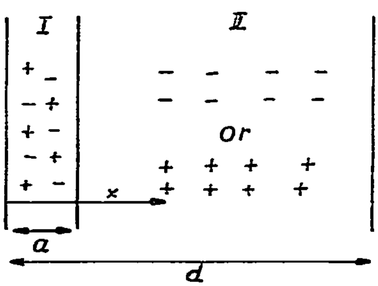


Fig. 1. The charge distribution in an ECD.

The calculation of such space charges can easily be performed if one assumes approximately that in space I a space charge of constant density ϱ_1 and in space II a space charge of constant density ϱ_2 exist. Assuming a negatively polarized source we have

$$E_1 = \left(\frac{\varrho_1}{\varepsilon_0} \cdot x\right) - c_1 \qquad V_1 = \left(-\frac{\varrho_1}{2\,\varepsilon_0} \cdot x^2\right) + c_1 x + c_2$$

$$E_2 = \left(-\frac{\varrho_2}{\varepsilon_0} \cdot x\right) - c_3 \qquad V_2 = \left(\frac{\varrho_2}{2\,\varepsilon_0} \cdot x^2\right) + c_3 x + c_4$$

with the conditions

$$x = 0 \rightarrow V_1 = 0$$
$$x = a \rightarrow E_1 = E_2,\ V_1 = V_2$$
$$x = d \rightarrow V_2 = V_0$$

Determining the constants c_1, c_3 and c_4 ($c_2 = 0$), we obtain

$$E_1 = \frac{1}{2\,\varepsilon_0}\left[\left(\frac{a^2}{d} - 2a\right)(\varrho_1 + \varrho_2) + 2x\varrho_1 + d\varrho_2\right] - E_0 \qquad (1)$$

$$E_2 = \frac{1}{2\,\varepsilon_0}\left[\frac{a^2}{d}(\varrho_1 + \varrho_2) + (d - 2x)\,\varrho_2\right] - E_0 \tag{2}$$

$$V_1 = E_0 x + \frac{x}{2\,\varepsilon_0}\left[\left(2a - \frac{a^2}{d} - x\right)\varrho_1 + \left(2a - \frac{a^2}{d} - d\right)\varrho_2\right] \tag{3}$$

$$V_2 = E_0 x - \frac{x}{2\,\varepsilon_0}\left[\left(\frac{a^2}{d} - \frac{a^2}{x}\right)\varrho_1 + \left(\frac{a^2}{d} + d - \frac{a^2}{x} - x\right)\varrho_2\right] \tag{4}$$

Eqns. 1–4 can be simplified for the purest carrier gases with $\varrho_2 = 0$ (case A) and for electronegative additions if ϱ_1 is negligible (case B), giving the values for E_1, E_2, V_1 and V_2 listed in Table I.

Table I also contains expressions modified for a positively polarized foil (case C). Considering potential and field dependences in these three cases (Fig. 2), it can be seen that up to the distance $x = a - (a^2/2d)$ the field is increased in case A, which means higher ionization currents compared with the space charge-free case. Case B leads to a decrease in the field, resulting in a higher recombination rate. Considering case C, we must assume a strong positive space charge, because the positive ions with their low mobility have a long drift path. Then the decrease in the field is so strong that under the same voltage conditions as in case B the current is much lower than with the opposite polarization of the source, and as a result the sensitivity of the ECD must be almost zero. This is the "reversed-field effect" of Aue and Kapila[10].

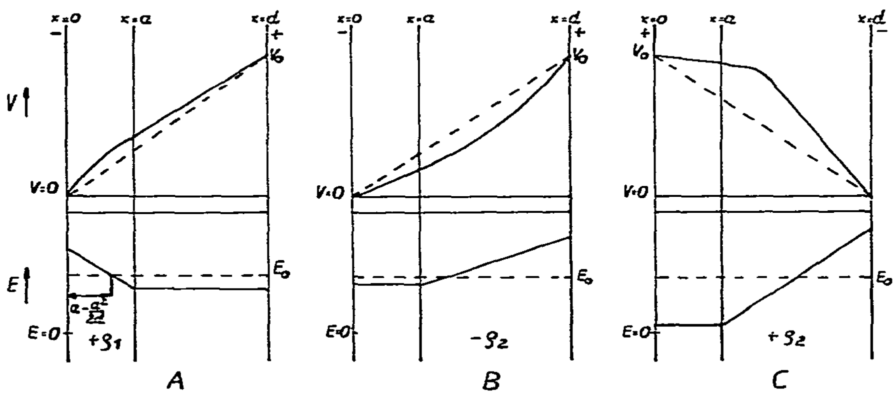


Fig. 2. Potential and field distribution in the cases of a positive space charge within space I (A), of a negative space charge within space II (B), and of a positive space charge within space II (C). The broken lines represent the space charge-free case.

The influence of space charges on the potential and field distribution using a pure carrier gas, a carrier gas with a small amount of contaminant (*e.g.*, nitrogen with a small oxygen content) and a carrier gas containing a higher concentration of an electronegative compound is shown in Fig. 3. For the pure carrier gas and a nega-

TABLE I

POTENTIAL AND FIELD DEPENDENCES UNDER VARIOUS CONDITIONS

Parameter	*Case A: negative polarization of the source,* $\varrho_1 = \varrho, \varrho_2 = 0$		*Case B: negative polarization of the source,* $\varrho_1 = 0, \varrho_2 = \varrho$		*Case C: positive polarization of the source,* $\varrho_1 = 0, \varrho_2 = \varrho$	
V_1	$E_0 x + \frac{x}{2\varepsilon_0}\cdot\varrho\left(2a - \frac{a^2}{d} - x\right)$	(5)	$E_0 x - \frac{x}{2\varepsilon_0}\cdot\varrho\left(d + \frac{a^2}{d} - 2a\right)$	(9)	$V_0 - E_0 x + \frac{x}{2\varepsilon_0}\cdot\varrho\left(d + \frac{a^2}{d} - 2a\right)$	(13)
E_1	$\frac{\varrho}{2\varepsilon_0}\left(\frac{a^2}{d} - 2a + 2x\right) - E_0$	(6)	$\frac{\varrho}{2\varepsilon_0}\left(d + \frac{a^2}{d} - 2a\right) - E_0$	(10)	$E_0 - \frac{\varrho}{2\varepsilon_0}\left(d + \frac{a^2}{d} - 2a\right)$	(14)
V_2	$E_0 x - \frac{x}{2\varepsilon_0}\cdot\varrho\cdot\frac{a^2}{(d - x)}$	(7)	$E_0 x - \frac{x}{2\varepsilon_0}\cdot\varrho\left(d + \frac{a^2}{d} - x - \frac{a^2}{x}\right)$	(11)	$V_0 - E_0 x + \frac{x}{2\varepsilon_0}\cdot\varrho\left(d + \frac{a^2}{d} - x - \frac{a^2}{x}\right)$	(15)
E_2	$\frac{\varrho}{2\varepsilon_0}\cdot\frac{a^2}{d} - E_0$	(8)	$\frac{\varrho}{2\varepsilon_0}\left(d + \frac{a^2}{d} - 2x\right) - E_0$	(12)	$E_0 - \frac{\varrho}{2\varepsilon_0}\left(d + \frac{a^2}{d} - 2x\right)$	(16)

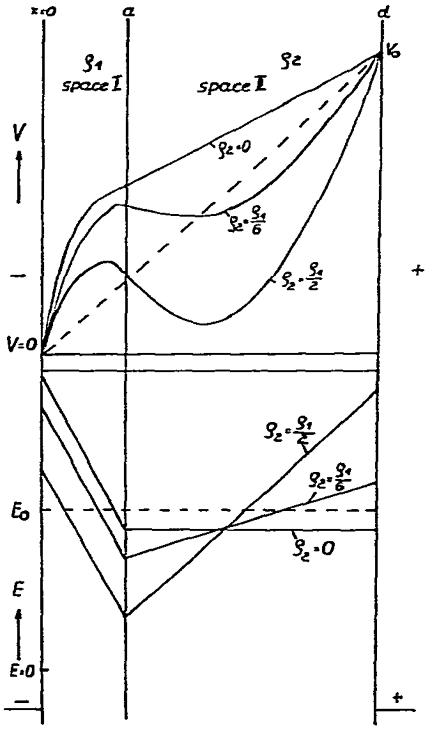


Fig. 3. Potential and field distribution in the case of a positive space charge ϱ_1 within space I and different negative space charges ϱ_2 within space II with a negatively polarized foil (arbitrary units).

tively polarized source $\varrho_2 = 0$. Assuming the case $\varrho_1 = 6\,\varrho_2$ is valid for the carrier gas with a small amount of contaminant and $\varrho_1 = 2\,\varrho_2$ for the additional electronegative compound, then in both instances the field values (arbitrary units) within the recombination range are lower than for the pure carrier gas and that as a result the recombination rate of positive ions and electrons increases. However, this also means that an electronegative sample (for example, a gas chromatographically separated compound) causes an additional decrease in the current due to space charges, provided that the negative ions formed within space I do not completely recombine in this region. The negative ions drifting to the anode in this instance form a space charge within space II and decrease the field and potential within space I.

EXPERIMENTAL

The d.c. ECD used for the space charge studies (see Fig. 4) was a parallel-plate ionization chamber with an internal radiation source (^3H, ^{63}Ni, ^{241}Am). The electrode distances could be varied from 0.25 to 30 mm.

Additional units were the power supply, a vibrating reed electrometer (Type VAJ-51, VEB RFT Messelektronik, Dresden, G.D.R.) and a recorder (Type Endim 621.01, VEB Messgerätewerk, Schlotheim, G.D.R.).

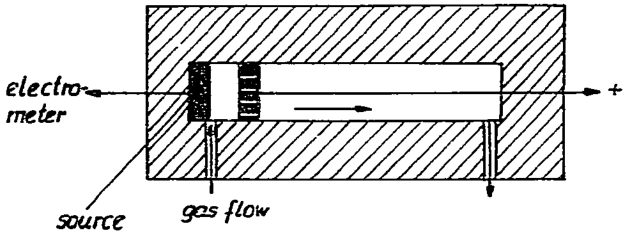


Fig. 4. Schematic diagram of the ECD.

RESULTS AND DISCUSSION

Dependence of the saturation current on the electrode distance

The dependence of the saturation current, i_s, on the electrode distance d, using ^3H, ^{63}Ni and ^{241}Am as radioactive sources is shown in Fig. 5. Total absorption of the radiation occurs at *ca.* 5 mm for ^3H, *ca.* 18 mm for ^{241}Am and *ca.* 25 mm for ^{63}Ni. Let us define an "effective range" extending from the radioactive foil to the distance at which the saturation current amounts to 95% of the saturation current at total radiation absorption. This range is 2 mm for ^3H, 11 mm for ^{241}Am and 15 mm for ^{63}Ni. To a first approximation we can say that charged carriers of both signs (space I) exist only in this part. The other region contains only positively or negatively polarized carriers, depending on the direction of the field (space II).

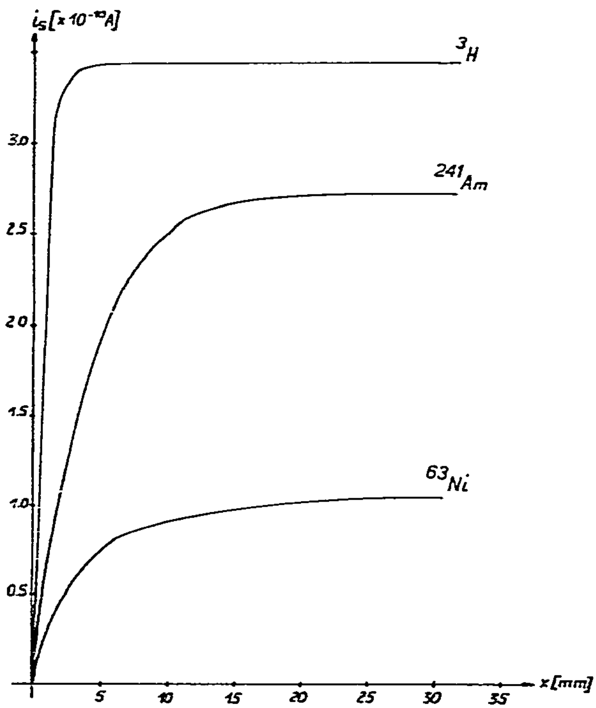


Fig. 5. Dependence of the saturation current on the electrode distance for ^3H, ^{63}Ni and ^{241}Am sources.

Current–field characteristics

Without the occurrence of space charges the current–field characteristics (except for the lower saturation currents within space I) should be identical. With the negatively polarized ^{3}H source negative space charges occur for electrode distances greater than 5 mm. If the source is positively polarized, positive space charges in space II arise for smaller electrode distances, affecting the potential and field conditions (see Fig. 6).

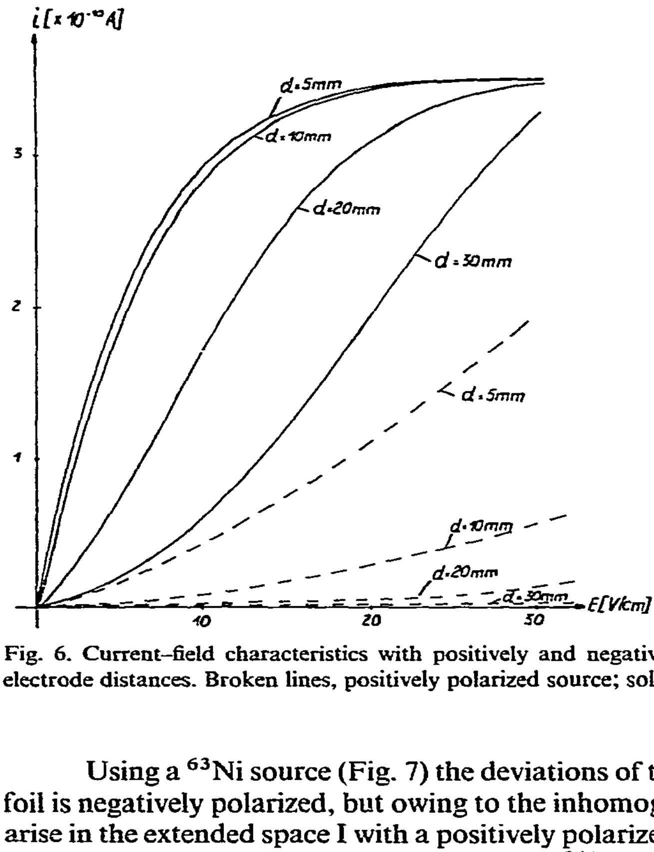


Fig. 6. Current–field characteristics with positively and negatively polarized ^{3}H sources and different electrode distances. Broken lines, positively polarized source; solid lines, negatively polarized source.

Using a ^{63}Ni source (Fig. 7) the deviations of the characteristics are small if the foil is negatively polarized, but owing to the inhomogeneous ionization space charges arise in the extended space I with a positively polarized foil so that the condition $\varrho_1 = 0$ within space I is not fulfilled. The use of the ^{241}Am source provides similar shapes of the curves.

Dependence of sensitivity on electrode distance

Fig. 8 shows the dependence of the sensitivity of the d.c. ECD on the electrode distance for oxygen samples with both polarizations of the foil.

Let us first consider the conditions for the negatively polarized foil. Using the ^{3}H source with an effective range of only 2 mm the sensitivity increases strongly at small distances; using the other sources ^{63}Ni and ^{241}Am, with effective ranges greater than 10 mm the sensitivity increases slowly at first and more strongly for greater distances.

A concrete example, the calculation of the density of the negative space charge

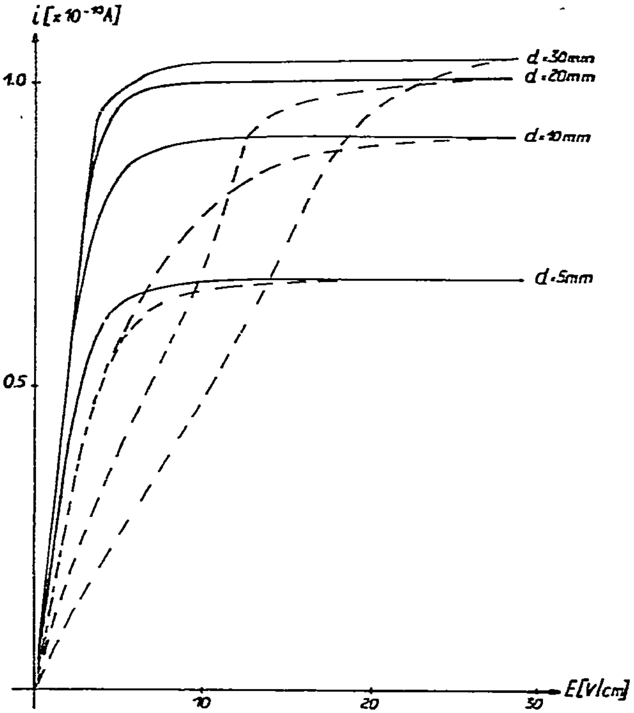


Fig. 7. Current–field characteristics with positively and negatively polarized ^{63}Ni source and different electrode distances. Lines as in Fig. 6.

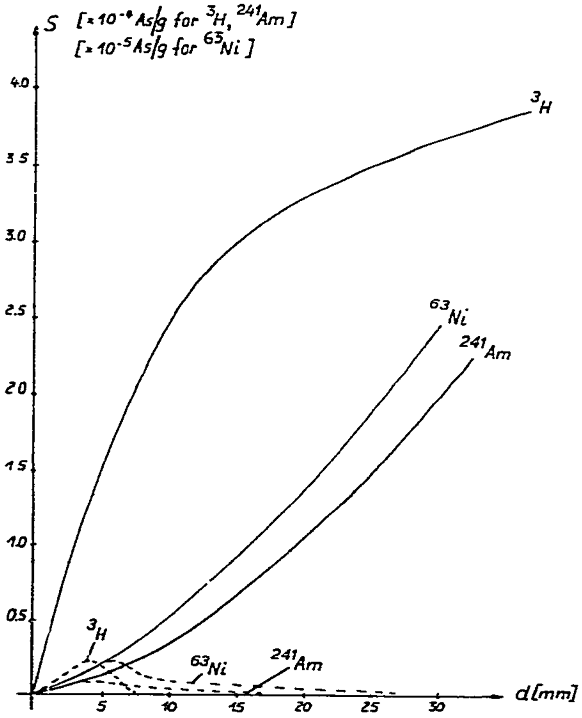


Fig. 8. Dependence of the sensitivity on the electrode distance with positively and negatively polarized ^{3}H, ^{63}Ni and ^{241}Am sources. Lines as in Fig. 6.

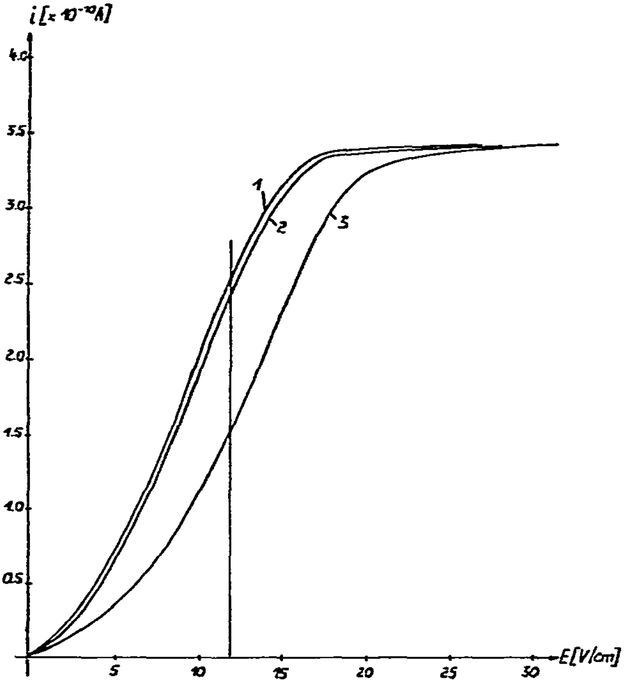
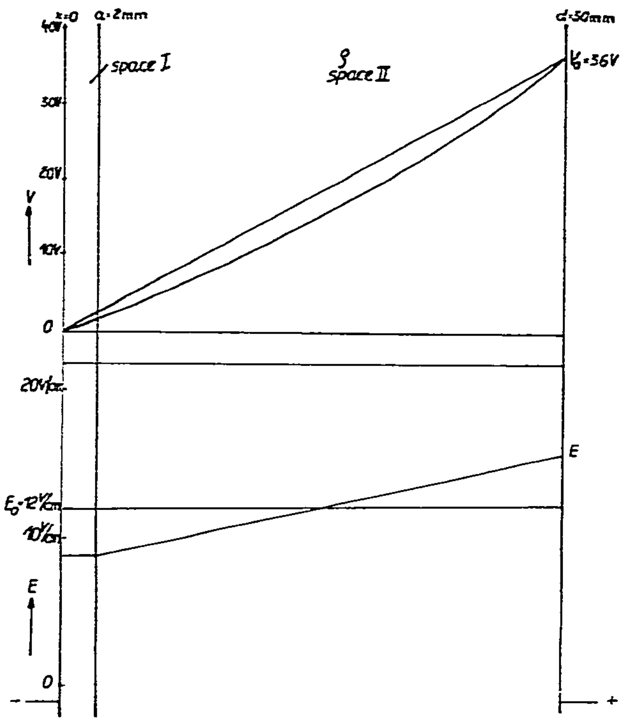


Fig. 9. Current–field characteristics using the ^3H source for a pure carrier gas and carrier gas doped with oxygen. 1, Pure nitrogen, $d \geqslant 2$ mm; 2, nitrogen + 70 ppm of O_2, $d = 2$ mm; 3, nitrogen + 70 ppm of O_2, $d = 30$ mm.

in space II and the calculation of the potential and field conditions under the influence of this space charge, will explain the increase of the sensitivity with increasing electrode distance. Fig. 9 shows the current–field characteristics for the pure carrier gas, being nearly independent of the electrode distance if $d \geqslant 2$ mm (curve 1), the decrease in the ionization current if the detector which works in the space charge-free region ($d = 2$ mm) is doped with 70 ppm of oxygen (curve 2), and shows the decrease in the current if the detector is doped with the same oxygen concentration but using a distance of 30 mm (curve 3). Then the deviation of curve 3 compared with curve 2 will be an effect of the space charge within range II. A simple method given by Grosse[11] makes it possible to determine the density of this charge. If we consider the field strength of 12 V/cm, then a corresponding current of $1.52 \cdot 10^{-10}$ A is valid for curve 3. The same current for curve 2 is reached with a field strength of 8.6 V/cm.

Assuming case B and putting this value in eqn. 9 or 11 with $x = a = 0.2$ cm and $d = 3$ cm, we obtain a mean space charge of $1.9 \cdot 10^{-13}$ C/cm^3. With this value the potential and field dependences shown in Fig. 10 were calculated. The field within space I is decreased by the negative space charge and as a result the recombination rate of electrons and positive ions will be increased.

When we consider the positively polarized foil, the effect of the small sensitivity predicted in the theoretical section is clearly seen. As soon as the electrode distances are large enough for positive space charges to occur, the sensitivity decreases. The calculation of the density of the positive space charges with ^3H as a radioactive source



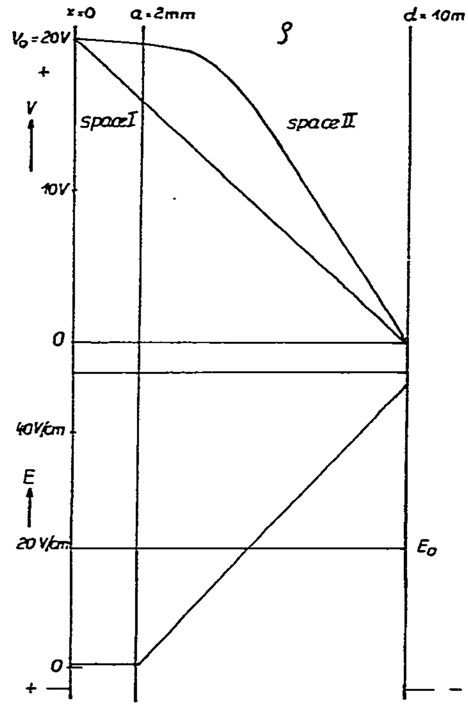


Fig. 10. Potential and field distribution in the case of a negative space charge ϱ within space II with a negatively polarized ^{3}H foil and an electrode distance of 30 mm.

Fig. 11. Potential and field distribution in the case of a positive space charge ϱ within space II with a positively polarized foil.

and an electrode distance of 10 mm (see Fig. 11) shows that in this instance the space charge is so strong that the field strength (E_0 = 20 V/cm in the space charge-free case) decreases to E = 0.6 V/cm, and the potential difference between $x = 0$ and $x = a$ is nearly zero. This means that the recombination rate of electrons and positive ions in the pure carrier gas is so high that the ionization current is small in comparison with the current in the opposite polarization (see Fig. 6), and a trace amount of an electronegative compound does not cause an additional decrease in the current.

CONCLUSIONS

The results of the theoretical and experimental studies of space charge phenomena in d.c. ECDs lead to the following conclusions:

(1) With a negatively polarized foil the sensitivity of the d.c. ECD increases considerably if, using a parallel-plate geometry, the electrode distance becomes greater than the range of the β-radiation, that is, if a negative space charge arises.

(2) With other geometries an increase in the sensitivity will be observed if conditions providing a unipolar current of negative particles exist.

(3) With an electrode arrangement providing a unipolar current of negative

particles, a hypercoulometric response occurs if the concentration of electrons is high enough for each sample molecule to be converted to a negative ion and if the ion–ion recombination rate is less than 100%, so that a negative space charge arises within the region of the unipolar current.

(4) With a postively polarized foil the sensitivity of the d.c. ECD caused by a strong positive space charge is nearly zero.

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