MONTANA STATE UNIVERSITY

Ion-ion, ion-molecule, and ion-electron reactions affecting the response of the electron capture detector to resonance electron capturing compounds
by Cornelius Andrew Valkenburg

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:
The electron capture detector (ECD) response to resonance electron capturing compounds is shown to be affected not only by the electron capture reaction, but also by the detailed nature of the subsequent competitive reaction dynamics. For aromatic molecules with a low electron affinity, two processes accompany the electron capture reaction. These additional processes are electron detachment from the molecular negative ion and the protonation of the analyte molecules. Results are presented in which the effects of these two undesired reactions are eliminated by the chemical doping of the detector make-up gas with a high proton affinity amine and an alkylmono-chloride. In the detector gas these dopants alter and stabilize the reaction dynamics and provide greatly increased sensitivity, linearity, and reproducibility of the ECD response to polycyclic aromatic molecules. For numerous PAH's, ECD responses were measured as a function of analyte concentration, detector temperature, dopant type, and dopant concentration. Identification of the charged species in the ECD plasma was accomplished by a specialized ECD interfaced to a quadrupole mass spectrometer.

Theoretical modeling of the constant current ECD response to resonance electron capturing compounds includes a kinetic model to explain the mechanism of response with the amine and alkyl monochloride dopants. The existing theoretical models of resonance electron capture in the ECD are Improved and supported by the results presented here.

Utilizing two ECD cells in series, experiments are described in which the tendency for regeneration of the parent molecule from the molecular anion by recombination with positive ions was investigated. The efficiency of molecular regeneration for molecules with a high electron affinity is determined from the ratio of the response in the tandem cells and the compound's known electron attachment rate. Theoretical models and results for compounds responding by a resonance and a dissociative electron capture mechanism are presented. Differences in the molecular anion behavior in the recombination reaction are discussed, as well as the application of this technique to tandem cell coulometry.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date___6-12-1987_____

To my wife Linda, and son Casey, for the joy and
optimism in life they have given me, and the hopes and
dreams we share for the future. To my parents, for their
unwavering support and faith in me.

VITA

Cornelius Andrew Valkenburg was born November 28, 1957 in Hamilton, Ontario, Canada, the son of Dutch immigrants, Cornelis and Johanna Valkenburg. He graduated in 1975 from Stevenson High School, Stevenson, Washington.

He majored in Biology at Carroll College in Helena, Montana, and graduated with honors in May of 1979. He then worked for one year as a chemical research technician with Oregon Graduate Center in Beaverton, Oregon. The year following was spent in research and development with Falls Chemicals in Great Falls, Montana.

In December of 1980 he was married to Linda Doig and they now have one child, Casey.

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He has accepted a position as a Senior Scientist with Lockheed, Las Vegas, Nevada, beginning February 1987.

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ABSTRACT

The electron capture detector (ECD) response to resonance electron capturing compounds is shown to be affected not only by the electron capture reaction, but also by the detailed nature of the subsequent competitive reaction dynamics. For aromatic molecules with a low electron affinity, two processes accompany the electron capture reaction. These additional processes are electron detachment from the molecular negative ion and the protonation of the analyte molecules. Results are presented in which the effects of these two undesired reactions are eliminated by the chemical doping of the detector make-up gas with a high proton affinity amine and an alkylmonochloride. In the detector gas these dopants alter and stabilize the reaction dynamics and provide greatly increased sensitivity, linearity, and reproducibility of the ECD response to polycyclic aromatic molecules. For numerous PAH's, ECD responses were measured as a function of analyte concentration, detector temperature, dopant type, and dopant concentration. Identification of the charged species in the ECD plasma was accomplished by a specialized ECD interfaced to a quadrupole mass spectrometer.

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Utilizing two ECD cells in series, experiments are described in which the tendency for regeneration of the parent molecule from the molecular anion by recombination with positive ions was investigated. The efficiency of molecular regeneration for molecules with a high electron affinity is determined from the ratio of the response in the tandem cells and the compound's known electron attachment rate. Theoretical models and results for compounds responding by a resonance and a dissociative electron capture mechanism are presented. Differences in the molecular anion behavior in the recombination reaction are discussed, as well as the application of this technique to tandem cell coulometry.

INTRODUCTION

Historical Review

The electron capture detector (ECD) for gas chromatography has seen considerable development in the last 30 years since its discovery by Dr. James E. Lovelock[1]. The detector is simple in construction and operation, is extremely sensitive to many compound classes, and has only recently been challenged by mass spectrometry in regards to detection limits for compounds to which it is sensitive. It is interesting to note that of those compounds to which the ECD is sensitive many are environmentally important pollutants of anthropogenic origin. The detector was pressed into service early in its stage of development because of its unparalleled sensitivity to compounds that were undetectable by the existing techniques of the time. Compounds of anthropogenic sources, particularly the halogenated pesticides, could be detected in sample concentrations as low as the parts per trillion level. The detector was instrumental in showing the ubiquity of pesticides and other man-made compounds throughout the biosphere. The effects of environmental contamination discussed in Rachel Carson's book, Silent Spring[2], could then be supported by an analytical method which was able to detect trace levels of persistent

pesticides such as DDT and their bioaccumulation in food chains.

A schematic design of a typical detector with a concentric coaxial anode is shown in Figure 1. It consists of a cylindrical volume through which gas chromatographic column effluents are passed. The walls of the detector are lined by a beta emitting radioactive source. Today, the most common radiation source is ^{63}Ni on platinum foil. The high energy beta particles ionize the detector gas, typically N_2 or Ar/10% methane, to produce positive ions and thermalized electrons. An electrically isolated electrode is placed within the detector and is biased to a positive electrical potential to collect the thermalized electrons within the cylinder. The flow of electrons (current) is then measured. The analytical signal is the decrease in current due to the removal of electrons by an analyte molecule capturing the thermalized electrons to produce a stable negative ion.

The sensitivity of the detector is related to the rate at which electron attachment to analyte molecules occurs. The attachment of an electron to a solute molecule is related to the electron affinity (EA) and the activation energy of the reaction. The larger the activation energy for attachment, slower is the attachment reaction. For those molecules with a significant activation barrier, higher detector temperatures will facilitate the attachment

Syringe   Capillary GC   ECD   Vent   Electrometer   Chart Recorder

Diluter ^{63}Ni Foil   Pin   Pulser   ω
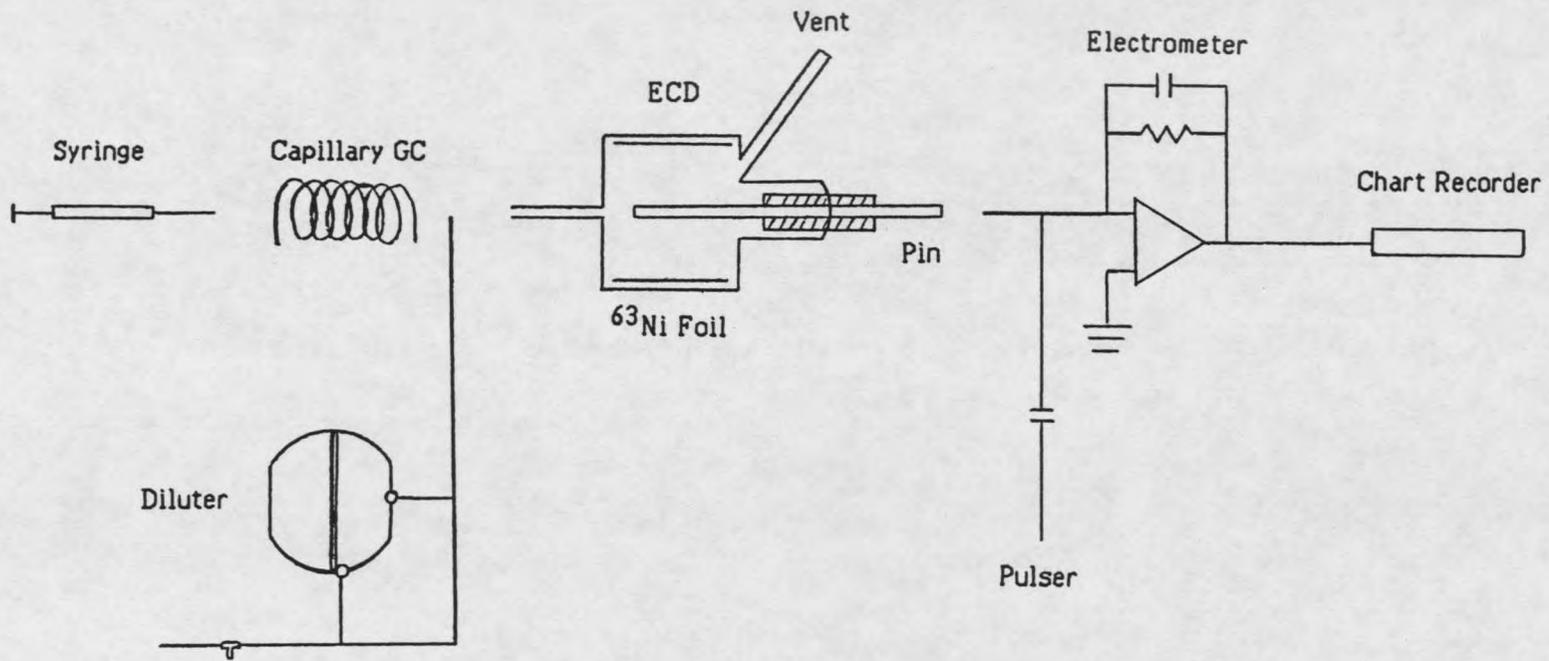
Fig. 1.   Schematic illustration of a fixed frequency
electron capture detector (ECD) configured for
chemical doping experiments.

of an electron. Therefore, at higher detector temperatures higher sensitivity is expected for molecules with a large EA, and a selective detector for compounds in this class is provided.

The first reported description and application of the ECD was by Lovelock in 1957[3]. This detector used a tritium embedded metal foil as a radiation source and was operated with a continuous +50 volts applied to the electrode. The direct current (DC) ECD was plagued with unusual responses, non-reproducibility, and non-linear calibration curves. Despite these limitations, the exceptional sensitivity of the detector propelled it into commercial development by instrument manufacturers, and it was widely used for trace residue analysis within a few years. The first reported application of the ECD to environmental problems was in 1961[4].

In the early 1960's Lovelock continued work on the development of the ECD and other ionization detectors. He suggested that the problems of reproducibility with the DC-ECD responses could be explained by contact potentials and space charge effects, and that a pulsed waveform potential should eliminate these effects[5]. He proposed that a pulsed ECD would allow for the electron capture reactions to occur under field free conditions and that the collection of negative ions would not complicate the response when pulse widths of small duration and amplitude were used.

Previous experiments on the amplitude of the voltage levels revealed that moderate voltages would collect the electrons and, with further increase in voltage levels, the less mobile negative ions would also be measured at the detector electrode[6]. Therefore, particularly with the pulsed ECD, the appropriate selection of voltage levels would result in the collection only of electrons. Developmental research was also conducted to determine possible types of carrier gases. Nitrogen or argon with 10% methane were selected as detector gases, because the electron capture response would not be perturbed by metastable reactions as found to occur with pure helium or pure argon gases. The pulsed ECD, where the response was taken as the difference in current (ΔI) with and without sample present, was found to improve the reproducibility of the detector, and gave linear responses over the first 10% of the dynamic range of the instrument.

In the mid 60's, Wentworth et al.[7] developed the first detailed explanation of the reaction dynamics occurring within the ECD, and improved the method of signal processing by using the response function, $(I-I^O)/I^O$, where I is the instantaneous current and I^O is the current in the absence of sample. This mode of signal processing gave linear ranges up to 90% of detector saturation, and facilitated the modeling of the reactions occurring within the EC cell. At pulse periods greater than 500 μsec the dynamics of the

reactions within the ECD were then described as a series of kinetically competitive reactions at equilibrium. However, this mode of signal processing required that the chromatographic conditions be quite clean, since only a small amount of an electron capturing impurity would significantly diminish the baseline standing current in the absence of sample.

Maggs et al.[6] greatly improved the method of signal processing for the pulsed ECD by developing the constant current (CC) ECD. In this mode of operation the cell current is held constant by a feedback loop to the pulsing portion of the circuit. The frequency of pulsing is increased to compensate for the electron loss processes due to analyte entering the cell. The signal measured is thus proportional to the pulse frequency. With this mode of signal processing the linearity of response is extended to 99% of detector saturation. The constant-current pulsed ECD is the one mode available on commercial GC-ECD systems used today.

Even with the improvements in the development of pulsed ECD signal processing, non-linear response versus concentration plots continued to be observed for some compounds. Within this group of compounds are the monochloroalkanes, the polyhalogenated hydrocarbons, and some of the polycyclic aromatic hydrocarbons (PAH's).

Polyhalogenated hydrocarbons are the compounds best suited for ECD detection since they have the fastest electron attachment rates and subsequently the highest molar sensitivities for the ECD. For these compounds non-linear calibration is caused by the significant proportion of sample destruction through the reaction with reagent electrons. This results in a detector concentration which is no longer proportional to the concentration of analyte eluting from the column. In 1983, Knighton and Grimsrud accounted for this effect with a new response function for the CC-ECD[9].

Monochloroalkanes were found to have high sensitivity in the low concentration region, but would quickly reach a limiting response which would not increase with larger concentration of sample[10]. Because they have moderate to small electron attachment rates, linear calibration was expected. Numerous explanations have been offered for the cause of this unusual behavior, yet the causative factor remains unknown. Studies on this interesting class of compounds will be presented in this investigation.

The PAH's are an environmentally important class of compounds due to man's uses of fossil fuels and their continual increased loading on the environment. Unfortunately, many of the PAH's, when analyzed in low concentration and/or with high detector temperatures, exhibit unusual peak shapes that are opposite to the normal

electron capture response, or have a complicated "W" shaped character to them[11,12]. These unusual peak shapes prevent accurate quantitation and unpredictable and non-linear calibration curves result. Since many of the PAH's have a low EA and poor sensitivity accompanied with the unusual responses, EC detection for these compounds is generally not favored.

Theoretical Modeling

Developments of theoretical models to explain the chemical dynamics within the ECD have paralleled the improvements in the processing of the detector signal. Wentworth et al.[7] were the first to give a detailed explanation of the chemical dynamics occurring within the pulsed ECD. The reaction models that will be presented here are based on reaction dynamics that were originally proposed by Wentworth, and will incorporate the most recent understanding of the reaction processes in the ECD.

These recently developed kinetic models have been applied to the responses of numerous compounds and explain the dynamics of the detector's responses for most compounds satisfactorily. However, for compounds which exhibit unusual responses and non-linear calibration curves, the current theoretical models are not effective in describing the reaction dynamics involved in the detector's response.

Two of the important issues in the debate concerning the ECD have been the distribution of charge density and whether or not charge neutrality exists. The current understanding of the charge distribution has been addressed by the use of a specialized ECD interfaced to a mass spectrometer[13,14]. The use of the atmospheric pressure ionization mass spectrometer (APIMS) has allowed the measurement of the positive and negative ions formed within the detector. The model favored here is that offered in 1980 by Gobby, Grimsrud, and Warden[15] and further supported by the work of Grimsrud and Connolly[16]. Their work was built on the understanding and observations of Wentworth et al.[7,17] and the APIMS observations of Siegel and Mckeown[18].

A summary of the current space charge model developed by Grimsrud et al. for the pulsed ECD is as follows. When ^{63}Ni radiation sources are used relatively uniform ionization throughout the cell is expected[16]. The application of short voltage pulses clears the cell of all electrons[7]. Positive ions left after a pulse are thought to create a space charge potential which is dissipated in time by space-charge-migration of the positive ions to the cell walls. The pulse itself does not measurably perturb the location of positive or negative ions in space. Over the range of pulse periods used in the CC-ECD, the total positive ion density remains relatively constant, since recombination of positive ions with electrons and negative

ions is approximately equal to losses by migration to the walls. The contribution of positive ion collection at the electrode is dependent on cell geometry and is not affected by pulsing or pulse polarity. It is dependent only on space-charge-driven-migration. Negatively charged species will be drawn towards the region of highest positive charge potential (in the center of the EC cell) to form a neutral plasma which contains an equal number of positive ions and negative ions. The plasma grows with time until the next pulse. Pulse periods less than 1000 μsec for normal cell geometry will be sufficient to prevent the charge-neutral plasma from expanding to the walls. The total number of negatively charged species within the detector at time "T" of the pulse will be a constant value. For example, a 50-volt pulse of 1 μsec duration, though sufficient to clear the detector of all electrons, will not remove the negatively charged ions from the charge neutral plasma. The kinetic equations modeling these reactions require that the negatively charged species be considered as populations rather than concentrations within the detector, since the negatively charged species are localized in the region within the charge neutral plasma.

From these studies on charge densities, better ECD geometries have been designed and improved interpretations of EC reaction dynamics were possible. With a better understanding of the ECD, limits for the frequency of

response in the CC-ECD could be established for optimum sensitivity and linear calibration curves.

The detector designed by Patterson[19] for the Varian 3700 series Gas Chromatographs, is an example of an ECD designed for small-bore capillary chromatography using the knowledge from this type of basic research to improve the detector's mode of operation. This small-volume detector was designed with a displaced coaxial anode so that the signal measured would only reflect the electron density. This was done by minimizing the collection of positive and negative ions at the electrode, normally a concern with a small-volume ECD necessary for capillary chromatography.

The reactions that are considered to be the most important in affecting the electron density within the electron capture detector are:

$$Beta\ particles + N_2 \xrightarrow{\ S\ } P^+ + electrons + Radicals \qquad (1)$$

$$AB + e^- \xrightarrow{\ k_1\ } AB^- \qquad (2)$$

$$AB^- \xrightarrow{\ k_{-1}\ } AB + e- \qquad (3)$$

$$AB + e^- \xrightarrow{\ k_d\ } A + B^- \ or \ A^- + B \qquad (4)$$

$$AB^- + P^+ \xrightarrow{\ R_1\ } Neutrals \qquad (5)$$

$$AB^- + X \xrightarrow{R_2} R^- + AB \qquad (6)$$

$$e- + P^+ \xrightarrow{R_3} Neutrals \qquad (7)$$

$$e- + Impurity \xrightarrow{k_b} Impurity^- \qquad (8)$$
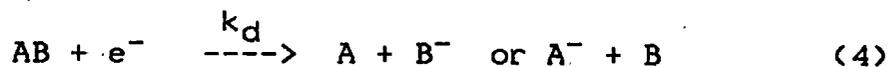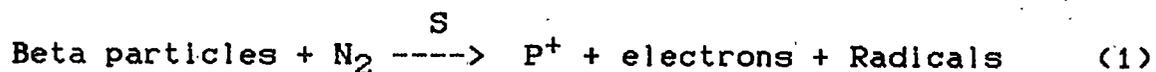
In reaction (1) beta particles react with carrier gas molecules to produce positive ions, radicals, and electrons. S is the rate of ion pair production. The positive ions formed are initially characteristic of the carrier gas but, through a series of rapid charge and proton transfer reactions, will eventually produce a terminal set of positive ions. These positive ions are characteristic of other neutrals with higher proton affinities than the carrier gas molecules[18]. About 35 ion pairs are formed per beta particle[15]. Reaction (2) is the attachment of a thermalized electron by analyte molecule AB, with k_1 as the second order rate constant of electron attachment. Reaction (3) is the electron detachment from the negative ion AB^-, with its rate of reaction denoted as k_{-1}. Reaction (4) represents the unimolecular dissociative electron capture of analyte AB to form a stable negative ion fragment with reaction rate k_d. Reaction (5) represents the recombination of negative ions with positive ions to produce neutrals with a recombination rate R_1. Reaction (6) is the loss of AB^- ions to compound X with a reaction rate R_2. Compound X will

include any compound or radical that may be reactive with the negative ion. It is included here to represent chemical dopants that will be discussed later in this investigation. Reaction (7) is the recombination of electrons with positive ions by recombination rate R_3. Reaction (8) is the loss of electrons due to column bleed and other carrier gas impurities with a reaction rate k_b. In the current theoretical models as applied to all of the above reactions, S, K_b, R_1, R_2, and R_3 are assigned constant values when the detector operating conditions are specified and stabilized.

The response of the detector is related to the ability of a molecule to capture an electron, and the stability of the negative ion formed. Because only the electron density is measured and the total number of negatively charged species is a constant value at time "T" of the pulse, the response of the detector's signal becomes a function of the number of negative ions relative to the number of electrons. This is assuming that the negative species in the detector each have the same rate of loss by recombination with positive ions. Therefore, the detector's sensitivity, which has been related to the electron attachment rate, must also include the fate and stability of the negative ion produced.

With the resonance electron capture of an electron, the system moves to a lower energy state, Delta G of this reaction is approximately equal to the EA of the molecule. The ion formed can dissipate this energy by collision with

buffer gas molecules within the detector. If the EA of the
molecules is not large, the negative ion formed by reaction
(2) can undergo simple electron detachment as depicted in
reaction (3). This process of detachment, if it proceeds at
a rate competitive with reaction (2), would result in a weak
and very small molar response for that particular compound.
The overall production of negative ions and the response of
the detector by this resonance electron capture process has
been related to the equilibrium of reaction (2) and (3)
combined[7,18,20]. For other systems, where reaction (3) is
not significant, the negative ion must be stable or
otherwise a dissociative electron capture mechanism, as
depicted in reaction (4), would occur. Typically, high
sensitivity and large molar responses are seen when
dissociative electron capture is operating. The major loss
process for a stable negative ion as depicted in reaction
(5) is the recombination of positive ions with negative
ions. Diffusion to the walls and ventilation out of the
cell can be neglected for all negatively charged species in
the space charge model, because these processes are slow
relative to recombination with positive ions.

The sum of the electron production and electron loss
process can be mathematically represented by these two
differential equations:

$$dN_{e-}/dt = S + k_{-1}N_{A-} - (k_1 n_A + R_3 n_{P+} + R_4 n_B)N_{e-} \qquad (9)$$

$$dN_{A-}/dt = k_1 n_A N_{e-} - (k_{-1} + R_1 n_{P+} R_2 n_{Rad} + k_d) N_{A-} \quad (10)$$

A capital N denotes a population and a small n denotes concentration. To obtain a numerical solution, the rates of the reactions, and the ion and molecule densities must be known.

Experimentation on the electron capture responses of CH_3I and CCl_4, for example, illustrates the importance of other reactions occurring within the ECD in addition to the direct electron capture process[21]. Indirect electron capture processes are important in interpreting the response differences between these two compounds.

The behavior of CCl_4 in the ECD is explained by a dissociative electron capture mechanism[22], with negative ion APIMS studies demonstrating the formation of Cl^-. The production of the stable Cl^- ion will, upon recombination with positive ions, produce a neutral species (HCl) which does not undergo further electron attachment[23]. The remaining neutral radical, $\cdot CCl_3$, is not believed to be reactive to electrons based on the APIMS studies of CCl_3Br [24]. The reaction of a CCl_4 molecule with an electron should then occur only once. Measuring the numbers of electrons reacted with a quantity of analyte molecules, along with the efficiency of the reaction, has been the basis for using the ECD as a coulometric cell[22,25,27]. Up to 90% efficiency can be expected from the reaction of CCl_4 with electrons, and

reasonably accurate analytical results have been obtained

using tandem cell coulometry[22,26].

The molecule CH_3I has a smaller k_1 value[28] than CCl_4 [29]

and therefore would be expected to have a slower electron

attachment rate and smaller molar response sensitivities

based on the above mechanism. However, hypercoulometric

results were found by tandem ECD cell coulometry. This

hypercoulometric result has been explained by the occurrence

of an additional reaction sequence[21]. The APIMS study

showed that CH_3I produces the stable negative ion I^- by

dissociative electron capture. Upon recombination with

positive ions, I^- produces HI which is thermodynamically

capable of undergoing further electron attachment and

regeneration of the I^- ion for recycling by the recombi-

nation/electron attachment process. This unusual reaction

sequence allows for an additional source of electron loss to

each analyte molecule and demonstrates the significant

impact that reactions other than electron capture may have

on the sensitivity of the ECD. Numerous studies, including

this investigation, have been done to determine the

importance of individual reactions and mechanisms involved

in the response of the detector.

Part of this study will examine a similar recombina-

tion/regeneration sequence to that just mentioned. It will

differ in that it will examine the importance of parent

molecule regeneration, where the molecular species being

studied is regenerated from the molecular anion by recombination with positive ions. Also to be examined in this investigation is the relationship between reactions (6) and (7) and the "W"-shaped peaks of low-EA PAH's. To understand these relationships a detailed examination of the existing theories as applied to resonance electron capture will be made.

A recent publication by Zlatkis et al.[20] discusses how the mechanism of response can be determined from the molar response of a compound relative to the operating detector temperature. Generally, for a compound responding by a resonance electron capture mechanism, highest molar responses are favored by the lowest detector temperature. This results from the higher electron detachment rates (reaction 3) as temperature is increased. A dissociative process is implied by an increase in molar sensitivity with increasing temperature.

In their model, Zlatkis et al. describe three different regions that can be observed when the molar response, (R), for compounds is plotted as ln $RT^{3/2}$ against 1000/T, where T is the temperature in degrees Kelvin. They describe an alpha, beta, and a gamma region in these plots; the alpha is where $k_{-1} > R_1[+] > k_d$, the beta region is where $R_1[+] > k_{-1} > k_d$, and the gamma region is where $R_1[+] > k_d > k_{-1}$. The alpha region describes resonance electron capture, and when plotted, gives a positive slope with a common Y-intercept

for compounds of similar structure[7,30]. The beta region
describes the process where electron detachment is not
competitive with the rate of recombination between positive
and negative ions. That is, resonance electron capture is
occurring, yet the negative ion is considered to be stable
to detachment relative to the negative ion loss rate by
recombination with positive ions. The beta region is
expected to give a negative slope. The gamma region
describes the dissociative electron capture process as the
dominant force in affecting the detector's response. An
increase in detector temperature tends to increase the
molecules instability, and favors further dissociation of
chemical bonds. Often, the fragment ion is more stable than
the molecular negative ion and plots with very steep
negative slopes are then observed. When steep negative
slopes are not seen, thermodynamic calculations or results
from APIMS studies must be used to distinguish between
stable resonance electron capture and dissociative electron
capture processes.

Though the Zlatkis model requires a number of assump-
tions, it has aided in the understanding of the mechanisms
of response and, indeed, the modeling does agree with the
experimental observations. Some of the assumptions used are
as follows:

1) The pulse frequency is directly proportional to the electron density and equations derived for electron density will apply to the CC-ECD.

2) Those observations and assumptions previously discussed for the space charge model are also applied here.

3) A steady state is reached for all charged species and the reactions can be described by kinetically competitive reactions at equilibrium.

4) The only temperature dependent rates of reaction are k_{-1} and k_d. All of the other reaction rates, including the electron attachment rate, k_1, are temperature independent. The electron attachment rate is considered temperature independent, since molecules with a positive EA would have a very low energy of activation for ionization to occur Therefore, ionization should not be assisted by temperature.

Selectivity and Chemical Doping

Recent advances in capillary gas chromatography and the use of selective detectors with high sensitivity have been a great aid to analysts. The advantages of selective detectors for gas chromatography are especially evident in environmental analyses. Complex environmental samples can produce extremely complicated chromatograms with a universal detector such as the flame ionization detector (FID), making

detection of a low-concentration target compound very
difficult if the baseline is complicated with coeluting
compounds. The simplicity of the ECD and its associated
electronics, as well as its sensitivity and selectivity to
many compounds of environmental interest, have brought about
its widespread use in trace residue analysis. The fact that
many environmentally important compounds are both mutageni-
cally active and sensitive to ECD detection make this detec-
tor particularly important to trace residue monitoring.

The selectivity of the ECD has also limited its
application to those areas of trace environmental analysis
for compounds in which the ECD is sensitive. For those
compounds to which the ECD is not sensitive, other selective
gas chromatographic detectors must be used. Other selective
detectors such as the photoionization, flame photometric,
flameless alkali, and alkali-flame ionization detectors have
been successfully used in environmental laboratories, each
being selective to particular classes of compounds. These
selective detectors, including the ECD, and others, have
recently been reviewed and their detection abilities and
limitations have been well described[31].

None of the other detectors, with the exception of mass
spectrometers, have the ultimate detection limits of the
ECD. The mass spectrometer approaches the sensitivity and
detection limits that the ECD has for certain high EA
compounds, but these limits are only being realized by

efficient research grade instruments operated by trained technicians applying some of the more recent developments in alternate ionization techniques. With its capability of mass filtering and various chemical ionization procedures, the mass spectrometer is considered to be the most universal and selective detector. Application of the mass spectrometer to environmental analyses has been extremely useful, although under its normal mode of operation with electron impact ionization (as currently required by the U.S. EPA), it too is limited in distinguishing isomers for some classes of compounds. The other selective detectors are more cost effective than the highly sophisticated mass spectrometer and for this reason their use is often preferred.

One of the requirements for the proper operation of the electron capture detector has been the need for high purity detector gases free from electron capturing impurities. Oxygen, commonly found in many carrier gases, was noted to destroy the standing current of the ECD. Therefore the carrier gas and make-up gas required effective oxygen scrubbers for normal ECD operation. In the early 1970's Van de Wiel and Tommassen[32] noted that when oxygen was present in the detector gas, not only was there a loss in baseline standing current, but the compound n-butyl bromide gave a response of larger magnitude. Grimsrud and Stebbins[33], capitalizing on this observation, intentionally doped the ECD with O_2 to cause alterations in the

selectivity of the detector and reported significantly
enhanced response values for a number of compounds. In
their mechanism proposed to explain these responses they
found that in addition to the reactions already occurring
within the ECD they could rationalize the enhancements by
adding these reactions:

$$O_2 + e- \rightleftharpoons O_2^- \qquad (11)$$

$$O_2^- + AB \longrightarrow \text{Stable negative ions and Neutrals} \qquad (12)$$

Reaction (11) depicts the resonance electron capture of
O_2 to produce the superoxide anion O_2^-. In reaction (12),
O_2^- is reacting with neutral unreacted solute molecules to
produce stable negative ions. This happens in addition to
the normal electron capture reaction. One ion commonly
observed in the APIMS spectrum of O_2-doped PAH's is the
$(AB + O)^-$ ion[34]. The O_2^- lost by reaction with analyte is
replaced by the kinetic equilibrium depicted in reaction
(11). The overall effect is that an increased rate of
electron loss is observed and a larger response is predicted
for some types of analytes in the ECD. It is interesting to
note that the sensitized response to analyte does not
involve direct reaction with the electron, but rather is an
indirect electron capture process. Though the overall
response to analyte is quite complicated for the O_2
sensitized response, the kinetic theory and its mathematical

derivations have been worked out[35]. Briefly discussed, the normal electron capture response will remain effective in the presence of O_2 with the sensitization dependent on the remaining amount of unreacted neutrals and their rate of reaction with O_2^-. Grimsrud et al., presented thermodynamic considerations on the reactions of different AB-type molecules with O_2^- [34].

With O_2 doping, the selectivity of the detector has been altered to include an even larger number of compounds. Some of these compounds previously exhibited little or no detection sensitivity. Linear and near-linear calibration curves have resulted, and an improved sensitivity for many compounds is easily seen in their chromatograms. The fact that compounds and their isomers are unique in their enhancement values, identification based on GC retention times and the enhancement levels is possible[36,37]. This doping scheme has been manipulated in a variety of ways, with isomer identification made possible even for coeluting peaks[37]. The O_2 sensitized ECD has been applied to the monitoring of methyl chloride in the atmosphere[38], and has also demonstrated its applicability to the analysis of many low concentration PAH's and their isomers[36,37].

Realizing that the reaction chemistry occurring within the ECD could be altered by chemical doping of the detector gas, and that responses could be generated by indirect electron capture, Phillips et al. developed N_2O doping of

the ECD[39]. They termed this selective electron capture sensitization (SECS). Nitrous oxide doping works in a very similar manner as O_2 doping and is explained by an equilibrium reaction sequence involving electrons. The reaction is driven to the right when the reagent ions produced react with the analyte molecules. The reagent ion thought to be of primary importance in the reaction with analyte is the O^- ion. Because the reagent ion is different than the one theorized for O_2 doping, the N_2O doping scheme predicts sensitization to differing types of compounds. The level of sensitization is highly dependent upon the neutral's ability to react with the O^- ion.

The ECD has been very important to trace residue analysis in environmental applications and through selective sensitization it has been able to respond to additional compound classes. Many difficult problems have been overcome with this simple, yet sensitive detector. Through careful characterization of the reaction dynamics and chemical doping possibilities, it is possible that many more compounds can continue to be analyzed by this increasingly versatile detector.

RESEARCH OBJECTIVES

This study was developed to give further consideration to the chemical dynamics occurring within the pulsed ECD. Numerous others have studied the resonance electron capture process and reasonable working models have been developed for many compounds as was summarized in the previous section[7,17,20,30]. The models previously generated for resonance electron capture were successful in explaining the temperature dependence and the mechanism of response[20,30]. These models utilized simplifying assumptions concerning the effects of the recombination processes to describe mathematically the signals observed, however these assumptions may not necessarily be valid for all cases. The present investigation will evaluate the assumptions that were previously made by testing the theoretical models against chemical systems which do not agree with the predicted linear calibration curves.

To determine how these anomalous results come about for some compounds, all of the reactions known to be occurring within the ECD were individually reviewed. Compounds were analyzed and chemical dopants were selected to demonstrate the various reactions in relation to the measured response of the ECD. Previously derived mathematical models required

steady-state approximations of the negative ion density to calculate the expected electron density. The calculated electron density was then related to a pulse frequency in the CC-ECD[8]. Because the normal response of the CC-ECD to an analyte is measured by means of an increase in the pulsing frequency, steady-state approximations as applied to long pulse periods may no longer be valid at higher frequency responses. Computer modeling of the resonance electron capture theories was done to examine the assumptions regarding the validity of steady-state approximations. Computer modeling was chosen to examine this relationship since the variables can easily be changed. The reiterations in the calculations necessary would otherwise be quite tedious by hand.

Another of the objectives of this study was the examination of positive ion/electron recombinations in the ECD reaction dynamics. The "W"-shaped response observed for some PAH's is believed to be the result of a competition between the positive ion/electron recombination reaction with the weak electron capture response. Anthracene and several other low EA PAH's, were carefully characterized according to their effect on the positive ion nature of the ECD. Using APIMS instrumentation, the response of the ECD to PAH's was examined relative to the positive ion composition of the ECD. Alterations in the positive ion

nature were through the use of chemical dopants with any changes in the measured ECD response noted.

A survey of chemical dopants was also done to see if some of these may possibly eliminate, enhance, or stabilize the reactions and/or the rates of the reaction that might affect the electron density during the elution of a sample. With the use of chemical dopants, it was hoped that the response of the ECD could be made to reflect only the electron capture reaction of the analyte by preventing any indirect electron loss or production reactions involving the analyte molecule. For example, a dopant that would preferentially react with trace O_2 rather than with the analyte should eliminate any sensitization of the analyte response caused by trace O_2.

In the last portion of this study, the importance of positive-negative ion recombinations was examined. This investigation, in particular, looked at the fate of a resonance electron capturing molecule after it had undergone electron capture followed by a positive ion recombination. The requirements for this analysis differed, in that tandem ECD cells were used, and the responses of higher EA compounds were measured. The tandem cells are two matched ECD cells hooked in series with one another. The signals from each cell are individually measured. Interpretations of the signal intensity and the ratios between the two cells are compared to literature values of the electron capture

rate constants. In theory, if the parent molecule is regenerated from its anion by the recombination with a positive ion, a response similar to that of CH_3I, should be observed in these detectors that have been used and characterized for coulometric analysis.

EXPERIMENTAL

Varian Instrumentation

A Varian 3700 gas chromatograph equipped with a flame ionization detector and a ^{63}Ni constant current electron capture detector was used to survey the aromatic hydrocarbons and determine their sensitivity to chemical doping schemes. The commercial EC cell on the Varian 3700 utilizes a displaced coaxial anode and is a Patterson engineering design. It has been well described elsewhere[19]. Design advantages of the Varian Aerograph ECD over conventional coaxial electrode geometry give it decreased levels of background currents from positive and negative ions, an increase in sensitivity through a smaller cell volume, and improved enhancement values to chemical doping techniques[40].

Analytical signals from the electrometer were recorded on a Varian 9176 strip chart recorder. Peak heights were measured with a ruler and converted to a frequency response $(f-f^o)$. Baseline levels of frequency were constantly monitored, and only when conditions were optimized with acceptable baseline levels would experiments be logged.

The ECD make-up gas was high purity nitrogen which was first passed through a water removing ($CaSO_4$ and molecular sieve 5A) trap followed by an oxygen removing (Alltech Oxy

Trap) trap. The cleaned N_2 gas was then sent through a flow controlling needle valve (Swagelock Flow controllers) before entering a 3.3-liter stainless steel dilution vessel. The output of the dilution vessel was connected to the make-up gas lines at the base of the detector housing. Overall flow rate of the gases through the detector was monitored by a soap-bubble meter connected to the exhaust of the detector, the flow rate being generally set to 40 ml/min.

For the gas chromatographic analysis of the aromatic hydrocarbons, samples were injected via a splitless injection port into a 30 meter, 0.32 mm ID., DB-1 fused silica capillary column (J & W Scientific). Carrier gas velocity through the column was maintained by measuring the time for the elution of the oxygen and solvent peak. This elution time was set to a fixed value by varying the pressure at the head of the column. The capillary column was necessary for the separation of the compound's response from other EC sensitive impurities in the sample. The splitless injection port temperature was generally held at 210° C for most of the PAH's. Detector temperatures were varied according to the nature of the experiment, but were always higher than the maximum column temperature to prevent contamination of the ^{63}Ni foil by condensation of column effluents.

Samples were first run with a flame ionization detector to determine the best chromatographic operating conditions.

FID retention times were characterized for a number of compounds and relative retention times were used to assign a signal in the ECD chromatogram to the response of the compound. It was necessary to use the FID first, since the normal ECD chromatogram observed for many of the PAH's studied were complicated by ECD responsive trace impurities in the weakly responding compound standards. Sample sizes of approximately 100 ng were used for the FID analysis. Chromatographic conditions chosen were those that gave good separation from the solvent, gaussian shaped peaks, and reasonable retention times. Generally, temperature programming was found to be the most effective method.

Hewlett Packard Instrumentation

A Hewlett Packard 5890A gas chromatograph (HPGC) was equipped with a ^{63}Ni constant current pulsed ECD using a conventional coaxial anode design. An EC cell of conventional design and geometry was chosen since fundamental studies on the physical processes and reaction dynamics have been predominately done with detectors of this design. Response enhancement values and their temperature dependence could then be better interpreted using a detector of conventional design. Information about the EC cell used in the HP-5890A was revealed through personal communications with Hewlett Packard engineers. The detector has a cell volume of 2.8 cm^3 and is lined with a ^{63}Ni foil of 12 ± 0.5

millicuries which produces a standing current of 8.1 to 9.9 nanoamps. The electrometer is a constant current design and uses a pulse width of 0.75 μsec. The reference current is set to obtain a baseline pulse frequency of 400 hz for either N_2 or Ar/CH_4.

The HP gas chromatographic system consisted of carrier and make-up gases of ultra high purity N_2 or $Ar/10\%$ CH_4 mixtures. Oxygen and H_2O were removed by conventional techniques as previously described. The column used was a 6-ft., .57 mm ID., SE-30 column (Hewlett Packard). The column flow rate was set to 10 ml/min using the same gas that was used for the make-up gas in the detector. Overall flow rate through the detector with the make-up and carrier gas was generally set to 40 ml/min. The glass-lined splitless injection port and make-up gas lines were adapted to the large-bore capillary column with a kit provided by the instrument manufacturer. The installation of the dilution vessel and carrier gas scrubbers were the same as described for the Varian GC system. When using the N_2 or Ar/CH_4 detector gases, reference currents for the commercial electrometer were adjusted to compensate for the differences in the carrier gases. Retention times of the samples analyzed on the HP GC-ECD system were identified by their chemically enhanced responses as determined for compounds that were enhanced on the Varian GC-ECD system.

Analytical signals from the HP commercial electrometer were measured with an Omniscribe 1 mv strip chart recorder and peak areas were integrated with an Apple II+ computer fitted with an Issacs Cyborg A to D interface. Control of the A to D interface and digitization of the data was accomplished with an Appligration software program. Range and attenuation of the electrometer was set for maximum sensitivity of the response.

Atmospheric Pressure Ionization Mass Spectrometer (APIMS)

The APIMS is a specialized ECD capable of measuring an ECD function as well as the positive and negative ions existing within the detector. This particular system has been completely described elsewhere[14], and only a brief review relative to the experiments in this study is presented here. A schematic diagram of the EC ionization source is given in Figure 2. The walls of the detector are lined with a 6-mCi ^{63}Ni foil which emits beta radiations producing positive ions, negative ions, and thermalized electrons. The ions are sampled in the source at a flow rate of 4 ml/min by a 20-μm aperture into a differentially pumped vacuum region containing a quadrupole mass filter with a channeltron ion counting detector. Differences in voltage potential biases allow the mass filter and channeltron detector to be set for positive or negative ion
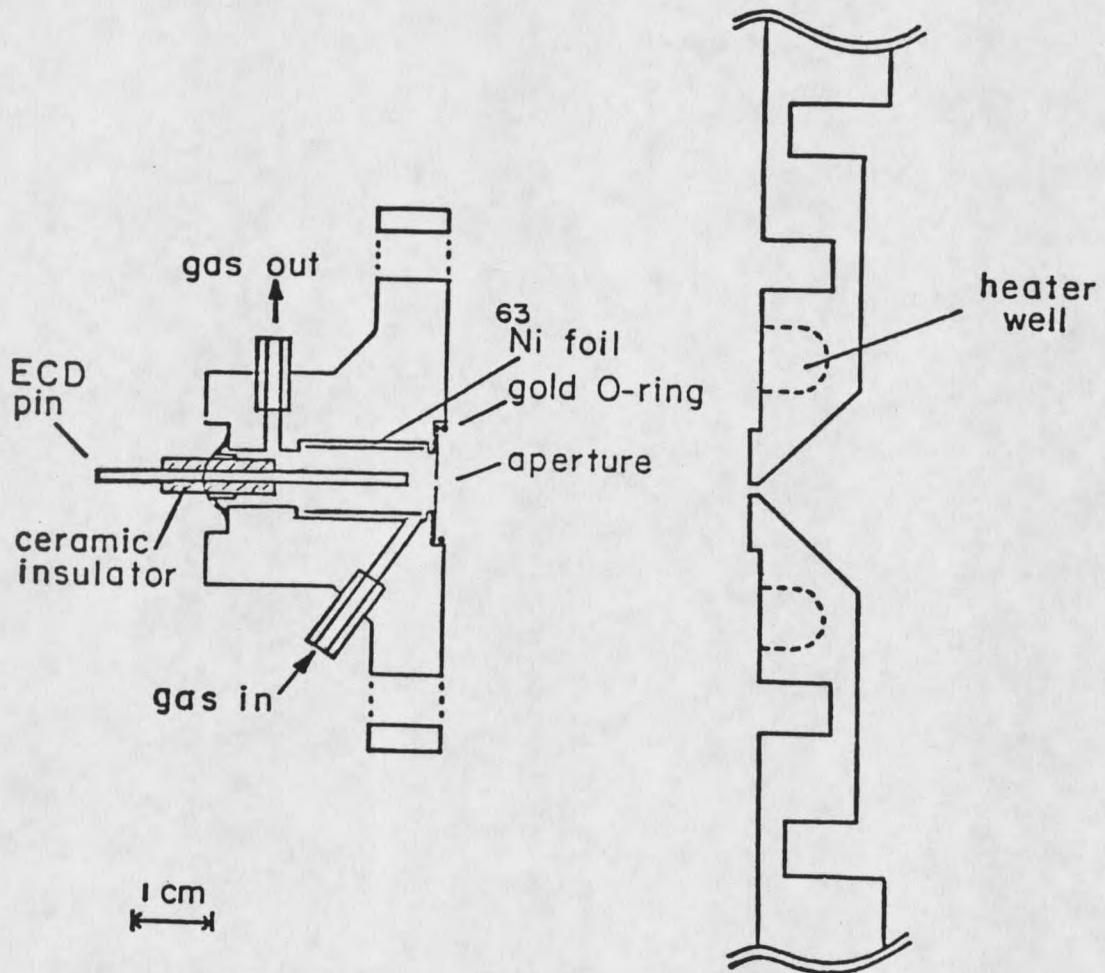
34

Fig. 2.   Specialized ECD/atmospheric pressure ionization
          mass spectrometer (APIMS) source used for the ECD
          signal and ion measurements.

detection. The stainless steel pin that protrudes through the center of the source in Figure 2 is the electrode by which the ECD function is obtained. Pulses of +50-volts and 1 μsec duration are applied to the pin with a constant frequency of 200 msec using an electrometer circuit designed by Grimsrud et al.[41]. The analytical signals from the source and the ion detector were recorded on a 2-pen Omniscribe strip chart recorder.

Positive ion signals were measured simultaneously with the ECD function, but the pulser was turned off for measurements of the negative ion signals[42]. Mass spectra were obtained by scanning of the quadrupole mass filter with identification of each mass by single ion monitoring.

To introduce samples into the ion source a simple isothermal gas chromatograph was utilized. The gas chromatograph was equipped with a standard injection port and a 1/8 in. x 1.5 ft. stainless steel column packed with 4% OV-101 on Chromosorb W. High purity N_2 was passed through O_2 and H_2O removing traps and then through a 3.3-liter stainless steel dilution sphere. This arrangement was then connected to the head of the column. No make-up gas lines were necessary since flow rates through the packed column were adequate. The effluent from the GC was introduced into the APIMS ion source by means of a heated 1/8 in. x 6 in. glass lined stainless steel transfer line.