Journal of Chromatography, 265 (1983) 145–157
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,919

EFFECT OF APPLIED FIELDS ON POSITIVE IONS IN THE PULSED ELECTRON-CAPTURE DETECTOR

M. J. CONNOLLY, W. B. KNIGHTON and E. P. GRIMSRUD*
Department of Chemistry, Montana State University, Bozeman, MT 59717 (U.S.A.)
(Received March 8th, 1983)

SUMMARY

Experiments are reported which indicate the effect of positive ions on the measured standing current and response of the pulsed electron-capture detector (ECD). These experiments include measurements taken with a specialized ion source on an atmospheric pressure ionization mass spectrometer, and also measurements of standing current obtained from two ECDs of coaxial cylindrical geometry but having different length-to-diameter ratios. Two opposing views of the means by which positive ions might be removed from a pulsed ECD are considered. The results of this study are shown to strongly support one of these.

INTRODUCTION

In almost all of the various types of electron-capture detectors (ECDs) for gas chromatography (GC) which are in use today, electrons are produced in an inert gaseous medium by beta radiation, typically provided by ^{63}Ni or ^{3}H nuclides. The formation of these electrons is, of course, accompanied by the formation of an equal number of positive ions. A question which then arises is: what effects, if any, do these positive ions have on the measured standing current (baseline frequency in the case of the constant-current ECD) and response of these detectors. Neutralization of a portion of the positive ions by recombination with electrons and with negative ions will occur in the gas phase. This will tend to lower the observed standing current and responses by lowering the populations of electrons. This affect has been recognized and characterized in several previous accounts of the ECD[1–3]. An additional cause for loss of signal can be envisioned, however, if a significant fraction of the positive ions are transported to and neutralized on the cell surface which serves as the electron-collecting anode. In the worst case, where all the positive ions somehow arrive at the anode, this cell would provide no measureable standing current and response to samples. As proof of this point we have, in fact, built and demonstrated such an undesireable cell[4]. For the sake of understanding ECDs in use today and for the sake of improving designs in the future, it is appropriate to seek an answer to the more specific question: to what extent is the ECD response and standing current of a given cell influenced by positive ion transport to the anode surface and how does this occur?

0021-9673/83/$03.00

For the direct-current ECD (d.c. ECD), the answer to the above question has never been seriously in doubt. With it, an electric field is continuously applied between the anode and cathode. As long as minimal care is given to proper cell design, the current measured at the anode will reflect the arrival of negatively charged species, only. No positive ion transport to this anode should occur because the applied field should continuously prevent the migration of positive ions in that direction. The response of the d.c. ECD is, however, subject to other complications such as the collection of negative ions at the anode and space-charge effects caused by the separation of oppsitely charged species[5].

For the pulsed ECD the question of positive ion contribution to the measured current and response is not so easily answered. This is because for only very short durations (typically a microsecond or less) an external field is applied to the cell in order to collect the electrons at the anode. For the great majority of time no electric field is being externally applied to any surfaces of the cell. The first model for the pulsed ECD was proposed in 1966 by Wentworth *et al.*[6]. This model has greatly assisted the development of various forms of the ECD and has been useful in explaining their responses. With respect to the role and behavior of positive ions, however, this early model is now recognized to have been inaccurate in its assumption that positive ions increase in concentration as they are formed, unabated by either the pulse which was assumed to remove all electrons or by the positive space-charge which would exist following the removal of electrons. In 1976 Siegel and McKeown[1] described quite a different positive ion behavior within their atmospheric pressure ionization mass spectrometry (API-MS) instrument. This instrument had an ion source which was very similar to an ECD with a primary difference being that no electric fields, d.c. or pulsed, were applied. Their measurements suggested that in a field-free source, the population of positive ions will not exceed the population of the negative charge carriers (which are electrons if the cell is free of electrophiles). They pointed out that this equality in the concentration of oppositely charged species occurs because at the relatively high charge densities present the diffusion rates of electrons and positive ions will be equal, each being determined by a single ambipolar diffusion coefficient. They argued further that similar electrostatic forces between all charged species should also be dominent forces in ECDs in which electric fields are externally applied. In 1979[7] and 1980[3] measurements from our laboratory were reported using an API-MS instrument where the ion source was an actual pulsed ECD. In these studies it was shown that a pulse applied to a central anode does remove all electrons, resulting in a momentary excess of positive ions, but that positive ion concentration does not then increase unabatedly. It was observed that with fast pulsing and frequent electron removal another means of positive ion removal replaces recombination as the dominant mode of positive ion loss. Guided by experiments described in those reports[3,7] we proposed that this loss occurs during the periods between pulses and is caused by the electrostatic repulsion which must then exist between the excess positive ions. Thus, positive ions were envisioned to migrate through the space-charge electric field which they themselves generate to the various surfaces of the cell all of which are at ground potential during the period between pulses. Within this view, which will be referred to here as the space-charge model, the nature of positive ion migration to cell boundaries will be determined primarily by the design of the cell. Depending on this design, the space-charge electric field could then

drive a significant fraction of the positive ions to the surface which served as the anode during the pulse.

An alternate means by which positive ions could be removed from a pulsed ECD can be envisioned by assuming that this loss occurs primarily during the application of each voltage pulse by the migration of positive ions to the cathode under the influence of the intermittent applied electric fields. This view has been favored by Wentworth and Chen[2] in a recent modification of the original model by Wentworth *et al.*[6]. They add the qualifying statement that this proposed means of positive ion loss most likely applies to the tritium source of plane parallel design where positive ions are formed in close proximity to the cathode. If this mode of positive ion loss is, in fact, the dominant one in the tritium source, it might then be at least partially operative in the ^{63}Ni source, particularly where high frequencies of pulsing are used. This mode of positive ion loss leads to a different prediction for positive ion contribution to standing current and response because with it, the positive ions will tend to be moved to the cathode and away from the anode by the pulsed fields for all cell designs.

Thus, at least two different and opposing views of the means by which positive ions are lost within the pulsed ECD presently exist in the literature. Resolution of this point is important to future practical developments of the pulsed ECD. We wish to report here measurements by a specialized API-MS instrument and two pulsed ECDs where experiments have been designed to specifically explore the means by which positive ion loss occurs. Measurements are reported over a winde range of pulse frequencies since one of the candidate mechanisms might be favored by very fast pulsing while the other might be dominant with slow pulsing. If this mixed result were supported by experiment, a particularly complex situation would exist with the constant-current ECD, where the dominant means of positive ion loss might switch from one mode to another on going from a condition of low sample (slow pulsing) to large sample (fast pulsing). On the other hand, if one or the other mode of positive ion loss is observed to be dominate at all pulse frequencies, a central clue to understanding the quantitative response of this important detector will be thereby provided. Also, the results of this study are critically relevant to the development of the ECD for gas phase coulometry[4,8,9].

EXPERIMENTAL

The API-MS instrument used here has been described in previous studies[2,7]. It has a specialized ion source, shown in Fig. 1, which has also been described in detail[10]. The ^{63}Ni disk shown in Fig. 1 is movable so that the distance between the disk and aperture could be varied. A quadrupole mass filter of the API-MS instrument is used to monitor the total positive ion content of the gas which passes through the aperture. We have previously calculated[2,10] that the volume of ionized gas sampled by the mass filter extends less than 1.0 mm into the atmospheric pressure source. For the measurements reported here the disk-to-aperture distance is generally not less than 2.0 mm, so that the distance between the beta source and observation volume is always greater than the dimensions of the observation volume. Various d.c. potentials and pulsed waveforms are applied to the source disk while the walls of the source are electrically grounded. Electronic devices for the applied waveforms were homebuilt as previously described[11].

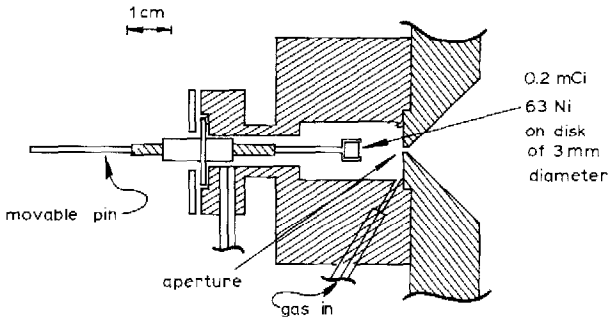

Fig. 1. Specialized atmospheric pressure ion source in which the distance between a ^{63}Ni-on-Pt disk and ion-sampling aperture is variable.

In most experiments 10% methane-in-argon was passed through traps containing $CaSO_4$ and 5A molecular sieve, through an Altech Oxy-Trap and then through the API-MS ion source or one of the ECDs. A flow-rate of 40 ml min^{-1} was used.

The ECDs were homebuilt from stainless steel. Each has a foil of 15 mCi ^{63}Ni-on-Pt which forms the cylindrical wall of the cell and each has a concentric anode made of 1/16-in. stainless rod. The internal dimensions of the two cells differ in that one has a length of 2.0 cm and a diameter of 1.0 cm and the other has a length and diameter of 1.4 cm. Various d.c. and pulse waveforms of fixed frequency were applied to the body of the ECDs while an operational amplifier electrometer[11] monitored the resulting current at the central pin of the ECD.

RESULTS AND DISCUSSION

The first measurements to be reported are those obtained from the API-MS using the specialized ion source shown in Fig. 1. With this source ionization is provided by a disk of ^{63}Ni which is movable with respect to the ion-sampling aperture. The API-MS signal is thought[3,10] to be proportional to the concentration of ions in the small volume of gas less than one millimeter from the aperture. When no electric fields are applied to this cell, the total positive ion signal observed by the mass spectrometer is a function of the placement of the disk as shown in Fig. 2, where both air and ultra-high-purity nitrogen have been used as the beta attenuating medium. As is expected[10] in both cases the total positive ion signal increases as the disk-to-aperture distance decreases. In a previous study[10] we analyzed field-free experiments such as these in order to quantitatively describe the nature of beta ionization and penetration into any imagined ionization cell. Consistent with the conclusions of that study, the air and nitrogen cases of Fig. 2 show very similar beta attenuating character because of their near equality of mass density. While the positive ion signals observed with nitrogen and air are nearly equivalent, the negative species which will be simultaneously present in each case are, of course, quite different. With air various negative ions[12] and essentially no electrons will be present while with pure nitrogen, only electrons will be formed. If one now alters the conditions of the ion source by applying intermittent pulses of 50-V amplitude and 1-μsec duration to the disk, the air and nitrogen experiments of Fig. 2 will no longer resemble each other. Using either

+50 V and −50 V pulses of various frequencies (periods from 1000 to 20 μsec) the air measurements of Fig. 2 are not measureably altered, while with nitrogen in the source, these pulsed waveforms cause large alterations in the API-MS signal. For the case of air, the lack of dependence of the API-MS signal on the application of pulses to the disk provides an early suggestion to the answer we seek. Since the positive ions which exist along the disk-to-pin axis decrease sharply in concentration with distance from the disk, a very significant perturbation in positive ion signal might have been expected if the ions in air were being moved significantly towards or away from the aperture by the applied pulses. Since absolutely no perturbations of signals in air are observed, even with high pulse frequencies where the period between 1-μsec pulses is only 20 μsec, the ions are apparently not being moved significantly by the intermittant electric fields.

As indicated above, with nitrogen in the ion source large perturbations of the API-MS signals are caused by pulsing. This behavior is also noted when an argon–10% methane mixture is used as the bulk gas and with it electrons, again, are the negatively charged species which accompany the positive ions. In the experiments to be related next, argon–methane has been used because in this gas mixture the drift velocity of the electron in an applied field is about one order of magnitude greater than that in nitrogen[13]. This will facilitate interpretation of our data by allowing us to assume with confidence that all electrons in the source are removed during the application of each pulse.

The effect of −50 V pulses of various frequencies applied to the disk on the total positive ion API-MS signal with argon–methane gas is shown in Fig. 3. It is seen

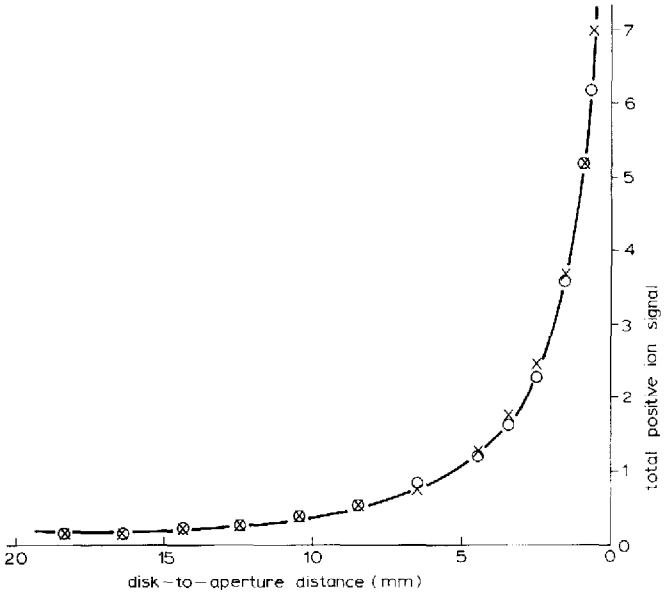

Fig. 2. Total positive ion signals measured by mass spectrometer as a function of disk-to-aperture distance. With nitrogen (×) in the source no external electric fields are applied. With air (○) the data is for the field-free condition and also where pulsed waveforms with frequencies up to 50 kHz are applied to the disk. The source pressure and temperature are 0.85 atm and 23°C (ambient). Units of positive ion signal are 10^4 counts per second.

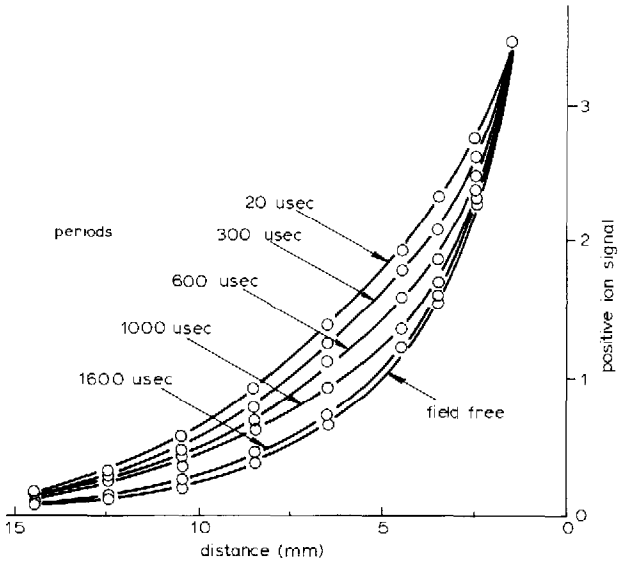

Fig. 3. Total positive ion signal of argon–10% methane mixture measured as a function of disk-to-aperture distance with various pulsed waveforms applied to the disk. 1-μsec pulses of -50 V were applied.

that at all disk-to-aperture distances between 2 and 15 mm, the application of these pulses causes an increase in the API-MS signal. This observation indicates that at these distances the act of pulsing increases the concentration of positive ions in the vacinity of the aperture. It is also clear that this effect is accentuated by increasing the frequency of pulsing. Another way of displaying the results of experiments such as shown in Fig. 3 is shown in Fig. 4A where the ratios of signals observed with pulsing and without pulsing (field-free) have been plotted as a function of disk-to-aperture distance. From this plot the relative pulse-induced increase in positive ion concentration at the observation point as a function of distance to the disk is directly observed. The data of Fig. 3 indicates that in the absence of applied pulses, the concentration of positive ions in any given region of space in front of the disk decreases sharply with distance from the disk, and that with the application of pulses, the positive ions tend to spread out in space so that the concentration gradient at any point along the disk-to-aperture axis is thereby decreased. We might now again ask our question: what force has caused this spread of positive ions? The pulse applied to the disk was of negative polarity. If the applied field, itself, were important in moving the positive ions, we might have expected a waveform of this polarity to pull the positive ions closer to the disk and thereby decrease the concentration of positive ions at the observed point along the disk-to-aperture axis. The opposite of this was observed suggesting a lack of importance of the pulsed field itself. The effect of the pulsed field on the API-MS signal is further characterized in parts B and C of Fig. 4, where either the width of the pulse or its polarity have been changed. The clear result is that these drastic alterations of the pulse characteristics have no measurable affect on the API-MS signal. Again, these experiments imply that under the conditions examined here, which should be directly applicable to those of the typical ^{63}Ni

detectors, positive ion distribution and motion is not significantly affected by the applied pulsed fields, themselves.

Clearly, however, the data of Figs. 3 and 4 indicate that some strong force has accompanied the act of pulsing and has significantly altered the distribution of positive ions within the argon–methane mixture. This can not be explained by diffusion (motion of a species through a concentration gradient), because there is no reason for the diffusion coefficients of the positive ions to have been increased by the intermittent pulses. The remaining explanation is that the positive ions tend to spread themselves in space following an electron-removing pulse by migration (motion of a charged species through an electric field) through the electric field generated by the excess positive ions, themselves. This migration will largely occur during the periods between the application of pulses. With faster pulsing, electrons are removed more frequently causing a larger time-averaged space-charge field and greater positive ion spreading. If the pulse serves only to remove electrons and create the positive space-charge, a change in its polarity should not alter the API-MS signal. This view is that of the space-charge model of the ECD[3] and appears to most adequately describe the experimental results of Figs. 3 and 4.

If a constant d.c. field is applied to the disk very different results from those

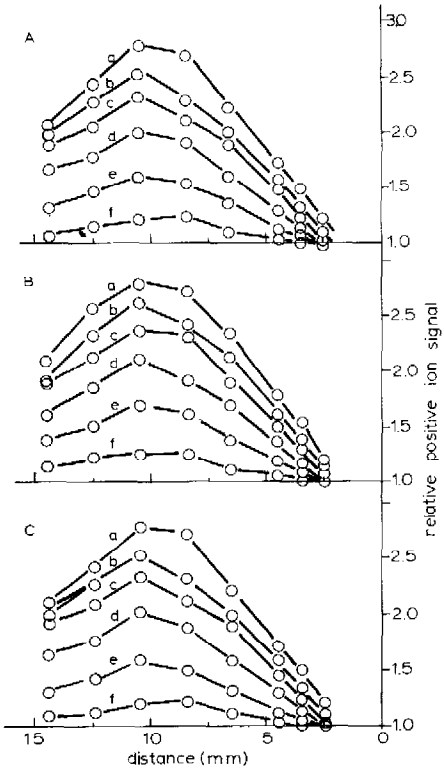

Fig. 4. Ratios of total positive ion signals measured with and without the application of various pulsed waveforms to the disk as a function of disk-to-aperture distance. The frequencies of pulsing expressed as the period between pulses are: 20 (a); 300 (b); 500 (c); 800 (d); 1200 (e) and 1600 μsec (f). A, 1-μsec pulses of −50 V; B, 2-μsec pulses of −50 V; C, 1-μsec pulses of +50 V.

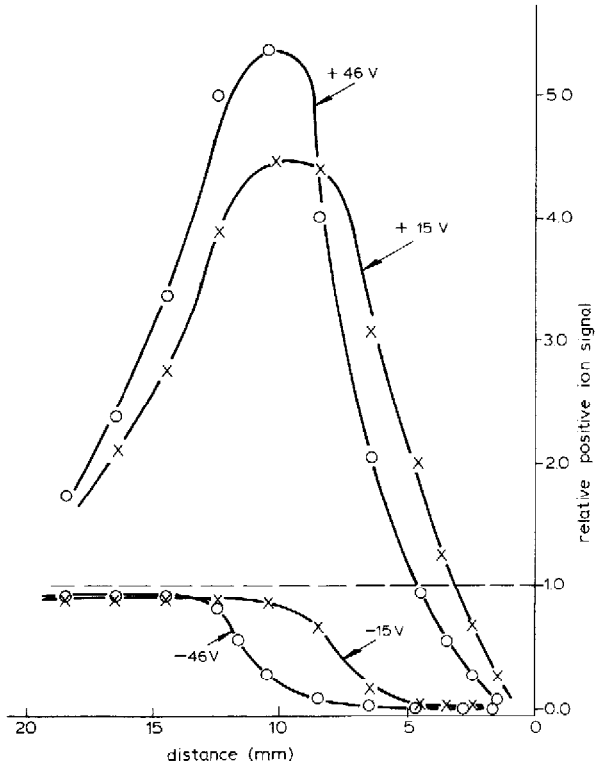

Fig. 5. Ratio of total positive ion signals measured with and without various d.c. potentials applied to the source disk.

reported above are observed. In Fig. 5 the effect of constantly applied fields on the API-MS total positive ion signal are shown. In this case a change in the polarity has drastic consequences. At 5.0 mm, for example, a positive potential of 15 V doubles the signal while a negative voltage of the same magnitude almost eliminates it. At all disk-to-aperture distances a positive d.c. potential appears to spread the positive ions out in space while a negative potential appear to pull them toward the disk. A larger positive voltage of 46 V appears to spread the positive ions out to greater distances from the disk than does +15 V. With a negative voltage applied to the disk, the signal is reduced only slightly when the disk is greater than 12 mm from the aperture, but is reduced much more drastically when closer than 5.0 mm. This is undoubtedly due to the greater electric field (volts/distance) which exists when the disk-to-aperture distance is small. These data clearly indicate that the space-charge dynamics of the pulsed and d.c. ECDs are entirely different where, in the d.c. ECD, positive ions are, indeed, driven towards the cathode by the applied field.

Returning to the pulsed ECD, the effects of positive ions on the standing currents obtained with the two pulsed ECDs shown in Fig. 6 will be discussed. Both of these detectors contain about 15 mCi of ^{63}Ni on platinum foils which form the cylindrical wall of each cell. Each has a concentric anode made of 1/16-in. diameter stainless steel. The two cells differ, however, in that one is 2.0 cm in length by 1.0 cm

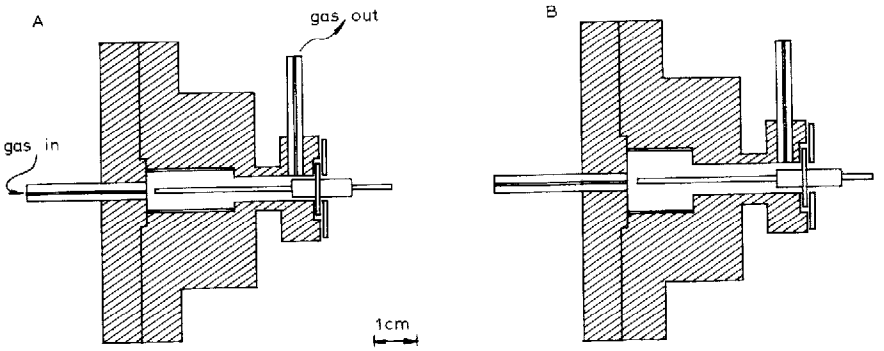

Fig. 6. Two ^{63}Ni ECDs of cylindrical, coaxial design. Interior dimensions are (A) 2.0-cm length, 1.0-cm diameter and (B) 1.4-cm length and diameter.

in diameter and the other is 1.4 cm in length and 1.4 cm in diameter. For each of these cells the standing currents measured with various types of applied electric fields are reported in Figs. 7 and 8.

Considering Fig. 7 first, the standing current of cell A measured with a d.c. negative polarizing voltage applied to the wall of the cell is shown as curve I_{DC}. With about -8 V applied to the wall a saturation level of current equal to 8.3 A is observed at the central anode. The application of greater voltages results in no further increase in current because with this and greater fields, all available electrons are being drawn to the anode and all positive ions are being pushed away from the anode to the cathode. The curve labelled I_N (normal polarity pulsing) shows the standing current measured at the central pin with the application of pulsed waveforms of negative polarity to the wall (-45 V was used, but the current measured was not dependent on the voltage selected between the range of 25–50 V). As the frequency is increased, the

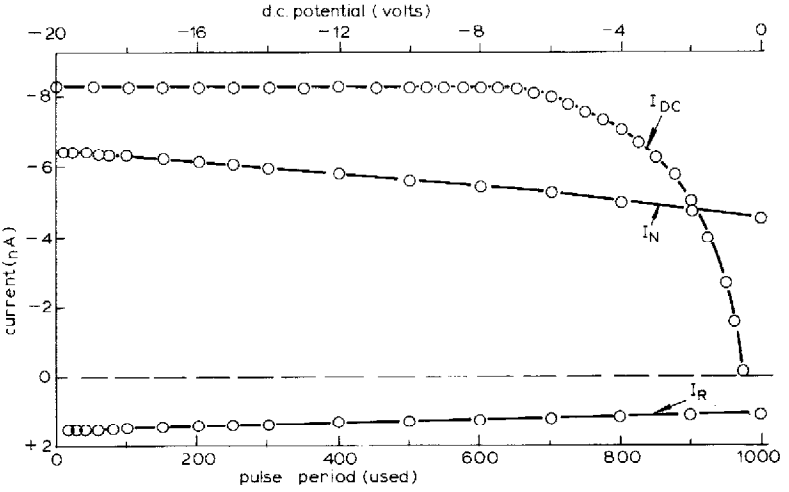

Fig. 7. Standing currents measured at the central pin of cell A with the following potentials applied to the cell block: I_{DC}, negative d.c. potentials from 0 to -20 V; I_N negative pulses of -45 V, 1-μsec duration and various pulse periods; I_R, positive pulses of $+45$ V, 1-μsec duration and various pulse periods.

measured standing current at the central anode increases smoothly and continuously until reaching a maximum value of 6.5 nA with very fast pulsing (period = 20 μsec). We have previously discussed in considerable detail the interpretation of the normal standing current of the pulsed mode for a cylindrical cell in terms of the space-charge model[3,4]. Within this view the normal standing current is described by the following equation

$$I_N = I_e(1 - \delta) \tag{1}$$

where I_N is the standing current observed with normal polarity pulsing, I_e is the negative current which would result from the collection of electrons, alone, at the anode, and δ is the fraction of the positive ions which migrate to the anode. The magnitude of δ will depend on cell design. The standing current measurements in Fig. 7 which constitute curve I_R were obtained by applying pulses of positive polarity to the cell wall (reverse polarity pulsing). Under this condition electrons will be drawn by the pulse to the cell wall and are, therefore, not measured by the electrometer which remains connected to the central pin. The current measured at the central pin is then due to the positive ions, alone, which are arriving at it. Within the view of the space-charge model, the magnitude of this positive ion flux to the pin with reverse polarity pulsing will be the same as with normal polarity pulsing because the only difference in the two experiments is that electrons are cleared by the pulses to different surfaces. As was strongly indicated by the API-MS measurements discussed above, all features of the positive space-charge created by electron removal should be independent of pulse polarity. In terms of the space-charge model the magnitude of current observed with reverse polarity pulsing is then thought to be expressed by

$$I_R = \delta I_+ = \delta I_e \tag{2}$$

where I_R is the measured standing current with reverse polarity pulsing and I_+ is the total positive ion equivalent of current arriving at all cell surfaces. Of course, I_e must equal I_+ (conservation of charge), so I_R will also be equal to the fraction, δ, times the electron current, I_e. According to this interpretation, the sum of I_N and I_R should equal I_e. With very fast pulsing of cell A the sum of I_N and I_R equals 8.0 nA. Another independent measure of I_e has been provided by the d.c. standing current measurement of 8.3 nA. Thus, the magnitudes of the two sets of measurements in the pulsed modes are in reasonable harmony with the d.c. measurements. Returning to the principle point of this study we might now ask: is the magnitude of δ dependent on the frequency of pulsing? A measurement of δ can be obtained from the pulsed experiments by taking the ratios of the two pulsed standing currents at any given frequency:

$$\frac{I_N}{I_R} = \frac{1 - \delta}{\delta} \tag{3}$$

Taking all pairs of standing currents in Fig. 7 from very fast to slow pulsing (periods of 20–1000 μsec), the values of δ observed are essentially constant, all lying between 0.18 and 0.19. In a previous report[7] we calculated that a value for δ of 0.25

might be expected from the space-charge model for the ^{63}Ni detector of infinitely long cylindrical geometry with a coaxial central anode. This calculation also assumed that ionization by beta radiation occurs perfectly uniformly throughout the cell volume. Cell A of Fig. 6 is of cylindrical coaxial design but is not, of course, infinitely long and has a length-to-diameter ratio of 2.0. Thus, longitudinal migration to the ends of the cell will tend to reduce the expected value of δ relative to that where radial migration, alone, would occur. Another factor which might be considered in adjusting our expected value of δ for a ^{63}Ni source is that the ionization rate at the center of a cell with a 1-cm diameter will be somewhat lower than in regions nearer the wall[10]. Thus, we would expect the measured value of δ for cell A to be somewhat less than 0.25, and the result $\delta = 0.18$ seems reasonable. In addressing the primary question under investigation here, the observation that the measured value of δ is relatively constant at all frequencies is most significant. This implies, as did the previous API-MS experiments, that the transport of positive ions is not significantly influenced by the applied field, itself, of the pulses, but is determined at all frequencies by the space-charge field existing between the application of pulses. If the alternate view[2] of positive ion loss was of importance to the ^{63}Ni cell, the applied field of the pulses would have tended to have drawn positive ions to the cathode in proportion to the frequency of pulsing and the measured value of δ would have been expected to be strongly dependent on the pulse frequency. Within this view I_N might have been expected to more closely approach the value of $I_{d.c.}$ as the frequency of pulsing was made very rapid. Thus, the constancy of the measured value of δ at all pulse periods strongly suggests that the space-charge means of positive ion loss is dominant under all conditions of this ^{63}Ni cell.

In Fig. 8, the corresponding standing current measurements with cell B (Fig. 6) are reported. With this cell reverse polarity pulsing results in a very small positive standing current indicating that a much smaller fraction of this cell's positive ions

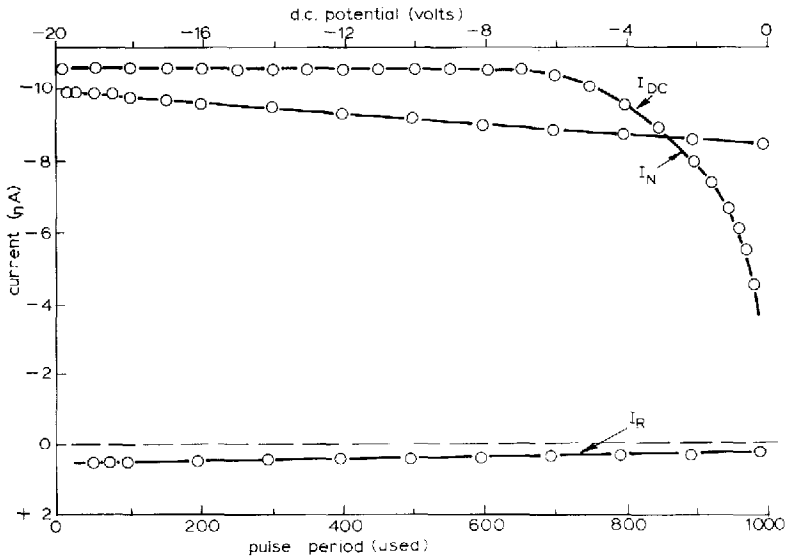

Fig. 8. Same experiment as in Fig. 7, but using cell B.

migrate to its central electrode. This is also implied by the observation that I_N more closely approaches $I_{d.c.}$ for this cell. Cell B differs from cell A in that its length to diameter ratio is 1.0, or one half that of cell A. Although it is cylindrical, its length is so truncated that a large fraction of the ions, which in a longer cell would migrate radially to the anode, will now migrate longitudinally to the ends of the cell. Another factor which will tend to decrease the positive ion migration to the anode of cell B is related to the increased attenuation of beta radiation at the center of this larger diameter cell. (We have previously described this effect in detail[10].) From the ratio of I_N and I_R at any given frequency in Fig. 8, the value of δ measured for this cell is only 0.05 and again is relatively constant for all frequencies. With fast pulsing I_N and I_R approach absolute magnitudes of 9.90 and 0.55 nA, respectively. The sum of these two currents, 10.45 nA, is again nearly equal to the saturation d.c. current observed, 10.6 nA. Thus, cell B differs from cell A in that the contribution of positive ions to the normal pulsed-mode standing current is much less than that of cell A. The space-charge model of positive ion loss offers a useful means of describing this dependence on cell design.

CONCLUSIONS

In recent years the role of positive ions in the pulsed ECD has been a matter of some controversy. It would probably be incorrect, however, to assume that an electron producing source in which positive ions were not formed would be simpler or better behaved. This is because in such an ECD it would be difficult to contain its electrons against the negative space-charge force which must accompany such a device. The positive ions which are formed in ECDs having beta-emitting nuclides actually provide an essential service by containing the electrons within the positively charged ionized gas. Furthermore, the nature and location of this containment can be predicted and controlled by appropriate design of the cell[3]. Therefore, at the present time it seems prudent to accept and use the positive ions for this function and learn how to understand and minimize their detrimental effects. This paper has provided additional understanding of the transport and fate of positive ions in a pulsed ^{63}Ni ECD and reaffirms the validity of the space-charge model[3] in predicting and interpreting their influence on responses observed with these devices. Although the ECD measurements reported here are of standing currents only, it has been clearly shown in previous studies[4,7] that responses to analytes will be similarly affected by the positive ions.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation, Grant Number CHE-8119857.

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