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## **Oxygen enhancement of thermal electron capture in a non-radioactive discharge source for a quadrupole mass spectrometer**

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### ABSTRACT

The electron-capture detector (ECD) is the most sensitive gas chromatographic detector available for certain compounds. In the process of developing a non-radioactive ECD based upon photoionization, we studied the enhancement of the ECD response by the addition of oxygen. This paper describes the results obtained by coupling the non-radioactive photoionization ECD to a quadrupole mass spectrometer. It describes the use of oxygen enhancement of the production of halide ions in a thermal electron-capture process. The production of the halide ions from aliphatic chloro compounds is much greater in the non-radioactive ECD than has been observed in typical radioactive ECDs. Indeed, the response to methylene chloride is equal to that of carbon tetrachloride. This result was unexpected. The exact mechanism for this enhancement is not known. The enhanced signal is smaller for bromobenzene and chlorobenzene.

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### INTRODUCTION

The electron-capture detector (ECD) is generally recognized as the most sensitive detector available for gas chromatography. However, it is also notorious for its difference in sensitivities<sup>1</sup>. For example, at room temperature, the response for carbon tetrachloride is  $10^5$  times that of methylene chloride<sup>2</sup>. One method for modifying this is to add oxygen to the carrier gas to enhance the response of the methylene chloride<sup>3</sup>. However, even the enhanced response of methylene chloride is less than that of carbon tetrachloride at 523 K. The enhanced response of methylene chloride does increase with decreasing temperature and would be closer to that of carbon tetrachloride at the temperature of our experiments.

We have recently described the development of a non-radioactive photoioniza-

tion electron-capture detector (PI-ECD)<sup>4,5</sup>. In this paper, we describe the use of this detector as a source for a quadrupole mass spectrometer. The first objective was to merely determine the relative production of ions from various compounds. These results were as expected. However, the study was extended to determine the enhancement of electron capture and these results were quite different from that which has been observed in the conventional radioactive ECD.

In this article we describe the coupling of the chromatographic detector to a mass spectrometer and present the relative values of the normal response *versus* the enhanced responses for aliphatic and aromatic chloro and bromo compounds. Finally, we present the optimum temperatures for the use of the selective-ion mode for the halide ions and show the relationship between the  $O_2^-$  ion current and the halide ion current.

## EXPERIMENTAL

The mass spectrometer and the basic atmospheric pressure ionization (API) source have been described previously<sup>6</sup>. In addition, an improved version of the microwave discharge ECD has been given<sup>4,5</sup>. The work on the oxygen enhancement was carried out with an earlier version of the microwave discharge source which will be described here. Briefly, the thermal electrons are generated through the interaction of energetic species with the carrier gas, helium-methane. The response of the detector is measured with and without oxygen. Both the halide ion intensity and the  $O_2^-$  current are measured in the selected-ion mode. The details of the data collection programs have been given earlier<sup>6</sup>. The mass spectrometer used in these experiments was an Extranuclear SpectraEL (Extranuclear Labs., Pittsburgh, PA, U.S.A.) having a nominal mass range of 2–400 a.m.u. It was modified to allow analysis of either positive or negative ions from an external high-pressure ionization source. The overall diagram of the various components is shown in Fig. 1. Two vertical cross sections of the actual

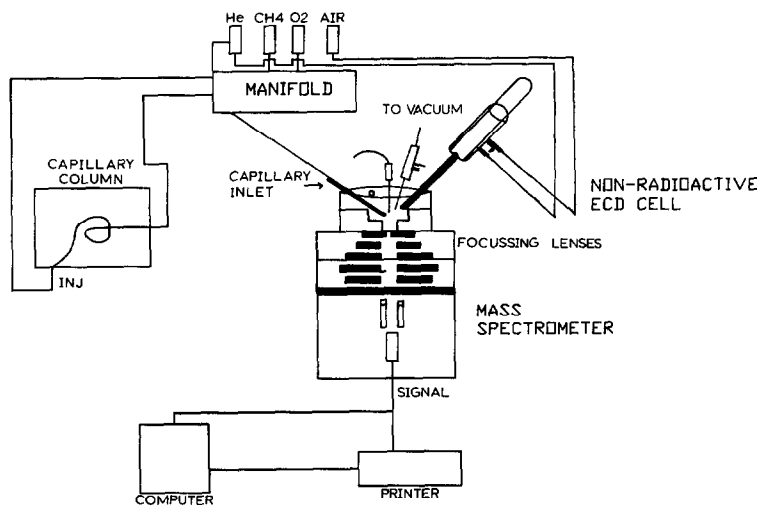


Fig. 1. Basic diagram of the experimental set up.

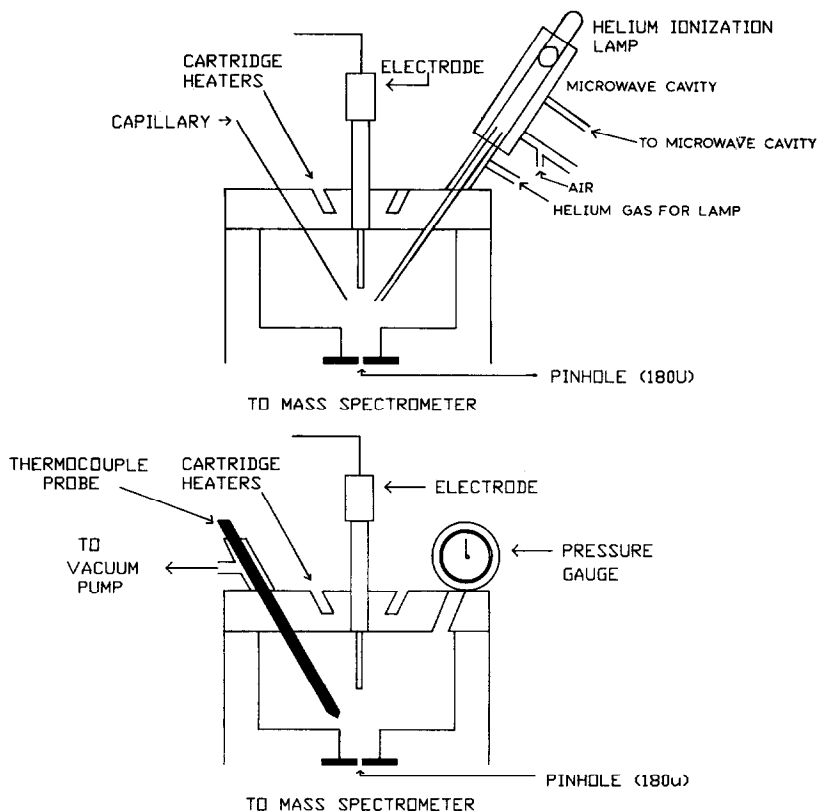


Fig. 2. Cross-sectional view of the interface; two views shown at right angles.

detector are shown in Fig. 2. The carrier gas for the chromatograph is 99.998% pure helium (Big 3 Industries, Houston, TX, U.S.A.). In Fig. 1, it can be seen that there are five entrances into the reaction zone. One serves as an inlet for the pre-mixed reactant gases to enter the reaction zone at 35°C to the horizontal plane. A second at the same angle serves as an inlet for the discharge lamp which produces the excited species. The third port serves as an inlet for the thermocouple and an exit for the gases. The fourth is an inlet for a stainless-steel electrode for the collection of electrons and the fifth is a connection to a pressure gauge.

The lamp is made of an outer quartz tube, 1/4 in. in diameter, with an entrance for the helium gas connected by means of a Kovar-Pyrex fitting and an inner quartz tube that is 18 in. in length that allows the excited species formed in the larger quartz tube to migrate down into the reaction zone. The gas flows exiting the fused-silica capillary column and the inner quartz tube intersect each other in the center of the reaction zone right above the pinhole below which stand the quadrupole of the mass spectrometer. The discharge tube is positioned inside an air-cooled microwave cavity (Ophos Instruments, Rockville, MD, U.S.A.) and is adjusted both in the position on the outer quartz tube as well as its entire length to give the minimum reflected power. The power used is generally about 40 W with a reflected power of 2 W. Helium

discharge is seen to be a very intense peach color and minor leaks in the system can easily be detected and correlated because of the change in the discharge from peach to purple, probably due to nitrogen in the air.

The high-pressure source is separated from the mass spectrometer by a 0.001-in.-thick stainless-steel disk (Optimation, Windham, NH, U.S.A.) with a pinhole aperture of 180  $\mu\text{m}$ . The mass spectrometer pressure is  $1 \cdot 10^{-4}$  Torr while the source pressure is about 10–20 Torr. The temperature in the ion source is measured with a thermocouple 1/16 in. in diameter (Type K Omega Engineering, Stamford, CT, U.S.A.). All of the five entrances are made leak-tight by having the lower flanges welded on to the main (top) flange of the mass spectrometer.

The data were collected as follows: the temperature of the detector was gradually raised from room temperature to 250°C and readings were taken every 15–20°C. Pure oxygen and pure methane were used as reagent gases both from Union Carbide, Linde Division (Somerset, NJ, U.S.A.). Once the optimum temperature was established, enhancement measurements were made first by taking measurements without oxygen and then taking them with oxygen. In order to remain in the linear region of the response, dilutions of the samples were made for the readings for the low-capture compounds. The gas in the reaction cell was about 20% methane and 80% helium or 20% methane, 40% helium and 40% oxygen.

The low-electron-capturing species such as methylene chloride were introduced as a solution through the gas chromatograph and the flow was adjusted to get adequate resolution of the peaks. Since actual flows at low pressures cannot be measured, they were approximated by flows at atmospheric pressure and read in terms of the number of Torr so as to be consistent from day to day.

All the compounds were reagent grade and were obtained from Baker, Fisher Scientific or Aldrich (U.S.A.). Of course, since samples are separated on the gas chromatograph, absolute purities are less significant. In addition, in the case of the enhancement values, the results are ratios and therefore any error due to purity will be cancelled out. The samples were diluted in reagent-grade hexane. All samples were injected with a 0.06- $\mu\text{l}$  liquid sampling valve to obtain good reproducibility.

All of the chromatograms were taken with a DB-5 Durabond column, 30 mm  $\times$  0.32 mm I.D., with a film thickness of 1  $\mu\text{m}$  at 298 K and a nominal flow-rate of 1 ml/min. The exact column conditions are not critical since the enhancement values are ratios, providing the compound under investigation is separated from its impurities.

## RESULTS

The absolute responses of the PI-ECD, the enhanced responses and the enhancement ratios are given in Table I. For comparison, the enhancement ratios for a standard ECD<sup>7</sup> are given in the last column of Table I. Eight compounds with varying degrees of ECD sensitivity have been studied. The absolute responses are calculated from the ion counts per mole calculated using the following formula:

$$R = I_{X^-, \text{peak}} W_{1/2} / \text{moles injected}$$

where  $R$  is the response,  $I_{X^-, \text{peak}}$  is the halide ion intensity at the peak, including all of

TABLE I

SENSITIZATION BY OXYGEN OF THE RESPONSE OF LOW-ELECTRON-CAPTURING COMPOUNDS IN A MICROWAVE DISCHARGE PI-ECD/COUPLED TO A MASS SPECTROMETER (MS)

The enhancement ratio is the ratio of the ion intensity with oxygen added to the ion intensity without the addition of oxygen.

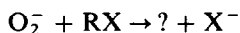
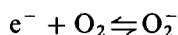
Compound	<i>R</i> (ion counts/mol)		Enhancement ratio	
	Without oxygen	With oxygen	ECD-MS	Standard ECD <sup>7</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub> Cl	2.4 · 10 <sup>9</sup>	1.4 · 10 <sup>15</sup>	5.9 · 10 <sup>5</sup>	2 · 10 <sup>2</sup>
CH <sub>2</sub> Cl <sub>2</sub>	1.8 · 10 <sup>12</sup>	2.9 · 10 <sup>15</sup>	1.6 · 10 <sup>3</sup>	1.1 · 10 <sup>2</sup>
CHCl <sub>3</sub>	5.9 · 10 <sup>12</sup>	1.7 · 10 <sup>15</sup>	2.9 · 10 <sup>2</sup>	5.0
CCl <sub>4</sub>	2.3 · 10 <sup>14</sup>	3.4 · 10 <sup>15</sup>	15.0	2.0
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	7.9 · 10 <sup>10</sup>	3.8 · 10 <sup>15</sup>	4.8 · 10 <sup>4</sup>	44.0
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	2.9 · 10 <sup>9</sup>	8.7 · 10 <sup>14</sup>	3.0 · 10 <sup>2</sup>	20.0
C <sub>6</sub> H <sub>5</sub> Cl	3.8 · 10 <sup>9</sup>	1.1 · 10 <sup>14</sup>	2.9 · 10 <sup>4</sup>	15.0
C <sub>2</sub> H <sub>5</sub> Br	8.7 · 10 <sup>10</sup>	4.1 · 10 <sup>14</sup>	4.1 · 10 <sup>3</sup>	50.0

the isotopes, and  $W_{1/2}$  is the width of the peak at half height. The moles injected are calculated from the volume of the sample loop, the dilution factor, the density and the molecular weight of the sample. (In the case of the Cl<sup>-</sup> ions a factor of 1.33 × the <sup>35</sup>Cl<sup>-</sup> peak was used. In the case of the bromine compound, a factor of 2 × the <sup>79</sup>Br<sup>-</sup> peak was used.) The temperature of the ECD was kept constant at 443 K for all compounds.

Although the ion intensities are generally higher at lower temperatures, residual water forms clusters with the anions and interferes with the reactions. At high temperatures no hydrates are formed and the specific ion-molecule reactions can take place.

We have carried out thermodynamic studies of the chloride, bromide, iodide, and O<sub>2</sub><sup>-</sup> reactions with water at the temperature of the detector. At temperatures lower than 400 K, the release of water molecules competes with recombination but we find that the kinetic model gives the equilibrium ratios of the ions and hydrates in the temperatures region above 450 K. Thus adiabatic cooling and declustering in the pinhole are negligible under these conditions.

It is generally believed that the enhancement reaction sequences is



The normal ECD response for compounds such as methylene chloride is low because there is a significantly large activation energy for dissociative electron attachment. Thus, if an ion molecule reaction is sufficiently exothermic then the ion molecule reaction rate can be larger than the electron molecule reaction and hence there can be an enhancement. However, for compounds such as carbon tetrachloride where the rate constant for dissociative electron attachment is a maximum, the ion

molecule reaction rate should be at most equal to that for the electron molecule reaction. The neutral products of the reaction are not specified. However, one possibility is the radical ROO. Alternatively, the reaction could be one between an excited  $O_2^-$  and RX. In addition to the change from an endothermic reaction to an exothermic reaction, there must also be a change in the concentration of the reactive species. This is because the electron molecule rate constants are significantly larger than ion molecule reactions even if the reaction is exothermic. We do not know the answers to these points at present but it is known that the oxygen enhancement reaction takes place even in the radioactive ECD at atmospheric pressure.

From the data given in Table I, it is clear that the relative responses for the PI-ECD are as expected for an ECD. For example, the response for carbon tetrachloride is the greatest while that for chloropropane is the smallest. The relative values are about  $10^5$  which is also observed in a standard ECD. The major differences are in the enhancement ratios. The enhanced response for the PI-ECD is much greater than that for the standard ECD. The enhanced responses for all eight compounds vary by about an order of magnitude. Indeed, if chlorobenzene and ethyl bromide are excluded, then the response factors vary by slightly less than an order of magnitude. On the other hand, the enhanced response in the standard ECD still varies by three

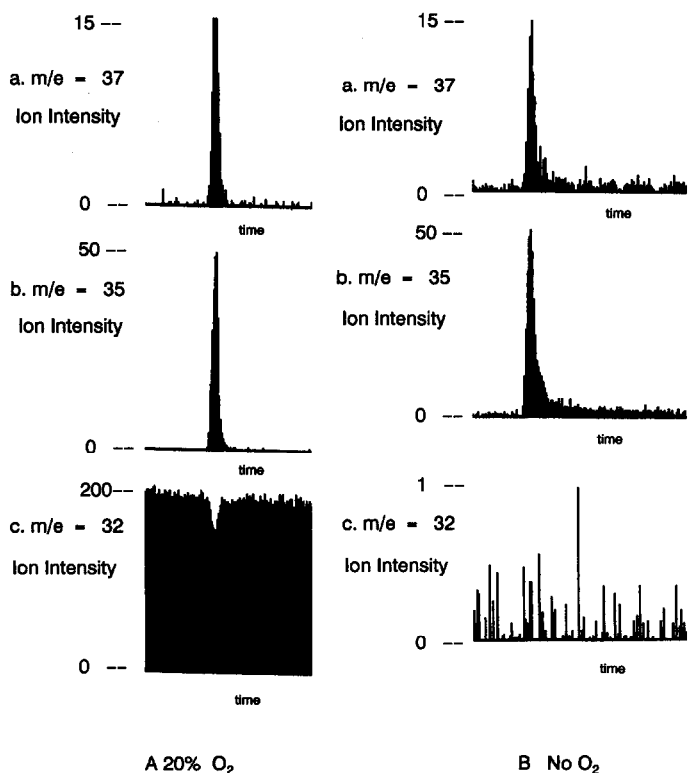


Fig. 3. Chromatograms for the injection of (A) 10 pmol of carbon tetrachloride with 20% oxygen  $O_2$  and (B) 100 pmol of carbon tetrachloride without oxygen. Attenuations: (A)  $\times 15$  (a),  $\times 50$  (b),  $\times 200$  (c); (B)  $\times 1$ . ECD temperature 441 K.

orders of magnitude. We do not understand this but recognize the value of using the PI-ECD in conjunction with a mass spectrometer as a non-selective halocarbon detector. By monitoring the intensity of the  $O_2^-$ , confirmation of the reaction can be made.

In Fig. 3 the selected-ion currents are shown for the injection of 10 pmol of carbon tetrachloride with oxygen and the injection of 100 pmol of carbon tetrachloride without oxygen. In Fig. 4, the selected-ion currents for the injection of 10 pmol of 1-chloropropane with oxygen and  $10^5$  pmol of 1-chloropropane without oxygen are shown. The plots are ion intensities at  $m/e$  32, 35 and 37 versus time. It is obvious that the responses for the two compounds are about the same in the system where oxygen is added and quite different without the oxygen. In Fig. 4, the differences in the peak shapes for the chromatograms with and without oxygen should be noted. Without oxygen, the peak is not symmetrical as expected for the large amount injected. The relative intensities of the chlorine isotopes is about 3:1 when the relative attenuations are taken into account. These chromatograms show that the increase in the halide ion

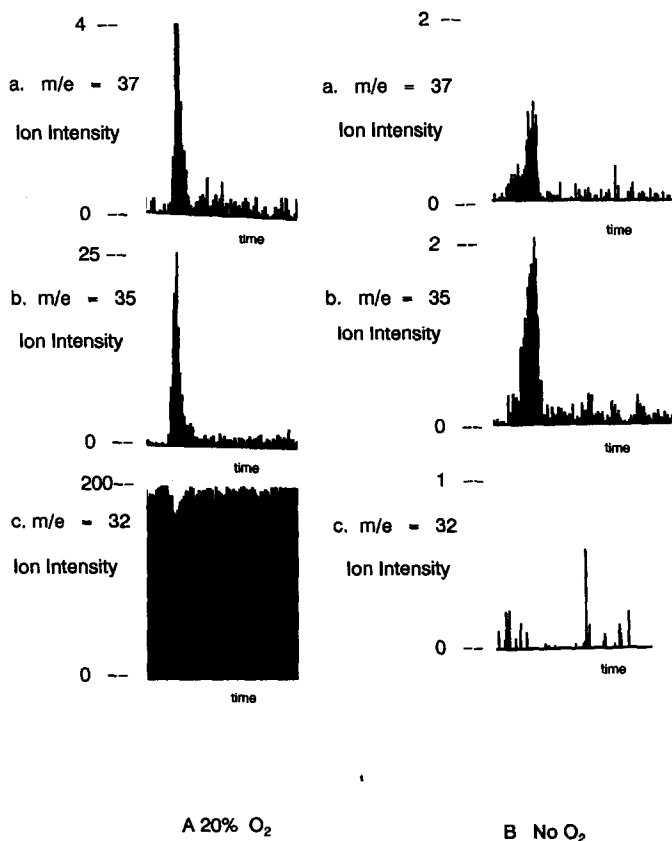


Fig. 4. Chromatograms for the injection of (A) 10 pmol of 1-chloropropane with 20% oxygen and (B)  $10^6$  pmol of 1-chloropropane without oxygen. Attenuations:  $\times 4$  (a),  $\times 25$  (b) and  $\times 200$  (c); (B)  $\times 2$  (a),  $\times 4$  (b) and  $\times 1$  (c). ECD temperature = 441 K.

occurs at the same time that there is a decrease in the  $O_2^-$  current. It should be noted that the decrease in the oxygen peak is less than the amount by which the chloride ions increases. No other peaks were observed in the mass spectrum as mass scans were taken during the time of elution of the gas chromatographic peak of interest.

It was also observed that the intensity of the halide ions varied linearly with the amount of compound injected.

## CONCLUSIONS

The ion intensities observed in a microwave discharge PI-ECD are similar to a standard ECD when no oxygen is added to the system. When oxygen is added to the system, the production of the halide ions is enhanced. For the aliphatic chloro compounds, the enhanced response is about constant. This is different from oxygen enhancement in a standard ECD. The enhanced response of olefinic and aromatic chloro compounds is less than that for aliphatic chloro compounds. This system offers potential for the development of a chloride-specific detector by using the PI-ECD with a mass spectrometer as a gas chromatographic detector. The response can be verified by observing the decrease in the  $O_2^-$  ion.

## ACKNOWLEDGEMENT

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