



Responses and mechanisms of positive electron affinity molecules in the N<sub>2</sub> mode of the thermionic ionization detector and the electron capture detector  
by Christopher Stephen Jones

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:**

Very little knowledge has been acquired in the past on the mechanistic pathway by which molecules respond in the N<sub>2</sub> mode of the thermionic ionization detector. An attempt is made here to elucidate the response mechanism of the detector. The basic response mechanisms are known for the electron capture detector, and an attempt is made to identify the certain mechanism by which selected molecules respond. The resonance electron capture rate constant has been believed to be temperature independent, and investigations of the temperature dependence of electron capture responses are presented.

Mechanisms for the N<sub>2</sub> mode of the thermionic ionization detector have been proposed by examining the detector response to positive electron affinity molecules and by measurement of the ions produced by the detector. Electron capture mechanisms for selected molecules have been proposed by examining their temperature dependent responses in the electron capture detector and negative ion mass spectra of the samples. In studies of the resonance electron capture rate constant, the relative responses of selected positive electron affinity molecules and their temperature dependent responses were investigated.

Positive electron affinity did not guarantee large responses in the N<sub>2</sub> mode thermionic ionization detector. High mass ions were measured following ionization of samples in the detector. Responses in the electron capture detector varied with temperature and electron affinity.

Results support a mechanism for the N<sub>2</sub> mode of the thermionic ionization detector where a high mass ion is formed during decomposition of the sample and reaction with inorganic species. Resonance electron capture rate constants are not temperature independent, and electron mechanisms were elucidated. Electron capture responses do not bear a strict dependence on electron affinity.

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MOLECULES IN THE N<sub>2</sub> MODE OF THE THERMIONIC  
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CAPTURE DETECTOR

by

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APPROVAL

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Christopher Stephen Jones

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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## VITA

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## ABSTRACT

Very little knowledge has been acquired in the past on the mechanistic pathway by which molecules respond in the  $N_2$  mode of the thermionic ionization detector. An attempt is made here to elucidate the response mechanism of the detector. The basic response mechanisms are known for the electron capture detector, and an attempt is made to identify the certain mechanism by which selected molecules respond. The resonance electron capture rate constant has been believed to be temperature independent, and investigations of the temperature dependence of electron capture responses are presented.

Mechanisms for the  $N_2$  mode of the thermionic ionization detector have been proposed by examining the detector response to positive electron affinity molecules and by measurement of the ions produced by the detector. Electron capture mechanisms for selected molecules have been proposed by examining their temperature dependent responses in the electron capture detector and negative ion mass spectra of the samples. In studies of the resonance electron capture rate constant, the relative responses of selected positive electron affinity molecules and their temperature dependent responses were investigated.

Positive electron affinity did not guarantee large responses in the  $N_2$  mode thermionic ionization detector. High mass ions were measured following ionization of samples in the detector. Responses in the electron capture detector varied with temperature and electron affinity.

Results support a mechanism for the  $N_2$  mode of the thermionic ionization detector where a high mass ion is formed during decomposition of the sample and reaction with inorganic species. Resonance electron capture rate constants are not temperature independent, and electron mechanisms were elucidated. Electron capture responses do not bear a strict dependence on electron affinity.

## INTRODUCTION

Gas Chromatographic Detection

The technique of gas chromatography (GC) was first demonstrated experimentally in the early 1950s (1). Since that time, the growth in applications of the procedure has been so great that the technique is now the most important and widely used of all the column chromatographic methods. An active area of research since the discovery of this technique has been the study of detection devices which respond to chemical compounds that elute from the gas chromatographic column. The function of a GC detector is to produce a measurable electrical signal by interaction with these compounds. In addition to signaling the moment of elution of a given compound, the detector provides the means by which the quantity of the chemical can be electronically measured and recorded.

Detection devices that produce an electrical signal by directly converting incoming compounds to gas phase ions have seen widespread success as GC detectors. Two devices that employ the formation of negative ions to produce a usable analytical signal are the  $N_2$  mode of

the thermionic ionization detector (TID-N<sub>2</sub>) and the electron capture detector (ECD). These are both selective GC detectors, responding only to compounds with molecular structures conducive to the formation of negative ions. The ECD has been especially popular for the selective detection of halogenated compounds, while the TID-N<sub>2</sub> has generally been used for the selective detection of nitrated and halogenated compounds. It was thought at the onset of this study that investigation of these two negative ionization techniques would produce converging results. Results, however, diverged somewhat, and the two techniques are quite distinct from one another.

#### Thermionic Ionization Detection

All methods of ionizing GC effluents involve the production of gas phase ions within the working volume of the GC detector by the application of energy in one form or another. In a TID, this energy is provided by a hot, solid surface known as the thermionic source. This thermionic emitter is positioned inside the detector housing so that samples eluting may impact the source surface, and any ionization produced is measured by an adjacent collector anode.



In 1964 Karmen and Giuffrida (2, 3, 4) demonstrated that a conventional flame ionization detector (FID) could be selective to halogen- and phosphorous-containing organic molecules if the flame was doped with an alkali salt. The thermionic source used in this study consisted of a wire mesh that had been treated with sodium hydroxide or sodium sulfate and subsequently heated in a hydrogen-air flame. Since that time, TIDs which use heated, alkali-impregnated sources have been widely used for the selective GC detection of nitrogen- and phosphorous-containing compounds (5-10). In these applications the thermionic source is heated either electrically in a reactive flameless atmosphere of hydrogen and air or by a hydrogen-air flame.

Many different thermionic emitter source compositions and configurations have been studied. These include the use of alkali reservoirs at the bottom (11) or above the top (12) of the flame, application of a rubidium silicate salt tip (10), a potassium chloride pellet (5), a cesium-ceramic cylinder with a nickel sub-layer (13), a rubidium silicate bead (7, 14, 15) and a rubidium-ceramic bead (8). Currently, all commercial TIDs are supplied with a thermionic emitter of one of the four following types:

- (a) a homogenous alkali-glass bead formed on a loop of bare platinum wire (14);
- (b) a ceramic cylinder core coated with an alkali salt activator and embedded with a heating coil (16);
- (c) multiply-layered cylindrical ceramic with a conducting sub-layer of nickel-ceramic that covers a loop of nichrome heating wire and a surface layer of alkali-embedded ceramic (13, 17);
- (d) a homogenous alkali-ceramic bead on a nichrome heating wire (8,9,18).

The sensitivity and selectivity of these nitrogen-phosphorous selective detectors depend upon the composition of the atmosphere surrounding the source, the source temperature, the hydrogen flow rate and the polarization voltage imposed upon the detector electrodes (9, 19, 20). Modern models generally employ thermionic sources composed of either a cesium- or rubidium-impregnated ceramic material. The ceramic sources are more resistant to melting than are the silicate sources, and the use of the higher molecular weight alkali metals allows a lower effective work function of the source surface to be established (8). The work function in this

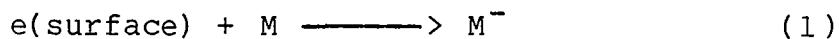
case is defined as the energy required to transfer an electron from the source surface to the gas phase (21).

The selective response mechanism of the flameless TID to nitrogen- and phosphorous-containing organic compounds has been explained (8) in terms of a lowering of the effective work function of the thermionic surface due to the presence of electronegative species at the gas-solid interface. The response is thought to occur due to electron transfer from the low work function surface to highly electronegative radical species, possibly  $CN$ ,  $NO_2$  and  $PO_2$ , which are believed to be produced in the reactive gaseous boundary layer adjacent to the hot surface. It has been pointed out that this mechanism may not be operative for all the nitrogen-phosphorous selective detectors. In detectors where a flame is employed, it is fairly well established that the mechanism is a gas phase ionization process (22-24). The heated alkali impregnated source generates gas phase neutral alkali atoms, and the response is due to an electron transfer from the alkali atoms to the sample. These detectors are sometimes called alkali flame ionization detectors to distinguish them from the thermionic process, which is defined as the emission of electrical charge from a heated solid surface (25).

More recently, Patterson and coworkers (13, 26) have shown that a flameless TID can also be used for the selective detection of certain electronegative molecules in an inert atmosphere of nitrogen. Using a highly cesium-enriched ceramic thermionic source and a relatively low surface temperature of about 400° to 600° C, Patterson and coworkers observed selective responses to certain classes of molecules, such as the dinitrotoluenes. Optimization of response and selectivity for this mode (TID-N<sub>2</sub>) requires a thermionic surface of very low work function (27), and this is accomplished by using a high cesium concentration in the source surface (28). Sub-picogram detection limits for these nitro-organics has been reported (27) for this mode of the TID, along with a very high specificity factor of 10<sup>8</sup> versus alkane hydrocarbons. Subsequent use of this detector for the specific analysis of nitrated polycyclic aromatic hydrocarbons in environmental samples has also been reported (29).

In this version of the TID, the analyte molecule itself appears to carry with it all of the ingredients necessary for occurrence of a surface-to-gas phase electron transfer. Beyond this general deduction, however, no more precise, descriptive evidence of the

surface ionization mechanism has been offered. Possible mechanisms by which the TID-N<sub>2</sub> mode responses might occur have been envisioned (28, 30). The first and simplest one is by direct electron transfer from the surface to the molecule to form a molecular negative ion as shown by Reaction 1.

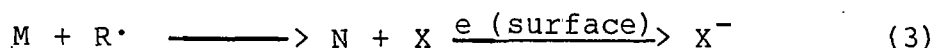


This possibility is a reasonable one in view of the fact that the compounds to which the nitrogen mode is known to respond have positive electron affinities (32). Another plausible mechanism, shown as Reaction 2,



is that the analyte molecule M is thermally decomposed on the hot surface of the thermionic source to form species N and X, one of which has a high electron affinity and abstracts an electron from the surface to form the negative ion X<sup>-</sup>. This possibility is attractive if one considers species X in Reaction 2 to be NO<sub>2</sub>. The NO<sub>2</sub> radical has a very high electron affinity (31, 32) and

specificity of response has been previously demonstrated to nitroaromatic hydrocarbons (13, 26, 29). An additional possibility is worthy of consideration since it is thought to be operative in the nitrogen-phosphorous mode of the TID. That is, gas phase radicals at the gas-solid interface might chemically alter the analyte molecule so as to again form an intermediate species X, which abstracts a surface electron as shown in Reaction 3.



While the presence of reactive radical species,  $R\cdot$ , might seem unlikely in an atmosphere of pure nitrogen, it is nonetheless possible due to either the presence of impurities in the nitrogen or due to the generation of reactive radical species from the analyte itself.

#### Electron Capture Detection: Design and Operation

Gas phase electron capture reactions have played a very central role in environmental analysis and analytical chemistry for nearly three decades. These reactions have been used for trace analysis in GC since Lovelock described the first ECD in 1958 (33). Currently the ECD

and the FID constitute the most widely used detection devices for gas chromatography. Following the introduction of this GC detector, it was soon recognized that the device was very sensitive and selective to certain groups of compounds, namely those that contain structures strongly conducive to the formation of negative ions. Many of these compounds are of environmental importance, and the ECD quickly became a useful tool for environmental analyses (34), even though the detector was very temperamental and the basic processes occurring within the cell were poorly understood. Today the detector remains a very important tool for the selective detection of pesticides in the environment (66), halocarbon aerosols in the atmosphere (67, 68), toxic chemicals in the workplace and disposal sites (69), drugs in human beings (70) and biologically active compounds in physiological fluids (70).

Like the TID-N<sub>2</sub>, the ECD functions by producing negative ions. The energy necessary for this ionization is derived from beta particles emitted by a radioactive source. The ECD is unusual among ionization detectors in that a high level of ionization is present within the cell even in the absence of analyte molecules (27). It is also unique in that it functions by redistributing electric

charges between different types of ionized species instead of changing the total amount of electric charges within the detector (27). The beta particles emanating from the radioactive source in the ECD cell collide with carrier gas molecules, resulting in the formation of secondary electrons, positive ions and radical species within the atmosphere of the detector cell. The secondary electrons are thermalized by further collisions with carrier gas molecules. By applying a potential difference across two electrodes in the cell, the thermal electrons can be collected and a current measured. When electron capturing analyte molecules elute into the detector cell, they react with the thermalized electrons present to produce negative ions and therefore reduce the population of these thermal electrons. This removal of electrons from the atmosphere of the electron capture cell is the basis of an electrical signal indicative of the analyte molecule.

Lovelock's first ECD (33) contained an ionization chamber with a tritium radioactive beta emitter and two electrodes that measured the current within the cell at a small constant potential, hence the term DC-ECD. The responses to different concentrations of sample were very non-linear and responses to different molecules were unpredictable. In 1963 Lovelock (35) used 10% methane in



argon as the carrier gas and the pulse sampling technique to eliminate much of the anomalous behavior observed in the original model of the ECD. The presence of methane in the detector cell aided in the deactivation of metastables by inelastic collisions, enhanced the thermalization of the secondary electrons and nullified deleterious electron mobility effects by increasing the drift velocity of the electrons. The application of a momentary, recurrent voltage pulse to collect the electrons affected behavior of the detector in several ways. In the DC mode of the ECD, Lovelock (35) observed that anomalous responses were due to space charge potentials that had arisen from the separation of the positive and negative charges in the detector cell. Anomalous responses in the DC-ECD also were attributed to contact potentials arising from contamination of cell surfaces, high applied voltages, and unpredictable electron energies. By applying voltage pulses, one can restrict the electron capture reactions to a field free atmosphere in the period between the pulses. This eliminates the effects of space charges and contact potentials that are the root of much of the anomalous behavior in the DC-ECD. Application of the voltage pulses, 0.5 to 1.0  $\mu$ sec width and 100 to 1000  $\mu$ sec period, eliminates the contribution to cell current from

the collection of negative ions because the width of the voltage pulse is of insufficient duration to draw these relatively immobile ions to the anode. The pulsed mode ECD also produces a much more stable baseline and this allows a wider range of chromatographic conditions to be employed. Still, after all the improvements that were realized with the introduction of this fixed frequency pulsed (FFP) detector, a linear response factor was available for only 10% of the dynamic range of the device.

From a better understanding of the chemical and physical phenomena taking place in the ECD, investigators were able to improve detector designs and signal processing. Kinetic studies and models of Wentworth, et. al. (36) and Wentworth and Chen (37) in the 1960s showing that events in FFP-ECD were a series of competitive kinetically controlled reactions led to a new method of signal processing that produced a linear region 90% of the dynamic range of the detector. Previous methods of obtaining an analytical signal used the difference in the cell current with and without analyte present as the response. The new method of using the decrease in cell current divided by the instantaneous cell current led to a much more cooperative device. Operation of this mode required very clean conditions so a high

standing current with long pulse periods could be achieved.

The replacement of tritium with  $^{63}\text{Ni}$  as the source of beta radiation (38) considerably broadened the scope of the ECD. The  $^{63}\text{Ni}$  allows operation at much higher temperatures than the tritium beta emitter and lengthened the list of compounds which could be analyzed with the ECD.

In 1971 a new method of signal processing for the ECD was introduced (39). In this new mode of detector, the cell current is held constant and equal to a reference current by varying the frequency of voltage pulses. When an electron capturing analyte molecule enters the cell, the population of electrons decreases and the frequency of pulsing increases. This change in frequency is used as the response to an electron capturing molecule, the change being proportional to the amount of the compound. This constant current pulsed ECD (CCP-ECD) was shown to exhibit linearity with sample concentration up to 99% of the dynamic range of the detector. This mode of signal processing is most commonly used in the commercial ECDs today.

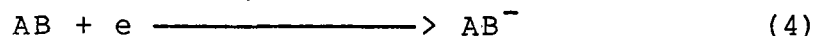
In the commercial models of the ECDs being employed presently, one of two detector geometries is usually

applied. One design is the coaxial ECD, first developed by Simmonds, et. al. (38). The anode of this detector is positioned concentrically within the ECD cell. Positive voltage wave forms are applied to the anode to collect the thermalized electrons within the detector cell. This cell design was employed in the collection of the electron capture data in this study. The other detector geometry that is very successfully used is the displaced coaxial ECD reported by Patterson (40). In this detector configuration, the anode is upstream from the actual detector cell. A narrow pulse of 0.64  $\mu$ sec width collects the electrons from the cell of 0.3 cc volume counter to the carrier gas flow. The advantages of this configuration are the tolerability to detector contamination and its large linear dynamic range (40). The detector provides a linear response to many compounds until electron density is reduced to 0.005 of its original magnitude.

#### Electron Capture Response Mechanisms

The first electron attachment response mechanisms were postulated in the kinetic studies of Wentworth and coworkers (36, 37, 41) for a FFP-ECD. The first of the

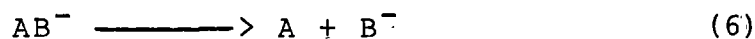
mechanisms proposed, designated as mechanism I, is depicted in Reaction 4.



This process is commonly known today as resonance electron capture. The rate constants for the forward electron capture reaction and the reverse detachment process are denoted by  $k_1$  and  $k_{-1}$  respectively. The molecular anion formed for this process, depending upon a number of physical and chemical properties, may be stable, or may detach to reform the original analyte molecule and electron as depicted in Reaction 4. If stable it will react further by recombination with positive ions as shown by Reaction 5.



where  $k_+$  is the recombination rate constant, or it may dissociate according to Reaction 6



where  $k_2$  is the dissociation rate constant. The potential energy curve for the formation of a stable molecular ion is shown in Figure 1. This figure portrays the case where the electron affinity of the analyte molecule AB is greater than zero. Molecules that undergo the process are usually large systems, often conjugated and containing electron attracting functionalities, allowing distribution of excess energy among many internal degrees of freedom. The rate constants for this process can be as high as  $10^{-7}$  cc mol<sup>-1</sup> sec<sup>-1</sup> (62) but vary greatly from compound to compound. This accounts for the high sensitivity and selectivity of electron capture detection. If the electron affinity is less than zero, a Franck-Condon transition leads to an unstable molecular anion which may disappear by autodetachment, or, if above the dissociation limit, may dissociate to A<sup>•</sup> + B<sup>-</sup>. Based on these competitive kinetic relationships, Wentworth and Becker (42) derived the relationship shown in Equation 7

$$\ln KT^{3/2} = \ln A + \ln \frac{k_+}{k_e} + \frac{EA}{RT} \quad (7)$$

between a molecule's electron affinity and its ECD response where A is composed of fundamental constants,  $k_+$  and  $k_e$  are the recombination rate constants for a



































































































































































































































































































