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Measurement of Ions within a Pulsed Electron Capture Detector by Mass Spectrometry

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Measurements of ions within an electron capture detector (ECD) have been made by the technique of atmospheric pressure ionization mass spectrometry (APIMS) where the ion source has been modified to be an actual ECD. By observing the dependence of ion signals on electrostatic fields applied to the ionization cell, new insight into the role of ions in influencing the measured ECD current is provided. It is shown that for this pulsed ECD, a positive current of significant magnitude exists which is an integral component of the normally measured ECD current, and that it is caused by the selective migration of positive ions to the sampling electrode during the period between pulses. The results are discussed relative to opposing views of the ECD, and are shown to strongly support one of these.

Electron capture detection (ECD) with gas chromatography (GC) has proved to be one of the most useful techniques available for the trace analysis of many environmentally important organic compounds. This success is due primarily to the very selective reactivity of the low-energy electron with certain classes of compounds in the gas phase. To improve our understanding of these reactions and the basis of ECD responses, several studies have had as their objective the identification of the negative ions formed under one-atmosphere, electron capture conditions. Using the technique called plasma chromatography, the formation of negative ions from substituted benzenes (1) and polychlorinated biphenyls (2), and the effects of oxygen (3) under electron capture conditions have been reported. By atmospheric pressure ionization mass spectrometry (APIMS), additional chemical (4, 5) and physical (6) detail of EC reactions have been made possible by the direct mass spectrometric analysis of one-atmosphere plasmas. In a recent study by Horning et al. (5), an APIMS ion source was modified to be an actual ECD complete with a cell electrode, so that the ECD function of this ion source could be obtained simultaneously with negative ion measurements. Not only might one expect this combination to provide an ideal means of studying EC reactions, but it also appears to constitute a promising technique in itself for the analysis of trace amounts of organic substances.

Because of the demonstrated success of APIMS for the sensitive measurement of ions formed within its ECD-like source, we have constructed a similar instrument designed specifically for the study of ECD chemistry. This instrument provides the simultaneous measurement of cell current and mass-analyzed ion currents as in the Horning study (5). With

it, however, we have made new observations which provide a new source of information for ECD events. We have found that, under electron capture conditions within the ion source, the measured intensity of negative ions formed by electron-capture reactions is strongly affected by the simultaneous application of the pulsed field used to obtain the ECD function of the source. We believe these interactions reflect changes in the rates of ion transport to boundary surfaces of the ionization cell and, therefore, provide added insight into the basis of the currents measured within the ECD.

EXPERIMENTAL

The vacuum envelope, quadrupole mass spectrometer, and pumping system of our APIMS has been described previously (7). A detailed view of its ion source is shown in Figure 1. The stainless steel ion source bolts onto the front flange of the vacuum envelope. A $5/8$ -inch nickel disk of 25- μ m thickness and containing a 20- or 25- μ m aperture in its center (Perforated Products, Inc., Brookline, Mass.) provides a controlled leak of the ion source contents into the vacuum region. Nitrogen carrier gas (Matheson, ultra high purity) flows continuously through the ion source at a rate of about 40–60 cm³ min⁻¹. The carrier gas is further purified by passing it through a filter containing CaSO₄ and 5A molecular sieve. The volume of the active region of the ion source is about 1 cm³, the approximate size of a conventional ⁶³Ni ECD. A platinum cylinder imbedded with 9 mCi of ⁶³Ni (New England Nuclear, Boston, Mass.) forms the wall of the active region. A $1/16$ -inch stainless steel pin protrudes into the ion source as shown via a ceramic feedthrough. The diameter of the cylindrical source is 1.0 cm.

Samples are introduced to the carrier gas stream via either a 3.4-L stainless steel exponential dilution sphere or at the injection port of a gas chromatograph (Aerograph Autoprep A-700). For GC a $1/8$ -inch, 1.5-foot stainless column packed with 3% OV-17 on Supelcoport 100/120 mesh was used. A heated, glass-lined stainless transfer tube connects the GC with the ion source.

For the ECD current measurement, a pulsed, positive voltage was applied to the ion source pin. The resulting total cell current was measured at the same pin using the circuit shown in Figure 2. Others (8) have used a similar approach to obtain the ECD signal from cells whose walls are electrically grounded. The operational amplifier shown is an RCA CA3140S. In all chromatograms reported here, the ECD current is the total unprocessed cell current. For the pulsed mode, 35-V, 2- μ s pulses of variable period were used. With a pulse period of 300 μ s, a standing current of about 2 nA was obtained at all temperatures. All ECD circuitry was home-built.

Ion measurements were usually made by monitoring one ion only during the course of an experiment. Detection of positive and negative ions was by the counting method (9) using a Channeltron 4039 electron multiplier (Galileo Electro-Optics Corp., Sturbridge, Mass.). An analog signal from a ratemeter (Ortec, Model 441) is recorded. The mass filter is a quadrupole

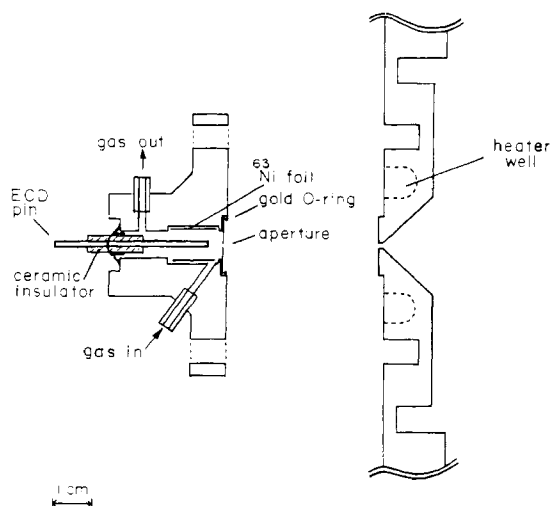


Figure 1. Electron Capture Detector ion source of mass spectrometer shown with the front flange of vacuum envelope

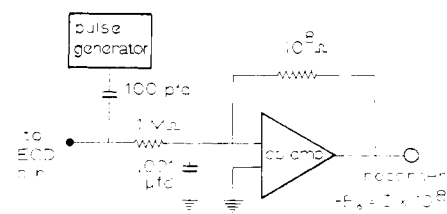


Figure 2. Circuit for measuring the ECD current at the ion source electrode

(Extranuclear, Model 162-8) capable of greater-than unit mass resolution up to about $m/e = 500$.

RESULTS AND DISCUSSION

Effect of Applied Fields on APIMS Signals. During our initial use of the specialized ECD/APIMS instrument described above, we looked for and usually found the negative ions of EC-active compounds which have been reported in other APIMS studies. These include the M and $M - Cl + O$ negative ions of *p*-chloronitrobenzene and tetrachlorobenzene (4), the M^- ion of SF_6 (10), and halide anions of simple aliphatic chlorocarbons and chlorofluorocarbons (10). With one exception (5), our instrument differs from other APIMS studies in that for the ECD function of the ion source, electrostatic fields can be applied to the ionization region. The presence of these fields was immediately noticed to have a pronounced effect on the negative ions observed under electron capture conditions. For example, in Figure 3 are shown two GC-ECD/MS analyses of azulene. In the first run, the elution of azulene is signaled by a reduction in the ECD standing current of about 10%. At mass 128, however, no negative ion corresponding to the M^- species was detected. In searching for other possible negative ions of azulene, such as the $M - H + O$ anion, none were found for this 0.5-ng sample as long as the ECD pulser was operative. In chromatogram b, however, the ECD pulser (+35 V, 300- μ s period applied to the ion source pin) was turned off just prior to the elution of azulene. An intense negative ion current corresponding to M was then observed. This behavior has been the rule for all negative ions we have observed under electron capture conditions and is not unique to the example shown. Ions such as Cl^- , Br^- , SF_6^- , SF_5^- , and those of the type $[M - Cl + O]$ all are affected by the applied fields in the same manner.

In demonstrating further the effects of pulsed fields applied to the ion source, the example of *p*-chloronitrobenzene (PCNB) will be used most frequently where the sample introduction method is gas chromatography. To show, however,

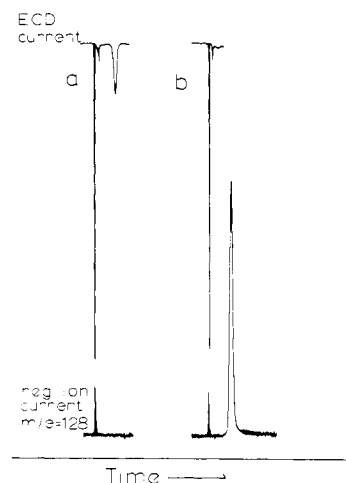


Figure 3. Two GC-ECD/MS analyses of azulene. (a) Both the pulsed, ECD current and the mass spectrometer ion current of the M^- ion of azulene are monitored simultaneously. (b) The ECD pulser is turned off just prior to the elution of azulene. Sample size, 0.5 ng. Source temperature, 150 °C

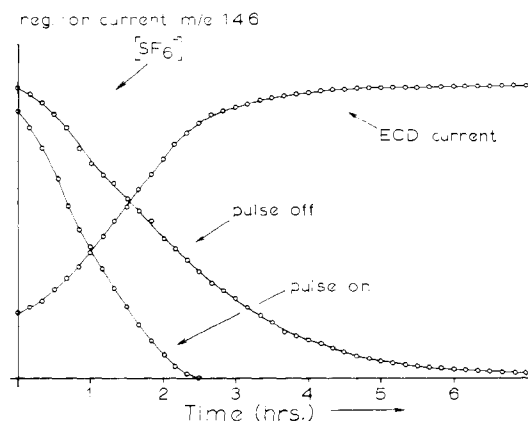


Figure 4. ECD current and SF_6^- ion currents measured by ECD/MS with ECD pulser alternately turned on and off. Sample is introduced via a 3.4-L exponential dilution sphere. Initial SF_6 concentration 30 ppb (v/v) in nitrogen. Gas flow rate, 60 mL min^{-1} . Source temperature, 200 °C. Pulse period, 300 μ s

that the observations to be described are independent of compound type and sample introduction method, the case of SF_6 introduced directly into the carrier gas stream via an exponential dilution sphere is first shown in Figure 4. The injection of the SF_6 causes a drastic reduction in the ECD current and a simultaneous appearance of an intense SF_6^- ion signal. As the SF_6 concentration decreases exponentially with time, the ECD current increases in a manner roughly similar to that predicted if a Beer's law relation between ECD current and SF_6 concentration is assumed. With the ECD pulser left on, the SF_6^- ion current decreases prematurely and goes to zero when the ECD current has returned to about 90% of the original standing current. By turning the ECD pulser off intermittently, a simultaneous trace of the SF_6^- current under the field-free ion source condition was also obtained. This ion current does not differ drastically from the "pulse on" ion current in the large sample or saturation condition, but diverges continuously from it as the SF_6 concentration decreases. Under the small sample condition where the ECD current is restored to 90% or greater, a sizable SF_6^- ion current is still measured only in the "pulse off" condition.

In Figure 5 is shown the effect of the pulsed field on the M ion of *p*-chloronitrobenzene (PCNB) where this time the sample is introduced by gas chromatography. Again, as in the case of SF_6 , the ion signal is decreased by the pulsed field

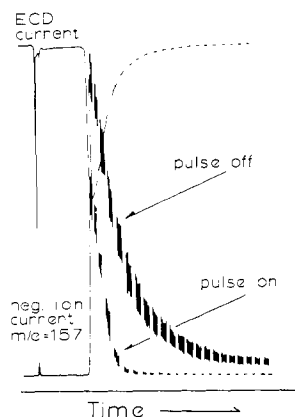


Figure 5. GC-ECD/MS analysis of *p*-chloronitrobenzene monitoring the molecular anion at $m/e = 157$. After the peak maximum, the ECD pulser is turned off and on alternately every 10 s. Sample size, 1.0 ng. Source temperature, 250 °C. Pulse period, 300 μ s. Column temperature, 95 °C

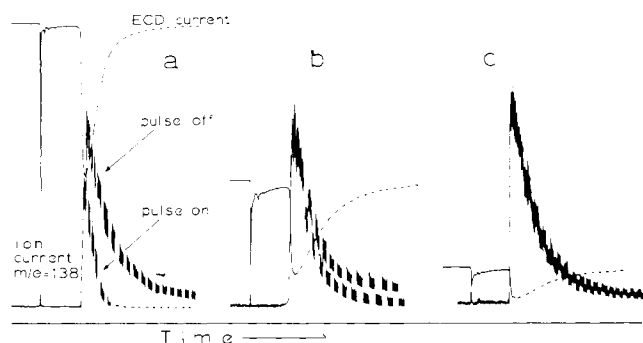


Figure 6. Effect of ECD pulse period on negative ion observed with the ECD/MS. Ion monitored is $M - Cl + O$ negative ion of *p*-chloronitrobenzene. Pulse periods are (a) 300 μ s, (b) 1.0 ms, (c) 2.5 ms. After the peak maxima, the ECD pulser is turned off and on alternately every 10 s. Sample size, 1.0 ng. Source temperature, 250 °C. ECD standing current in (a) is 2.2 nA

and is caused to go to zero as the ECD response returns to about 90% of the original standing current. Again, the ion signal observed with the pulser turned off seems to reflect better the degree of negative ion formation which might be predicted from the ECD response. In Figure 6 is shown the effect of varying the pulse period of the ECD pulser on the ion signal of the $M - Cl + O$ anion of PCNB. Using a period of 300 μ s, the ion signal is reduced by the field's presence in a manner precisely the same as that of the M^- ion. With longer pulse periods, the ECD current is lessened as expected (11). Also, with longer pulse periods, the perturbation of the ion signals by the field is observed to be not so severe. About 1 to 3 ms appears to be enough time to allow the perturbation caused by the pulse to relax significantly back toward an equilibrium position. Perhaps not coincidentally, this is about the same amount of time required for an apparent steady-state electron concentration to be achieved in ECD studies when ^{63}Ni ionization is used (8, 12).

In Figure 7 is shown the effect of the pulsed field (300- μ s period) on the $M + 1$ positive ion of PCNB. The applied field clearly has no effect on the positive ions for all sample concentrations. In Figure 8 is shown the effect of reversing the polarity of the pulser (to -35 V) on the negative ions of PCNB. The fascinating result is that pulsing negative vs. positive makes no difference on the negative ion perturbation. Clearly, the cause of the negative ion perturbation cannot be related to a simple repeller field affect since, if it were, a negative field would assist the ejection of negative ions out of the ion source.

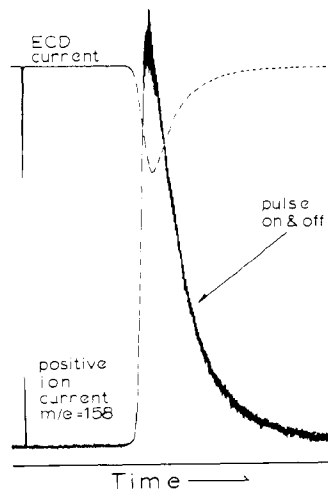


Figure 7. Effect of ECD pulser on positive $M + 1$ ion of *p*-chloronitrobenzene. Pulse period, 300 μ s. Pulser turned on and off alternately every 10 s. Sample size, 0.3 ng. Source temperature, 250 °C. Column temperature, 87 °C

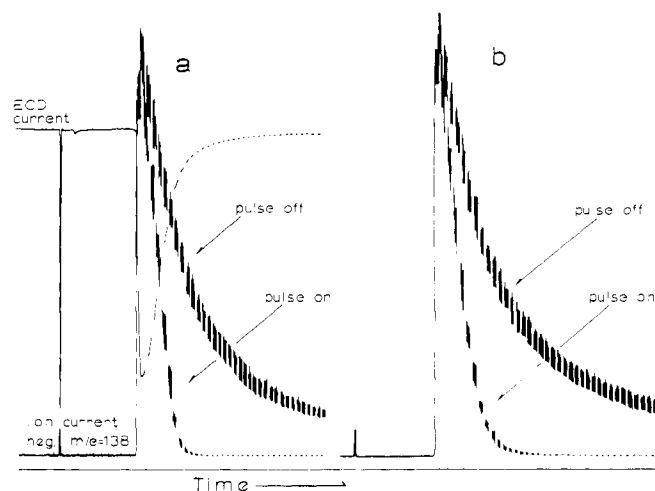


Figure 8. Effect of polarity of the ECD pulser on the negative ion signal of the ECD/MS. Pulse characteristics; (a) +35 V, (b) -35 V, both 2- μ s pulse width, 300- μ s pulse period. Sample, *p*-chloronitrobenzene. Ion monitored $M - Cl + O$ negative ion. $T = 250$ °C. Pulser turned on and off alternately every 10 s

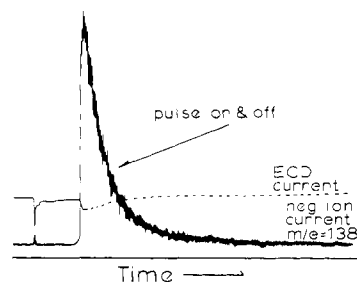


Figure 9. Effect of ECD voltage pulses on negative ions of sample with carrier gas doped with 1 pph oxygen. Sample, 1 ng *p*-chloronitrobenzene. Ion monitored, $M - Cl + O$ negative ion. Source temperature, 250 °C. ECD pulser is turned off and on alternately every 10 s

Finally, in Figure 9 is shown the effect of the ion source field when oxygen has been added to the carrier gas so that the negative reactive species present are probably O_2^- (13) instead of electrons. This saturated condition is indicated by the low ECD standing current which accompanies the addition of oxygen. Under this condition no perturbation of the negative

ion signal is caused by the ECD field.

In summarizing the above set of measurements, it is clear that a pulsed field can alter APIMS signals under certain conditions of the ion source. These effects are strongest in the low-sample or weak-response condition where electrons are the predominant negatively-charged species. Under this condition using pulse frequencies of about 3 kHz or greater, the negative ion signals, only, are destroyed. Since an ECD response is observed, however, it seems likely that negative ions are actually being produced within the ion source.

Candidate Models of the ECD. If it is assumed that the ion measurements of our ECD/MS reflect the transport (diffusion and migration) of ions to the grounded walls of our ECD ion source, these measurements provide a means of adding further detail to physical events occurring within the ECD. Thus, we have tried to merge an explanation of the above experiments with the literature views of the ECD.

Conventional View. In the ECD, β radiation initiates a series of chemical reactions which, even in the absence of added sample, will produce steady-state concentrations of electrons, positive ions, negative ions (with sample present), free radicals, and molecular reaction products (14). For the pulsed ECD, a generally accepted model of the role of electrons and ions in determining the measured current has evolved (8, 12, 15–21) which states: (1) the current measured is due to electrons which are drawn to the more positive electrode during the application of short voltage pulses; (2) the relatively immobile ions contribute little to the current; and (3) the entire ionization cell is cleared of electrons during each pulse. Thus, this view holds that the ECD current is a direct measure of the steady-state electron concentration achieved at the end of the field-free period between pulses. Experiments such as those of Wentworth, Chen, and Lovelock (16), Devaux and Guiochon (22), and Simmonds et al. (12) in which the effects on the ECD currents of variations in the pulse width, pulse period, and pulse voltage were determined have provided persuasive evidence of the above general model. Further detail of ECD events, though not essential to its operation, has sometimes included: (4) positive ions will be in very large excess of electrons because the electrons diffuse quickly to cell boundaries (even during the field-free period between pulses); and (5) the charge associated with negative ions formed by electron capture is quickly lost because of a much faster recombination between positive ions and negative ions than exists between positive ions and electrons (8, 18, 19, 21).

Recently, Siegel and McKeown (6) have presented several criticisms of the above view. They argue that, under the ECD condition of relatively high ion density, positive and negative particles do not move independent of one another as they may in weakly ionized gases, but all move with one characteristic "ambipolar" diffusion constant. Using an APIMS with a ^{63}Ni ionization source, they provide experimental evidence indicating that strong electrostatic forces between ions and electrons (which are ignored in the conventional view of the ECD) cause the maintenance of charge balance in the field-free ionization source of their APIMS. Thus, it appears that point 4 of the conventional view is incorrect. Siegel and McKeown also argue with support from the literature and their APIMS experiments that point 5 is incorrect. Our own measurements by APIMS support Siegel and McKeown in this later point. For example, if during the GC elution of a large sample of CCl_4 , the total positive ion intensity is monitored, this signal increases about 50% while the source is saturated with CCl_4 . Apparently, the recombination of positive ions with negative ions (Cl^-) is actually slower than that of positive ions with electrons.

Modified View A. While Siegel and McKeown (6) did not address directly the effect of an applied field which must be

present if the ionization call is to function as an ECD, they maintain that positive and negative charge densities must remain numerically equal in the ECD. Thus, within the view of Siegel and McKeown, it is more difficult to envision what the measured ECD current is due to. A view which may follow most naturally from Siegel and McKeown's concepts is that only a very small distance from the electrode surface (one Debye length) is sampled with each voltage pulse. According to McDaniel (23), a highly ionized volume of gas is to be considered a plasma where "when in contact with a physical boundary, a plasma forms a protective sheath about itself. The sheath, in effect, separates the main body of the plasma from its environment. Unlike the main body, the sheath is not electrically neutral and strong electric fields may be present in it. The thickness of the sheath is of the order of a Debye length". Thus, within Siegel and McKeown's concepts and McDaniel's description of a plasma, the current one measures from an ECD may reflect the motion of electrons and possibly ions only within one Debye length from electrode surfaces. This distance can be calculated from the equation (23).

$$\lambda_d = \sqrt{\frac{\epsilon k T}{4\pi e^2 n}}$$

where n is the ion density, ϵ is the dielectric constant, e is the charge of an electron, k is the Boltzmann constant, and T is temperature. Assuming a reasonable value for n to be $2.4 \times 10^8 \text{ cm}^{-3}$ (6), λ_d becomes $33 \mu\text{m}$ at 300°C . Since a typical ECD cell has an inside diameter on the order of 1 cm, this model suggests that only a minor portion of the total ECD volume is sampled during individual voltage pulses. This model contradicts point 3 of the conventional model and constitutes generally a radical departure from earlier ideas.

Modified View B. An alternative view might be considered which recognizes the importance of electrostatic forces between ions and electrons, but does not depart so drastically from the conventional view. This view insists that all electrons within the ECD are removed with each pulse, and then considers the effects of the positive space-charge field created by the excess positive ions during the period between pulses. We feel that this view has considerable merit, because point 3 of the conventional view is strongly supported in different ways by the ECD literature. Because this is a crucial detail of ECD theory, the support of point 3 might be recalled. The experiments of Wentworth, Chen, and Lovelock (16), Devaux and Guiochon (22), and Simmonds et al. (12) have already been referred to. Experiments by Hastings, Ryan, and Aue (14) and also by Lovelock (19) have shown that the electron capture reactions in an ECD cell can be stopped by the application of a continuous potential of about 50 V. These experiments suggest that the applied field's presence is felt throughout the cell, not just within a Debye length from the electrodes. In other experiments (19, 24, 25) it has been shown that a near-coulometric relationship exists between electrons lost and moles of sample present in the ECD's response to some polychlorinated molecules. Either point 3 of the conventional view is valid or this relationship is coincidental. Later in this article a theoretical argument supporting point 3 of the conventional view will also be presented.

Interpretation of Results. We would now like to consider how the mass spectrometric measurements reported here might be related to the ECD models discussed. As an aid for this discussion, in Figure 10 is shown a pictorial model of ions and electrons in a pulsed ECD which may be taken to represent modified view B if the events suggested are assumed to take place throughout the entire cell or, alternatively, may represent modified view A if the events pictured are thought to occur only at short distances (one Debye length) from the

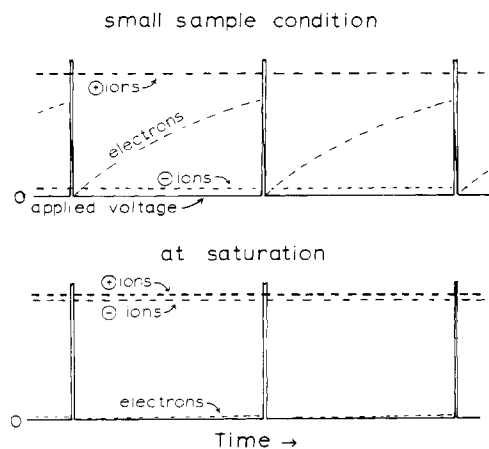


Figure 10. Representation of the concentrations of charged particles within a region of the pulsed ECD. This region exists throughout the entire cell volume or alternatively near the wall of the ECD. The saturated condition is caused by the presence of an adequately high concentration of electron capturing molecules in the carrier gas

cell wall. During a short voltage pulse, the electrons are removed from the entire cell or from the region immediately adjacent to the cell wall. The relatively sluggish positive ions are not so strongly affected by the short pulses, and the result is that a positive space-charge is created. During the time immediately following the pulse, the positive space-charge will tend to hold the few negative ions which may be present in the small sample condition within the space-charge region, and the negative ions are not observed (thus, Figure 3). The positive ions, meanwhile, are allowed to diffuse to the cell boundaries (thus, Figure 7). With longer periods between pulses, electron concentration is allowed to increase to a point where charge neutrality may be achieved during the latter portion of the period and the effect of pulsing on the negative ion signals at this lower frequency is much less (thus, Figure 6). The positive space-charge which retards the negative ion signals is created by the removal of electrons, and it might be expected that this post-pulse condition could be created by pulses of either polarity. Thus, pulsing the pin positive or negative causes the identical effect on the negative ions (Figure 8). In the large sample condition, or with negative ions in large excess over electrons (saturation), electrons play a minor role in the maintenance of charge neutrality and the effect of pulsing the ECD on the negative ion signals vanishes (Figure 9).

The ECD/APIMS data cannot be explained solely by the conventional view of the ECD and clearly indicate the importance of electrostatic forces between charged particles. The data seem very consistent with modified view B, but, however, may also be explainable by the less-well defined modified view A. From the experiments we have described, one can make an interesting prediction which perhaps can be used to test the candidate views further. That is that at least some of the current measured in the pulsed ECD should be due to a selective positive ion migration to the sampling electrode during the period between pulses, when negative ions (as we have shown experimentally), and undoubtedly also electrons, are held within the space-charge region, while positive ions are allowed to diffuse out. This current would tend to subtract from the large negative current caused by drawing electrons to the pin during a positive pulse. We have tested this prediction by performing a simple experiment. The ECD pulser was altered to produce negative, 35-V pulses (as used in Figure 8). The negative pulses will repel electrons away from the sampling electrode, and a positive ECD current should be observed due to the arrival of positive ions to the pin during the period between pulses as we predict for the

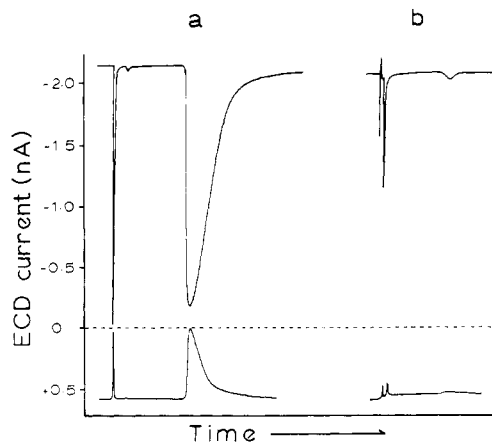


Figure 11. ECD current observed at the collection pin of the ion source using normal positive voltage pulses (upper trace) and using negative pulses (lower trace). During chromatograms of (a) 3 ng *p*-chloro-nitrobenzene, (b) 10 ng anthracene. ECD temperature, 250 °C. Pulse period, 300 μ s

small- or no-sample condition. Two chromatograms using negative pulses are shown in Figure 11 in the lower traces while the normal ECD current caused by positive pulses during repeated analyses is shown in the upper traces. The very striking result is that in the backwards configuration, a remarkably high positive standing current results (0.28 as high as that of the conventional configuration). Furthermore, a very sensitive response to the electron-capturing compound, PCNB, occurs. The positive current goes to zero (and a response occurs) in the saturated condition because negative ions have replaced electrons, and the pulses then create no region of positive space-charge. That the response is due to an electron capture reaction is supported by the lack of response to the larger anthracene sample which captures electrons only weakly, but which we know from our APIMS measurements undergoes positive ion-molecule reactions very readily.

In determining whether this large positive ion current is consistent with either of the modified views, again modified view A has not yet been sufficiently defined as to allow this assessment to be made for it. It will be shown, however, that the magnitude of current observed with the application of negative pulses is in good agreement with modified view B. If the entire cell volume is cleared of electrons during a pulse, after this pulse a certain fraction of the positive ions will migrate to the sampling pin causing the positive current, and some will migrate to the cell wall which is electrically grounded. The fraction of the total positive ions present which will move toward the pin will be determined by the field generated by the positive ions themselves. If one assumes that initially following the removal of a pulse, positive ions are uniformly distributed throughout the cell, the electrical potential at any point within the cell can be calculated by solving Poisson's equation (26). Assuming infinite cylindrical symmetry, Equation 1 is thereby derived for the boundary conditions, that

$$V = \frac{\rho_0}{4\epsilon_0} \left[(b^2 - a^2) \frac{\ln(r/b)}{\ln(b/a)} + (b^2 - r^2) \right] \quad (1)$$

potential V , equals zero at radii, $r = a$ and $r = b$, where a is the radius of the sampling pin and b is the radius of the cylindrical cell cross section. ρ_0 is the density of the positive ions, and ϵ_0 is the permittivity of free space. For our cell, $a = 0.79$ mm and $b = 5.0$ mm. Assuming that ρ_0 is about 2.4×10^8 ions/cm³ (6), the electrical potential calculated from Equation 1 is plotted as a function of r in Figure 12, curve

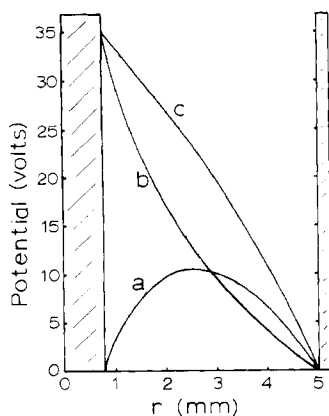


Figure 12. Calculated electrical potential, V , within our cylindrical ECD as a function of distance, r , from the center of the sampling pin as predicted by modified view B. Curve a shows the potential just as the pin is grounded after a voltage pulse, when all electrons have been removed, and a uniform distribution of positive ions remains. Curve a is calculated from Equation 1 in text. Curve b is the potential expected across the cell during the first instant a +35-V pulse is applied to the central pin. Curve b is calculated from the equation, $V(\text{volts}) = 35 \times \ln(b/r)/\ln(b/a)$. Curve c is also the potential expected during the applied pulse, but after all electrons have been removed, about 1 μs later. Curve c is the sum of curves a and b

a. This curve shows that the potential caused by the presence of the uniformly distributed positive ions rises from zero at the cell boundaries to a maximum which occurs at $r_{\text{max}} = 2.57$ mm. Thus, we might expect space-charge repulsive forces to cause the positive ions within $r = 2.57$ mm to move toward the sampling electrode, and the ions beyond this distance to move toward the cell wall. The ratio of ions which may eventually arrive at the surfaces at $r = a$ and $r = b$ is equal to the ratio of the volumes of the cell within and beyond r_{max} and is given by

$$\frac{I_a^+}{I_b^+} = \frac{(r_{\text{max}}^2 - a^2)}{(b^2 - r_{\text{max}}^2)}$$

where I_a^+ and I_b^+ are the positive ion currents arriving at the sampling electrode and the grounded wall, respectively. For our cell this treatment predicts I_a^+/I_b^+ to be 0.33. We can now compare this prediction of modified view B with the experimental result shown in Figure 11, in which the observed positive current, I_{net}^+ obtained with negative pulses is 0.28 as large as the negative current, I_{net} observed using positive pulses. According to modified view B, I_{net}^+ might be viewed as being simply I_a^+ , while I_{net} is equal to the electron current accumulated during pulses, I_e , minus the current due to the arrival at the pin of positive ions during the period between pulses, again equal to I_a^+ . Thus,

$$\frac{I_{\text{net}}^+}{I_{\text{net}}} = \frac{I_a^+}{I_e - I_a^+}$$

A reasonable assumption within modified view B is that $I_e = I_a^+ + I_b^+$. Thus, the last equation becomes

$$\frac{I_{\text{net}}^+}{I_{\text{net}}} = \frac{I_a^+}{I_b^+}$$

and the ratio of the two measured currents in Figure 11, noted to be 0.28, is a direct measure of I_a^+/I_b^+ . This value compares very favorably with the predicted value, 0.33, and strongly supports the validity of modified view B.

Also shown in Figure 12 are the results of additional calculations which we feel further support modified view B over modified view A. Curve b in Figure 12 is the calculated

potential throughout the cell during the application of a positive, 35-V pulse when the cell contains an equal number of positive and negative particles uniformly distributed. This is the condition we might expect to exist during the first instant of a pulse before any electrons have been removed. Curve c is the potential expected throughout the cell near the end of this same pulse (about 1 μs later) when all electrons have been removed by the pulse. Curve c is obtained by the simple addition of curves a and b. While curve c has some convex curvature as a result of the positive ion space-charge field, it still has a negative slope at all radii from the pin, supporting the assumption that all electrons within the cell will have been drawn to the anode. Only with the application of smaller voltages would curve c acquire a flat or positive slope, causing an incomplete collection of electrons at the pin. The insistence of modified view A that charge neutrality must be maintained at distances greater than one Debye length from the cell boundaries does not, therefore, seem appropriate to the pulsed ECD during the application of the pulse. The forces between charged particles appear to become dominant only during the period after the pulse.

CONCLUSIONS

We have demonstrated here the existence and theoretical basis of a previously unrecognized component of the current measured with a pulsed ECD. The importance of positive ions in affecting the ECD current is undoubtedly a function of the cell geometry and anode placement. In certain practical applications of the ECD, such as its use as a gas-phase coulometer (19, 24, 25), it is essential that either the positive ion contribution to the measured current be eliminated, or that its contribution be understood to the extent that a correction for its presence can be applied.

The incorporation of an ECD sampling pin into the ion source of an APIMS is very easily done and provides a powerful combination of functions which should be useful for trace organic analysis. In the use of such an instrument, however, an appreciation of the interdependence of negative ion signals and the pulsed field used for the ECD function is advised.

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Mass Spectrum Dictionary for Library Searching

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When data can be arranged according to some ordering principle (e.g., numerical or alphabetical), powerful searching techniques can be applied to retrieve information. An explicit set of procedures is proposed for constructing a precisely ordered mass spectrum dictionary. Performance tests on the proposed system show that on average less than 1% of the spectra need to be examined in searching for a given unknown. The mass spectrum dictionary is economical on storage and it will accommodate spectrum variability likely to be found in a library search environment.

Searching a large library of mass spectra for the best-match candidates with some particular query spectrum can be a time consuming process. A number of systems that perform well on this task have been proposed (1-7). One of the most successful of the library search techniques is the method due to Heller (4) which employs an inverted file structure. One of the only real criticisms of this system is that it is very costly both in terms of file generation and file maintenance. The other really serious problem is the size of the file (although there are ways to alleviate this problem (8)).

These problems have prompted the development of a system that is comparable in performance but which requires neither the overhead of file maintenance nor large amounts of storage for the search file.

Searching large amounts of data can be efficient provided the items can be ordered in some way. For instance, searching a file as large as a telephone directory by computer can be made a simple and efficient task using a binary search algorithm (9). The binary search algorithm guarantees to find any item in an ordered file of N items in at most $\log_2 N$ steps. For example only 16 comparisons are necessary to locate any item in an ordered file of 32 000 items. This efficiency is derived by taking advantage of the order in the file.

Returning to the mass spectrum context, we find that searching a library of mass spectra for the best match with some unknown spectrum is comparable to searching a telephone directory in which the names are in random order. Obviously such a search system is very inefficient because there is no way of taking advantage of any inherent order in the data. Series displacement indices (7) and ion series analysis (5, 6) have been suggested as ways of reducing the portion of the file that needs to be searched. These methods do not, however, possess the specificity that is desirable in searching large files; that is, they do not eliminate enough candidates from the search.

This leads to the question as to whether we can impose some ordering principle on a library of mass spectra. Any attempt at such a task must take into account the inherent variability in the data. In particular, there can be considerable differences

in intensity information for representations of a mass spectrum measured on different instruments.

A careful examination of a large number of mass spectra reveals that, in general, there are considerable differences in both mass and intensity representations for compounds that are closely similar structurally. Grotch has shown that, when intensity information is discarded altogether, we still have a very selective representation (10). It might therefore seem reasonable that the mass information could be used in some way to order a file of spectra. However, using the mass information alone still does not completely remove the intensity variation problem. It will be shown in the next section that certain intensity related constraints can be placed on the selection of masses for an ordered representation.

MASS SPECTRUM DICTIONARY CONSTRUCTION

In order to construct a mass spectrum dictionary, a fixed range for selecting masses must be predetermined (for this to work the mass range 40 \rightarrow 99 is used). This range is divided up into 6 ranges of 10 mass units (i.e. 40 \rightarrow 49, 50 \rightarrow 59, ...). The selection rules that are then applied to cope with spectrum variability are as follows.

(1) Select the mass of the most intense peak in each range (relative ion abundance is used for the intensity scale, range is 0 to 100%).

(2) Make the following checks to determine if there is any possibility of ambiguity in the selection made: (a) If the most intense peak in a range is less than or equal to 1%, assign it to the zero mass for the range and mark it as not ambiguous. (b) If the most intense peak in a range is greater than 1% and less than or equal to 10%, mark it as ambiguous. (c) If the ratio of the most intense to the second most intense peak in a given 10 amu range is less than 1.4, flag it as ambiguous. (The 1.4 criterion was a heuristic choice made after carefully examining over 200 spectra that included a number of duplicates.). (d) All other peaks that are the most intense in their respective ranges are considered as unambiguous.

The preceding steps divide the ranges and selected peaks into two categories: (1) those that are definitive and unambiguous, and (2) those for which instrumental variations may lead to either no mass or another mass being selected as the most intense for that particular range.

With this information in hand it is possible to consider how representations that can be ordered may be constructed.

Construction of Abbreviated Mass Spectral Representations Suitable for Ordering. The representation for each unambiguous range is just the value of the integer mass for that range modulo 10 (e.g., mass 43 has the representation 3, and 57 has the representation 7).

The representations for those ranges that have been flagged as possibly ambiguous must be treated differently. They are given two possible representations: (1) the representation they