



Application of the O<sub>2</sub>-doped ECD to isomer differentiation  
by James Allen Campbell

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 addition of oxygen to the nitrogen carrier gas of a constant current electron capture detector (BCD) is shown to provide increased sensitivity and isomer distinction for environmentally important compounds such as polychlorinated biphenyls, polycyclic aromatic amines and hydroxides with appropriate EC-enhancing tags, chloroanthracenes and chlorophenanthrenes, methylanthracenes and methylphenanthrenes, and 2,3,7-trichlorodibenzo-p-dioxin. In most cases, the isomers of these particular compounds can be distinguished from the other isomers based solely on the measured response enhancements.

The oxygen doped BCD has been applied to compound identification where only partial resolution with capillary column gas chromatography is obtained. In addition, in instances where several compounds coelute and have the exact same retention times, the mole fraction of each component in the unresolved peak can be determined.

Atmospheric pressure ionization mass spectrometry (APIMS) gives an indication of the ions formed with and without the presence of oxygen in the source. For the chloroanthracenes, methylanthracenes, and methylphenanthrenes, actual oxygen incorporation is observed when oxygen is present. In contrast, for the polycyclic aromatic amines derivatized with trifluoroacetic anhydride (TFAA), the reaction with oxygen to produce an induced response involves a charge transfer between the oxygen anion and the analyte molecule.

Several TFAA derivatives of the aminoanthracenes and aminophenanthrenes were examined using electron impact mass spectrometry and chemical ionization mass spectrometry. Negative chemical ionization mass spectrometry with methane and isobutane as the reagent gases was evaluated as a method of isomer differentiation of these compounds and shows considerable promise.

In order to improve the precision involved in the measurement of response enhancements, two methods with parallel and series arrangement of the ECDs were utilized. The parallel arrangement with dual columns represents a significant improvement in the reproducibility of response enhancement measurements. The series detector arrangement seems to be confusing in view of possible additional reactions in the detectors.

The addition of ethyl chloride to an electron capture detector increased the response of anthracene and similar molecules with a low normal BCD response and those that react with the gaseous electron through a resonance type of reaction mechanism. The addition of ethyl chloride to the detector does not significantly increase the baseline frequency, in contrast to the addition of oxygen. The negative ions formed in this reaction have been identified.

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TO ISOMER DIFFERENTIATION

by

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A thesis submitted in partial fulfillment  
of the requirements for the degree

of

Doctor of Philosophy

in

Chemistry

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APPROVAL

of a thesis submitted by

James Allen Campbell

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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Signature James A. Campbell  
Date July 27, 1984

DEDICATION

I would like to dedicate this thesis to the memory of my father who recently passed away. He had his own particular definition of love and will always be remembered in my thoughts and actions. In addition, this is dedicated to the living, my mother, my wife, and son whose constant encouragement made this all possible.

## VITA

James Allen Campbell was born December 14, 1948 in Wolf Point, Montana, the younger of two sons of Donald W. and Harriet V. Campbell. He attended public schools in Montana and graduated from Stanford High School in May, 1966.

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## ACKNOWLEDGEMENT

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## ABSTRACT

The addition of oxygen to the nitrogen carrier gas of a constant current electron capture detector (ECD) is shown to provide increased sensitivity and isomer distinction for environmentally important compounds such as polychlorinated biphenyls, polycyclic aromatic amines and hydroxides with appropriate EC-enhancing tags, chloroanthracenes and chlorophenanthrenes, methylanthracenes and methylphenanthrenes, and 2,3,7-trichlorodibenzo-p-dioxin. In most cases, the isomers of these particular compounds can be distinguished from the other isomers based solely on the measured response enhancements.

The oxygen doped ECD has been applied to compound identification where only partial resolution with capillary column gas chromatography is obtained. In addition, in instances where several compounds coelute and have the exact same retention times, the mole fraction of each component in the unresolved peak can be determined.

Atmospheric pressure ionization mass spectrometry (APIMS) gives an indication of the ions formed with and without the presence of oxygen in the source. For the chloroanthracenes, methylanthracenes, and methylphenanthrenes, actual oxygen incorporation is observed when oxygen is present. In contrast, for the polycyclic aromatic amines derivatized with trifluoroacetic anhydride (TFAA), the reaction with oxygen to produce an induced response involves a charge transfer between the oxygen anion and the analyte molecule.

Several TFAA derivatives of the aminoanthracenes and aminophenanthrenes were examined using electron impact mass spectrometry and chemical ionization mass spectrometry. Negative chemical ionization mass spectrometry with methane and isobutane as the reagent gases was evaluated as a method of isomer differentiation of these compounds and shows considerable promise.

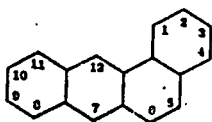
In order to improve the precision involved in the measurement of response enhancements, two methods with parallel and series arrangement of the ECDs were utilized. The parallel arrangement with dual columns represents a significant improvement in the reproducibility of response enhancement measurements. The series detector arrangement seems to be confusing in view of possible additional reactions in the detectors.

The addition of ethyl chloride to an electron capture detector increased the response of anthracene and similar molecules with a low normal ECD response and those that react with the gaseous electron through a resonance type of reaction mechanism. The addition of ethyl chloride to the detector does not significantly increase the baseline frequency, in contrast to the addition of oxygen. The negative ions formed in this reaction have been identified.

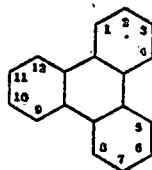
## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and substituted polycyclic aromatic hydrocarbons (SPAHS) are present as environmental pollutants formed from both natural and anthropogenic sources. Natural sources include forest and prairie fires and in situ synthesis from degraded biological material. Anthropogenic sources of PAHs and SPAHs include the burning of coal refuse banks, residential fireplaces, and commercial incinerators.

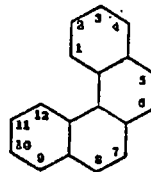
PAH mixtures can be extremely complex, since they can contain numerous isomeric compounds. A case in point is a simple sample containing the isomeric compounds with four-fused rings. These would include benz[*a*]anthracene (A), triphenylene (B), benzo[*c*]phenanthrene (C), chrysene (D), and naphthacene (E). The structure and numbering scheme for these compounds are shown below.



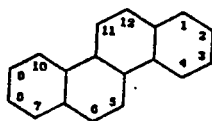
A



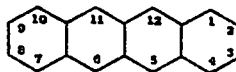
B



C



D



E

It follows that for example, a monosubstituted (amine, chloride, methyl, etc.) naphthacene has three isomers. Accounting for all of the isomeric possibilities for the five compounds for monosubstitution, the total number is 29. For a disubstituted naphthacene, the number of isomers is 20, and a disubstituted benz[*a*]anthracene has 66 isomers. The total number of disubstituted isomers for the five compounds then probably exceeds 100. As the number of substituted positions increases, the number of possible isomer combinations becomes enormous. This can pose quite a challenging problem for the analytical chemist to identify possible isomers in a sample. Even if the sample contained a single component, one isomer of the sixty-six possible disubstituted isomers of benz[*a*]anthracene, the problem of identification is still complex. Mass spectrometry, which is normally used for this type of analysis, alone is frequently unable to provide positive identification because of the large number of possible isomers for a given molecular mass. In addition, for some substituted PAHs, a strong dependence of carcinogenicity and mutagenicity on the position of substitution has been found. In view of these observations, identification of specific isomers is extremely important. Therefore, a technique which provides assistance in the identification of substituted PAHs will be a welcomed addition to the arsenal of analysis techniques presently available to the analytical chemist.

In the next section the background and history of some of the more environmentally important substituted polycyclic aromatic

hydrocarbons which include the polychlorobiphenyls, polycyclic amines and hydroxides and dioxins will be discussed followed by a short review of the typical analytical techniques for the identification of PAHs and SPAHs. The history and development of the electron capture detector (ECD) and the use of oxygen as a dopant will be reviewed. A discussion of the model for instrumental response with oxygen doping and the application of other dopants will follow.

#### Polychlorobiphenyls (PCBs)

Chlorinated biphenyls have been available as commercial products with a variety of applications for over fifty years. They were marketed under the trade name of Aroclors by Monsanto in North America and in other parts of the world under various names, such as Clophen (G.F.R.), Phenoclor (France), and Kennechlor (Japan). These PCB formulations, since their development in 1929, have been utilized chiefly as electrical coolant and insulating fluids in transformers and capacitors, but also in heat exchange and hydraulic systems, as plasticizers in paints, adhesives, caulking compounds and dye-carriers in carbonless copy paper. Their escape from these systems or their disposal in wastes has led to worldwide environmental contamination with PCBs. The presence of PCBs in the environment became apparent only after the ECD had been extensively applied to the monitoring of organochlorine pesticide residues, during the early 1960s. Chromatograms of wildlife sample extracts were found to exhibit many electron-capturing responses which could

not be attributed to organochlorine pesticide residues. These were first identified as PCBs by Jensen (1) who confirmed their presence with mass spectrometry.

Because of their resistance to breakdown and their other physical properties which are similar to those of the organochlorine pesticides, particularly DDT and its metabolites, the PCBs tend to bioaccumulate towards the top of the food web, namely in the fatty tissues of predatory fish, mammals and birds. PCBs have been found in all parts of the environment. Their presence and distribution have been reviewed by Risebrough *et al.* (2), Peakall (3), Jensen (4) and Nisbet and Sarofin (5). Pal *et al.* (6) have reviewed the fate of PCBs in soil-plant systems as well as in other environmental substrates. Fishbein (7) has reviewed some of the chromatographic and biological properties of the PCBs.

#### Polycyclic Aromatic Amines and Polycyclic Aromatic Hydroxides

The occurrence of polycyclic aromatic amines (PAA) in coal-derived liquids and residues was reported as early as 1958 by Karr *et al.* (8). Other workers have implied or demonstrated the presence of PAAs having one or two aromatic rings in synfuel products (9,10). More recently, however, even more highly mutagenic polycyclic aromatic amines (PAAs) have been detected in some synfuels materials (11-14) and have been found to be the determinant mutagens in some coal-derived materials (13,15-17). These species include recognized or suspected carcinogens such as 1-aminonaphthalene, 2-aminonaphthalene, 4-aminobiphenyl, 1-

anthracene, and 2-aminoanthracene (18-20). Lee, Later, and Wilson have found that mutagenic activity within an isomer group is structure dependent (21).

Many hydroxy type compounds have been shown to be present in synthetic fuel products and several methods have been developed for their isolation (22-25). Compounds such as hydroxyfluorenes, hydroxynaphthalenes, and hydroxybiphenyls have been identified in these synfuels (23). These compounds like the polycyclic aromatic amines may possess mutagenic and carcinogenic characteristics (25).

#### Chlorinated Dioxin

Chlorinated dioxins were first synthesized as early as 1872 by German scientists, but only recently has an enormous interest been focused on the polychlorodibenzo-p-dioxins (PDDs) and in particular one of the 22 isomers of the tetrachlorodibenzo-p-dioxin (TCDD) group, 2,3,7,8-TCDD, as a result of an explosion of a safety valve in an industrial plant producing trichlorophenol at Sevesco in northern Italy in July 1976. As the explosion was the result of overheating of the plant reactor, 2,3,7,8-TCDD, the most toxic (26) compound of the series, was produced in much larger amounts than in the normal process, where its concentration is restricted to low parts per million levels (27).

Times Beach, Missouri, has a most unenviable reputation as the town too poisoned to live in. Just a few miles west of St. Louis, its fate has been sealed as the result of some poor waste disposal practices, insufficient environmental laws in the early 1970s, and

political pressures for action. Because of the contamination and the federal government's decision to buy the town, Times Beach is expected to virtually disappear.

The story traces back to the 1960s and begins with agent orange. Hoffman-Taft, one of the original defendants in the agent orange trial, made 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) for the Department of Defense for a while, but ceased production in 1969, about the time ecological concerns led the military to halt spraying. In November of 1969, the plant in Verona, Missouri, was leased to North Eastern Pharmaceutical and Chemical company, and then later sold to Syntex Agribusiness, which let the pharmaceutical company stay to produce hexachlorophene.

According to EPA's records, wastes from the plant were being disposed of properly by shipping them to a waste facility owned by what is now Rollins Environmental Service near Baton Rouge, Louisiana. But in early 1971, allegedly to save money, North Eastern contracted with a firm called Independent Petrochemical to haul away its sludge bottoms. Independent, in turn, subcontracted the job to Russell Bliss, a waste oil hauler in Missouri. The records show that Bliss hauled away 18,500 gal of waste bottoms containing dioxin from the Verona plant, which he apparently stored in waste oil tanks near Fronenac, Missouri, between February and October 1971. But Bliss used some of this contaminated waste oil to spray horse arenas in May of 1971. Three stables apparently were sprayed, and the consequences were severe. Over the next few days and weeks, hundreds of animals got sick and died, including at

least 65 horses. One six-year old child, the daughter of one of the stable owners, developed an inflamed and bleeding bladder after playing in the soil of the arena, and three other children and one adult complained of skin lesions after exposure to the stables. All of the symptoms disappeared after exposure was halted and have not recurred.

State of Missouri investigators, reasoning that something must have been in the oil that was sprayed, sent samples for analysis. The Center for Disease Control, with few clues to go on, took until 1974 to identify dioxin as the toxic compound in the oil. They eventually determined that the oil was contaminated at about 33 ppm, a level far higher than any that occurred in Vietnam from agent orange. Crystals of trichlorophenol found during the soil analysis led the investigators to the Hoffman-Taft plant in Verona, and the thinking was that 2,4,5-T production was the culprit. But it was then discovered that the hexachlorophene wastes made by North Eastern had been disposed of improperly.

Spraying began in Vietnam in January 1962, using a variety of herbicide mixtures. Small amounts were used at first, but the amounts jumped at the end of 1965 and heavy use continued until 1969. Mounting concerns about damage to Vietnam's ecology led to a tapering off and finally a halt to the spraying of 2,4,5-T in 1970. Of the seven or so herbicide formulations used, the most significant was called agent orange, an oily liquid that was a 50-

50 mixture of the n-butyl esters of 2,4,5-T and 2,4-dichlorophenoxyacetic acid (2,4-D).

The major source of PCDDs is the massive production and use of pentachlorophenol (PCP) and other chlorophenols that are widely used as herbicides, insecticides, and wood preservatives. These compounds contain a variety of chlorine-containing contaminants and by-products that have different structures but a behavior that is similar to that of the PCDDs, and also their molecular weights lie in the same range. In addition, chlorinated dioxins have been found on fly ash particulate matter generated by municipal incinerators (28) and chimney particulate matter from wood combustion (29).

The overall picture indicates dioxins are extremely toxic and carcinogenic based on animal studies, but the picture is much less clear about human health effects. Dioxin's lethality is compared to other poisons in Table 1. It is clear that an analytical technique that would distinguish isomers of the dioxins, as well as the previously described compounds, would be of tremendous importance.

#### Analytical Techniques for PAH and SPAH Identification

As previously indicated, PAH mixtures can be extremely complex, since they contain numerous isomeric compounds. The success of the chemical analysis, whether it be quantitative or qualitative (of even a single component), hinges on the resolving power and sensitivity of the analytical method employed.

Table 1. Dioxin's lethality compared to other poisons

| Substance                  | Animal     | Minimum lethal dose (moles per kg body weight) |
|----------------------------|------------|------------------------------------------------|
| Botulinum toxic a          | Mouse      | $3.3 \times 10^{-17}$                          |
| Tetanus toxin              | Mouse      | $1.0 \times 10^{-15}$                          |
| Diphtheria toxin           | Mouse      | $4.2 \times 10^{-12}$                          |
| 2,3,7,8-TCDD               | Guinea Pig | $3.1 \times 10^{-9}$                           |
| Bufotoxin                  | Cat        | $5.2 \times 10^{-7}$                           |
| Curare                     | Mouse      | $7.2 \times 10^{-7}$                           |
| Strychnine                 | Mouse      | $1.5 \times 10^{-6}$                           |
| Muscarin                   | Cat        | $5.2 \times 10^{-6}$                           |
| Diisopropylfluorophosphate | Mouse      | $1.6 \times 10^{-5}$                           |
| Sodium cyanide             | Mouse      | $2.0 \times 10^{-4}$                           |

Source: EPA

In the following sections, the most important analytical techniques for the analysis of PAHs and substituted PAHs will be discussed. The emphasis will be placed on chromatographic methods, mass spectrometry, and spectroscopic methods.

### Chromatographic Methods

#### High Performance Liquid Chromatography

A major advantage of HPLC for the determination of PAHs is the general applicability to even completely involatile compounds of interest. Ultraviolet (UV) absorption and fluorescence detectors are generally used in series; the UV detector is universal for PAHs, whereas, the fluorescence detector provides high specificity.

Several workers (30-32) have described the use of variable wavelength UV detection to achieve some degree of selectivity. Thoms and Zander (33) used complete UV absorption spectra of PAHs for the identification in HPLC effluents. Other researchers (30,34) have employed absorbance ratios at several wavelengths for qualitative analyses.

Selective fluorescence quenching of certain PAHs in the presence of nitromethane has been investigated as a selective detection system for HPLC. Sawicki et al. (35) and later Dreeskamp et al. (36) reported that in the presence of nitromethane, the fluorescence emission of six-membered ring PAHs were quenched to a much greater degree than those containing a fluoranthenic structure. Recently, Konansh et al. (37) investigated further the potential of this phenomenon for the selective detection of the

benzofluoranthene isomers in the presence of the benzopyrene isomers and perylene.

A recent development in spectroscopic detection of PAHs in chromatographic effluents is the use of multichannel rapid scanning spectrometers. These detectors permit the recording of fluorescence spectra "on-the-fly", thereby eliminating stop flow or valving to trap the chromatographic peak in the flow cell. Jadamec et al. (38) described the use of such a system for the characterization of petroleum fractions for the determination of the source of oil spills.

The potential of the combination of liquid chromatography-mass spectrometry (LC/MS) for the separation and identification of organic compounds has generated considerable research interest in the past few years. At present, two LC/MS approaches are available, i.e., direct liquid injection and depositing the effluent onto a moving belt from which the mobile phase is evaporated prior to introduction into the mass spectrometer. Both of these approaches transfer only a small portion of the LC solute into the MS. Christensen et al. (39) recently described a new LC/MS interface that combines several of the advantages of both the direct liquid injection and moving belt techniques. The LC effluent is concentrated by evaporation as it flows down an electrically heated wire. The concentrated effluent then flows through a small needle valve and is sprayed into the MS ion source.

Dark et al. (40) using the moving belt method, demonstrated the LC fraction of coal liquid samples with structural

characterization by LC/MS. Using LC retention data on two different columns and the molecular weight data, they identified a number of aromatic compounds with molecular weights up to 250 in the coal liquid. Other applications of LC/MS involving PAH separation and identification have been reported (41,42). A review of the LC/MS techniques by McFadden (43) emphasized the current applications of this technique. Many other applications of LC/MS have been reported involving PAHs (43-45). For isomer distinction, this suffers from the same problems associated with the use of the mass spectrometer which will be discussed in more detail later. In the future, LC/MS probably will find greater application in the determination of higher molecular weight PAHs that are not particularly amenable to GC analysis.

#### Gas Chromatography

The extreme complexity of the PAH mixtures demands the greatest resolution possible in their analysis, and in this respect, as chromatography with packed columns has fallen far short of the capabilities of glass capillary columns. Capillary column gas chromatography was refined by a number of workers and the present standard was reached in 1975 when Lee (46) showed that acid-leaching of Lewis acids from the glass from which capillaries were made greatly improved the deactivation and efficiency of columns. Figure 1 shows a chromatogram of coal tar PAH obtained with an acid-leached column, subsequently coated with SE-52. The

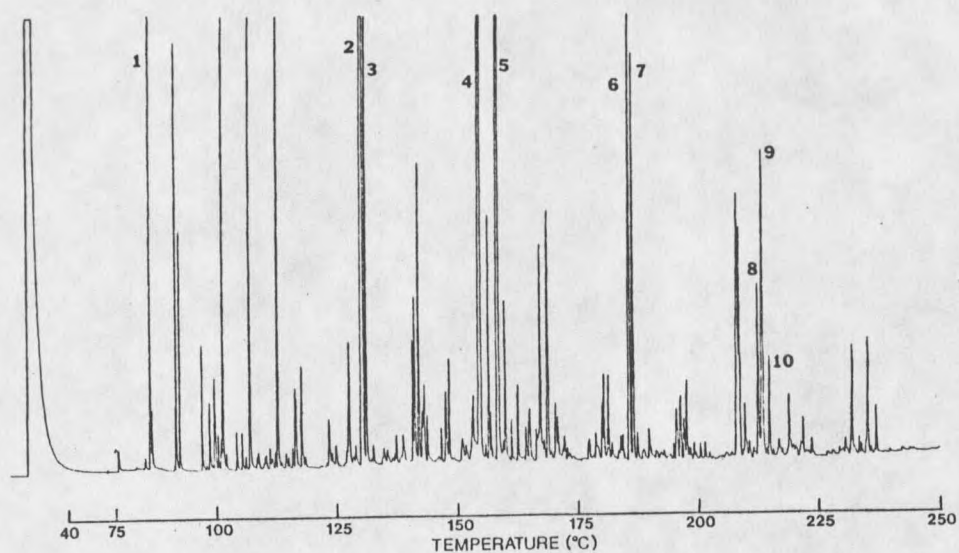


Figure 1. Capillary Column Gas Chromatogram of Coal Tar. Peak (1) Naphthalene, (2) Phenanthrene, (3) Anthracene, (4) Fluoranthene, (5) Pyrene, (6) Benz(a)anthracene, (7) Chrysene, (8) Benzo(a)pyrene, (9) Benzo(e)pyrene, (10) Perylene. (Reference 46).

performance of this column, as measured by the resolution between the isomer pairs phenanthrene-anthracene, benz[a]anthracene-chrysene, and benzo[e]pyrene-benz[a]pyrene, represents the best resolution currently available. Fused silica columns are now used almost universally. Liquid crystal phases show pronounced selectivity for PAHs in column chromatography and allow the resolution of a variety of isomer pairs such as anthracene and phenanthrene.

The most widely used gas chromatographic detector for PAHs is the flame ionization detector (FID). This is a result of its universally accepted characteristics of excellent response linearity, sensitivity, and reliability. Response increases with molecular weight and response factors are similar for most structural isomers.

As early as 1965, Cantuti *et al.* (47,48) showed that the response of the electron capture detector (ECD) for PAHs was dependent on the structure of the compound, and that the detector could be selective for PAHs in hydrocarbon mixtures. Bjorseth and Ekland (49) measured the ECD/FID response ratios for 29 PAHs, and found that many isomers could be differentiated by measurements of these ratios.

#### Mass Spectrometry

In the last decade, mass spectrometry (MS) has gained wide acceptance for the analysis of PAHs. New rapid scan techniques coupled with high resolution chromatography and improved data

systems have greatly surpassed any other method or combination of methods used for PAH analysis.

#### Electron Impact

The electron impact mass spectra of PAHs are generally quite simple, mainly consisting of an intense molecular ion and lower intensity ions due to the loss of one to four hydrogen atoms. Doubly charged molecular ions are quite common and are usually near twenty percent of the abundance of the molecular ion. In most cases, differentiation of PAH isomers by electron impact mass spectra alone cannot be achieved. Even in the cases of isomers with very different structures, such as fluoranthene and pyrene, the mass spectra are most often indistinguishable. Figure 2 compares the EI mass spectra of the four-ring isomers, triphenylene, chrysene, benz[a]anthracene, naphthacene, and benzo[c]phenanthrene. All the mass spectra are essentially identical except for the benzo[c]phenanthrene. In this case, steric interaction between the protons on and 1 and 12 carbons facilitates the loss of these two protons with the subsequent formation of the benzo[ghi]fluoranthene ion. A large number of electron impact mass spectra for PAHs have been compiled and may be found in several reference books (50,51).

Mass spectrometry coupled with gas chromatography has been used to confirm the presence of PCB residues and characterizing the molecular composition of PCB formulations. Coupling of the gas chromatograph and mass spectrometer is normally carried out in such

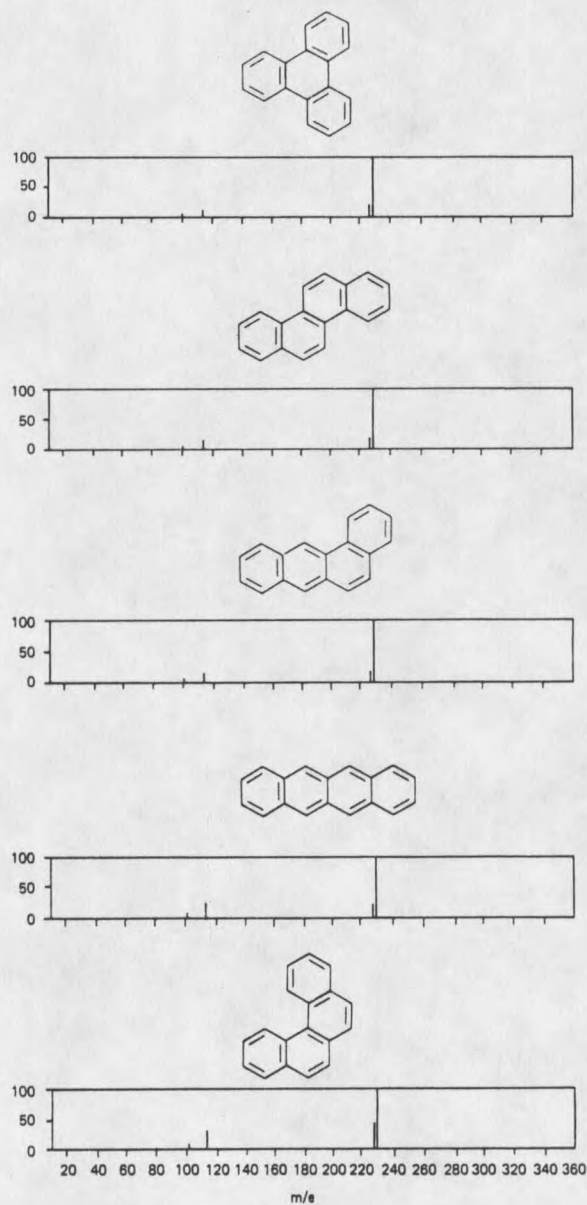


Figure 2. Electron Impact Mass Spectra of Triphenylene, Chrysene, Benz(a)anthracene, Naphthacene, and Benzo(c)-Phenanthrene. (Reference 64).

a way that a chromatogram-type readout analogous to that produced by conventional GC detectors is produced. The usual source of the GC signal is a total-ion-current monitor located between the ion source and mass-analyzing magnet (52). An extensive review of MS applications to pesticide residue analysis has been written by Biros (53). Bonnelli (54) reports that cleanup of PCB samples and separation from pesticides are not as important with GC/MS techniques as with conventional gas chromatography. Detailed investigations of primary ion spectra and fragmentation patterns of synthesized individual PCB isomers have been made (55,56). It was concluded (57) that the primary ion spectra of different isomers are virtually indistinguishable with the result that the use of mass spectrometry for structural studies of PCBs is limited.

Several researchers have recently reported procedures for isolating an amine-enriched fraction from synthetic crudes (58,59). This procedure, while effective, is not suitable for rapid analytical scale determinations. Derivatization of amines with fluorinated anhydrides, which is effective for all sterically unhindered amines (60,61) is a very useful step in any amine analysis. For example, trifluoroacetylation introduces a foreign element which is appropriate for selective spectroscopic identification procedures (62) and renders the compound more EC responsive. In addition, derivatized amines have characteristic fragmentation patterns. The parent ion gives the molecular weight of the derivatized compound. Two other major ions are present: (1) the  $(M - 97)^+$  ion corresponds to the loss of the trifluoroacetic

anhydride group and (2) the other prominent ion in the mass spectrum results from the loss of HCN from the  $(M - 97)^+$  fragment. Similar fragmentation patterns have been observed with the perfluoropropionic anhydride derivatives with the major fragment ion corresponding to the loss of the PFP group,  $(M - 147)^+$ . Later, Lee, and Wilson (59) have identified several PAAs in a solvent refined coal liquid with the use of EC-enhancing derivatization procedures with subsequent GC/MS and GC/ECD analyses. Aromatic amines have also been determined in cigarette smoke using column-chromatographic isolation procedures followed by derivatization with pentafluoropropionic anhydride and subsequent GC/MS analyses (63).

The analysis of dioxin is usually done with gas chromatography and mass spectrometry. But there's considerably more to it than that. Normally, dioxins are present, if at all, at levels ranging from parts per million down to the vanishing point. They coexist with many other compounds, and many of these are present in much larger amounts and capable of interfering with the analysis. The first step is to transfer the dioxins (and other chlorinated organics) from the sample matrix to an organic liquid, by a series of extractions. An isotopically labeled internal standard is added to help determine how much sample is lost in later steps, and to assist in quantitation. The organic extract is cleaned up with aqueous base and acid solutions and distilled water. Then the organic extract undergoes a sequence of preliminary liquid chromatographic separations, using a variety of columns and

eluents. All the fractions are recombined and concentrated for GC/MS analysis.

Usually, the sample first goes through a GC/low-resolution MS system for preliminary screening. This can show that TCDDs, for example, are present, but it isn't sensitive enough to distinguish among the various isomers. If TCDD or other dioxins of interest are revealed by this preliminary analysis, the sample then goes to a second GC/high-resolution MS analysis. The present and amount of specific isomers like 2,3,7,8-TCDD then can be determined from the ratios of certain key mass fragments. With such techniques, and depending on the nature of the sample, it's possible to detect and quantify dioxins down to low parts-per-trillion levels with reasonable confidence. In the case of a simple sample like water, one can go even lower, down to the parts-per-quadrillion level, by taking a very large sample and concentrating the dioxins into a much smaller volume by solvent extraction. In the case of more complex samples, like soils, this approach is probably beyond the capabilities of today's analytical labs. Other techniques such as MS/MS and LC/MS have been utilized for dioxin analysis.

The analytical problems involved in searching for, identifying and determining PCDDs in environmental, biological and industrial matrices cannot be solved using an ECD alone because of the presence of interfering compounds. However, if highly selective and reliable purification and clean-up of the sample is possible, an ECD can be of immense value as a auxillary detector in routine work.

Once the sample has been purified, the use of a very good capillary column with an ECD can be competitive with, and is perhaps better than, an inefficient packed column followed by a low-resolution mass spectrometer.

#### Chemical Ionization (CI)

Conventional chemical ionization (CI) mass spectrometry, using methane or isobutane as reagent gases, produces mass spectra of PAHs that also appear quite simple. The most abundant ion is the  $(M+1)^+$  or protonated molecular ion, and various adduct ions. Recent studies (64,65) indicate that the mass spectra of different isomers appear in most cases to be practically identical. A typical example is shown in Figure 3 which illustrates the methane CI mass spectra of phenanthrene and anthracene.

The use of a mixed charge exchange-chemical ionization reagent gas for mass spectrometry of PAHs which differentiates between isomers has recently been reported (66,67). The relative rates of the charge exchange and proton exchange reactions, and hence the ratio of the abundance of the  $(M+1)^+$  ion to the abundance of the  $M^+$  ion will vary according to the proton affinity and/or ionization potential of each PAH. Since the ionization potentials of PAH isomers are dependent on the specific structure of the molecule, the argon-methane reagent can produce quite different spectra for different isomers. This can be seen in Figure 4, in which a comparison of the argon-methane CI spectra for anthracene and phenanthrene is illustrated.

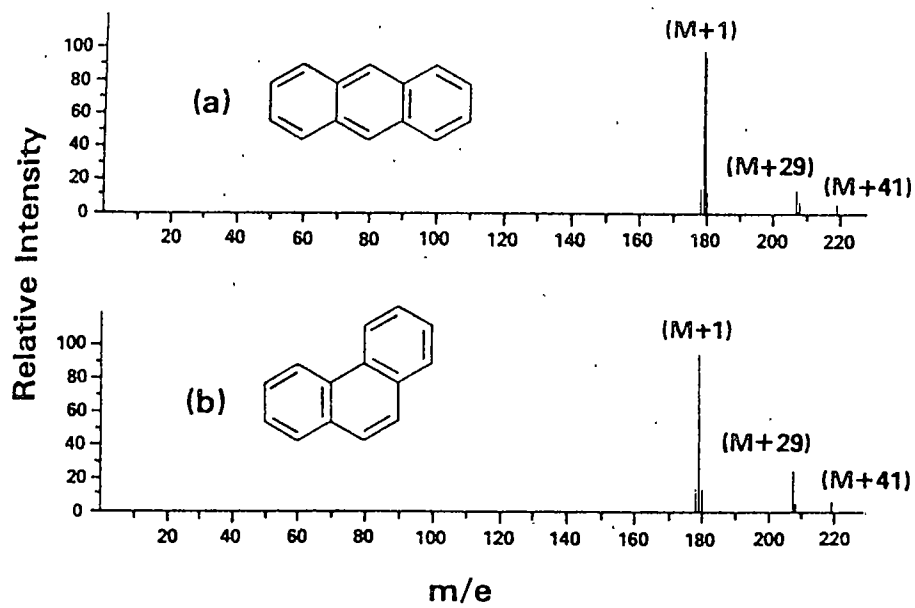


Figure 3. Methane chemical ionization mass spectra of anthracene and phenanthrene. (Reference 64).

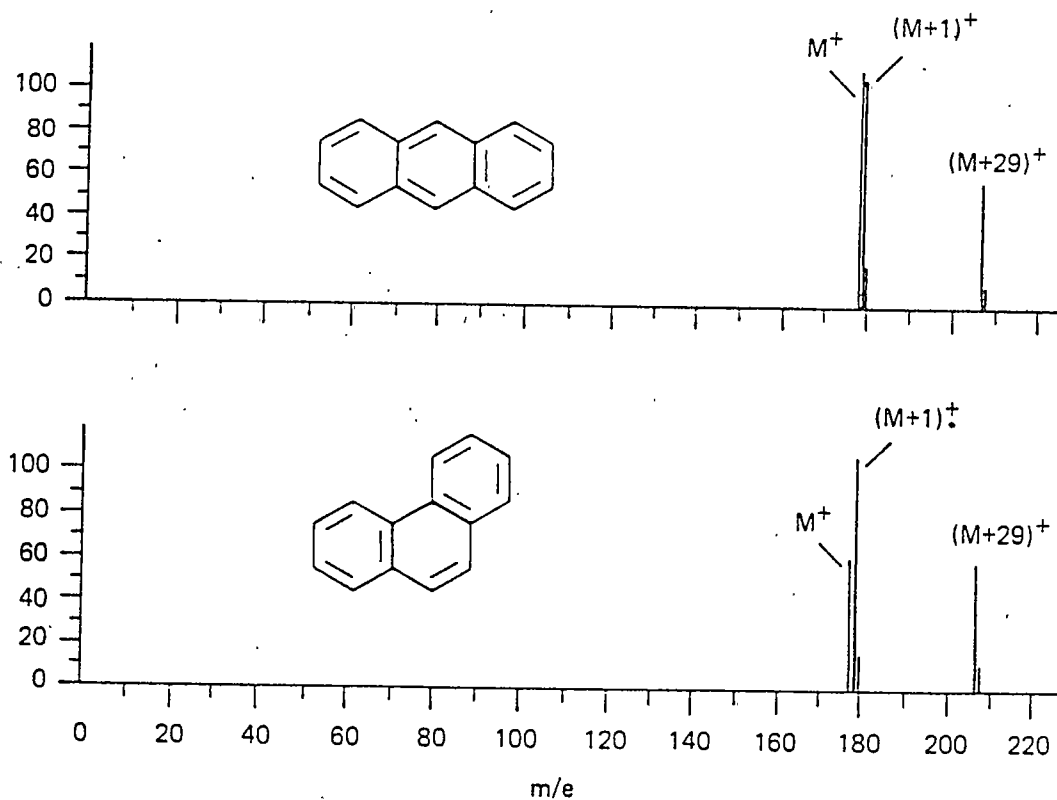


Figure 4. Argon-methane chemical ionization mass spectra of anthracene and phenanthrene. (Reference 64).

Hunt (68) has also shown that careful selection of reagent gases based on proton affinities can provide a means for differentiating PAH isomers. For example, the use of  $C_2H_5OD$  as a reagent gas can produce different spectra for phenanthrene and anthracene.

Shushan et al. (69) recently described a method in which both B and E are scanned so that (B/E) is held at the constant value required to transmit stable daughter ions of designated parent ions with preselected (m/e) ratio; in this way fragment ions formed in the first field-free region, from the preselected parent ions, are successively transmitted. The daughter-ion spectra of the four isomers, chrysene, triphenylene, benz[*a*]anthracene, and naphthacene showed considerable differences in the relative abundances of the  $M^+$ ,  $(M-H)^+$ , and  $(M-2H)^+$  ions.

### Spectroscopic Methods

#### UV Absorbance

The limitations of relatively low sensitivity and the poor specificity of spectra containing broad lines severely restrict the applications of ultra-violet (UV) absorption spectroscopy in the analysis of PAHs. Recent approaches to the luminescence analysis of PAHs have been aimed at increasing the sensitivity and selectivity of the methods through the use of new excitation sources and dispersive systems, more sophisticated detectors, and data systems (70,71).

## Nuclear magnetic resonance

Conventional single-scan NMR may confirm the presence of a given class of compounds and may be applied to the identification of specific individual compounds. Keefer *et al.* (72) investigated the methods of identification of methyl-substituted PAH from environmental samples by continuous wave  $^1\text{H}$ -NMR. The identities of 4-methylpyrene and 2-methylpyrene were identified from their different chemical shifts. Pulse Fourier-transform  $^1\text{H}$ -NMR can be applied with much more facility to small samples. Bartle *et al.* (73) were able to identify by FT  $^1\text{H}$ -NMR PAHs in mixtures separated from atmospheric dust and from the condensates of tobacco and marijuana smoke; pulse FT spectra at 90MHz allowed identification of both parent PAH and their methyl derivatives.  $^{13}\text{C}$ -NMR spectroscopy is a promising technique when sufficient sample is present. Sensitivity is relatively poor at the concentration levels normally found in environmental samples for NMR in the analysis of PAHs.

## Infrared

The chief disadvantages in the conventional IR spectroscopy of PAHs in the environment are the absence of unique features in the spectra and the lack of proportionality between band strengths and concentration, and until the introduction of matrix isolation (MI) FT-IR there were few applications reported. Wehry *et al.* (74,75) have conducted detailed investigations of the applicability of MI FT-IR in the quantitative and qualitative analysis of PAHs.

Most of the techniques discussed have several limitations for PAH differentiation. These include sensitivity or sufficient sample size as in the spectroscopic methods and in general, inability to distinguish isomeric compounds as in the case of both EI and CI mass spectrometry. Even in the case of capillary column gas chromatography (see Figure 1), the retention times for some of the isomer sets of PAHs are almost identical. Based strictly on retention times alone, positive identification would be difficult. As will be pointed out, the O<sub>2</sub>-doped ECD provides a very sensitive means for compound identification and provides assistance in the clarification of complex chromatograms where peaks are incompletely resolved.

#### Electron Capture Detector History and Development

The electron capture detector, along with the flame ionization detector, provide gas chromatography with its most commonly used detectors. For the ECD, a radioactive isotope is used as a source of beta electrons which bombard the carrier gas resulting in the formation of a plasma of positive ions, radicals, and thermal electrons. The application of a potential difference to the electron capture cell allows the collection of thermal electrons, which defines the standing current. The electron capturing species introduced in the carrier gas stream reacts with the thermal electrons to produce negative ions. The decrease in detector current due to the removal of thermal electrons by

reaction with electron capturing compounds forms the basis of the detector response.

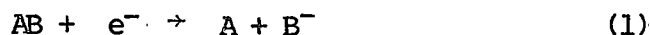
Lovelock first reported the use of the electron capture detector (ECD) for the detection of solutes in the effluent of a gas chromatography column in 1958 (76). The first ECD consisted of a simple enclosed ionization chamber containing a radioactive source (tritium as the beta particle emitter) and a pair of D.C. electrodes to monitor the cell current at a constant low potential. The response to vapor concentration was nonlinear and the response factors varied greatly for different compounds and in an unpredictable manner. In spite of these disadvantages, the electron absorption method using a simple ion chamber was utilized by Goodwin et al. (77) and Watts and Klein (78) for environmental problems, particularly the analysis of trace pesticides.

Lovelock introduced the pulse sampling technique to reduce the sources of anomalous responses (79) which were shown to be related to space charge effects, high applied voltages, contact potentials, and unpredictable changes in electron energy. Brief pulses of 0.5 to 1.0 microsecond width and 100 to 200 microsecond period of sufficient magnitude to collect all of the electrons present in the plasma are used, rather than a steady D.C. potential. The current measured reflects the chemical events occurring within the gaseous plasma during the field-free period between pulses. If the difference in standing current which accompanies sample elution is taken as the ECD response, the linear dynamic range of the constant frequency pulsed ECD varies from 50 times the detection limit to

500 times the detection limit, depending upon the type of radioactive source used. This linear range corresponds to only about 10% reduction in the standing current. For certain substances the sensitivity may be three to four times higher in the constant frequency pulsed mode than it is in the D.C. mode.

The pulse sampling procedure had several advantages over the D.C. mode. Most of the time no field is applied to the detector and the free electrons are in thermal equilibrium with the gas molecules. In addition, the electrons don't drift out of the plasma so that negative ion formation occurs in the region where the positive ions are also present and where recombination can most efficiently take place. The electron sampling period was so brief that no significant movement of the negative ions can occur; and as a result, the accuracy of the measurements are not affected by space charge effects or by the collection of negative ions at the anode. Also, a pulse amplitude of 30 volts is sufficient for the complete collection of the electrons. With the pulsed mode, the effects of contact potential effects are rarely if ever encountered if reasonably fast pulsing is used. Another important advantage of pulsed electron capture detection is that it provides an inherently more stable baseline than D.C. operation. This allows the use of column oven temperature programming to improve peak shape and reduce analysis time. For the reasons discussed, the pulse sampling technique provided for an increase in reproducibility over the previous D. C. mode.

Wentworth (80) derived a response relationship based on steady state kinetic relationships. In addition, Wentworth and coworkers showed two major mechanisms of electron attachment, dissociative capture and resonance capture which could be distinguished based on their temperature dependence (81). In the first case, the negative ion dissociates and forms radicals and ions or a radical ion which can subsequently react further (Reaction 1), and in the second case, a stable negative ion is formed which will only recombine with the positive species or react with the radicals (Reaction 2). The reactions are listed as follows:



For compounds that react with thermal electrons by a dissociative mechanism, the response is higher at higher detector temperatures. Compounds capturing electrons by Reaction 2 have their highest response at low detector temperatures and are thereby easily differentiated from those capturing electrons through Reaction 1.

Simmonds developed the coaxial ECD with a gold foil plated with a  $^{63}\text{Ni}$  source capable of temperatures up to  $400^\circ\text{C}$  (82). Previously used titanium tritide sources could not be heated above  $225^\circ\text{C}$  without producing a radioactive hazard. In 1971, a high temperature  $^3\text{H}$ -Sc source became available (83). The temperature limit of this source was  $325^\circ\text{C}$  and had a high sensitivity to

pesticides. A  $^{147}\text{Pm}$ -Au foil capable of operating at temperatures to  $400^\circ\text{C}$  has also been used as an ECD source with properties comparable with those of  $^{63}\text{Ni}$  (84). One of the major advantages of using  $^{63}\text{Ni}$  as the radioactive source is that with the sustained use of oxygen over long periods of time (several years), no decrease in sensitivity or detector performance is noticed.

Maggs *et al.* (85) described a new mode of operation of the pulsed ECD in which the detector current is held constant while the frequency of the applied pulses is varied. When a compound enters the detector and absorbs electrons, the pulse frequency will increase to collect more electrons and keep the current at the predetermined level. The average current  $I_{\text{cell}}$  is proportional to the concentration  $[n_e]$  of free electrons in the cell, and the frequency  $f$  of the applied pulses as follows:

$$I_{\text{cell}} \propto [n_e]f \quad (3)$$

Hence, when only carrier gas is in the cell,  $[N_e]$  is relatively large and  $f$  is low. This pulse frequency with pure carrier gas can be defined as the base frequency,  $f_0$ , of the system. Typically,  $f_0$  is so low that the time between pulses is about 1000 times longer than the width of each pulse. Hence, for most of the time there is no polarization voltage across the cell. When an electronegative sample enters the EC cell, it converts some of the free electrons in the cell to negative ions. As a result,  $[n_e]$  decreases and  $f$  increases in order to keep  $I_{\text{cell}}$  constant. The passage of an electronegative sample through the electron capture cell produces

an output signal with peak height proportional to the frequency difference ( $f_A - f_O$ ) where  $f_A$  is the frequency corresponding to a sample concentration  $[A]$  within the EC cell. Maggs *et al.* (85) have shown that ( $f_A - f_O$ ) is proportional to  $[n_a]$ , so that there is an inherently linear relationship between peak height signal and sample concentration.

Patterson (86) has reported a displaced coaxial  $^{63}\text{Ni}$  ECD which uses a narrow pulse width (0.64  $\mu\text{sec}$ ) and has a 0.3 ml cell volume with the carrier gas flow counter to the electron flow. This arrangement permits sufficient electron collection to ensure satisfactory detector response. A linear dynamic range of nearly five orders of magnitude can be obtained from this cell. A major advantage of the wide linear dynamic range of this constant current ECD is its general tolerability to modest levels of detector contamination (86). Patterson also found that the response of this ECD is linear until the electron density is reduced to less than 0.5% of its original magnitude. The Varian ECD that is used in our oxygen-doping studies is designed after the one reported by Patterson (86).

#### APIMS and Plasma Chromatography

The recent development of two analytical techniques: plasma chromatography (87) and atmospheric pressure ionization mass spectrometry (88,89) has added to the understanding of reactions occurring in the ECD and the oxygen-doped ECD. Both of these instruments have  $^{63}\text{Ni}$  ionization sources very similar to the ECD in

terms of pressure and temperature. Instead of measuring electron density as in the ECD, these devices allow measurement of the ions produced from electron-molecule and ion-molecule reactions.

Karasek and Kane (90) found that at 125°C 90% of the electrons in their ion source of a plasma chromatograph react with oxygen and water in the air to form water clusters of the form  $(\text{H}_2\text{O})_n\text{O}_2^-$  where  $n$  varies as a function of water concentration and temperature. They also observed that the addition of  $\text{H}_2\text{O}$  to nitrogen containing appreciable oxygen resulted in a much larger decrease in electron concentration resulting in the formation of more  $(\text{H}_2\text{O})_n\text{O}_2^-$  than the presence of oxygen by itself.

Spangler and Collins (91) similarly identified  $\text{O}_2^-$  and  $(\text{H}_2\text{O})\text{O}_2^-$  as the predominant negative ions in plasma chromatography using zero grade air as the carrier gas. They also studied the effects of water concentration upon the identity and concentration of reactant ions. Dzidic *et al.* (92), with an APIMS, identified  $\text{O}_2^-$  and its hydrated forms in high purity nitrogen carrier gas thought to contain approximately 100 ppm  $\text{O}_2$  and 10 ppm  $\text{H}_2\text{O}$ . In addition, they studied the reactions of *m*-chloronitrobenzene and *p*-chloronitrobenzene in an API source. The *m*-isomer reacts through electron attachment, and this leads to a stable  $\text{M}^-$  radical ion. The reaction sequence for *p*-chloronitrobenzene leads to two negative ions: chloride ion and the nitrophenoxide ion of mass equivalent to  $(\text{M}-\text{Cl}+\text{O})$ . Grimsrud *et al.* (93) also observed the  $(\text{M}-\text{Cl}+\text{O})$  anion of *p*-chloronitrobenzene and other chlorinated compounds when using their GC/APIMS. Horning and coworkers (94) observed  $\text{O}_2^-$

and  $(\text{H}_2\text{O})\text{O}_2^-$  to be the predominant ions in the negative ion spectra at  $100^\circ\text{C}$  for nitrogen carrier gas containing approximately 2 ppt oxygen (V/V). In a study of negative ion formation for polychlorinated biphenyls, using a plasma chromatograph, Karasek (95) found that the presence of a single chlorine atom in one or both rings was not sufficient to form  $\text{M}^-$  ions, but that the presence of three or more chlorine atoms always led to negative organic ions.

#### Use of Oxygen As An ECD Dopant

Grimsrud and Stebbins (96) reported the effect of oxygen on the response of a constant-current  $^{63}\text{Ni}$  electron-capture detector. Because of the greatly increased linear dynamic range and the high temperature capabilities of this instrument, oxygen contamination of the carrier gas was found to be much less harmful to the chromatogram baseline than had been previously reported for earlier ECD models. They also found that adding oxygen to the carrier gas increased the baseline frequency and the baseline frequency increased with lower detector temperatures. This is consistent with a resonance electron capture mechanism proposed for oxygen and similar compounds (Reaction 2). Water itself produced very little or no effect when the oxygen concentration was low, but at high concentrations the baseline frequency becomes significantly affected.

For the highly chlorinated molecules (e.g. tetrachloroethane, pentachloroacetone, and tetrachloroethylene), the effect of oxygen

was observed only at high levels of oxygen doping and at lower detector temperatures. However, 1-chlorobutane showed large response enhancement factors, 14 and 55, with 800 to 2000 ppm added oxygen, respectively. Anthracene exhibited somewhat different response characteristics, even at low concentrations of  $O_2$  (150 ppm) the response enhancement was 15.

Other researchers have utilized  $O_2$ -doping, primarily for the purpose of increasing the sensitivity for a specific compound. Simmonds has used high purity nitrogen carrier gas containing added oxygen (100 ppm V/V) for the analysis of carbon dioxide and nitrous oxide in the atmosphere (97). The addition of oxygen to the carrier gas produced a signal for carbon dioxide while preserving the usual response to nitrous oxide, thereby allowing analysis of both gases from a single sample of ambient air. Simmonds postulated a charge transfer mechanism involving  $O_2^-$  to be responsible for the increased response to  $CO_2$  using oxygen doped carrier gas. His mechanism is almost identical to that discussed by Grimsrud and Stebbins (96) and Miller and Grimsrud (98).

An oxygen doped GC/ECD is currently being used for the continuous on-line monitoring of bis(chloromethyl)ether in the workplace environment of Dow Chemical Company, Midland, Michigan (99). This fully automated system performs the monitoring tasks previously done by operator-assisted GC/MS with considerably less

expensive equipment and significant financial savings in operator expense.

Rasmussen and coworkers (100) recently reported the use of the use of oxygen doped nitrogen carrier gas to measure latitudinal distribution of methyl chloride in the atmosphere with a constant current  $^{63}\text{Ni}$  electron capture detector. These data were obtained from any analysis procedure very similar to that reported by Grimsrud and Miller (101,102). More recently, Rasmussen and Khalil (103) have reported the first measurement ever of ambient atmospheric concentrations of  $\text{CHClF}_2$  (Freon 22). These measurements were obtained with an oxygen doped ECD operated at  $275^\circ\text{C}$  using the techniques previously described by Rasmussen *et al.* (100).

A mechanism for oxygen doping was proposed by Grimsrud and Stebbins (96) and was similar to that mentioned by Van de Weil and Tomassen (104). Through an ion molecule reaction  $\text{O}_2^-$  and the sample molecule coupled to the electron attachment-detachment equilibria with  $\text{O}_2$ . If the rate of this  $\text{O}_2^-$  route of electron attachment is faster than the rate of direct electron attachment, an enhanced ECD response would be expected. The following reactions were proposed to account for this mechanism.



The last reaction indicates the reaction of the analyte molecule with the gaseous electron, the basis of the normal ECD response. A measured response enhancement is thought to reflect the ratio of the rates of Reactions 5 and 6 and may depend strongly on small variations in the structure of the substrate molecule.

Using published thermodynamic data, Grimsrud and Stebbins (96) calculated the relative concentrations of the ions,  $O_2^-$ ,  $O_2(H_2O)^-$ , and  $O_4^-$ . The clear results of this consideration is that in dry (1 ppm of water) carrier gas,  $O_2^-$  is considered to be the dominant negative ionic species at the temperatures studied. Even with 2000 ppm of oxygen added at the lowest detector temperature examined, 150°C,  $O_4^-$  will be only 0.002 as abundant as  $O_2^-$ . Kinetic considerations of the electron attachment-detachment equilibrium with  $O_2$  have enabled them to explain the oxygen dependence of the baseline frequency.

The enhancement of response to 32 simple chlorinated molecules of a constant-current electron capture detector caused by the addition of oxygen to its carrier gas was determined by Miller and Grimsrud (98). The effect of size and isomeric differences for alkyl, vinyl, allyl, and phenyl chlorides were examined. As shown in Figure 5, the response enhancements for several isomeric dichloro compounds are illustrated. This was probably the first clear indication that oxygen addition could be used for isomer identification. The response enhancements obtained for the trans isomer of dichloroethylene was 3.9, the cis by 5.5, and the 1,1-dichloro isomer was enhanced by only 1.1 at 300°C with an oxygen

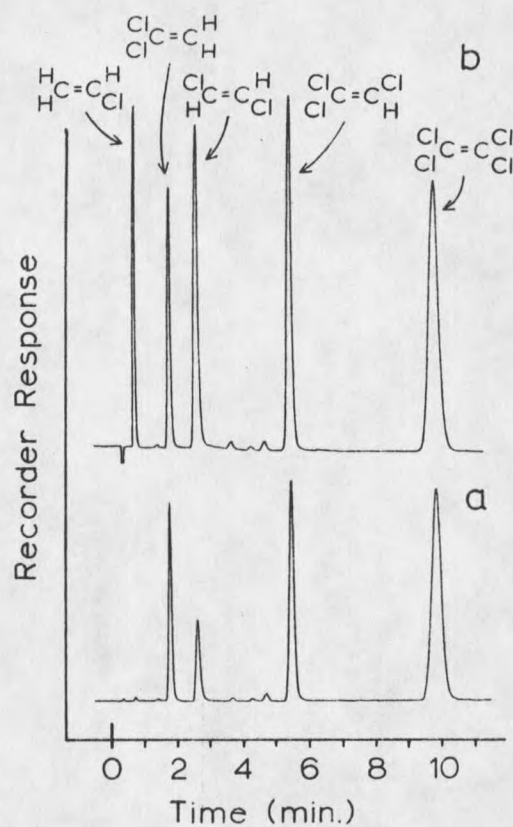


Figure 5. Typical chromatograms in the studies of oxygen's effects on ECD responses. The bottom chromatogram is with normal ECD conditions and the top ones are with 0.20% oxygen in the carrier gas. (Reference 98).

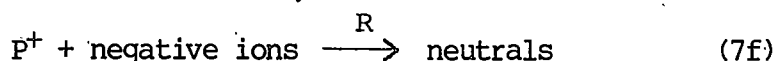
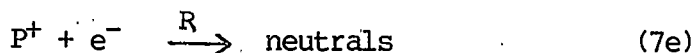
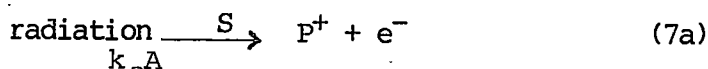
concentration of 2.0%. In that same study, they found that the number of chlorine atoms per molecule had a large effect on the ECD response and on the response enhancements. As an example, the ECD responses increased by a factor of nearly  $10^4$  in going from  $\text{CH}_3\text{Cl}$  to  $\text{CCl}_4$ , while the corresponding response enhancements decrease from 113 to 1.2. In addition, they showed a correlation between the bond dissociation energy and measured relative rates of reaction with  $\text{O}_2^-$  for several selected chlorinated hydrocarbons.

The enhancement of electron capture detector response with the addition of oxygen to the carrier gas was extended to polycyclic aromatic hydrocarbons and related chlorohydrocarbons (105). Large aromatic molecules possess EC sensitivities and exhibit oxygen induced response enhancements of magnitudes sufficient to allow their measurement in trace analysis schemes involving gas chromatography. The measured RE values are dependent on subtle structural variations, and in fact, can be used to detect structural differences among isomers that can't be resolved by existing forms of mass spectrometry. For example, triphenylene and chrysene have identical mass spectra and have the same retention times even on capillary columns, but their RE values are 3.0 and 140, respectively. Another example includes the isomers phenanthrene and anthracene. Based solely on response enhancements, these two compounds can be distinguished. The RE value for phenanthrene was determined to be 4.6, while that of anthracene was 62.

Model for Instrument Response with Oxygen Doping (97)

The formulation of the model for instrument response with oxygen doping is similar to that described by Gobby, Grimsrud, and Warden (106) of a clean gas condition of the ECD. The model for  $O_2$ -doping by Grimsrud and Miller (98) differs in that oxygen is always present and the removal of a constant fraction of electrons to the electrometer during each sampling pulse and the achievement of a steady-state condition for all charged particles during the period between pulses is assumed. All neutral and ionic species are assumed to be uniformly mixed within the ECD so that their presence can be described by one concentration expression. While an assumed even distribution of electrons may be suspect in the undoped, pulsed ECD where a significant space-charge, positive ion field may exist following the removal of electrons by a sampling pulse (93), this assumption is much more valid in the  $O_2$ -doped ECD, because most of the negative charge carriers are ions which are not removed with each pulse and overall charge neutrality within the ECD should be quickly reestablished (107). The assumption that a steady-state condition is achieved during the time between pulses is reasonable in this instance because the rates of electron attachment to  $O_2$  and detachment from  $O_2^-$  will be faster than the pulse frequency.

The following reactions might be expected to occur in an oxygen-doped ECD during the period between sampling pulses:



The  $^{63}\text{Ni}$  ionization of the carrier gas molecules to positive ions and electrons is presented in Reaction 7a. Reaction 7b shows the direct electron capture of the analyte molecule A. Reaction 7c is electron attachment and detachment with oxygen and 7d is an ion-molecule reaction between  $\text{O}_2^-$  and A. Reactions 7e and 7f are the recombination reactions of positive ions with electrons and with negative ions. It is assumed that the recombination Reactions 7e and 7f occur with the same rate R. Siegel and McKeown (107) have considered this point in detail for conditions within the ECD.

They have also shown that other possible loss mechanisms for charged particles in a ECD at equilibrium, such as diffusion to the walls or ventilation, contribute very little to the total loss rate which is dominated by recombination. These loss mechanisms are not considered to be important during the steady-state portion of the period between pulses.

Grimsrud and Miller (98) assumed that the total positive ion density remains fairly constant and independent of the amount of  $\text{O}_2$

or sample present. It is also assumed that during the field-free period between the ECD sampling pulses that charge neutrality within the cell will be obtained.

$$n_+ = \left( \frac{S}{RV} \right)^{\frac{1}{2}} \quad (8)$$

where  $S$  is the ion-electron production rate from the  $^{63}\text{Ni}$  source,  $R$  is the rate constant for recombination,  $V$  is the volume of the cell,  $R$  is the recombination rate, and  $n_+$  is the number density of the positive species. For a 7.5mCi  $^{63}\text{Ni}$  source of 0.3 ml volume,  $S$  is about  $1.3 \times 10^{11} \text{ s}^{-1}$  assuming 17-keV average primary energy and one ion pair per 35-eV primary energy (107). Taking  $R$  to be about  $3 \times 10^{-6} \text{ mL s}^{-1}$  (107),  $n_+$  is calculated to be about  $3.8 \times 10^8 \text{ mL}^{-1}$ . Grimsrud et al. (93) have obtained experimental support for the assumptions leading to the previous equation using the ECD/APIMS instrumentation described above and elsewhere (93). They noted that in the saturated condition (all negative species are ions), that the total positive ion signal is equal to the total negative ion signal. Also, upon changing the source from a condition of electron predominance to saturation, the total positive ion signal of our APIMS does not change drastically, but increases only about 50%. With high levels of oxygen doped into the carrier gas, the total positive ion signal is altered almost negligibly as sample enters the ion source, because in this case ions are the predominant negative charge carriers at all times.

In the absence of added sample and relating the rate equations with the fact that each approaches a steady state condition at the end of each field-free period, an expression for the electron density can be obtained.

$$\eta_e = \frac{S(k_{-0} + R\eta_+)}{V(k_{-0}R\eta_+ + k_0\eta_0^2 R\eta_+ + R^2\eta_+^2)} \quad (9)$$

For a frequency-modulated ECD the pulse frequency,  $f$ , is thought to be inversely related to the population of electrons existing at the instant of the sampling pulse (86,108). Also, the frequency will be proportional to the cell current demanded by the electrometer. Therefore, the following equation can be written:

$$f = \frac{KI}{V\eta_e} \quad (10)$$

For the instrument we normally use, the electrometer current,  $I$ , is held constant at 0.3nA when nitrogen is used as the carrier gas.  $K$  is an empirical proportionality constant. This term includes unknown factors for the electron collection process, such as the fraction of electrons collected during the 0.6 $\mu$ s, 50-V pulses in nitrogen (86), and the contribution to the overall current of positive ion migration to the collection electrode during the period between pulses (93). Substitution of Equation 9 for  $\eta_e$  and arithmetic reduction yields the following equation:

$$f_0 = \frac{KI}{S} R\eta_+ + \frac{KI}{S} \frac{R\eta_+ k_0}{k_{-0} + R\eta_+} \eta_0^2 \quad (11)$$

where the frequency is given as  $f_0$  to indicate this is the corresponding baseline frequency with oxygen-doped carrier gas and no sample ( $n_A = 0$ ).

With sample present in the oxygen-doped ECD and application of a steady-state condition, an expression for  $f$  can be obtained.

$$f = \frac{KI}{S}(k_{eA}n_A + Rn_+) + \frac{KI}{S} \frac{k_{-o}k_o k_{oA}n_A + Rn_+k_o}{k_{-o} + k_{oA}n_A + Rn_+} n_{O_2} \quad (12)$$

The response of a constant-current ECD is then taken as the increase in frequency,  $f-f_0$ , caused by the presence of sample molecules.

An expression for this response can be derived from Equations 11 and 12 and reduced to the following expression :

$$f - f_0 = \frac{KI}{S}(k_{eA}n_A) + \frac{KI}{S} \frac{k_{-o}k_o k_{oA}n_A}{(k_{-o} + k_{oA}n_A + Rn_+)(k_{-o} + Rn_+)} n_{O_2} \quad (13)$$

The first term is the contribution to the response of the electron capture reaction 7b while the second term is the contribution due to the assistance provided by  $O_2^-$ .

An expression for the oxygen-induced response enhancement(RE) is obtained in Equation 14 by dividing the total response,  $f-f_0$ , by

the contribution of the normal EC response,  $KI/S(k_{eA}n_A)$

$$RE = 1 + \frac{k_{-O} k_O k_{OA}}{k_{eA} (k_{-O} + k_{OA} n_A + Rn_+) (k_{-O} + Rn_+)} \cdot n_{O_2} \quad (14)$$

If  $k_{-O}$  is much larger than  $k_{OA}n_A$  and  $Rn_+$ , the above equation can be simplified. This appears to be justified under the experimental conditions used. As an example, at  $300^\circ\text{C}$   $k_{-O} = 1 \times 10^5 \text{s}^{-1}$  (calculated from its second order rate constant in nitrogen (109) of  $k_{-O} = 1.9(+0.4) \times 10^{-11} (T/300)^{3/2} e^{-4900/T} \text{mLs}^{-1} \times n_{N_2} = 1.3 \times 10^{19} \text{mL}^{-1}$ ,

the number density of the buffer gas at 1 atm pressure,  $300^\circ\text{C}$ ).

The product,  $Rn_+$ , will be about  $3 \times 10^{-6} \text{mL}^{-1} = 1100 \text{s}^{-1}$ . The product  $k_{OA}n_A$  will vary with the sample A and its concentration. The very fastest ion-molecule reactions occur with a rate constant of about  $1 \times 10^{-9} \text{mLs}^{-1}$  (110). The concentration of the monochloroalkane samples were about 0.1ppm or  $1.3 \times 10^{12} \text{mL}^{-1}$ , at  $300^\circ\text{C}$ . For these cases  $k_{OA}n_A$  will be less than  $1.3 \times 10^3$ , considerably smaller than  $k_{-O}$ . Equation 14 is reduced to Equation 15

$$RE = 1 + \frac{k_O}{k_{-O}} \cdot \frac{k_{OA}}{k_{eA}} \cdot n_{O_2} \quad (15)$$

The ratio  $k_O/k_{-O}$  in Equation 15 is the equilibrium constant for Reaction 7c. In an oxygen carrier gas,  $k_O = 1.4(+0.2) \times 10^{-29} (300/T) e^{(-600/T)} \text{mL}^2 \text{s}^{-1}$  (109) and  $k_{-O} = 2.7(+0.3) \times 10^{-10} (T/300)^{1/2} e^{(-5590/T)} \text{mLs}^{-1}$  (109). The ratio of these rates yields an equilibrium constant which will apply to Reaction 7c in any

buffer gas since the dependence of the third body cancels in the ratio. Equation 16 can be written

$$RE = 1 + 2.7 \times 10^{-16} T^{-3/2} e^{\frac{4990}{T}} \text{ mL} \cdot \frac{k_{oA}}{k_{eA}} \cdot n_{O_2} \quad (16)$$

where T is the temperature in degrees Kelvin. Under conditions used by Miller et al. (98) with 2 ppt O<sub>2</sub> ( $5.4 \times 10^{16} 273/T \text{ mL}^{-1}$ ) the previous equation reduces to the following:

$$RE = 1 + 8.8 \frac{k_{oA}}{k_{eA}} \quad \text{at } 250^\circ\text{C} \quad (17)$$

$$RE = 1 + 3.1 \frac{k_{oA}}{k_{eA}} \quad \text{at } 300^\circ\text{C} \quad (18)$$

$$RE = 1 + 1.2 \frac{k_{oA}}{k_{eA}} \quad \text{at } 350^\circ\text{C} \quad (19)$$

Expressions for the overall response,  $f - f_0$ , with oxygen doping can be derived from Equation 13 in the same manner as above. At 300° C, the following relationship is obtained:

$$f - f_0 = \frac{KI}{S} (k_{eA} + 3.0 k_{oA}) n_A \quad \text{at } 300^\circ\text{C} \quad (20)$$

The experimental characterizations of oxygen doping determined (98) thus far are in good agreement with the model developed. It has been shown that the base-line frequency,  $f_0$ , increases linearly with oxygen concentration as required by Equation 10 (101) and is illustrated in Figure 6. It has also been shown that with oxygen doping the response is linearly related to sample concentration throughout the linear range of our instrument as required by Equation 20. In addition it has been shown (see reference 98,

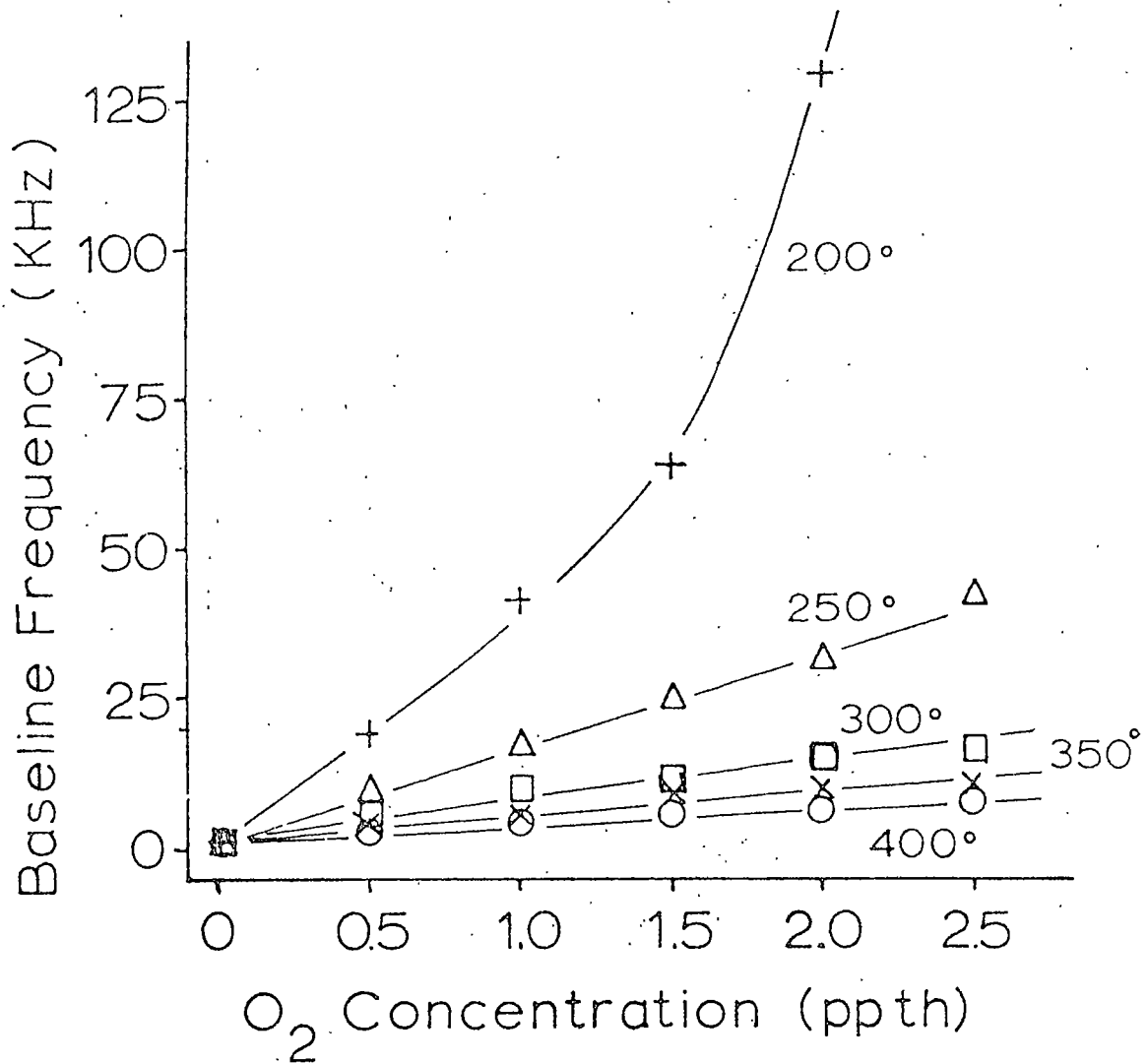


Figure 6. Effect of oxygen on the baseline noise at several detector temperatures. (Reference 101)

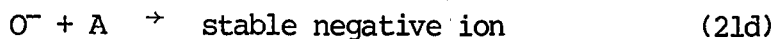
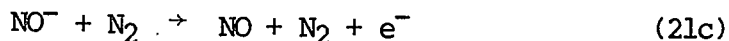
Figure 2) that the relationship between  $RE - 1$  and oxygen concentration is a nearly linear one as required by Equation 15. The general observation that these plots show some curvature from 0 to 1% oxygen is possibly due to small but notable changes in the total positive ion concentration caused by small changes in the effective recombination rate,  $R$ , as the predominant negative species present are changed from electrons to negative ions.

The temperature dependence of response enhancements predicted by Equations 17-19 also appear to be in harmony with experiments which might be reasonably used to test this relationship. For example, 1,2-dichloroethane has an ECD response which appears relatively insensitive to temperature change (98). Its relative oxygen-induced response value is high suggesting a large value of  $k_{OA}$  for it. It is reasonable to assume that this rate constant will also be relatively insensitive to temperature, as fast ion-molecule reactions generally are (110). Since the ratio of  $k_{OA}/k_{eA}$  for 1,2-dichloroethane might then be assumed to be insensitive to temperature change, the  $RE - 1$  values as predicted by Equations 39a-c should have relative values of approximately 8.5:3.0:1.2 at 250°C, 300°C, and 350°C, respectively. The response enhancements for 1,2-dichloroethane are 161, 69, and 22 at those temperatures, which yield relative values for  $RE - 1$  of 8.8:3.7:1.2, in good agreement with the above expectations. The ratio of the ion-molecule and electron capture rate constants,  $k_{OA}/k_{eA}$ , which caused these relatively large enhancements is deduced to be equal to about 20.

The experimental results in general give credence to the model for oxygen doping proposed by Grimsrud and Miller (98).

#### Other dopants

Fehsenfeld and coworkers (111) reported that the sensitivity of the ECD to  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$  could be enhanced by the addition of nitrous oxide to the carrier gas. Shortly thereafter, Sievers and coworkers (112) further characterized the  $\text{N}_2\text{O}$  enhancement process and demonstrated that a nitrous oxide chemically enhanced ECD responds to alkanes with about the same sensitivity as the flame ionization detector. The proposed mechanism for this enhancement process (112) postulates that a fast irreversible charge exchange ion-molecule reaction between  $\text{O}^-$  and the sample is responsible for the detector response. The proposed reaction mechanism is illustrated in the following equations :



Electrons are attached (Equation 21a ) and released (Equation 21c). The concentrations of electrons,  $\text{O}^-$ , and  $\text{NO}^-$  in the ECD depend on the rate constants for Equations 21a-d , the concentration of  $\text{N}_2\text{O}$  in the  $\text{N}_2$  carrier gas, and the operating temperature of the detector. Thus, any compound, analyte A, that can react with  $\text{O}^-$  or  $\text{NO}^-$  to form a stable negative ion ( Equation 21d) will interrupt the

reaction cycle, causing a reduction in the electron density and a detector response. This technique has been termed "selective electron-capture sensitization (SECS)". Goldan *et al.* (113) were able to detect part per billion levels of vinyl chloride using the  $N_2O$  doped ECD. This represents a very significant improvement when compared to the normal ECD detection limit for vinyl chloride of approximately 1-5 ppm (V/V). In a recent publication, Sievers *et al.* (114) determined the response enhancements of water, phenols, amines and aromatic and heterocyclic compounds using the  $N_2O$  doped ECD. From a comparison of the  $N_2O$  signal enhancements with those obtained by Miller *et al.* (105) several interesting features were noted. As an example, triphenylene and dibenzothiophene exhibited relatively large enhancements with  $N_2O$  addition, although they were among the least enhanced compounds when  $O_2$  was added. Substitution of a methyl group at the 9-position of anthracene decreased signal enhancement slightly with  $N_2O$ , while the response enhancement values increased by a factor of two with  $O_2$  addition. Water exhibited a relatively large enhancement factor, 260 and could be sensitively detected with selective electron capture sensitization. In general terms, doping with  $N_2O$  gives smaller enhancement values, and at the same time, is less dependent on isomer.

The reaction with  $O^-$  is more exothermic than with  $O_2^-$  and not as selective.

## RESEARCH OBJECTIVES

The objective of this study is to apply the O<sub>2</sub>-doped ECD to isomer differentiation of substituted polycyclic aromatic hydrocarbons , particularly in instances where no assistance for identification is provided by conventional forms of mass spectrometry. Also, the use of oxygen-induced response enhancement for the quantitative analysis of completely unresolved or partially resolved components of gas chromatographic peaks was evaluated.

For compounds whose normal ECD response is very low, the use of EC-enhancing chemical tags was examined. Again, isomer differentiation with the O<sub>2</sub>-doped ECD was studied.

Also worthy of examination was the use of the APIMS for indication of the ions formed with and without the presence of oxygen in its source for different compounds. A comparison of response enhancements determined from the APIMS measurements and the O<sub>2</sub>-doped ECD was made. In addition, conventional forms of mass spectrometry were evaluated for isomer distinction.

In order to improve the technique of oxygen enhancement measurements, the use of two ECDs for simultaneous electron capture and oxygen-sensitized electron capture detection was examined. Both a parallel and series arrangement of the two ECDs was tested in order to improve the precision of the enhancement measurements.

## EXPERIMENTAL

### Instrumentation

A Varian 3700 gas chromatograph equipped with an Aerograph Flame Ionization Detector (FID) and a  $^{63}\text{Ni}$  constant current electron capture detector (ECD) was utilized to obtain the response enhancement data reported here. The EC cell is a ceramic-metal assembly capable of operation at temperatures in excess of  $400^{\circ}\text{C}$ , for short periods of time. Figure 7 presents an illustration of the unique cell geometry of the Aerograph ECD (86). The cell has displaced coaxial cylinder geometry with the larger cylinder containing a 7.5 mCi  $^{63}\text{Ni}$  foil and the second cylinder serving as the electron collector. Carrier gas from the GC passes through the collector cylinder first, and then up through the foil cylinder. This particular arrangement minimizes the diffusion and convection of electrons into the collector cylinder (86). In addition, the number of long-range beta particles striking the collector is reduced. In effect, this cell minimizes the "field-free" background current, which is defined as the contribution to the cell current which does not vary with the pulse frequency (86). The cell is polarized by applying negative voltage pulses of 50V amplitude and 0.64 microsecond width to the walls of the large cylinder while grounding the collector cylinder. The net result is that the movement of electrons within the foil cylinder is against

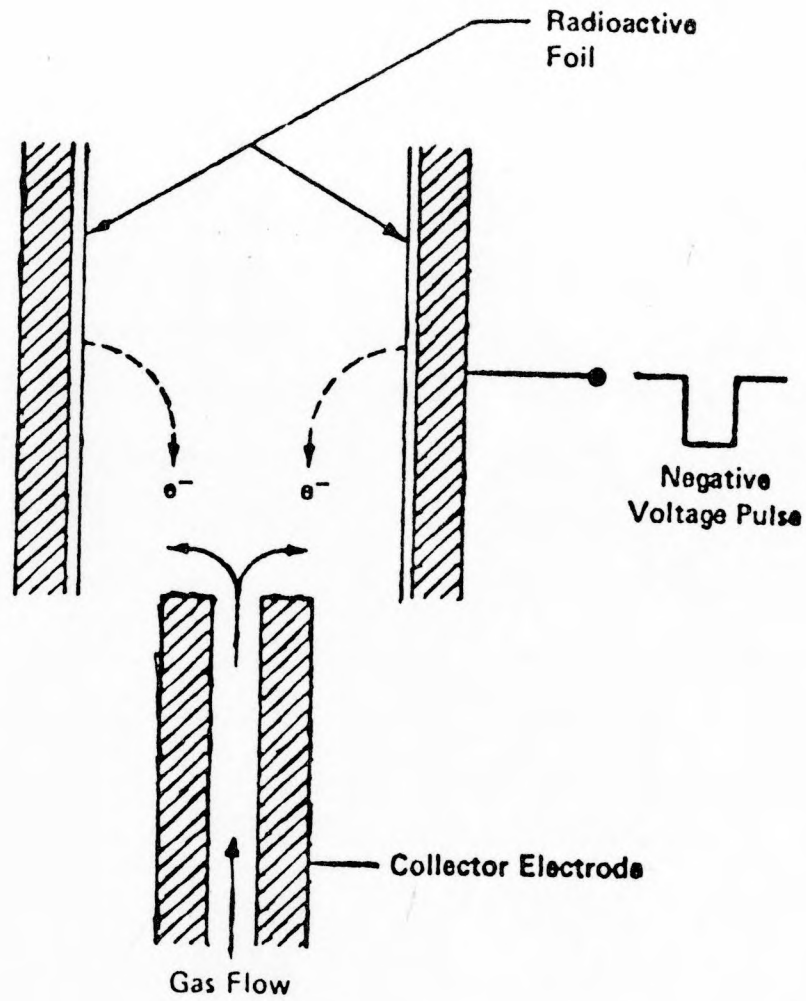


Figure 7. Schematic illustration of the displaced coaxial cylindrical ECD used in this work.

the gas flow. A fraction of electrons are collected during the time the pulse is on. As a result, the unique geometry has allowed the cell volume to be made very low(0.3 ml) for increased sensitivity.

The cell current is held constant at 0.3nA using nitrogen as the carrier gas through the use of the electronic circuit illustrated in Figure 8. The cell current,  $I_{\text{cell}}$ , is combined with an external reference current such that their difference is the input to the electrometer. The electrometer output determines the magnitude of  $I_{\text{cell}}$ . The system works by electronically varying the pulse frequency to maintain the relationship  $I_{\text{cell}} = I_{\text{ref}}$ . Since the pulse frequency is the quantity which is always changing in this method of operation, the output signal is a voltage proportional to that frequency.

Using the GC/ECD system just described, the data for this study were collected. In addition, a small portion of the data were obtained using the flame ionization detector to compare the retention times in instances where more than one peak was eluted. The Aerograph FID has a linear range greater than  $10^7$  and a detection limit of less than  $2.7 \times 10^{-12}$  g-c/sec (115). This FID uses a ceramic flame tip to minimize the effects of sample degradation at metallic surfaces. The small contribution to the system noise by the electrometer allows the FID system to operate at a maximum sensitivity of  $1 \times 10^{-12}$  A full scale. Retention times were determined for all the compounds discussed by using the flame ionization detector prior to the ECD analysis.

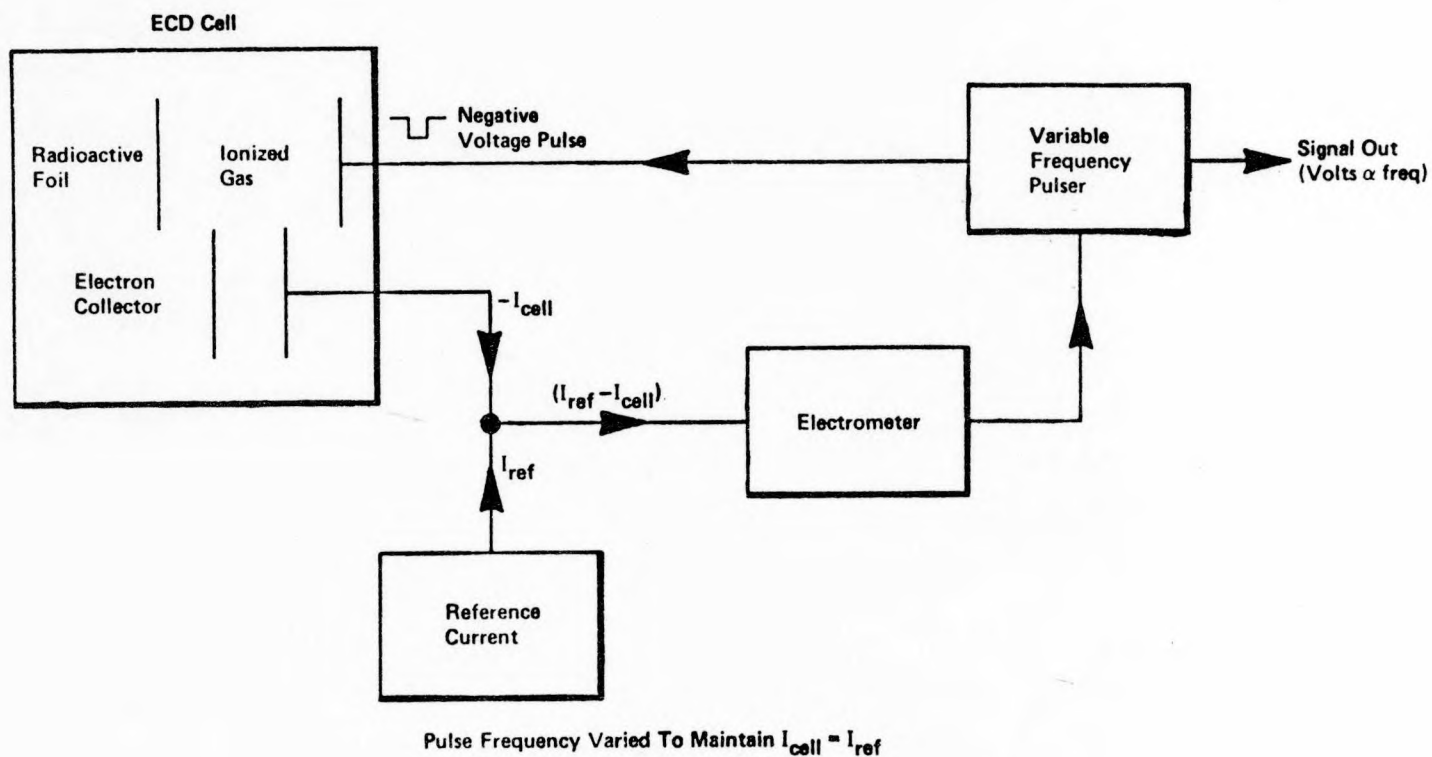


Figure 8. Block diagram of the electronic components of a constant current ECD.

Chromatograms were recorded on a Varian Model 9176 strip chart recorder or a BBC Goerz Servogar 303 three pen recorder.

#### Chromatographic Parameters

For the chlorinated biphenyls, a SE-52 capillary column, .25mm i.d. X 15m, was used at a constant oven temperature of 180°C. The detector temperature was 300°C and the injector was maintained at 210°C.

A 1.5-ft length by 1/8 inch stainless steel column packed with 4% OV101 on Chromosorb W was used for the mixture analyses of the chloroanthracenes. The temperature of the oven for packed column separations was 170°C and the injector was at 200°C. The detector was maintained at a temperature of 300°C. A SE-52 capillary column (15m X 0.25mm i.d.) was also used in the study of the chloroanthracenes. The oven was temperature-programmed as follows: 90°C for 3 min, 20°C increase per minute to 200°C, and hold at 200°C for 10 min.

A SE-52 column of 0.25mm i.d. and 15m length was used with He as the carrier gas and nitrogen as the make-up gas for the amine and hydroxy derivatives. The detector was maintained at either 250°C or 300°C and the injector temperature was 220°C. Isothermal conditions of the column were generally used for both the amine derivatives and the methoxy compounds. For the naphthalenes the column temperature was 130°C, anthracenes 180°C, phenanthrenes 230°C, fluorenes 190°C, pyrenes 230°C, and the benzo(c)phenanthrenes and chrysenes 230°C. A temperature program

of the oven was used for the mixture analysis and is as follows: 150°C for 1 min, 10 C increase per minute to 230°C, and then hold at 230°C for 10 minutes.

The methylanthracenes and methylphenanthrenes were analyzed with series detectors which will be discussed in more detail later at a detector temperature of 250°C, injector was at 210°C, and the oven at 180°C. Again, a SE-52 column of 0.25 mm i.d. X 15m was used.

The sample of 2,3,7-trichlorodibenzo-p-dioxin was analyzed at a detector temperature of 250°C, injector 210°C, and the oven isothermally programmed at 180°C. The capillary column previously discussed was used.

The make-up gas for the capillary column studies was nitrogen and was passed through two traps containing 13X molecular sieve and  $\text{CaSO}_4$ . Two oxygen scrubbers (Alltech Oxy-Trap) were added to the carrier gas line to remove residual oxygen from the nitrogen gas stream. When heated to 200°C, this scrubber is specified to reduce oxygen content to less than 0.1 ppm. The addition of the scrubbers and traps eliminated the need for using ultra-high purity nitrogen as the carrier gas in packed column work or the make-up gas in capillary column studies.

An SGE on-column injector model OCl-2 was utilized for analyzing the chloroanthracenes and the temperature used was as follows: 50°C for 3 minutes, 10°/min to 200°C, and then hold at 200°C for three minutes. The detector temperature was maintained at 300°C.

For capillary column analyses, the injection port is modified to reduce its volume by placing a glass liner inside a piece of stainless steel tubing. As a result, the chromatographic quality is definitely improved.

#### Oxygen Addition

With the packed column experiments, oxygen was normally added in the carrier gas prior to the detector after the column. In earlier studies, the oxygen was added prior to the injector, and oxygen has had no detrimental effects on the lifetime or performance of the columns used since the oven was not elevated in temperature. Either technique provided identical response enhancements.

For the experiments utilizing the capillary columns, oxygen was added as a make-up gas after the column just prior to the detector by combining the carrier gas flow with nitrogen gas containing 2.4% oxygen. This has been accomplished by using the H<sub>2</sub> flow system into the universal detector base upon which our ECD is mounted. The hydrogen inlet is located at the back of the instrument and is normally used for H<sub>2</sub> addition to the flame ionization detector at the base of the detector. This is illustrated in Figure 9. By adjusting the flow rate of the nitrogen containing oxygen make-up gas to produce a baseline frequency indicative of some known oxygen concentration, measurements can be made at a constant oxygen level. From one determination to the next, a precise level of oxygen is adjusted by

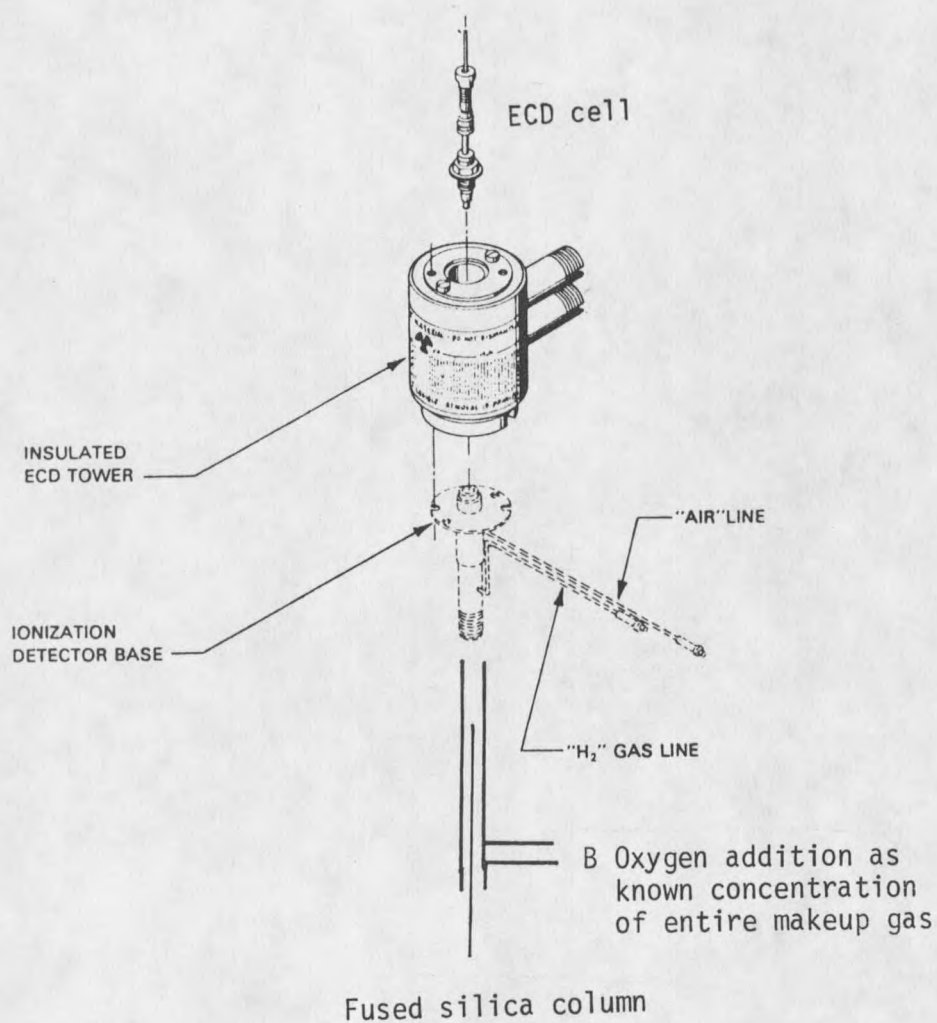


Figure 9. Diagram illustrating positions for addition of oxygen.

fine-tuning the oxygen flow until a preselected magnitude of baseline frequency is obtained. A known concentration of nitrogen containing oxygen can also be added as the entire make-up gas at position labelled B in Figure 9. Either experimental design or method of adding oxygen has produced accurate response enhancement values for the compounds studied.

#### Measurement procedures

The ECD chromatograms of individual compounds or mixtures which were easily separated from each other by gas chromatography were first obtained using nitrogen carrier gas or make-up gas as in the case of capillary columns. Oxygen was added to the make-up gas and the analysis of each compound was repeated. A signal enhancement value is calculated by dividing the response of the  $O_2$ -doped ECD by the response observed with normal electron capture for the same amount of compound.

$$\text{Response enhancement (RE)} = \frac{\text{peak height with oxygen}}{\text{peak height without oxygen}} \quad (22)$$

All compounds were analyzed at least three times both with and without oxygen.

#### Sample Preparation

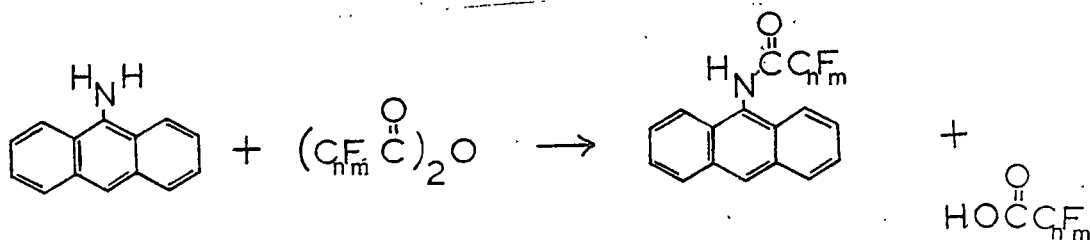
The following chemicals were purchased from Aldrich Co: 3,4,5-, 2,4,5-, 2,4,6-, 2,3,6-, 2,3,5-, 2,3,4-, 3,5,4'-trichlorobiphenyl, 1-, 2-, and 9-chloroanthracene, 9-chlorophenanthrene, 1-, 2-, and 9-aminoanthracene,

9-aminophenanthrene, 1-, 2-, and 4-aminopyrene, 2-, 3-, and 4-aminobenz(c)phenanthrene, 2,7-, 1,8-, 1,5-diaminonaphthalene, 2,4-, 1,5-, 1,4-, and 1,7-dimethoxynaphthalene, 9-methoxyphenanthrene, 4,5- and 1,9-dihydroxyphenanthrene, 9-amino-3-methoxyphenanthrene, 12-methoxy-7-methylbenz(a)anthracene, 5-methoxy-7-methylbenz(a)anthracene, 8-methoxy-7-methylbenz(a)anthracene, 2-methylanthracene, 9-methylanthracene, and 9,10-dimethylanthracene. The hydroxy isomers of chrysene and 2,3,7-trichlorodibenzo-p-dioxin were obtained from the National Cancer Institute's Standard Chemical Carcinogen Reference Repository. Samples of 1-, 2-, 3-, and 4-aminophenanthrene, 1-, 2-, 3-, 4-, and 9-aminofluorene, 2-, 3-, 4-aminobiphenyl, and the 1- and 2-aminonaphthalene and the 1-methylanthracene, 1-, 2-, 3-, 4-, and 9-methylphenanthrene were all kindly supplied by Doug Later and Milton Lee of Brigham Young University. The 2-, 3-, and 4-chlorobiphenyl and 2,3-, 3,5-, 2,4-, 4,4'-, 2,6-, 3,3', 2,5-, and 2,2-dichlorobiphenyl were all supplied by Richard Geer of Montana State University.

Standards for the chloroanthracenes, chlorophenanthrenes, methylanthracenes, methylphenanthrenes and chlorobiphenyls were prepared in the following manner. One to five mg of the solid samples were dissolved in 10.0 ml of thiophene-free toluene. This mixture was subsequently diluted with a known volume of toluene. If necessary, the second mixture was further diluted such that the resulting sample size was sufficient to produce small, but easily measurable peaks. Those sample sizes varied considerably and encompassed a wide range of concentrations. For example, sample

sizes range from 1 ng to .01 ng per injection produced easily measured peaks for most compounds.

The polycyclic aromatic amines (PAA) were derivatized by using a procedure similar to that utilized by Later *et al.* (116). Approximately 10-20 mg of each was dissolved in 10.0 ml of benzene. A 2-ml aliquot was placed in a 5-ml flask with 1 ml of 0.05M triethylamine in benzene. Next, 30  $\mu$ l of trifluoroacetic anhydride (Aldrich Chemical Co.) or perfluoropropionic anhydride (Fluka) was added to the mixture. The flask was sealed and heated in a water bath at 60° C for 15 minutes. The reaction mixture was then cooled for several minutes, 1 ml of 10% aqueous ammonia solution was added to terminate the reaction, and the mixture was then shaken for 5 minutes. Finally, the organic and aqueous phases were allowed to separate and the benzene layer containing the derivatized amines was recovered and diluted with a known volume of benzene for subsequent GC/ECD analyses. The 9-isomer of fluorene (HCL salt) was treated with base before undergoing the reaction with either trifluoroacetic anhydride or perfluoropropionic anhydride. The general reaction for the amine with either trifluoroacetic anhydride or perfluoropropionic anhydride is shown in the following reaction.



Masuda and Hoffman (117) used PFPA derivatization to identify and quantify 1- and 2-aminonaphthalene in cigarette smoke condensate and reported yields exceeding 95% of several standard polycyclic amines to PFPA-amide derivatives (118). Similar yields were observed by Later et al. (116) for the PFPA-amides, however, somewhat lower conversion yields, 85-95%, were obtained for the PAA-TFAA derivatives.

Due to the limited solubility in benzene, the procedure for preparing derivatives of the diaminonaphthalenes and 2,7-diaminofluorene differed somewhat from the previous procedure. Approximately 100 mg of the diamino compound was dissolved in 0.5 ml of tetrahydrofuran (THF) and diluted to 2 ml with benzene in a 5-ml flask. Next, 100  $\mu$ l of TFAA and 0.5ml of .5M triethylamine in benzene was added to the solution. The flask was sealed and heated in a water bath at 60° C for 30 minutes. The reaction mixture was then cooled and allowed to evaporate under a steady stream of nitrogen. The solid residue remaining was then dissolved in 0.5 ml of THF and diluted with 10 ml of benzene for subsequent ECD analysis.

The methoxy and dimethoxy derivatives were prepared in the following manner. Two test tubes (20 X 150mm) were connected in series with glass tubing through neoprene stoppers so that incoming nitrogen bubbled through the solutions in the test tubes. In the first test tube 10 ml of ether was added. To the second test tube, 1 ml of ether, 1 ml of 2-(2-ethoxyethoxy) ethanol, 1.5 ml of 37%

aqueous potassium hydroxide solution, and approximately 0.2mg of N-methyl-N-nitroso-p-toluenesulfonamide (Diazold, Aldrich Chemical Co.) were added. The nitrogen flow was adjusted to about 10ml/min. The vial containing the hydroxide in either ether or THF was positioned so that the gas bubbled through the sample. The reaction was allowed to proceed for about 10 min until the yellow color of diazomethane persists in the sample vial. The reaction solution was then allowed to evaporate to dryness and the solid residue remaining was redissolved in toluene for subsequent analysis by GC/ECD. Standard precautionary procedures associated with the use of diazomethane were strictly adhered to.

All organic solvents were of pesticide grade, the water was deionized and doubly distilled, and the derivatization reagents were used without additional purification. The stock ammonia solution (Baker) was extracted three times with equal portions of methylene chloride to remove any organic contaminants.

### Parallel Detectors

#### Dual Columns

Two fused silica columns, SE-30, of 0.25 mm i.d. and 6m length were placed in the injector port and used with He as the carrier gas and nitrogen as the make-up gas. When desired, oxygen was added by combining the nitrogen make-up gas with about 7 ml/min of nitrogen containing 2% oxygen. An oxygen concentration of about 3 ppt is thereby maintained in the doped detector. From one determination to the next, a precise level of oxygen is adjusted by

fine-tuning the oxygen flow until a preselected magnitude of baseline frequency is observed. The two detectors were maintained at 300°C and the injector temperature was 210°C. Isothermal conditions of the two columns were generally used to determine the enhancements for the individual compounds. The column temperature was held constant at 140°C. A splitless injection of 0.4  $\mu$ l was used where each injection contained an amount of sample in toluene to produce small, but easily measured peaks.

#### Splitter

Using a commercially available capillary column effluent splitter(Varian) as illustrated in Figure 10, an experimental design was utilized with one column(SE-52, 0.25 mm i.d. X 15m) and parallel detectors. The temperature of the column was 210°C, the injector was 220°C, and both detectors were maintained at 300°C. Helium was used as the carrier gas with nitrogen as the make-up gas. As discussed previously, the oxygen was added to one detector and adjusted to a preselected baseline frequency.

#### Series Detectors

In this experiment, an SE-52 capillary column 0.25 mm i.d. X 15m was used with helium as the carrier gas and nitrogen as the make-up gas. The effluent stream from the first ECD is connected to the second one with a portion of glass-lined stainless steel tubing(1/16 inch o.d. X 1.5 ft.). The tubing was wrapped with heat tape and heated to a temperature of 210°C. Both detectors were

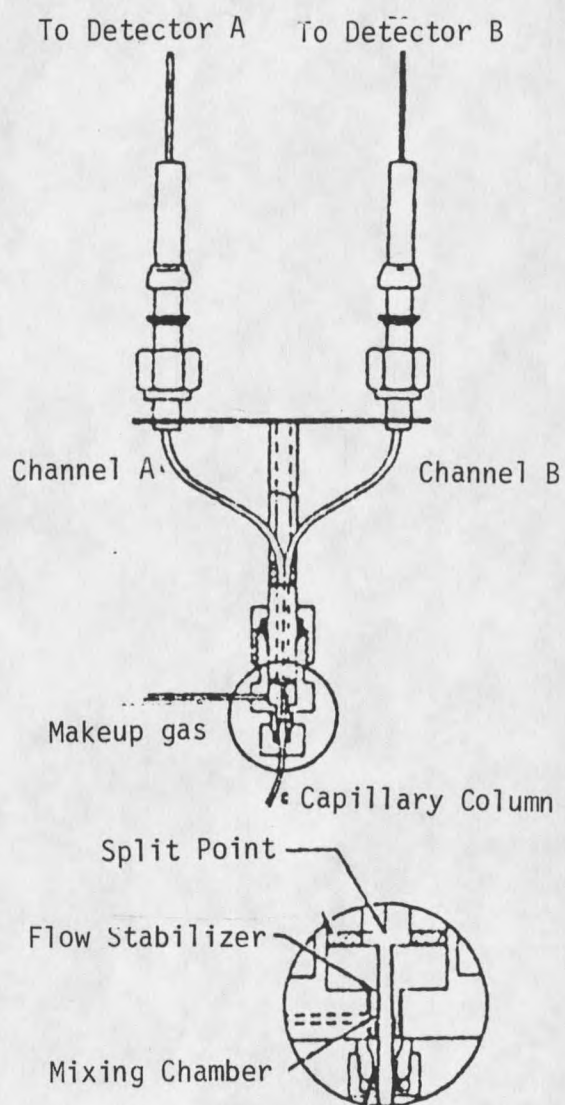


Figure 10. Schematic of the Varian capillary column effluent splitter.

maintained at a temperature of 300°C. Isothermal conditions were used to determine individual response enhancement values. For the chloroanthracenes and 9-chlorophenanthrene the oven temperature was 180°C. The temperature program for the separation of 9-chlorophenanthrene and 2-chloroanthracene was as follows: 140°C for 2 min, 5° per minute to 200°C, and hold at 200°C for 5 minutes. In this type of arrangement oxygen can be added to both detectors simultaneously.

#### Tandem Cells

This unique cell design is shown in Figure 11. Instead of having a coaxial pin design, this cell has the anodes coming in from the side of the cell and the pins are encompassed by high temperature ceramic material. Each volume contains a  $^{63}\text{Ni}$  foil of approximately 7.5 mCi and both cells are contained within the same block with a small transfer space between the cells. The effluent from the first cell flows into the second cell. In addition, each cell has its own electronics package patterned after previous work by Knighton and Grimsrud (119). This allows both cells to be monitored simultaneously and the second cell has the capability of adding oxygen. In other words, both the normal ECD response can be recorded as well as the oxygen-induced response simultaneously. This design is in its preliminary stage, but shows significant promise for analyses.

#### Mass spectrometric parameters

The samples were dissolved in benzene to prepare 1  $\mu\text{g}/\mu\text{l}$

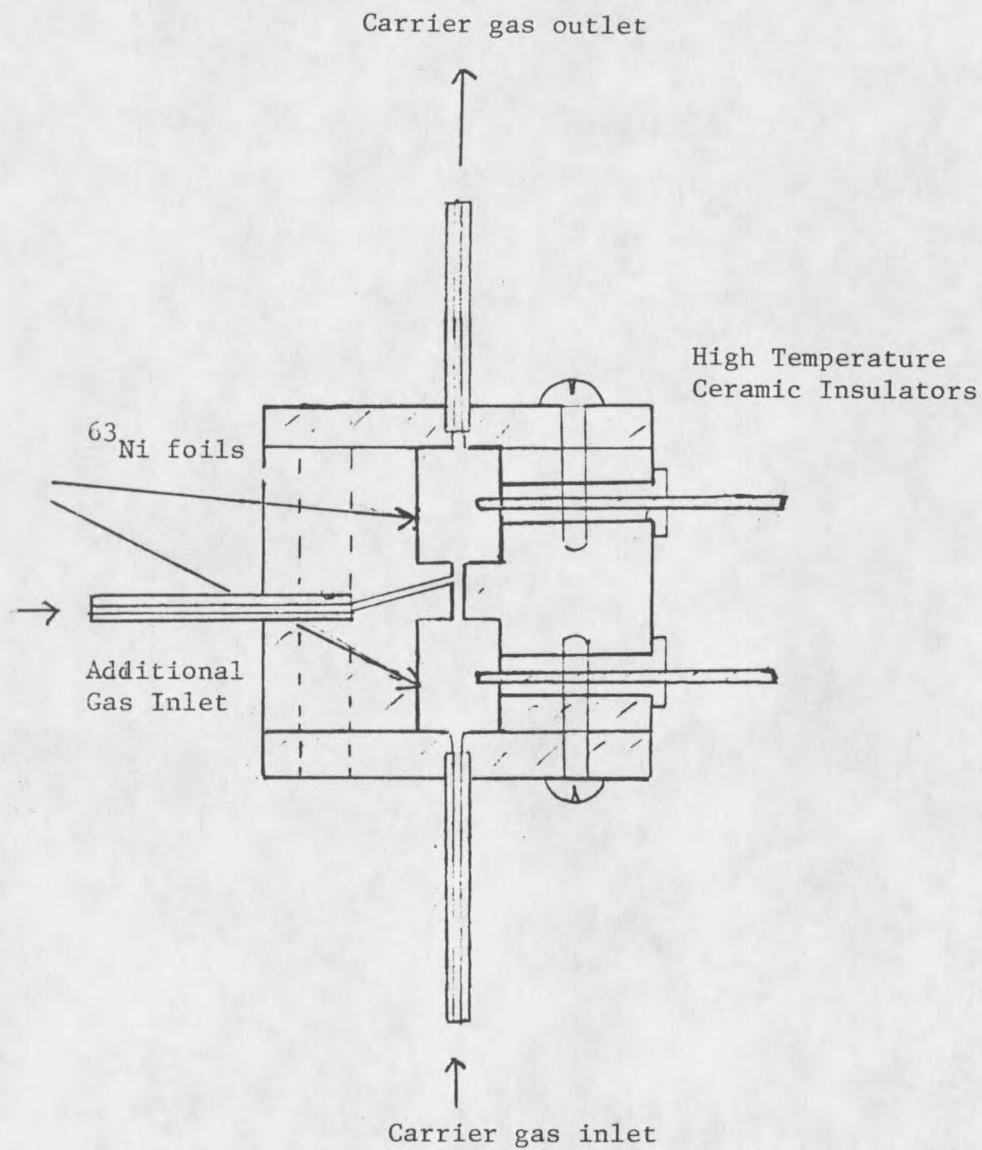


Figure 11. Tandem cell configuration.

solutions. One to five  $\mu$ l of the solution were introduced into a VGmm16 GC/MS/DS equipped with a 4% OV101 column (1/8 inch o.d. X 6ft) with a flow rate of 30 ml/min. The temperature of the column was 220°C, injector was 230°C, and the ion source temperature was also 230°C. The transfer lines were maintained at 230°C. The CI spectra were measured using 99.5% methane and isobutane (Matheson) over the range of m/e 50 to 400, at 1.5 sec/scan and a 1 sec interval. The ionization chamber was maintained at a pressure of  $2 \times 10^{-5}$  mbar (.2 torr) for both methane and isobutane. The accelerating voltage was 4.0 kV and the emission current was 100 amps. Mass calibration files were generated with perfluorokerosene (PFK). The electron impact spectra were obtained with an electron energy of 70 eV.

The B/E scans were performed with the VG 7070 GC/MS/DS equipped with a 4% OV101 column (1/8 inch o.d. X 6ft.) with a flow rate of 30 ml/min. The temperature of the column was 200°C and the injector was 210°C. The source was maintained at 200°C and the transfer lines were heated to 200°C. The spectra were measured using 99.95% isobutane (Matheson) over the range of m/e 60 to 500 at 1.0 sec/scan at a 1 sec interval. The ionization chamber was maintained at  $2 \times 10^{-5}$  mbar. The accelerating voltage was 6.0 kV, electron voltage was 90 eV, and the emission current at 0.5mA. Helium was used as the collision gas and the spectra were recorded with a UV recorder.

Atmospheric Pressure Ionization Mass Spectrometry (APIMS)

An atmospheric pressure ionization mass spectrometer (APIMS) was used for certain aspects of this study to identify ionic species with and without the presence of added oxygen. This homebuilt APIMS has an ECD as the ion source of internal volume (1 ml) typical of  $^{63}\text{Ni}$  ECD's and includes a coaxial pin which serves as the ECD anode. A five-eighth inch nickel disk of 25  $\mu\text{m}$  aperture in its center provides a controlled leak of the ions source contents into the vacuum region of a quadrupole mass filter. Figure 12 illustrates the ion source and schematic of the APIMS used in these studies. With this instrument, the ECD response to an electron capturing compound can be monitored along with mass spectral measurements of the ions simultaneously formed in the API source. In addition, the ions formed in the presence of oxygen can also be monitored. The APIMS was mass calibrated with  $\text{SF}_6$  and hexachlorobenzene. An Aerograph gas chromatograph with a 1.5ft packed column containing 4% OV101 on Chromosorb W was used to introduce selected samples into the APIMS. The temperature of the ion source was 250°C, and the carrier gas was nitrogen at a flow rate of 40 ml/min. By combining the carrier gas with about 7 ml/min of nitrogen containing 2% oxygen after the column and before the cell, an oxygen concentration of approximately 3 ppt was obtained when desired. Negative ions with and without oxygen present in the carrier gas can be identified both by single-ion monitoring of chromatographic effluent and also by performing mass scans during the elution of the substances of interest. Usually,

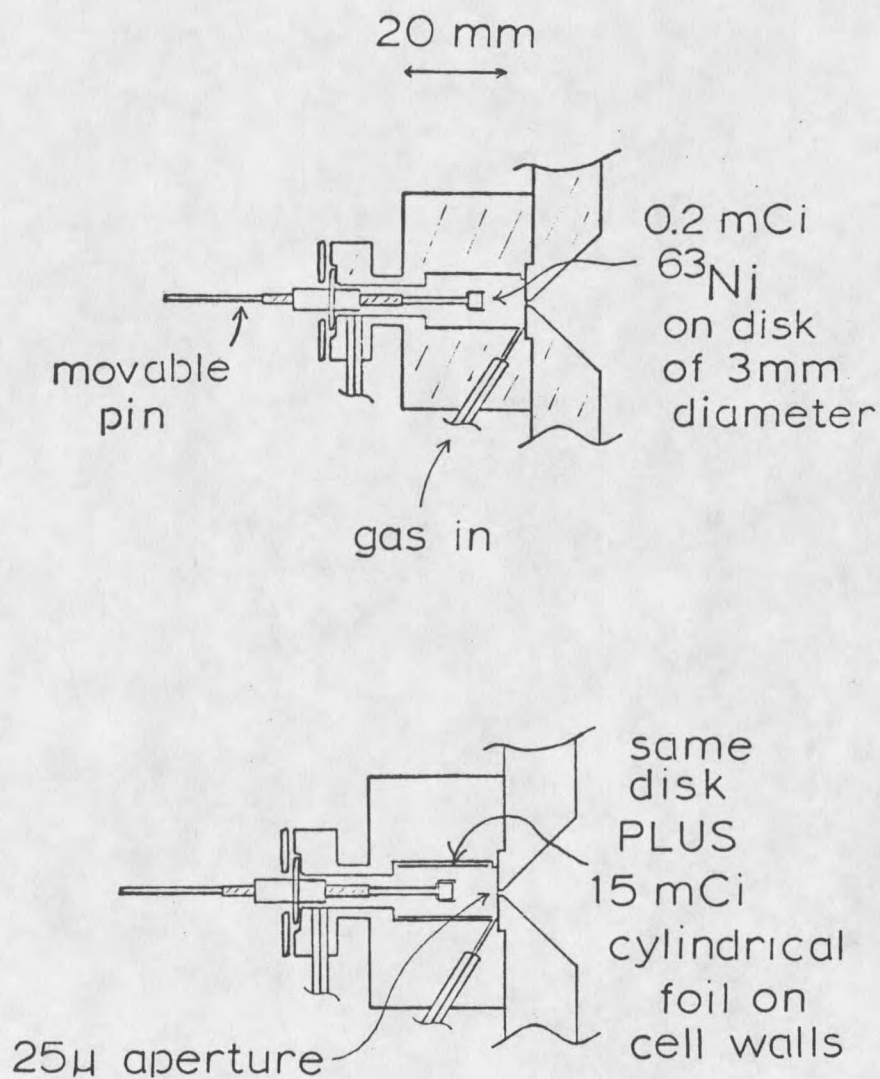


Figure 12. Two sources used in the APIMS studies.

higher column temperatures were used for single-ion monitoring than mass scanning. In the scanning mode, one normally scans a 100 mass range in approximately 10 sec. In using lower column temperatures, the peak elution time is long enough to allow to scan the desired range. For single ion monitoring, one needs a high a signal as possible and that is why a higher column temperature is desired.

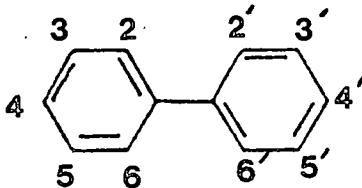
## RESULTS AND DISCUSSION

The first portion of this study will be discussed in sections corresponding to the various sets of isomeric compounds examined: polychlorobiphenyls, chloroanthracenes and chlorophenanthrene, polycyclic aromatic amines, polycyclic aromatic hydroxides, methylanthracenes, and methylphenanthrenes, and 2,3,7-trichlorodibenzo-p-dioxin. The second portion will be involved with the techniques utilized in optimizing the precision with which individual response enhancement measurements can be made.

Polychlorobiphenyls (PCBs)

## Isomer Differentiation

The numbering scheme and structure for the PCBs is shown as follows:



and a typical chromatogram indicating the response enhancements is indicated in Figure 13. The response enhancements for the monochloro, dichloro, and trichlorobiphenyls are listed in Table 2. For the monochlorobiphenyl compounds studied, the 4-isomer can be distinguished from the other two. Based solely on response enhancement values, the 3-isomer could not be differentiated from the 2-isomer. The 3,5-isomer can easily be distinguished from the

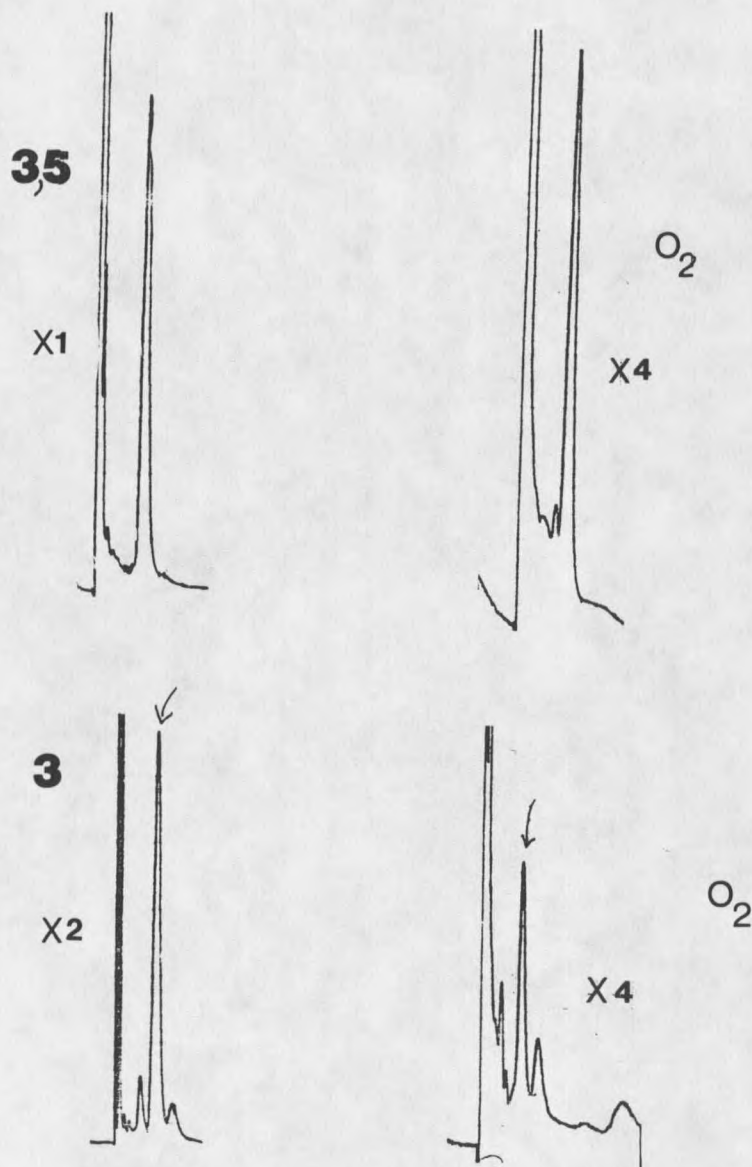


Figure 13. The response of ECD to 3-chlorobiphenyl (bottom) and 3,5-dichlorobiphenyl (top). The chromatograms on the left are with normal ECD conditions and the ones on the right are with 0.20% oxygen in the detector at 250°C.

Table 2. Response Enhancements (R.E.) for the Chlorinated Biphenyls

| <u>Chlorinated Biphenyls</u> | <u>R.E.</u> |
|------------------------------|-------------|
| 2                            | 1.0         |
| 3                            | 1.1         |
| 4                            | 1.6         |
| 2, 3                         | 2.1         |
| 3, 5                         | 4.0         |
| 2, 4                         | 2.3         |
| 4, 4'                        | 2.5         |
| 2, 6                         | 1.5         |
| 3, 3'                        | 1.0         |
| 2, 5                         | 1.9         |
| 2, 2'                        | 1.0         |
| 3, 4, 5                      | 2.1         |
| 2, 4, 5                      | 2.2         |
| 2, 4, 6                      | 2.6         |
| 2, 3, 6                      | 2.3         |
| 2, 3, 5                      | 2.1         |
| 2, 3, 4                      | 2.2         |
| 3, 5, 4'                     | 2.1         |

others, in view of its relatively high response enhancement. The 4,4'-isomer can be differentiated from the 2,6-, 3,3'-, 2,3-, 3,5- and 2,2'-chlorobiphenyls but not the rest of the dichlorobiphenyls. The 2,2' and 3,3' dichlorobiphenyls can be distinguished from the others based on their low enhancement values. The 2,4,6-trichlorobiphenyl isomer can be differentiated from the others, but based solely on enhancement values, the others could not be distinguished. As one increases the number of chlorine atoms, the response enhancement does not decrease. Even as the number of chlorine atoms increases to three and four, the response enhancements remain clustered around two. In an examination of the alkylchlorides, Miller *et al.* (98) found that as the number of chlorine atoms increased, the normal ECD response increased and the response enhancement usually decreased. It is also interesting to note that the response enhancements for all the biphenyl compounds are very low as compared to other compounds studied. This is probably due to the arrangement of the rings.

#### Chloroanthracenes and Chlorophenanthrene

##### Isomer Identification

The three isomers of chloroanthracene and 9-chlorophenanthrene have identical mass spectra which are shown in Figure 14 and 15, respectively and the relative ion intensities are listed in Table 3. The ions observed with the largest intensities are the parent ion at  $m/e$  212 and the ion at  $m/e$  176 which represents a loss of HCl from the parent ion. Therefore, no distinction is expected to

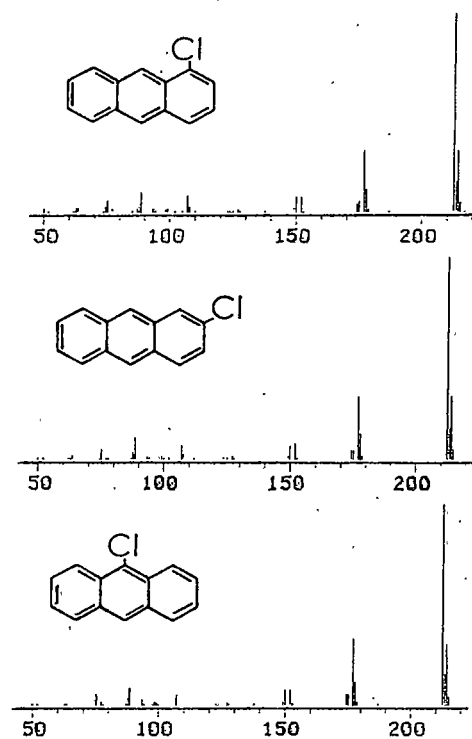


Figure 14. The electron impact mass spectra for 1-, 2-, and 9-chloroanthracene.

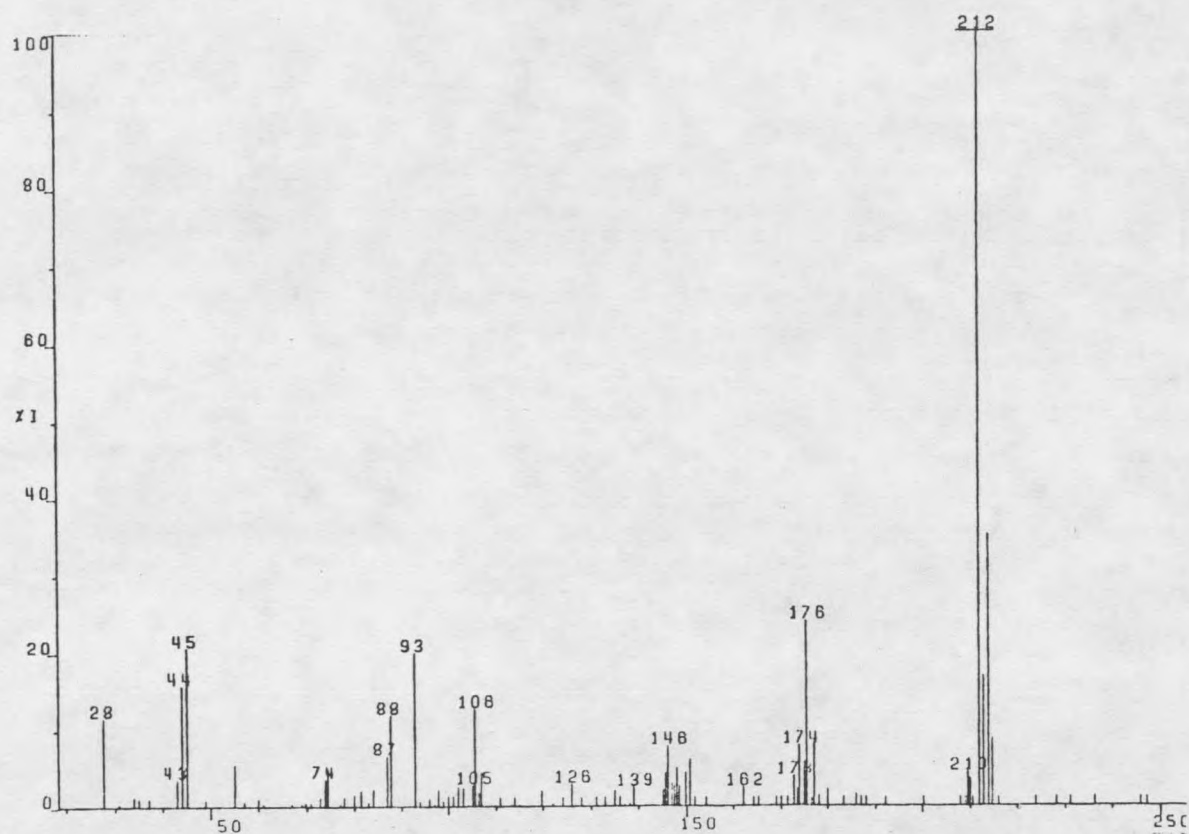


Figure 15. The electron impact mass spectrum of 9-chlorophenanthrene.

Table 3. Relative Abundances for the Chloro Isomers of Anthracene and Phenanthrene

| <u>M/E</u> | <u>% Abundance</u> |           |           |           |
|------------|--------------------|-----------|-----------|-----------|
|            | <u>1A</u>          | <u>2A</u> | <u>9A</u> | <u>9P</u> |
| 75.1       | 6.0                | 5.0       | 6.0       | 4.9       |
| 88.1       | 10.5               | 10.6      | 8.9       | 11.8      |
| 106.0      | 7.5                | 6.9       | 6.3       | 4.1       |
| 150.1      | 8.0                | 7.5       | 7.9       | 4.1       |
| 151        | 8.2                | 7.8       | 7.9       | 6.0       |
| 175        | 5.6                | 5.3       | 5.9       | 5.6       |
| 176        | 31.1               | 30.7      | 32.6      | 23.9      |
| 177        | 12.3               | 12.6      | 12.0      | 8.1       |
| 212        | 100                | 100       | 100       | 100       |
| 213        | 16.2               | 15.8      | 16        | 16.7      |
| 214        | 31.1               | 30.6      | 29.2      | 34.9      |

be provided by conventional forms of mass spectra. In Figure 16, typical chromatograms are shown from which determinations and response enhancements are obtained. The first chromatograms are for the pure isomers of 1-, 2-, and 9-chloroanthracene and 9-chlorophenanthrene. For each pair of chromatograms the lower one is obtained with approximately 3.0 parts per thousand oxygen continuously present in the detector at 300° C. It is seen that the response of each of the pure isomers is enhanced by oxygen's presence, but by differing magnitudes. The response to the 1-isomer is enhanced by 4.0, to the 2-isomer by 6.9, to the 9-isomer by 21.0, and the 9-chlorophenanthrene by 1.8. In addition the data in Figure 17 indicate that the magnitude of the response enhancement observed for the isomers of chloroanthracene is a relatively constant value over at least two orders of magnitude change in concentration above the lowest concentration levels used here. This fact is extremely important and eliminates determining calibration curves for these compounds. The response enhancement values can be utilized to provide positive identification in cases where mass spectrometry fails.

#### Mixture Analysis (120)

If the composition of mixed peaks are to be determined from the measured response enhancement, it is necessary that the enhancement of a mixed peak,  $RE_{mix}$ , be expressible as the sum of the contributions of the individual components as shown in Equation 23.

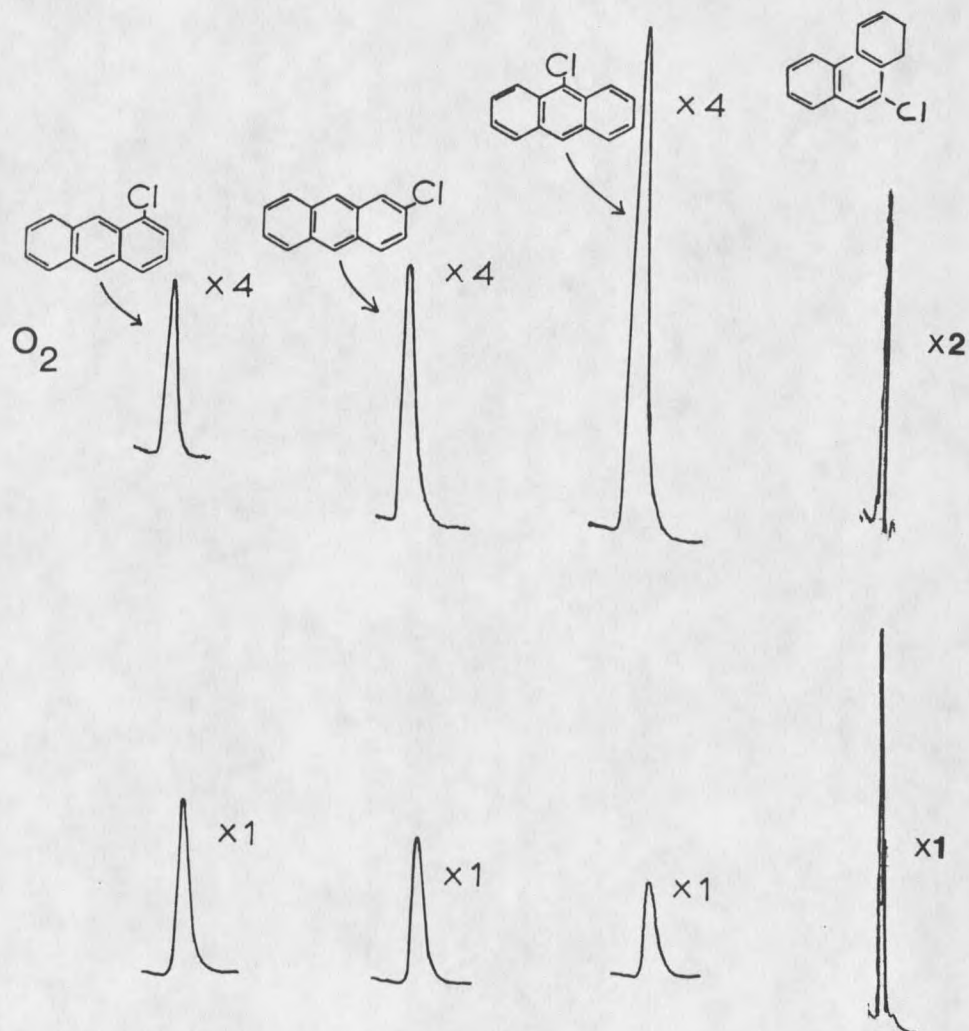


Figure 16. ECD responses to 1-, 2-, and 9-chloroanthracene, and 9-chlorophenanthrene (bottom) and chromatograms with 0.30% oxygen present in the detector (top). Detector temperature is 300°C.

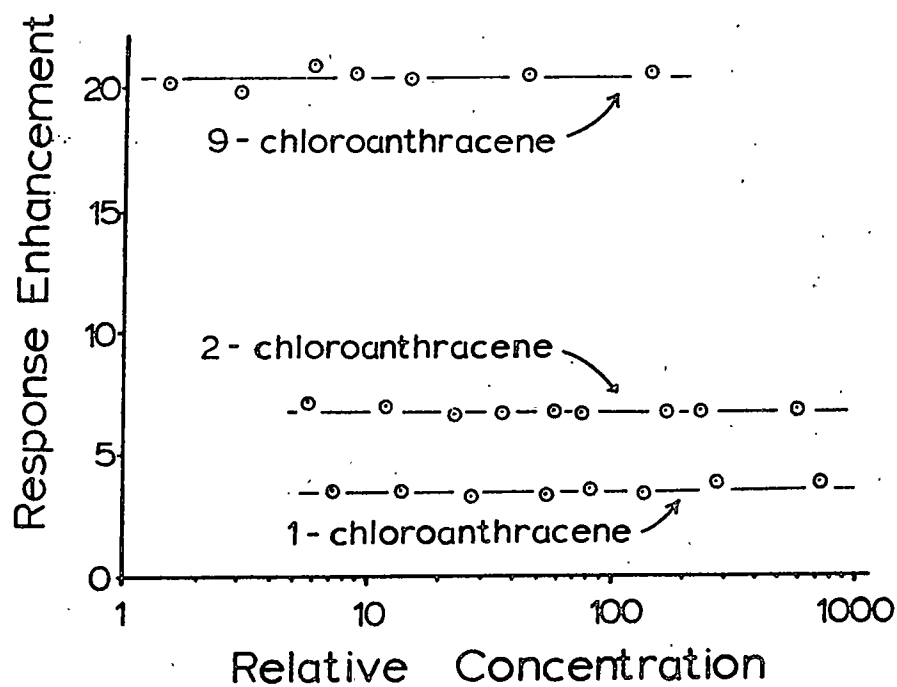


Figure 17. Oxygen-induced response enhancements for the chloroanthracenes as a function of concentration. A relative concentration value of 1.0 corresponds to 10 ng injected.

$$RE_{mix} = \sum X_i RE_i \quad (23)$$

where  $RE_i$  is the oxygen-caused response enhancement of the individual components,  $X_i$ , is the molar fraction of substance  $i$  in the mixture peak and  $\sum X_i = 1$ . An example of a two-component mixture is indicated in Figure 18. In order to test the validity of this relationship the response enhancements of many different mixtures of the chloroanthracenes have been measured. For the three possible sets of two-component mixtures, the results are shown in Figure 19 where the measured enhancement is plotted as a function of the molar fraction of one of the sample components. These data indicate that the measured enhancements are linearly related to the molar fraction of each component and that Equation 23 does, indeed, describe the response enhancement expected for a binary mixed peak. It would be relatively straight forward, therefore, to determine the relative amounts of two isomers known to be present in a mixed binary peak of unknown composition. For these cases the unknown quantities sought,  $X_1$  and  $X_2$ , are obtained from the application of Equation 23 and the trivial relationship that the sum of the mole fractions is equal to one, i.e.,

$$X_1 + X_2 = 1 \quad (24)$$

It is reasonable to expect that Equation 23 will also be applicable to three component peaks. The last pair of chromatograms in Figure 20 is seen to support this expectation, since response enhancements measured for the individual isomers and

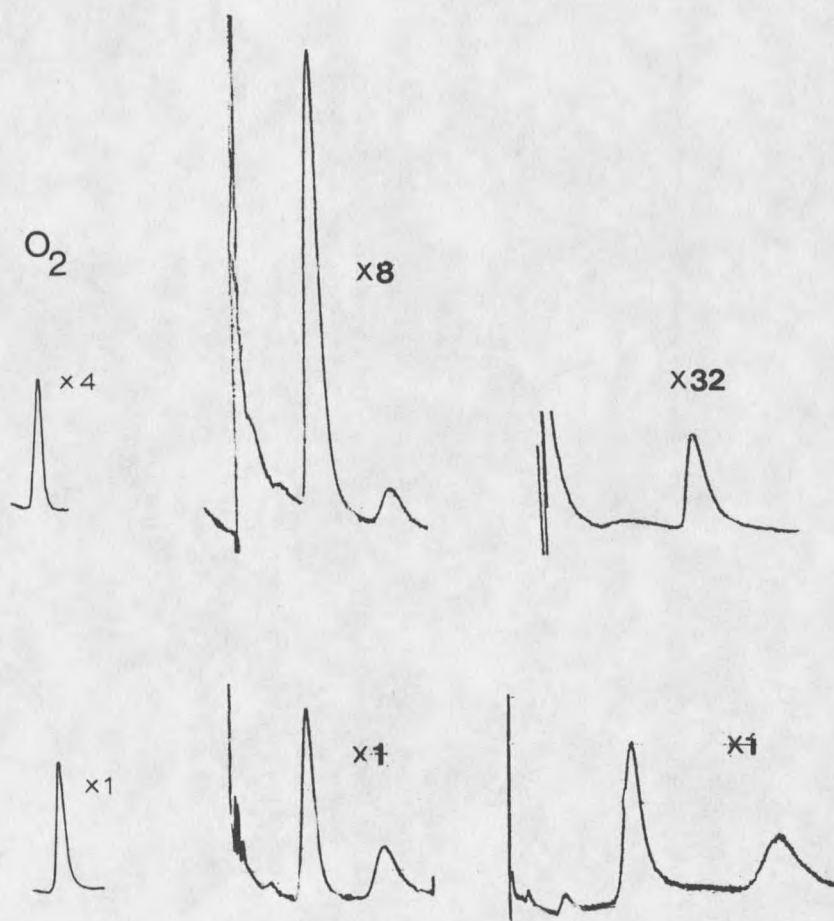


Figure 18. Normal ECD responses for 1- and 9-chloroanthracene and a mixture of the two (bottom chromatograms) and with the addition of 0.30% oxygen in the detector (top) at a temperature of 300°C. Mole fraction of 1-chloroanthracene is 0.19 and for 9-chloroanthracene is 0.81 in the mixture.

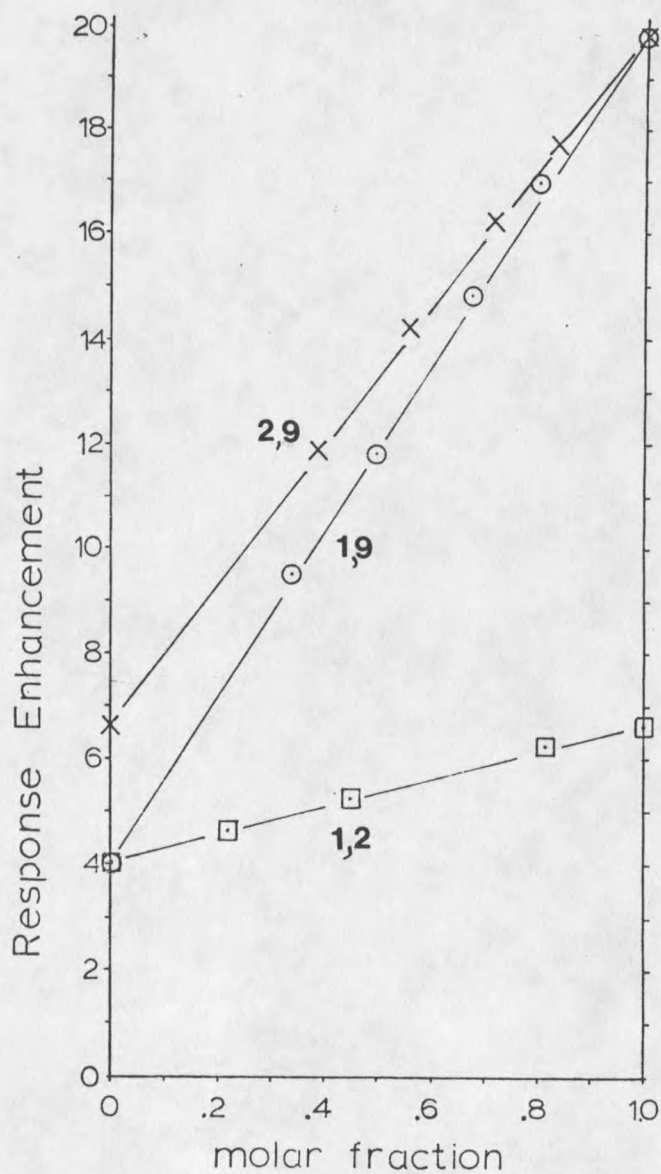


Figure 19. Response enhancements of two-component mixtures as a function of the molar fraction of one of the components. The mixtures are composed of 1- and 2-chloroanthracene ( $\square$ ), 1- and 9-chloroanthracene ( $\circ$ ), and 2- and 9-chloroanthracene ( $\times$ ).

from the known molar ratios of each in the mixture, a value of 11.1 is predicted ( $0.35 \times 4.0 + 6.9 \times 0.29 + 0.37 \times 21.1 = 11.1$ ).

Unfortunately, for the three component mixture system, the relative composition of an unknown mixed peak is not uniquely determined by a single enhancement measurement as in the binary case. In this case a single  $RE_{mix}$  value has many possible solutions when applied to Equation 23 since there are then three unknowns and only two equations relating them. For the chloroanthracenes under consideration here a solution to this problem is provided by repeating all enhancement measurements at a different detector temperature. The above measurements have indicated that at 300° C, the measured enhancements are  $RE_1 = 4.0$ ,  $RE_2 = 6.9$ ,  $RE_9 = 21.1$  and  $RE_{mix} = 11.2$ . With a detector temperature of 350°C, these enhancement measurements are found to be 2.5, 3.4, 15.6, and 7.6, respectively. Figures 20 and 21 illustrate the chromatograms obtained at 300°C and 350°C, respectively. With the data at 350° C, Equation 23 can be used a second time to provide the third equation necessary to determine uniquely the molar ratios in the three component mixtures. Applying this procedure to the synthesized mixture of three isomers, the data indicate that the molar ratios are  $X_1 = 0.32$ ,  $X_2 = 0.31$ , and  $X_9 = 0.37$ . These values are in good agreement with the known values of 0.35, 0.28, and 0.37, respectively. The equations needed to solve these three component systems are as follows:



Figure 20. ECD responses to pure isomers of chloroanthracene and a mixture of isomers without oxygen (lower chromatograms) and with 0.30% oxygen (upper chromatograms) in the detector at 300°C. Samples amounts are 2.9, 2.3, and 1.5 ng for the 1-, 2-, and 9-chloranthracene isomers respectively. The mixture contains molar fractions of these components of 0.35, 0.28, and 0.37, respectively.



Figure 21. ECD responses to pure isomers of chloranthracene and a mixture of all three isomers without oxygen (lower chromatograms) and with 0.30% oxygen (upper chromatograms) in the detector at 350°C. Sample amounts are 2.9, 2.3, and 1.5 ng for the 1-, 2-, and 9-isomers, respectively. The mixture contains molar fractions of these of 0.35, 0.28, and 0.37, respectively.

$$RE_{MIX(T_1)} = X_1 RE_1 + X_2 RE_2 + X_9 RE_9 \quad (25)$$

$$RE_{MIX(T_2)} = X_1 RE_1' + X_2 RE_2' + X_9 RE_9' \quad (26)$$

$$X_1 + X_2 + X_9 = 1 \quad (27)$$

In solving the three-component problem it is essential to recognize that the new set of RE values obtained at a second detector temperature must not be proportionately related to the second set. That is, if the new set were merely half, for instance, of the original set, no additional information will be obtained by the analysis at the second temperature. The reason for this is made clear by inspection of Equation 26 which is seen to be unchanged if all the RE values are simply altered by a proportional factor. Also, for this reason, no new information concerning the sample is expected by altering the amount of oxygen used in the detector for the enhancement measurement. We have previously shown that for the constant-current ECD that this change merely increases or decreases all RE values in proportion.

Also, with this detection scheme, it is important to recognize the situations where peak height rather than peak area can be used as the measure of detector response. With the short packed column used for these studies, the retention times of the three chloroanthracenes were indistinguishable. In this case their peak height or peak area could be used as a measure of response and the

same values for  $RE_{MIX}$  and  $RE_i$  are obtained (this is true as long as the normal and oxygen-sensitized responses are linearly related to sample concentrations over the concentration range of interest.) However, for the cases where the components of a mixed peak are partially separated by the column, care must be taken to use the peak area, only, as the measure of response. Then the method as outlined can be used for the quantitation of partially resolved mixed peak. For these cases, the use of the peak height as the measure of response will cause systematic error because at the instant of the peak maxima, the molar ratio of components in the detector differs from the molar ratio of these components in the original sample.

For chromatographic separations where only partial resolution of a mixed peak is observed, the use of the oxygen-sensitized ECD can be helpful in providing an indication of the nature of that partial separation. Consider, for example, the two chromatograms shown in Figure 22. The same mixture of the three chloroanthracenes as was previously described ( $X_1 = 0.35$ ,  $X_2 = 0.29$ ,  $X_3 = 0.37$ ) is now partially separated into a doublet by the use of a capillary column. The question one might ask is to which portions of this doublet do the individual isomers contribute. This question could be answered by very precise measurement of the retention times of the individual components or by the analysis of several prepared standards containing varied and known amounts of each of the three isomers. Alternatively, this information is provided very clearly and simply by repeating the analysis once

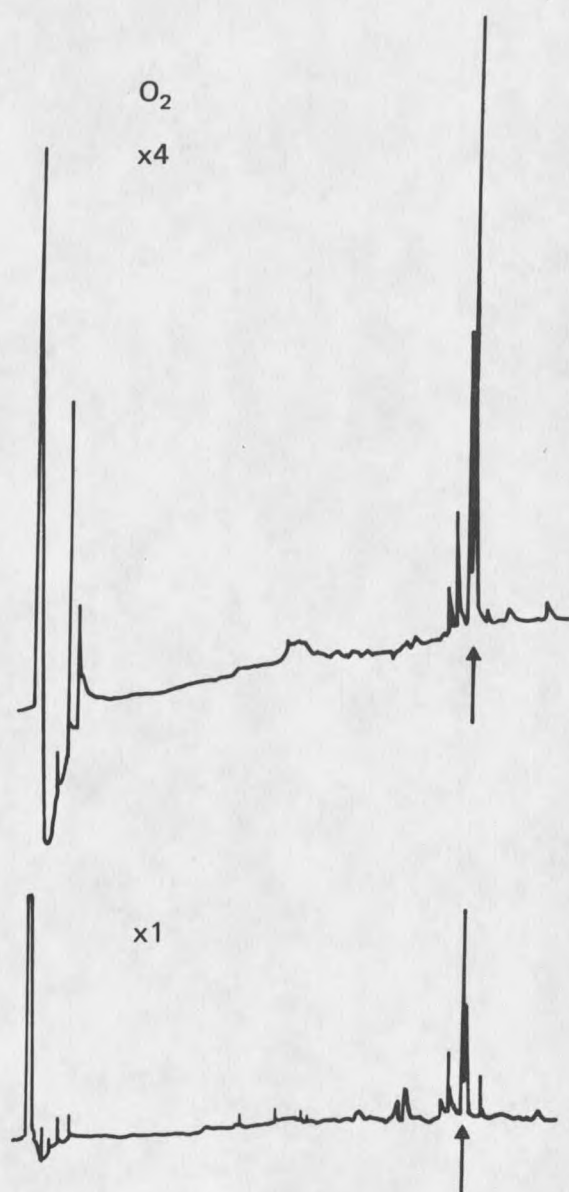


Figure 22. Capillary column gas chromatograms of the three-component mixture shown in Figure 20. The arrows indicate the point of elution of the chloranthracene isomers. The lower chromatogram is with normal EC detection and the upper is with 0.30% oxygen in the makeup gas. Detector temperature is 300°C.

with oxygen in the detector. By a comparison of the two chromatograms in Figure 22, it is evident that the second peak of the doublet is due to the 9-isomer, alone, since its enhanced by about 21 times in the presence of oxygen. The first peak is enhanced by 5.4 and, therefore, is a composite of approximately equimolar quantities of the 1- and 2-isomers. In correct terms  $X_1 = 0.55$  and  $X_2 = 0.45$ . The calculated response enhancement for this mixture of components should be  $0.55 (4.0) + 0.45 (6.9) = 5.3$  which agrees quite well with the experimental value. Since the same sample analyzed here is the same three-component mixture shown previously in Figure 19, the above deductions are correct.

In addition, the same three-component mixture was analyzed with the oxygen-sensitized ECD using an on column injector. The sample is actually injected on to the column through a cold injector. The results are shown in Figure 23. Again, the enhancements give an indication of the identity of the components. In using the type of logic discussed previously, it is obvious that the first peak is approximately an equimolar mixture of 1- and 2-isomers. In view of the large enhancement value obtained for the last peak, the identity of that peak is definitely the 9-isomer. The results indicate that for compounds that may be extremely unstable in a hot injector (thermally labile), this type of system will still lend itself for isomer identification.

It is anticipated that the detector scheme described here could be useful for the analysis of many electron capture-active compounds where the relative amounts of potentially present

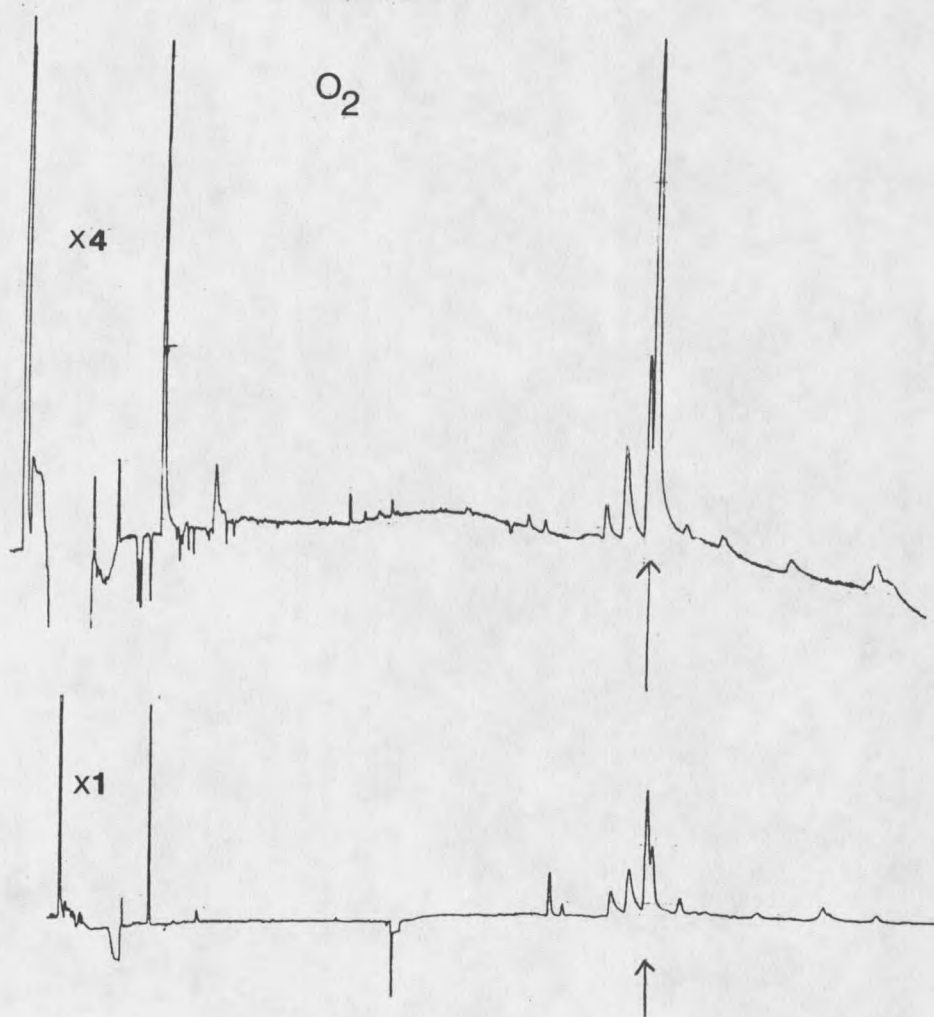


Figure 23. Capillary column gas chromatograms of the three-component mixture in Figure 20 with an on-column injector. The arrows indicate the point of elution of the chloroanthracene isomers. The lower chromatogram is with normal EC detection and the upper is with 0.30% oxygen in the makeup gas. Detector temperature is 300° C.

structural isomers under consideration meet certain minimum requirements of the method demonstrated here for the chloroanthracenes. First, the measured response enhancements of the pure isomers must be unique for each isomer. Second, the normal and the oxygen-sensitized responses of the ECD must be linearly related to the concentration of each analyte over the concentration range of interest.

#### Atmospheric Pressure Ionization Mass Spectrometer (APIMS)

In order to examine the ions formed by the chloroanthracenes with and without the presence of oxygen, the APIMS was used. An example of the negative ion API mass spectral scan taken during the elution of 9-chloroanthracene with and without added oxygen is illustrated in Figure 24.

The APIMS results for the chloroanthracenes and 9-chlorophenanthrene are shown in Table 4 obtained from single-ion monitoring. Some interesting features come immediately to attention. Without any oxygen present in the system, both the 2-isomer and 1-isomer form primarily the  $M^-$  ion.

The ratio of the  $M^-/(M + O_2)^-$  is 6 and 3, respectively for the 1- and 2-isomers. The 9-chloroanthracene and 9-chlorophenanthrene show primarily the  $(M-Cl+O_2)^-$  species. In the presence of oxygen (approximately 3 ppt), both the 2-isomer and 1-isomer form primarily the  $(M+O_2)^-$  species while both the 9-chloroanthracene and 9-chlorophenanthrene form almost entirely  $(M-Cl+O_2)^-$ . These results are consistent with other researchers who have found

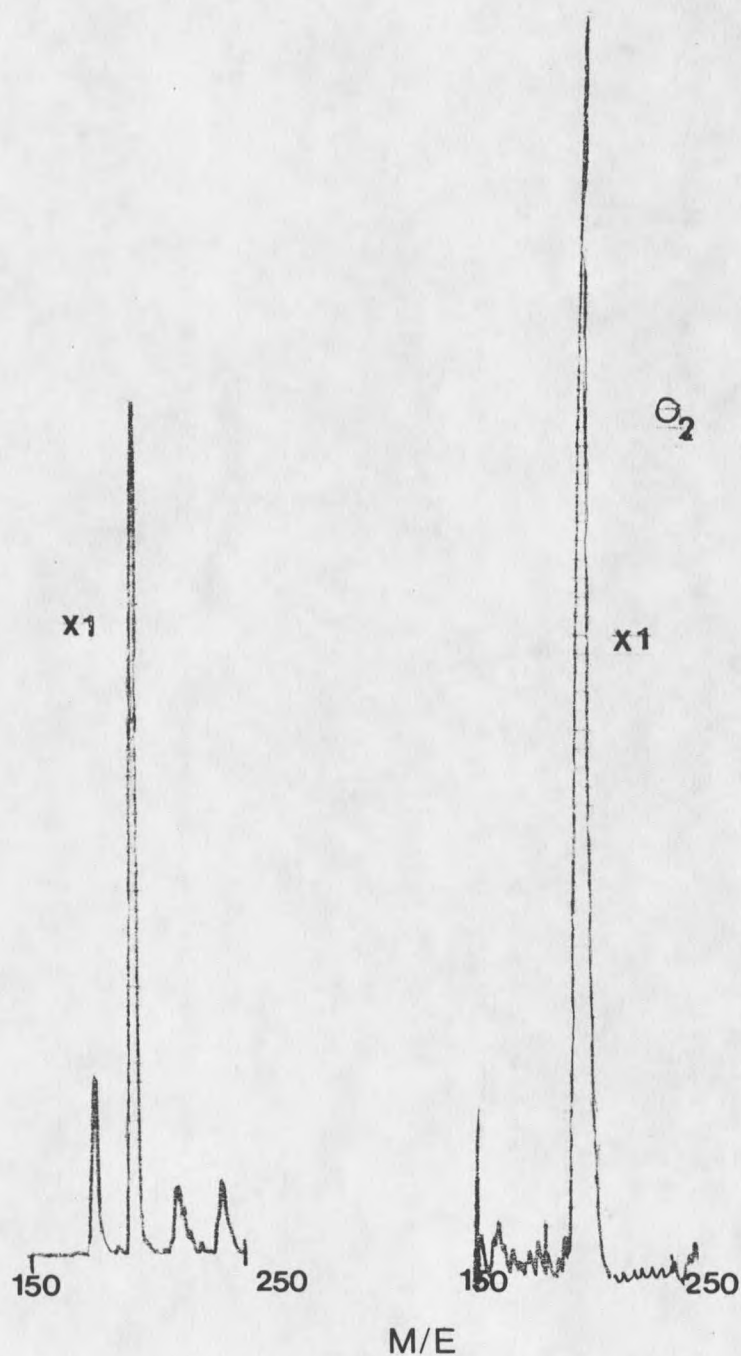


Figure 24. Negative API mass spectral scans taken during elution of 9-chloroanthracene without and with added oxygen at a source temperature of 250°C.

Table 4. APIMS Results for the Chloronthraces and 9-chlorophenanthrene from Single-Ion Monitoring <sup>a</sup>

without Oxygen

| <u>M/E</u>                             | <u>1A</u> | <u>2A</u> | <u>9A</u> | <u>9P</u> |
|----------------------------------------|-----------|-----------|-----------|-----------|
| 212(M-)                                | 2800      | 3000      | 200       | 100       |
| 244(M+O <sub>2</sub> ) <sup>-</sup>    | 500       | 1000      | 1500      | 1000      |
| 194(M-CL+O) <sup>-</sup>               | 100       | 100       | 100       | 100       |
| 209(M-CL+O <sub>2</sub> ) <sup>-</sup> | 250       | 100       | 4000      | 4000      |
| 228(M+O) <sup>-</sup>                  | 500       | 100       | 500       | 100       |
| TOTAL                                  | 5000      | 6000      | 6500      | 6000      |

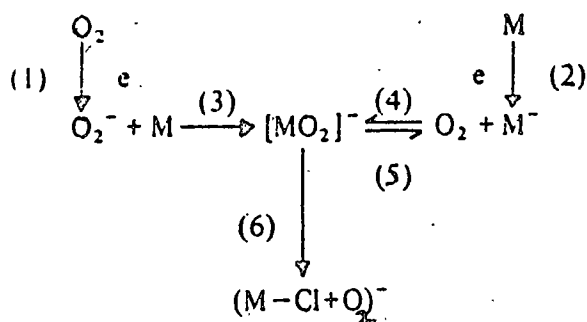
with Oxygen <sup>b</sup>

| <u>M/E</u> |      |      |      |      |
|------------|------|------|------|------|
| 212        |      | 50   |      |      |
| 244        | 600  | 4300 | 100  | 100  |
| 194        | 100  | 50   | 50   |      |
| 209        |      | 50   | 6500 | 3500 |
| 228        |      |      | 100  | 100  |
| TOTAL      | 1000 | 4000 | 6500 | 4000 |

<sup>a</sup> Source temperature is 250°C.

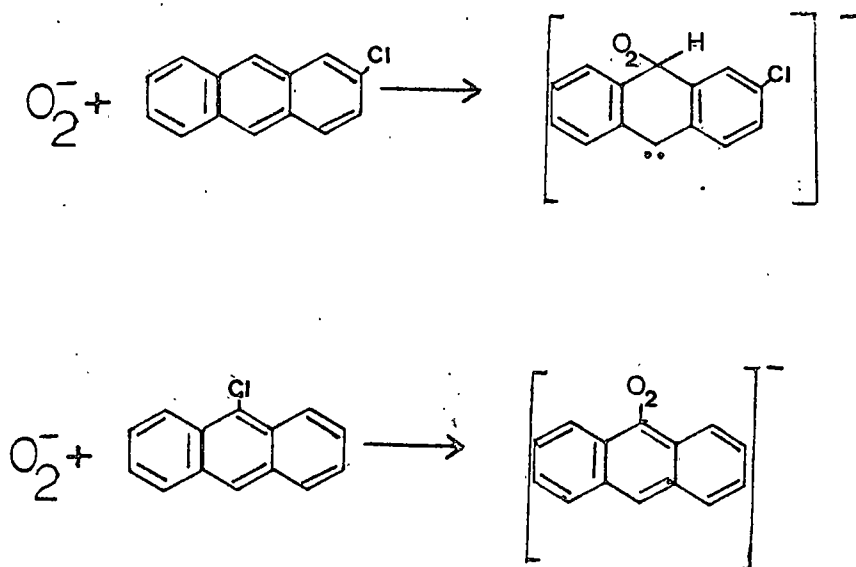
<sup>b</sup> Oxygen concentration is about 3ppt.

similar reactions with other chlorinated species (91,92,94). It is reasonable to be able to distinguish the 9-isomers from the other two based on their propensity to form the  $(M-Cl+O_2)^-$  species in the presence of oxygen in the APIMS. One could also possibly be able to do binary mixture analysis (for example, 9-chloroanthracene and 2-chloroanthracene) based on the ratio of the  $(M-Cl+O_2)^- / (M+O_2)^-$  species. The following reaction sequence is postulated for the chloroanthracenes and chlorophenanthrene and their reaction with  $O_2$  in the API source. This is similar to that of Horning and coworkers (92,94).



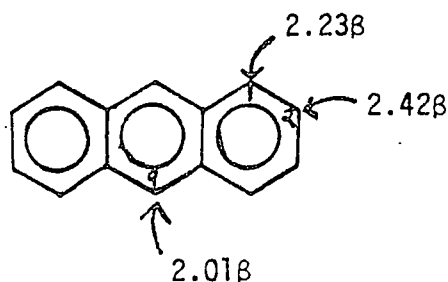
For the isomers of chloroanthracene and chlorophenanthrene, an intermediate  $(M+O_2)^-$  is formed by reactions 1 and 3 or 2 and 4. This intermediate may remain intact, as in the case for 1- and 2-chloroanthracene, or dissociate, through reaction 6 to form  $(M-Cl+O_2)^-$  ions which are observed for 9-chloroanthracene and 9-chlorophenanthrene. Another result of the API studies indicates that the position of attack by  $O_2^-$  occurs at the 9 or 10 position of 9-chloroanthracene as well as the other chloroanthracene isomers. In

both the 1- and 2-isomer, the presence of the  $(M+O_2)^-$  species and for the 9-isomer, the presence of  $(M-Cl+O_2)^-$  species with oxygen clearly indicates that the attack by  $O_2^-$  takes place at the 9 or 10 positions of chloroanthracene. The nucleophilic attack of  $O_2^-$  on chloroanthracene probably occurs by the following reaction.



These predictions are also consistent with results calculated from simple Huckel theory for the simple molecules with no substituents. The values of  $E_{LUMO}$  and  $L^-$ , which are readily available (121) or easily calculated for polycyclic aromatic hydrocarbons and provide a useful guide to the behavior of all PAHs in the ECD, with and without  $O_2$  doping.  $E_{LUMO}$  is defined as the calculated energy of the lowest unoccupied molecular orbital and  $L^-$  is the calculated resonance energy lost by removal of a specific atom from the  $\pi$ -electron system. In a simple molecule like

anthracene there are essentially only three positions for a single substituent. These positions with their corresponding  $L^-$  values are:



These values indicate that probable nucleophilic attack by  $O_2^-$  would occur at either the 9 or 10 position. In other words, the earlier computer predictions actually form the foundation of the proposed mechanism and the ions observed in the APIMS give additional support. Use of inductive and resonance parameters in the framework of Huckel theory satisfactorily accounts for the electron affinity for different substituents and positions of the substituents of several compounds. As an example, Wentworth *et al.* (122) utilized Huckel calculations to predict the difference in normal ECD responses for simple molecules as 1- and 2-napthaldehyde. Grimsrud *et al.* (123) have used  $E_{LUMO}$  and  $L^-$  values to correlate normal ECD response and reactivity with  $O_2^-$ , respectively. Their results correlate reasonably well with compounds such as anthracene, phenanthrene, triphenylene, and pyrene. It is postulated at this point that computer calculations (Huckel or extended Huckel) might be precise enough to predict differences in response with  $O_2^-$  as a function of isomer and substituent position.

The positive ions were also examined by APIMS and they consisted of  $MH^+$  for the chloroanthracenes and 9-chlorophenanthrene compounds.

#### Polycyclic Aromatic Amines (124)

Many compounds of biomedical and environmental interest, particularly those containing polar functional groups, are thermally labile at the temperatures required for their separation and cannot be determined directly by gas chromatography. To permit these compounds to be separated by gas chromatography the technique of derivatization was developed. The classic reasons for derivative formation are: to improve the stability of the compound; to improve the chromatographic performance of the compound by reducing undesirable column interactions; and to change the separation properties of the compound by a purposeful adjustment of its volatility, thus eliminating peak overlaps. In addition, derivatization includes the use as a means of introducing a detector-oriented tag into a molecule and as the means for maintaining the chromatographic integrity of the compound during its passage through the gas chromatographic column. The amines are derivatized not for the purpose of improving the thermal stability of the compound, but to increase its detector sensitivity. Figures 25 and 26 illustrate chromatograms of the underivatized amines of anthracene and the derivatized amines, respectively. The thermal stability is not altered and the retention times are very much the same in the two chromatogram. Figure 27 shows the ECD response of

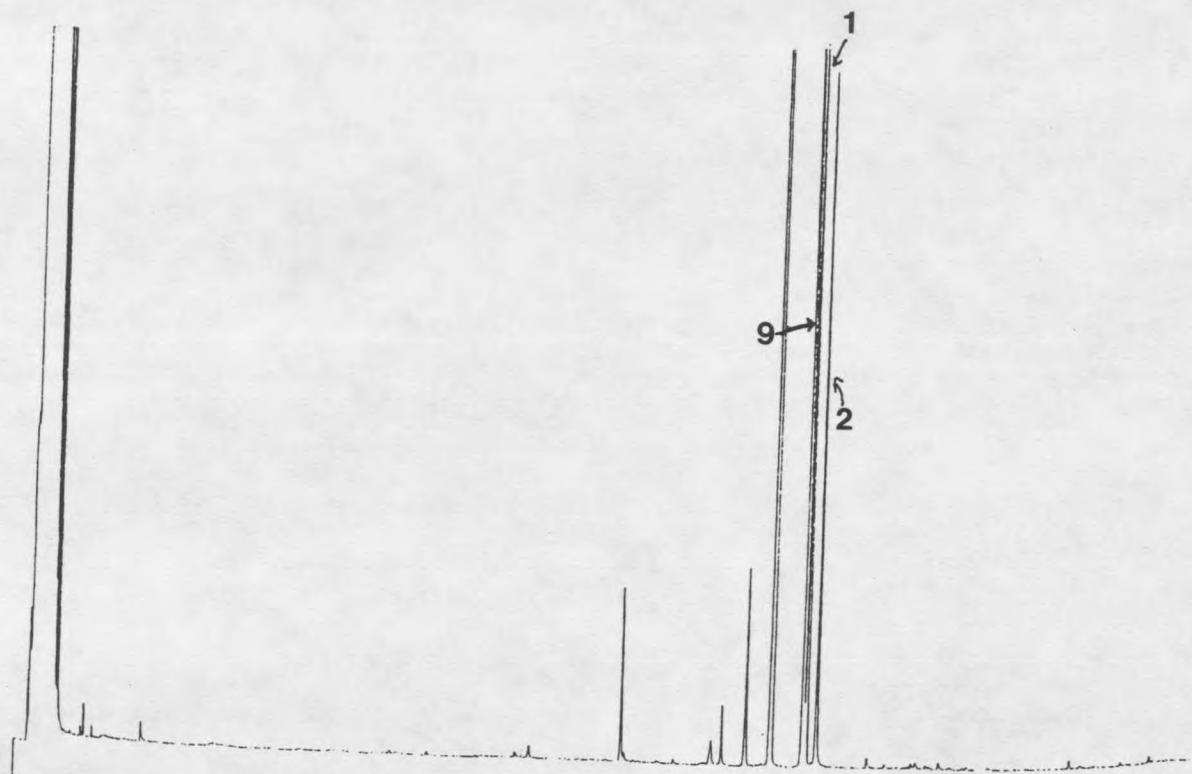
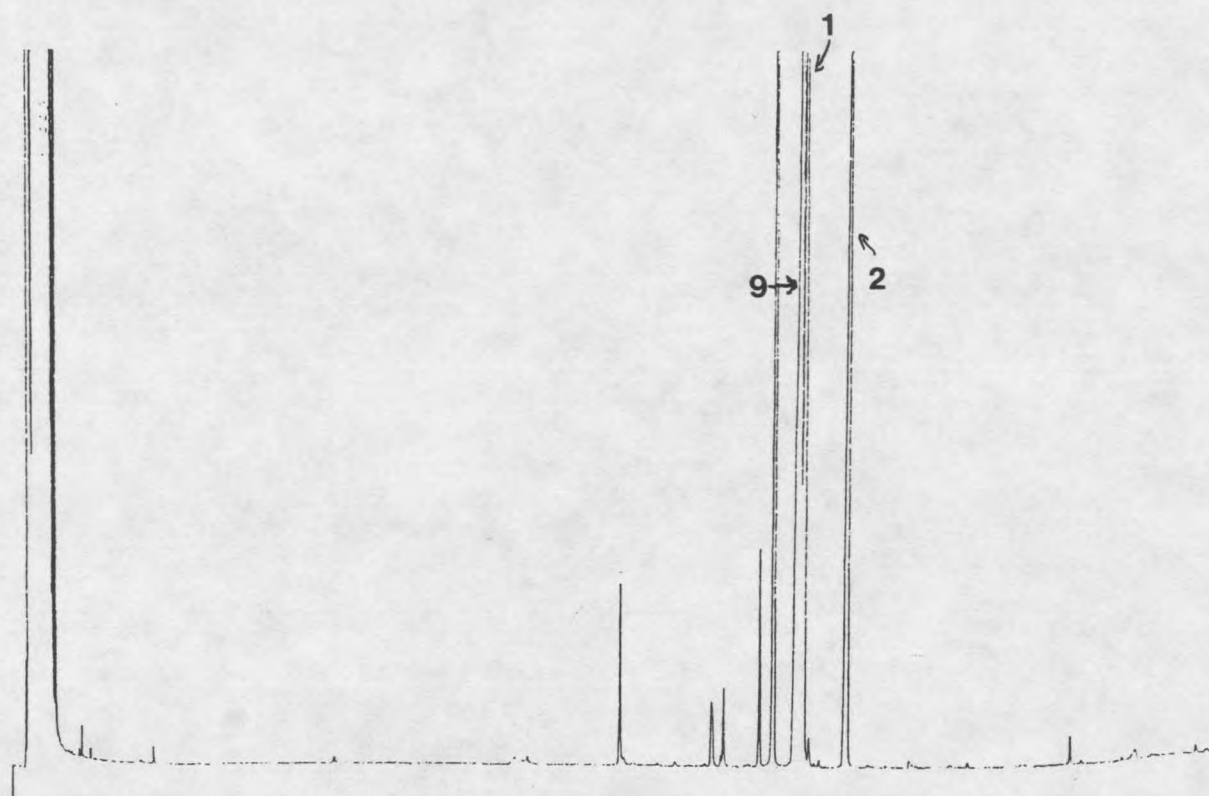


Figure 25. Flame ionization detector response to underivatized amines of 9-, 1-, and 2-aminoanthracene.



100

Figure 26. Flame ionization detector response to TFAA derivatives of 9-, 1-, and 2-aminanthracene.

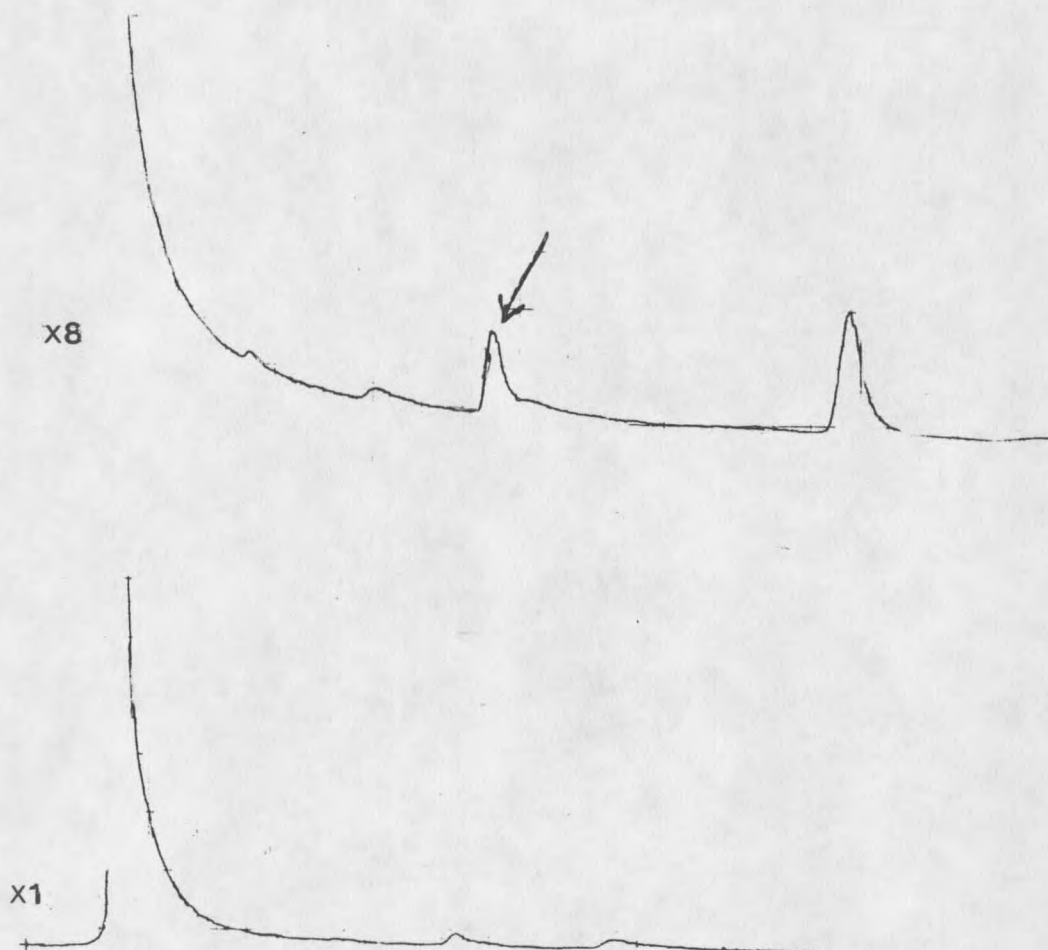


Figure 27. Normal ECD response to 9-aminophenanthrene (TFAA) (top Chromatogram) and underivatized (bottom) 9-aminophenanthrene. Concentration of underivatized is approximately 100 times derivatized compound. Detector is at 300°C.

the derivatized and underivatized amine of 9-phenanthrene. The concentration of the underivatized amine is approximately 100 times that of the derivatized amine. As a result, the derivatization procedure increases the detector sensitivity for the specific derivative.

#### Normal ECD Response of Derivatives

Martin and Rowland (125) have compared the response of the electron capture detector to various derivatives of pharmaceutically important amines. Clarke *et al.* (126) have assumed that electron attachment occurs at the carbonyl group of the amide but is destabilized by a contribution to the resonance form by the lone pair of electrons in nitrogen. This contention is further supported by the increased sensitivity of aromatic amines in which the electron density on the amino nitrogen is lowered by the electron-withdrawing ability of the benzene ring. Clarke also stated that the  $\text{CF}_3$  group by itself does not appear to hold any great advantage for electron-capture. Its power lies in enhancing the polarity of an adjacent carbonyl group.

#### Temperature Dependence

The effect of detector temperature on detector response to a particular compound is of considerable analytical significance. The response as a function of detector temperature gives an insight into the mechanisms involved in electron capture.

Figure 28 illustrates the response for the TFPA derivative of 4-aminophenanthrene and the PFPA derivative of 3-aminophenanthrene

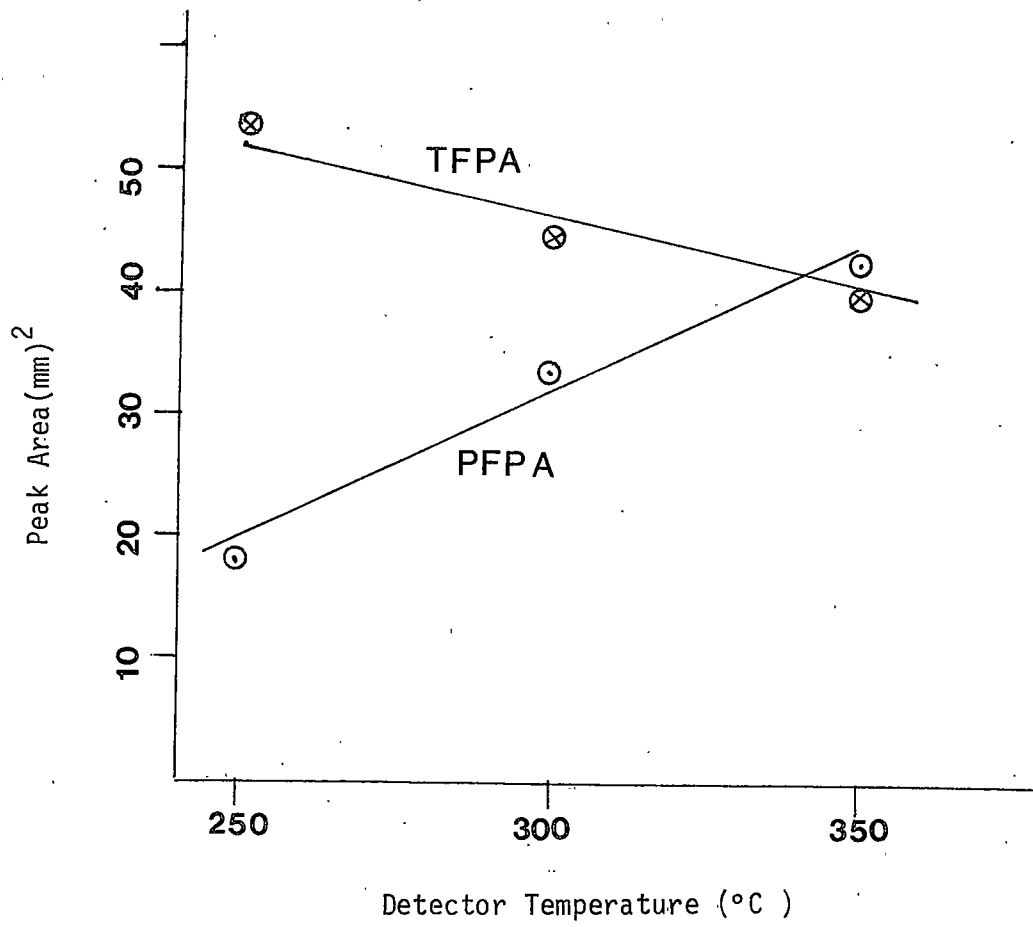


Figure 28. Normal ECD responses as a function of detector temperature for 3-aminophenanthrene (PFPA) and 4-aminophenanthrene (TFPA).

for detector temperatures of 250<sup>o</sup>, 300<sup>o</sup>, and 350<sup>o</sup>C. As one can see, for the 4-aminophenanthrene(TFAA), the response decreases as the temperature decreases over the designated temperature range. In contrast, the response for the PFPA derivative of 3-aminophenanthrene has its highest response at the highest detector temperature. This is indicative of a dissociative type of mechanism. In other words, this type of derivative follows an electron capture response similar to Reaction 1. This is similar to results obtained by Zlatkis and coworkers (127,128) for the pentafluoropropionate derivatives of n-hexylamine and cyclohexylamine. In addition, this difference in response for the two derivatives might give an insight into the characteristics of the two derivatives discussed in more detail later.

#### Isomer Differentiation

In Figures 29 and 30, typical chromatograms from which the response enhancements for the TFAA and PFPA derivatives have been determined. The chromatogram on the left is obtained by normal EC detection at 300<sup>o</sup>C detector temperature, and the one on the right is obtained with 3 ppt oxygen continuously present in the detector, again at 300<sup>o</sup>C. The magnitude of the enhancement is again determined by the ratio of the peak heights, with and without added oxygen. Table 5 lists the response enhancements determined in this way for all of the aromatic amines studied where either the trifluoroacetic anhydride(TFAA) derivative, the perfluoropropionic anhydride (PFPA) derivative, or both were examined. Table 5 also

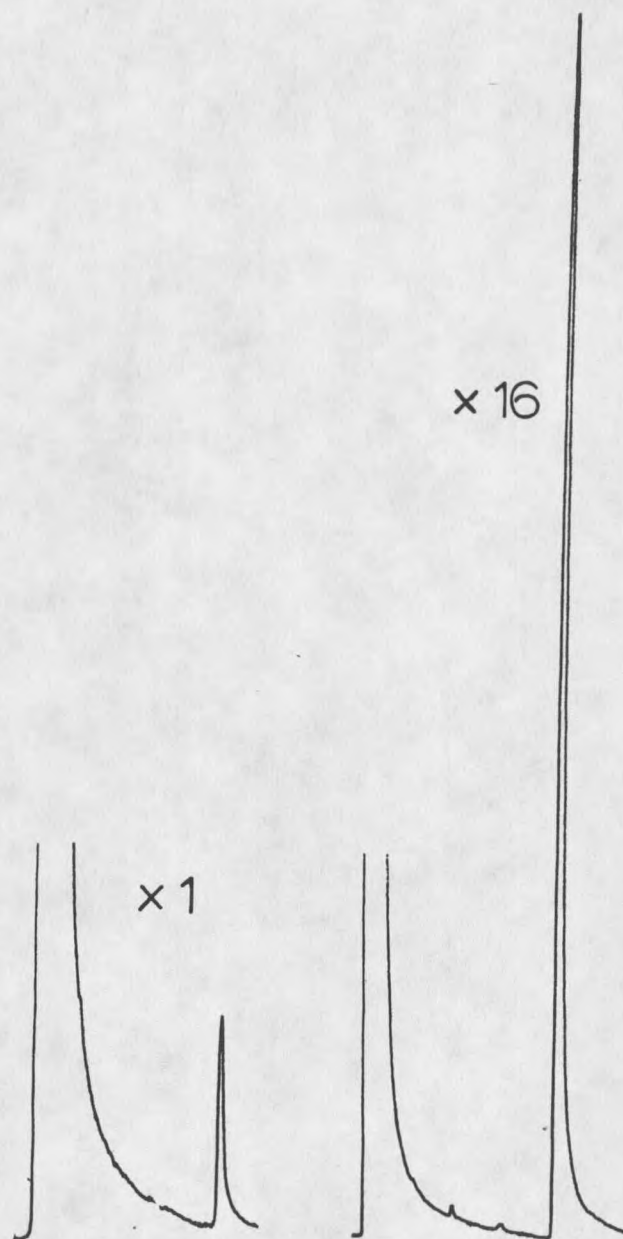


Figure 29. Capillary column gas chromatograms of the TFAA derivative of 2-aminofluorene. The chromatogram on the left is with normal EC detection and the one on the right is with 0.30% oxygen in the makeup gas. Detector temperature is 300°C.

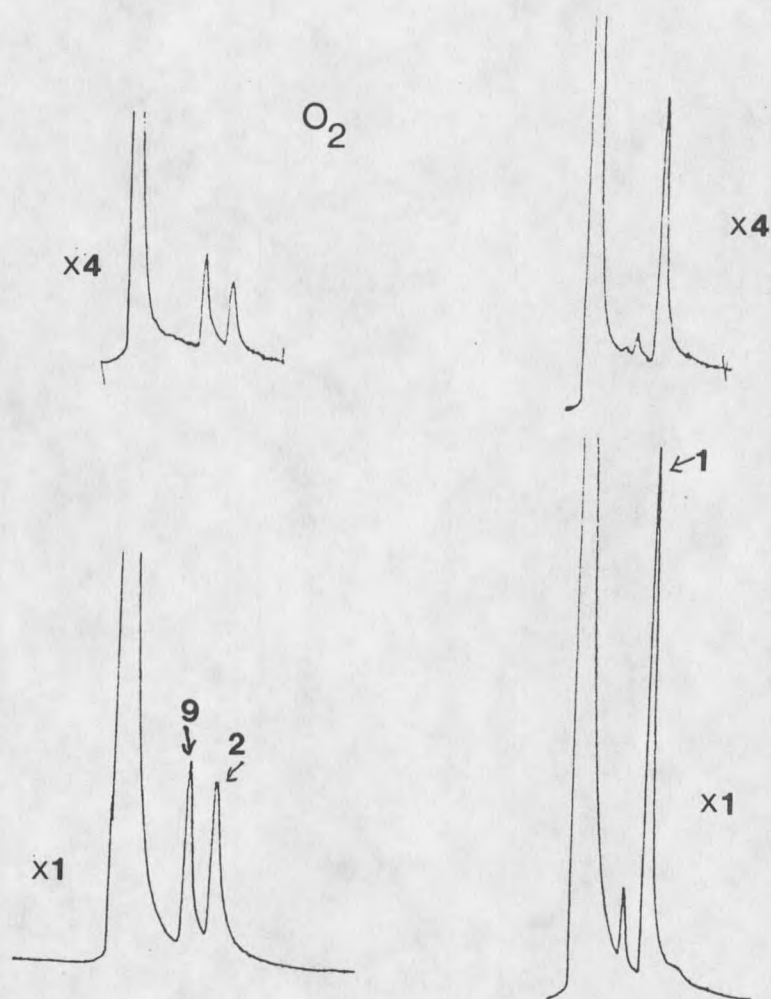


Figure 30. Capillary column gas chromatograms of the PFPA derivatives of 9-aminophenanthrene, 2-aminoanthracene, and 1-aminoanthracene. The top chromatograms are with 0.30% oxygen in the makeup gas. The bottom chromatograms are with normal EC detection. Detector temperature is 300°C.

Table 5. Oxygen Induced EC Response Enhancements for the Trifluoroacetic Anhydride (TFAA) and Perfluoropropionic Anhydride (PFPA) Derivatives of Various Polycyclic Aromatic Amines <sup>a</sup>

| <u>Amine</u>           | <u>Response Enhancement</u> |             |
|------------------------|-----------------------------|-------------|
|                        | <u>TFAA</u>                 | <u>PFPA</u> |
| 2-aminobiphenyl        | 106                         | 1.3         |
| 3-                     | 124                         |             |
| 4-                     | 102                         | 1.4         |
| 1-aminonaphthalene     | 125                         | 1.9         |
| 2-                     | 110                         | 1.7         |
| 2,7-diaminonaphthalene | 2.4                         |             |
| 1,8-                   | 1.6                         |             |
| 1,5-                   | 1.0                         |             |
| 1-aminoanthracene      | 5.5                         | 2.1         |
| 2-                     | 1.3                         | 1.7         |
| 9-                     | 10.2                        | 2.7         |
| 1-aminophenanthrene    | 32                          | 1.1         |
| 2-                     | 62                          |             |
| 3-                     | 74                          | 1.4         |
| 4-                     | 40                          | 1.3         |
| 9-                     | 32                          | 2.1         |
| 1-aminofluorene        | 56                          | 1.6         |
| 2-                     | 96                          | 2.6         |
| 3-                     | 96                          | 1.2         |

TABLE 5 (cont'd.)

|                     |     |     |
|---------------------|-----|-----|
| 4-                  | 71  | 1.4 |
| 9-                  | 1.7 | 1.1 |
| 2,7-diaminofluorene | 9.8 |     |
| 1-aminopyrene       | 2.8 |     |
| 2-                  | 4.5 |     |
| 4-                  | 2.9 |     |
| 2-aminobenzo(c)     | 6.4 |     |
| phenanthrene        |     |     |
| 3-                  | 5.3 |     |
| 4-                  | 4.8 |     |

<sup>a</sup> EC detector temperature is 300°C. Oxygen concentration in the doped detector is 3.0 parts per thousand.

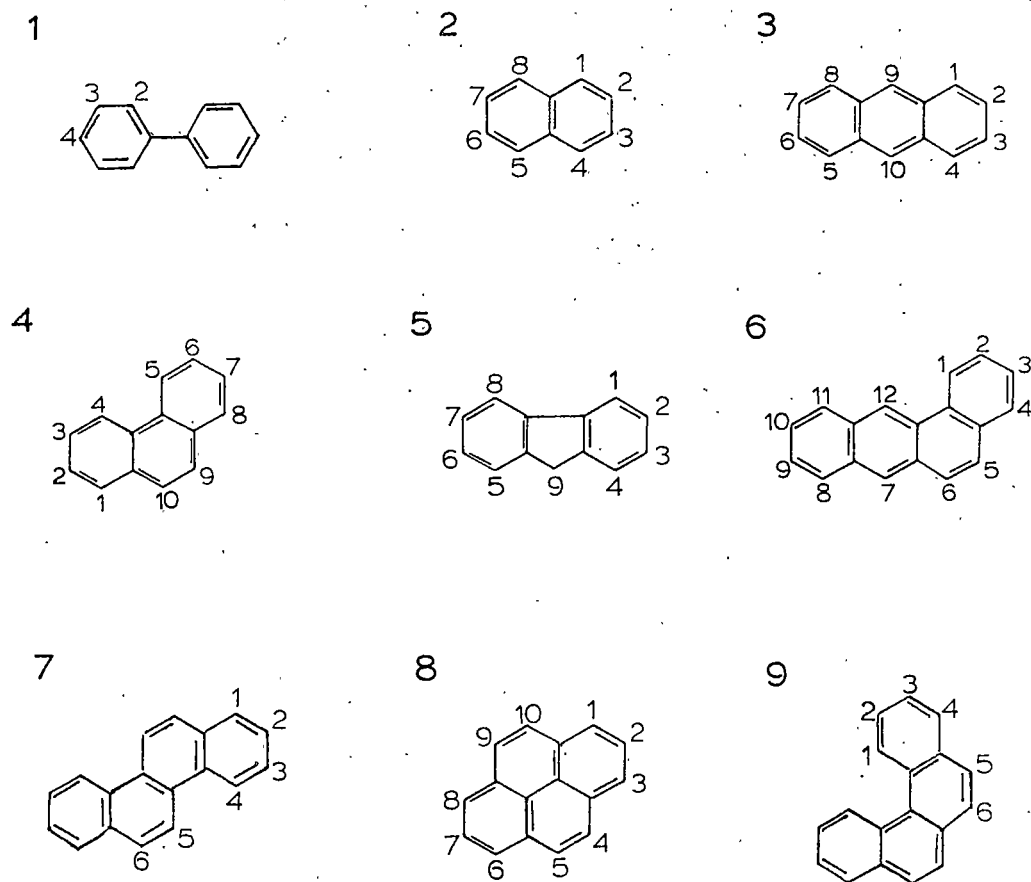


Figure 31. Structure and numbering scheme for biphenyl (1), naphthalene (2), anthracene (3), phenanthrene (4), fluorene (5), benz(a)anthracene (6), chrysene (7), pyrene (8), and benzo(c)phenanthrene (9).

lists the enhancements for the TFAA derivatives of several diamino compounds. The results listed in Table 5 are obtained from the average of at least three determinations. The structure and numbering scheme for each group are shown in Figure 31.

In considering the data listed in Table 5, a prominent feature immediately apparent is that the response enhancements of the PFPA derivatives are consistently much smaller than those of the TFAA derivatives. Later, Lee, and Wilson (116) found that the normal ECD response to a PFPA derivative was nearly an order of magnitude greater than that of a TFAA derivative for a given PAA. Our observations of relative EC sensitivity concur with this earlier report and this undoubtedly causes the large differences in RE values between the two derivative groups. That is, the oxygen enhancements of the PFPA derivatives are smaller because their normal electron capture rates are greater. This leaves less opportunity for response enhancements by oxygen addition. While the PFPA results show some variation among isomer sets, it appears that the TFAA derivatives are superior for the purpose of isomer distinction and each specific isomer group will be discussed in more detail below.

In considering the TFAA derivatives of the PAAs listed in Table 5, it is evident the RE differences among members of isomeric sets frequently exceed the  $\pm 6\%$  estimated standard deviation associated with the method. This value was determined by ten repetitive analyses for one of the isomers with and without the presence of oxygen in the detector. Considering each group in the

order listed, the enhancement value for the 2-biphenyl isomer is  $106 \pm 7$ , for 3-biphenyl the value is  $124 \pm 9$ , and the 4-biphenyl is  $102 \pm 7$ . From enhancement data, one could distinguish the 3-biphenyl isomer from the other two. For the two monosubstituted naphthalene isomers, the enhancements,  $125 \pm 8$  and  $110 \pm 7$ , differ somewhat more than the uncertainty of individual measurements. The three anthracene isomers are easily distinguished with the enhancements,  $1.3 \pm 0.1$ ,  $5.5 \pm 0.3$ , and  $10.2 \pm 0.6$ . For the five phenanthrene TFAA derivatives, only the 1- and 9-isomers do not have clearly unique enhancement values. The 3-aminophenanthrene isomer, one of the most mutagenic tested by Later *et al.* (129) can easily be distinguished from the 1-, 4-, and 9-isomers of phenanthrene and is barely distinguishable from the two isomer. Among the five aminofluorenes, all except the 2-and 3-derivatives can be be differentiated. It is interesting to note that the lowest enhancement is obtained with the 9-isomer of this group. Of the aminopyrene TFAA derivatives, perhaps only the 2-isomer is distinguishable from the other two. The isomers of benzo(c)phenanthrene also indicate barely distinguishable response enhancement values. It appears that as the size of the fused-ring structure is increased, the RE values become smaller and less isomer dependent. This is probably because the normal response is then too large and little increase in response is possible with oxygen addition. For the same reason the response enhancement

values for the diamino compounds are expected to be considerably less than those obtained for the monoamine derivatives .

Nevertheless, in the case of the diaminonaphthalenes, the 2,7-isomer can easily be discerned from the 1,8- and the 1,5-isomers.

For the cases where the RE values are low due to a normal EC response which is made too large by derivatization, the use of another, less EC sensitive chemical tag may be warranted.

#### Mixture Analysis

A readily apparent and powerful application of oxygen-induced response enhancements will be to support the assignment of individual peaks in gas chromatography with EC detection. Moreover, the technique should also provide assistance in the clarification of complex chromatograms where peaks are incompletely resolved (120). For example in Figure 32, two of the three anthracene TFAA derivatives are only partially separated by a temperature programmed capillary column. Knowing the enhancement expected for each isomer, one can quickly associate each isomer with its contribution to the partially resolved doublet by reanalyzing the sample with oxygen in the detector make-up gas. The partially resolved peaks are almost twice as much as the second component. These paired chromatograms establish that the first peak of interest is the 9-isomer and the second peak is the 1-isomer. By retention time alone, this assignment would have been difficult with this chromatographic system. Another more

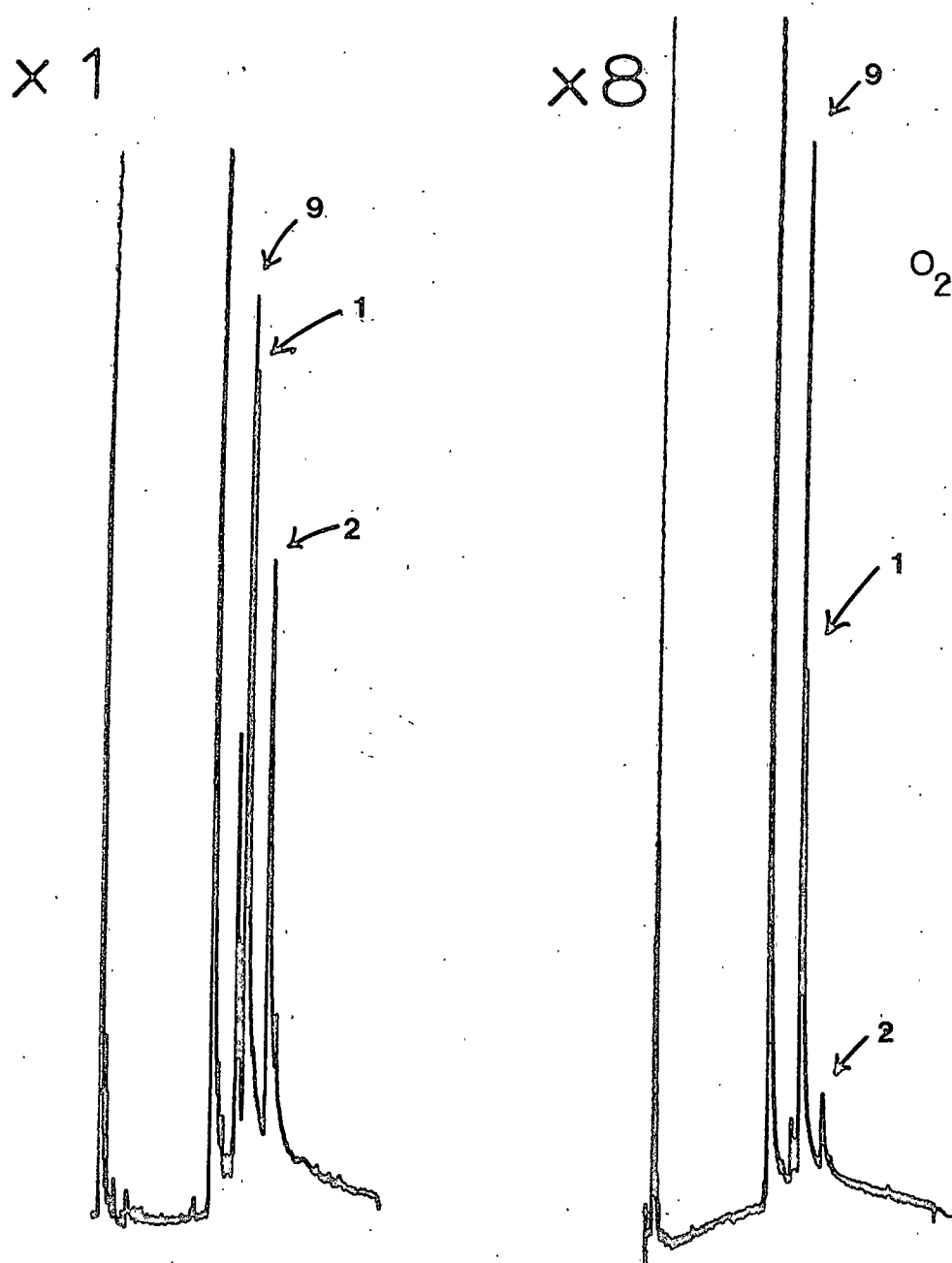


Figure 32. Capillary column gas chromatograms of a three-component mixture of 9-aminoanthracene (TFAA), 1-aminoanthracene (TFAA), and 2-aminoanthracene (TFAA). The chromatogram on the left is with normal EC detection and the one on the right is with 0.30% oxygen in the makeup gas. Detector temperature is 300°C.

challenging problem occurs in the case of exactly coeluting peaks. For example, Figure 33 shows chromatograms of a sample containing equal quantities of the TFAA derivatives of 9-phenanthrene and 1-anthracene for which no separation is provided by the column. The response enhancement observed for the single peak of interest which contains both compounds is 19.3. The composition of this mixed peak can be obtained by the following relationship:

$$RE_{MIX} = X_1 RE_1 + X_9 RE_9 \quad (28)$$

where  $RE_{MIX}$  is the response enhancement of the mixture,  $RE_1$  and  $RE_9$  are those of the pure isomers, and  $X_1$  and  $X_9$  are the mole fractions of the two isomers, where

$$X_1 + X_9 = 1 \quad (29)$$

For this case,  $RE_1$  and  $RE_9$  are 5.5 and 32, respectively. The measured value of  $RE_{MIX}$  thereby indicates that  $X_1 = 0.48$  and  $X_9 = 0.52$ , which agrees very well with the known composition of the mixture ( $X_1 = 0.50$  and  $X_9 = 0.50$ ). In addition, linearity studies have shown that both the normal ECD response as well as the oxygen-induced responses are linear over a concentration range of 100. In other words, the response enhancement as a function of concentration is fairly linear over this range for the TFAA and PFPA derivatives examined.

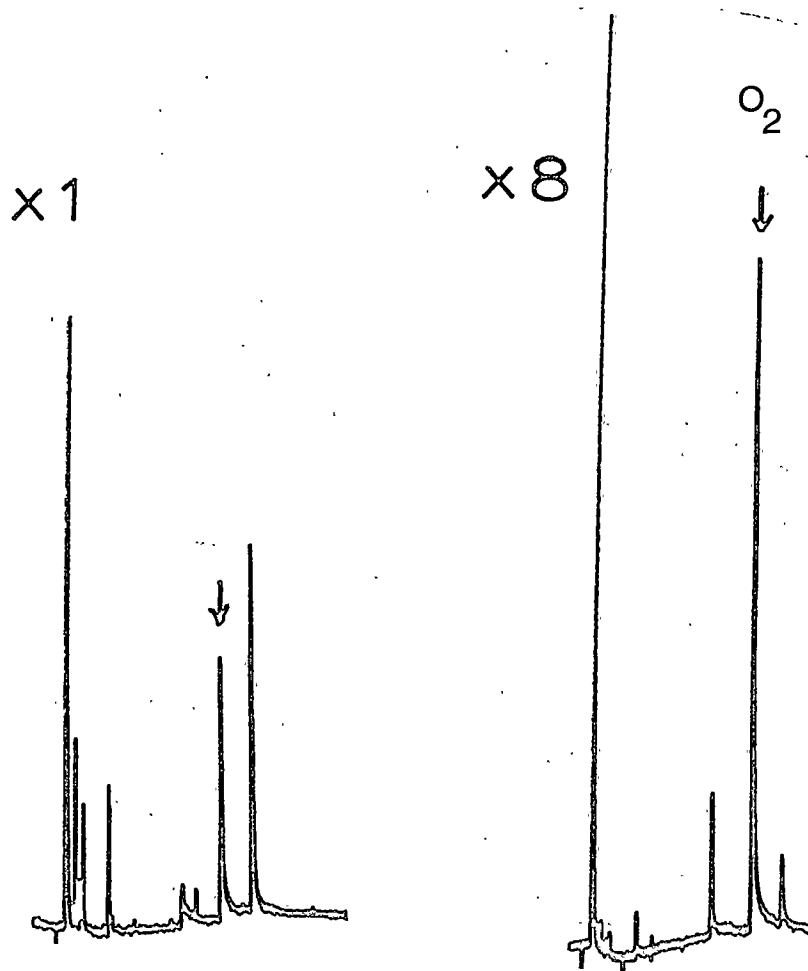


Figure 33. Capillary column gas chromatograms of the two-component equimolar mixture of the TFAA derivatives of 1-aminoanthracene and 9-aminophenanthrene. The arrows indicate the point of elution of the compounds. The chromatogram on the left is with normal EC detection and the one on the right is with 0.30% oxygen in the makeup gas. Detector temperature is 300°C.

Atmospheric Pressure Ionization Mass Spectrometry (APIMS)

In order to gain further insight into the chemical basis of the measurements of response enhancements with the TFAA and PFPA derivatives, we have identified the negative ions formed in the detector by the use of an atmospheric pressure ionization mass spectrometer (APIMS) where the ion source is, in fact, an ECD (92). The salient feature of the API mass spectrum of every PAA derivatized with TFAA was that the only negative ion observed with or without added oxygen is the parent  $M^-$  ion. Additional APIMS results for one set of isomers are shown in Table 6. This table indicates the relative  $M^-$  ion intensities observed for the TFAA derivatives of 1-aminoanthracene, 2-aminoanthracene, 9-aminoanthracene, and 9-aminoanthracene in a series of single-ion mass chromatograms under the identical oxygen-free and oxygen-doped conditions. It should be noted that the temperature of the EC detector was 300° C and that of the APIMS source was 250° C. If these measurements are compared with the corresponding RE measurements indicated in Table 6, it is seen that the relative increase in ion intensities caused by addition of oxygen in the APIMS experiment correlate quite well with the RE determinations by the ECD for this set of isomers. For example, of the four compounds the APIMS response to the 9-aminophenanthrene TFAA derivative increases most strongly with added oxygen (X9) and the measured RE value for this isomer is also the largest (X32). At the other extreme, no increase in the  $M^-$  intensity for the

Table 6. Relative Parent Negative Ion Intensities by APIMS for the TFAA Derivatives of Several Polycyclic Aromatic Amines (a)

| <u>Amine</u>        | <u>no O<sub>2</sub></u> | <u>with O<sub>2</sub></u> (b) |
|---------------------|-------------------------|-------------------------------|
| 1-aminoanthracene   | 1.0                     | 2.5                           |
| 2-aminoanthracene   | 1.0                     | 1.0                           |
| 9-aminoanthracene   | 1.0                     | 4.0                           |
| 9-aminophenanthrene | 1.0                     | 9.0                           |

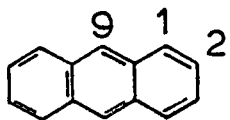
(a) Analyte concentrations were adjusted to produce similar negative ion intensities without adding O<sub>2</sub>.

(b) Oxygen concentration is 3.0 parts per thousand.  
Source temperature is 300°C

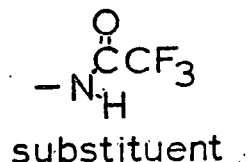
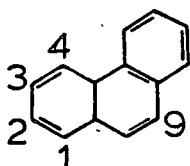
2-aminoanthracene derivative was caused by oxygen and the RE value for this compound was only 1.3. In all cases, it is noted that oxygen causes a greater ECD enhancement than API mass spectral enhancement. The larger EC enhancement is expected and is attributed to the mode of signal processing with the constant-current, frequency-modulated ECD as has been previously described (98,130).

In view of the preliminary results discussed above of the oxygen-doped ECD and APIMS studies of the TFAA derivatives of 1-, 2-, 9-aminoanthracene and 9-aminophenanthrene, the study was extended to include the other isomers aminoanthracene and aminophenanthrene were studied in much the same way with 0.20% oxygen in both the ECD and API at the same temperature of 250° C (131). The structures of the eight compounds examined are illustrated in the following:

anthracene



phenanthrene



The ECD responses to each of these were obtained and were similar to that illustrated in Figure 29. Chromatograms such as these were recorded without and then with 0.20% oxygen in the detector at a temperature of 250° C. The ratio of ECD responses with and without oxygen to each PAA derivative was thereby determined for at least three separate sets of measurements. The average values of these oxygen-induced response enhancements (RE) are shown in Table 7. It is seen that a very wide range of RE values are obtained, from a low value of 1.0 (no enhancement at all) for 2-aminoanthracene (TFAA) to an enhancement of 107 for 3-aminophenanthrene (TFAA). Furthermore, the RE values measured for the other members of this isomeric group are spread almost evenly throughout the range so that each isomer is uniquely indicated by its RE fingerprint.

Each PAA was then analyzed by GC/APIMS where conditions within its ion source were set nearly to those of the ECD. In Figure 34, for example, API mass spectral scans during the elution of the 9-aminophenanthrene derivative with and without added O<sub>2</sub> are shown. As in this case and the preliminary data discussed earlier, the striking feature of all mass spectra observed is that under these conditions, with or without added oxygen, the only negative ion

Table 7. Oxygen-Induced ECD and APIMS Response Enhancements for the Trifluoroacetic Anhydride Derivatives of Aminoanthracenes and Aminophenanthrenes <sup>a</sup>

| <u>Amine</u>        | <u>ECD</u> | <u>APIMS</u> |
|---------------------|------------|--------------|
| 2-aminoanthracene   | 1.0        | 1            |
| 1-aminoanthracene   | 3.1        | 2            |
| 9-aminoanthracene   | 8.1        | 4            |
| 1-aminophenanthrene | 19         | 9            |
| 4-aminophenanthrene | 34         | 13           |
| 9-aminophenanthrene | 43         | 16           |
| 2-aminophenanthrene | 72         | 20           |
| 3-aminophenanthrene | 107        | 29           |

<sup>a</sup> ECD and APIMS source temperature is 250°C. Oxygen concentration in doped detector is 0.20%.

<sup>b</sup> Reproducibility of ECD and APIMS enhancement measurements are approximately  $\pm 7\%$  and  $\pm 15\%$ , respectively.

observed for this entire set of molecules were due to the parent,  $M^+$ , ion at  $m/e$  289 and its  $^{13}C$  isotope peak at  $m/e$  290. The isotope peak at  $m/e$  290 is not resolved from the base peak at 289 in Figure 34 because the response time of the pulse counting detector is too slow to follow the relatively fast mass scan rate used here. With slower scanning over the parent ion mass region, alone, these two peaks are resolved and exhibit the expected 5.7 to 1.0 ratio. No fragment or oxygen adduct ions were seen for these compounds in spite of their frequent appearance elsewhere in the atmospheric pressure ionization of other aromatic hydrocarbons (92,123). The API results suggest that the ionization of these molecules under oxygen free conditions occur by simple electron capture

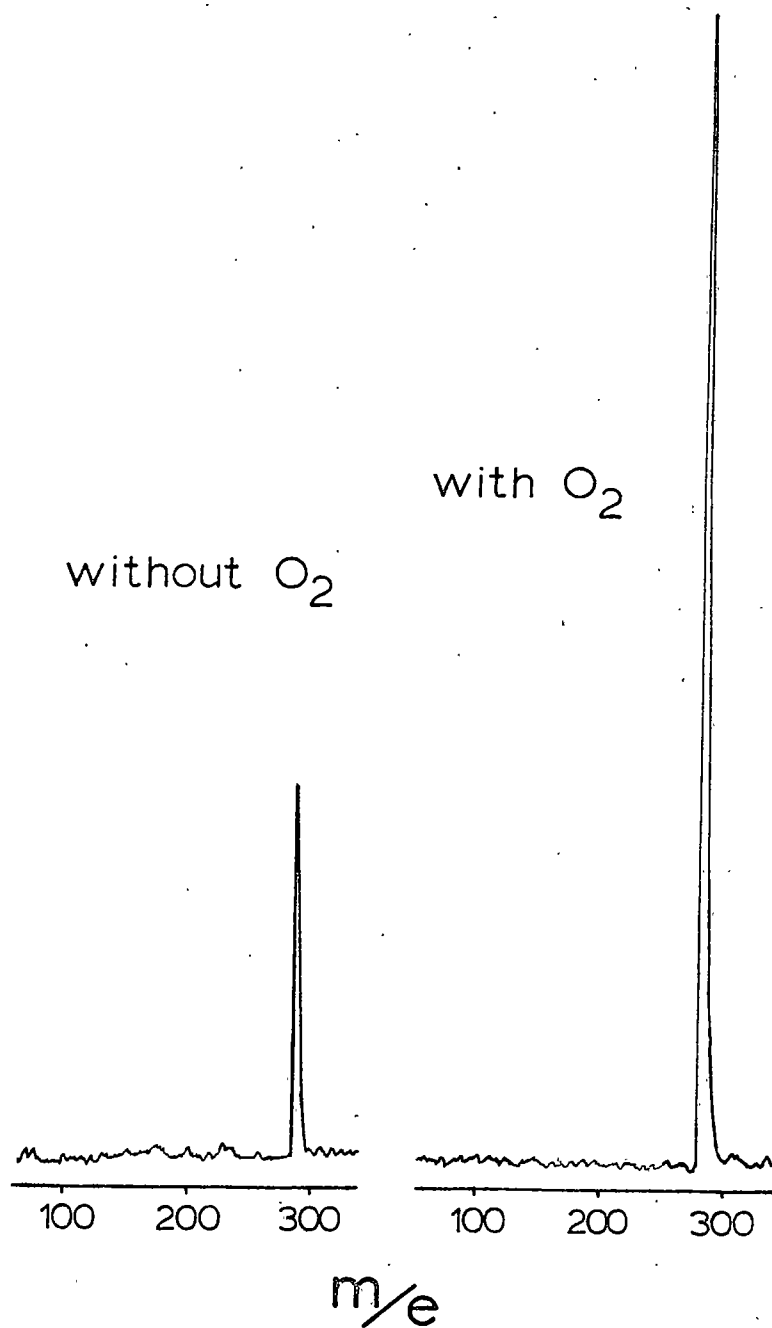
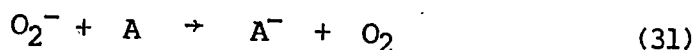


Figure 34. Negative ion API mass spectral scans taken during elution of TFAA derivative of 9-aminoanthracene without and with .20% added oxygen at a source temperature of 250°C.



and with added oxygen occurs by charge transfer,



to form the parent negative ion in both cases. Clearly, the mass spectra, themselves, provide no information from which isomer identity can be determined. It should be noted that the charge transfer reaction of  $O_2^{-}$  with the analyte molecule, in this particular instance the TFAA derivatives, is in contrast to the actual oxygen incorporation observed with the chloroanthracene and chlorophenanthrene molecules. In addition, the temperature dependence of the TFAA derivatives indicated a resonance type mechanism for electron capture. This is supported by the fact that in the APIMS, the only ion observed without oxygen is the  $M^{-}$  ion.

By performing paired single ion monitoring experiments such as that shown in Figure 35, the enhancement of the APIMS parent negative ion signal caused by oxygen was measured for each isomer studied. The magnitude of the APIMS enhancements (average of at least three determinations) is also shown in Table 7 alongside with the ECD data discussed previously. As with the ECD results, the magnitude of the APIMS enhancements of the parent negative ion intensities were also very dependent on the structural differences within this isomeric group. It is also evident in Table 7 that the relative order of the observed ECD and APIMS enhancements are the same. For both methods, the 2-aminoanthracene derivative shows the

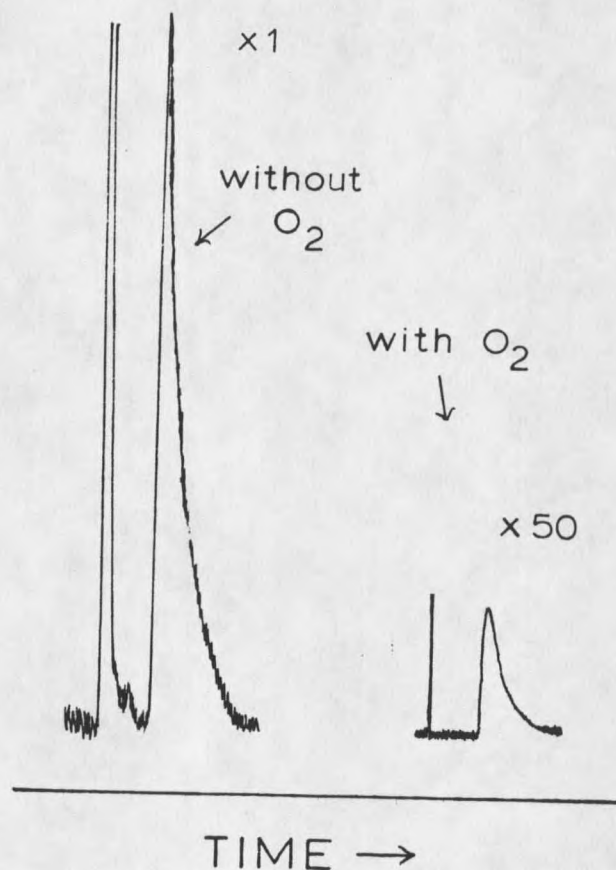


Figure 35. Single-ion APIMS monitor of the negative ion intensity at  $m/e$  289 for the 1-aminophenanthrene (TFAA) derivative without and with added oxygen (.20%) at a source temperature of 250°C.

lowest enhancement, the 3-aminophenanthrene derivative shows the greatest enhancement, while the enhancements of the other six compounds are relatively evenly spread throughout the observed ranges. The fact that the oxygen-induced enhancements measured by the ECD are uniformly greater than those measured by the APIMS is expected. This is thought to be largely due to the nature of the frequency-based response of the constant-current ECD which causes the observed ECD response enhancement to exceed the actual ratio of rates in Reaction 30 and 32. This effect has been previously described in a detailed model of the O<sub>2</sub>-doped ECD. The fact that the order of reactivity of the compounds listed in Table 7 are the same for both methods provides additional support for that model.

The experiments reported here suggest that Reactions 30 and 31 provide the basis of the responses observed in the atmospheric pressure ionization cells and that the only measurable characteristics of these reactions that provides an indication of compound identity is the ratio of the rate constants for Reactions 30 and 31. This rate constant ratio appears to more easily and reproducibly measured by the ECD than by the APIMS. The reproducibility of the ECD and APIMS enhancement measurements are approximately  $\pm 7\%$  and  $\pm 15\%$ , respectively. These results further support our earlier suggestion that an analysis scheme which provides normal and oxygen-enhanced ECD responses to a chromatographic effluent provides a very simple, but powerful aid for the identification of the components of complex mixtures by gas chromatography.

Several PFPA derivatives were also examined with the APIMS system. For those examples, without oxygen the ions observed were  $M^-$  at  $m/e$  339, an ion at  $m/e$  319 which corresponds to  $(M-HF)^-$ , and an ion at  $m/e$  309. In the presence of oxygen the same species were observed with the  $M^-$  ion increasing slightly in intensity. Figure 36 illustrates the API mass spectral scans during the elution of the PFPA derivative of 4-aminophenanthrene with and without added oxygen. These results are consistent with the results obtained of the detector response as a function of detector temperature. Those results suggest a dissociative type mechanism for electron capture, and the ions observed without oxygen in the APIMS support this evidence.

#### Mass Spectral Analysis of TFAA and PFPA Derivatives (132)

The TFAA derivatives of the isomers of aminoanthracene and aminophenanthrene and several PFPA derivatives of the same group were examined with electron impact (EI) and both negative and positive chemical ionization (NCI and PCI) mass spectrometry with isobutane and methane as reagent gases to disclose the characteristics and evaluate the possibility of isomer distinction.

The EI spectra of the TFAA derivatives of 1-aminoanthracene and 4-aminophenanthrene are shown in Figures 37 and 38, respectively and the relative intensities of the common ions observed in the EI spectra for all eight isomers are listed in Table 8. Figures 39 and 40 illustrate the isobutane PCI for 1-aminoanthracene and 4-aminophenanthrene TFAA derivatives. The relative intensities of the

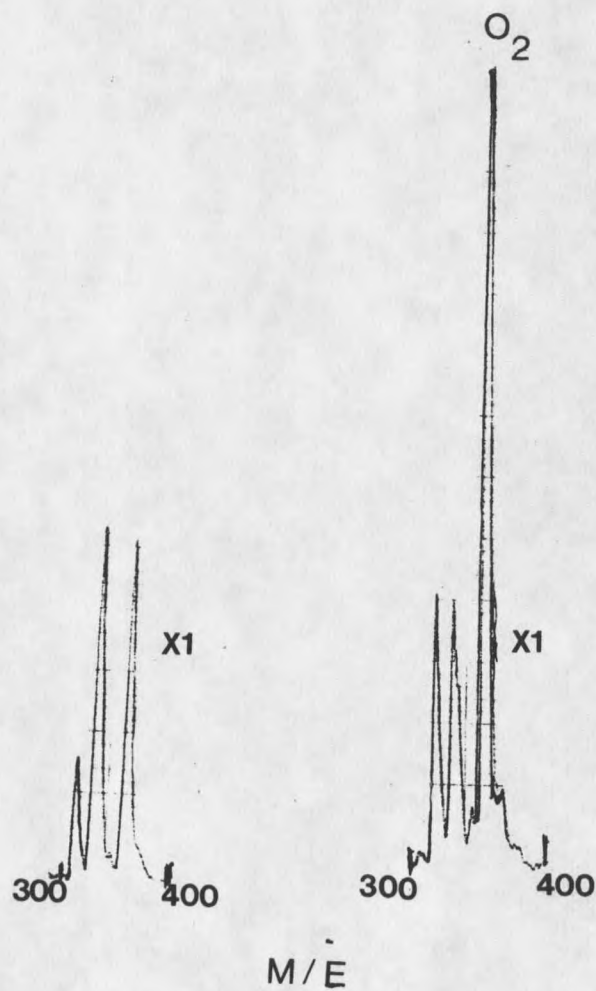


Figure 36. Negative ion API mass spectral scans taken during elution of derivative of 3-aminophenanthrene (PFPA) with (right) and without (right) .20% added oxygen. Source temperature is 250°C.

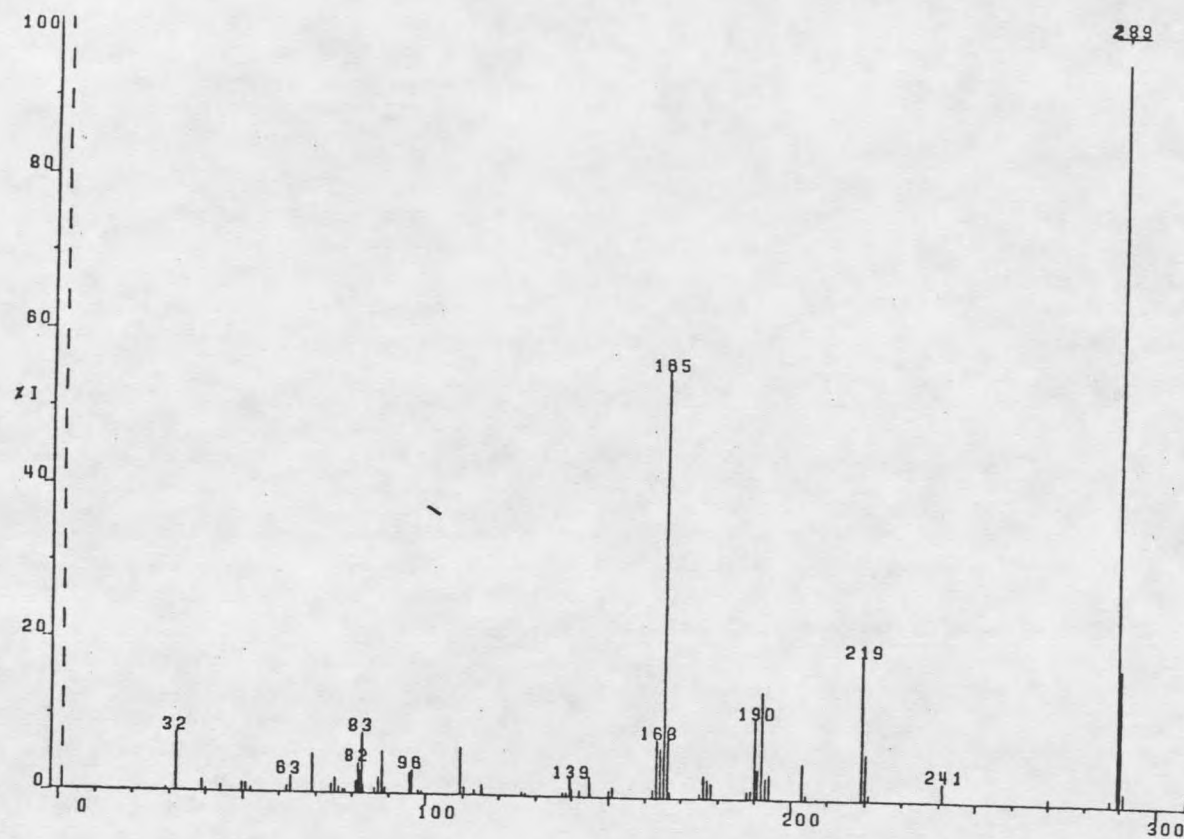


Figure 37. Electron impact mass spectrum of 1-aminoanthracene (TFAA).

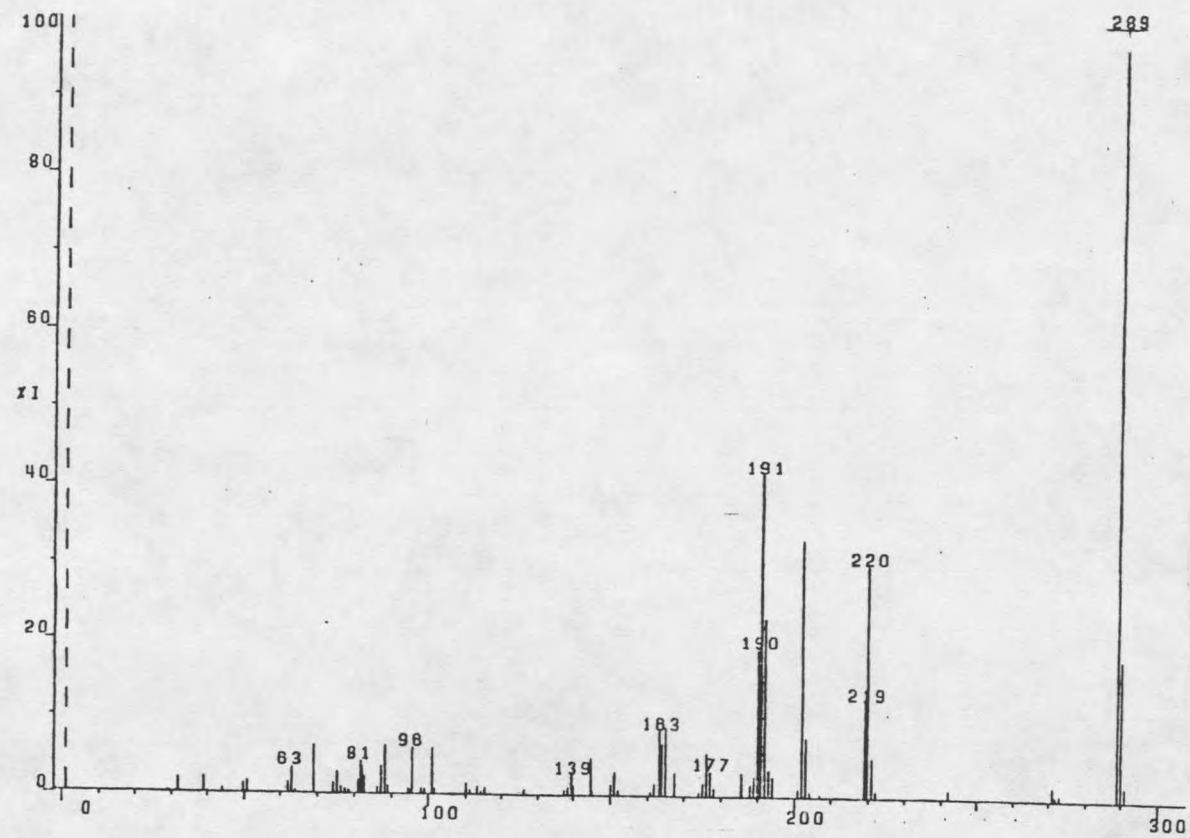


Figure 38. Electron impact mass spectrum of 4-aminophenanthrene (TFAA).

Table 8. Ion Intensities from the Electron Impact Mass Spectra of the TFAA Derivatives of the Aminoanthracenes and Phenanthrene.

| <u>Amine</u> | <u>M/E (% Abundance)</u> |            |            |            |            |            |            |            |
|--------------|--------------------------|------------|------------|------------|------------|------------|------------|------------|
|              | <u>289</u>               | <u>220</u> | <u>219</u> | <u>202</u> | <u>192</u> | <u>191</u> | <u>190</u> | <u>165</u> |
| 1A           | 100                      | 6          | 18         | 0          | 14         | 4          | 11         | 55         |
| 2A           | 100                      | 4          | 21         | 0          | 2          | 0          | 9          | 55         |
| 9A           | 100                      | 0          | 32         | 0          | 87         | 11         | 22         | 46         |
| 1P           | 100                      | 8          | 15         | 0          | 23         | 3          | 10         | 48         |
| 2P           | 100                      | 3          | 11         | 0          | 20         | 0          | 7          | 39         |
| 3P           | 100                      | 0          | 11         | 0          | 24         | 3          | 7          | 41         |
| 4P           | 100                      | 30         | 12         | 33         | 23         | 42         | 19         | 0          |
| 9P           | 100                      | 5          | 10         | 0          | 6          | 3          | 8          | 77         |

common ions observed are shown in Table 9. The isobutane NCI for the same two derivatives are illustrated in Figures 41 and 42, and the intensities for all eight isomers are listed in Table 10.

Figures 43 and 44 illustrate the methane PCI for 1-aminoanthracene and 4-aminophenanthrene, respectively with the intensities listed in Table 11. The methane NCI for the same two compounds is shown in Figures 45 and 46 and the relative intensities for all eight isomers are listed in Table 12.

The EI spectra for the 1- and 2-aminoanthracene (TFAA) and the 2- and 3-aminophenanthrenes derivatives are quite similar. The intensities of the parent  $m/e$  289 and the fragment ions of  $m/e$  192 and 165 are almost equal in intensity. The fragmentation pattern

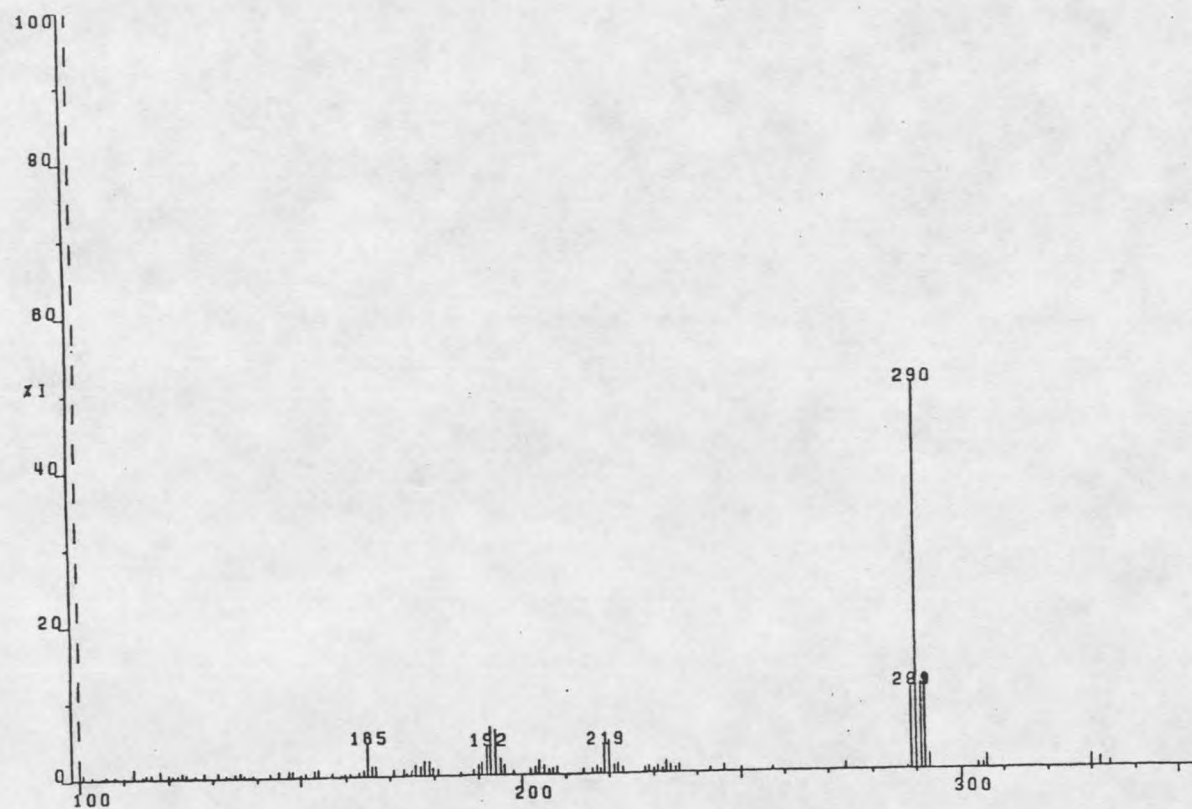


Figure 39. Isobutane positive chemical ionization mass spectrum of 1-aminoanthracene (TFAA).

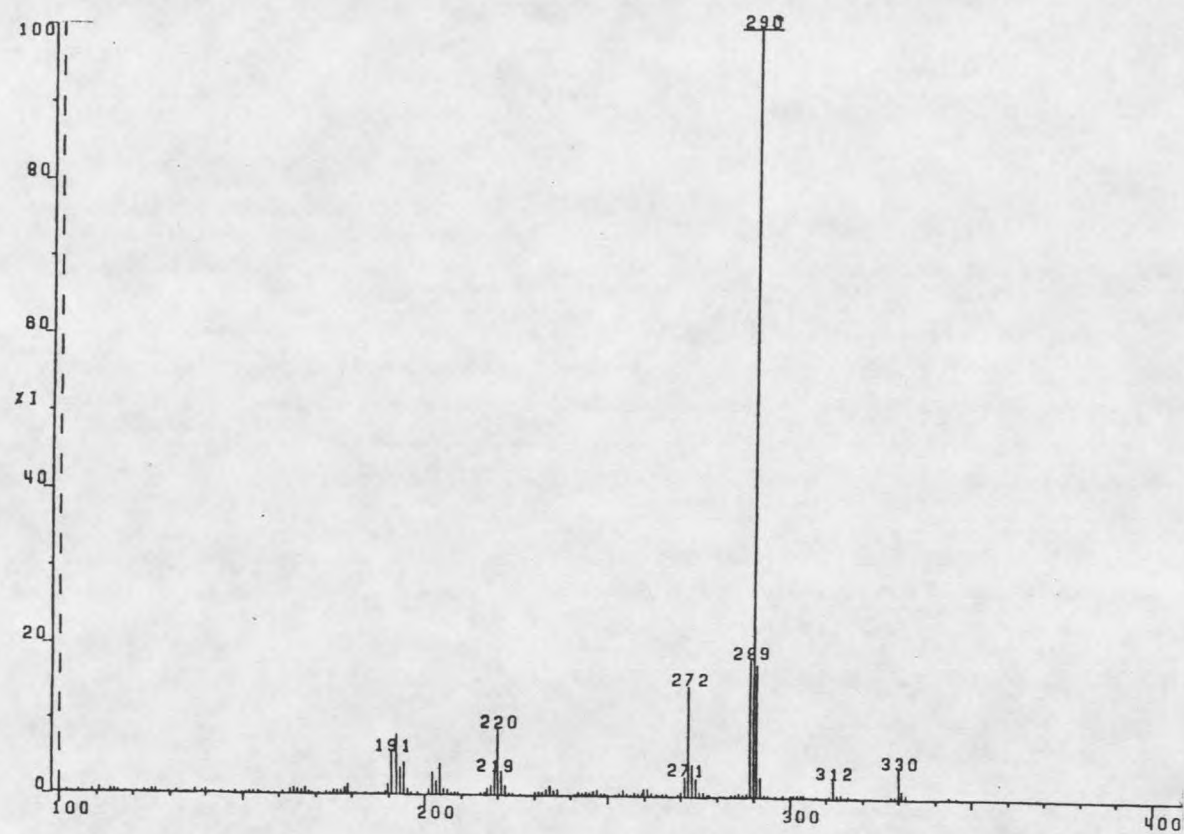
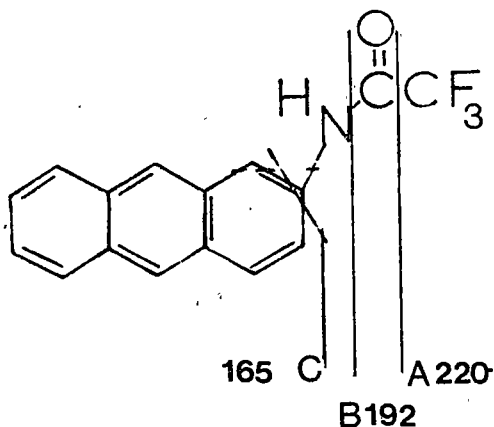


Figure 40. Isobutane positive chemical ionization mass spectrum of 4-aminophenanthrene (TFAA).

giving rise to these ions and others is shown in the following scheme:



The ion intensities of  $m/e$  192 for the 9-aminoanthracene derivative,  $m/e$  202 for 4-aminophenanthrene and  $m/e$  165 for the 9-aminophenanthrene would distinguish those isomers from the others.

Table 9. Ion Intensities from the PCI (isobutane) Mass Spectra of the TFAA Derivatives of the Isomers of Aminoanthracene and Phenanthrene

|              | <u>M/E (% Abundance)</u> |            |            |            |            |
|--------------|--------------------------|------------|------------|------------|------------|
| <u>Amine</u> | <u>292</u>               | <u>291</u> | <u>290</u> | <u>289</u> | <u>272</u> |
| 1A           | 22                       | 23         | 100        | 21         | 0          |
| 2A           | 12                       | 15         | 100        | 21         | 0          |
| 9A           | 4                        | 18         | 100        | 20         | 0          |
| 1P           | 2                        | 18         | 100        | 15         | 0          |
| 2P           | 2                        | 17         | 100        | 16         | 0          |
| 3P           | 6                        | 17         | 100        | 17         | 0          |
| 4P           | 2                        | 21         | 100        | 20         | 20         |
| 9P           | 3                        | 17         | 100        | 20         | 0          |

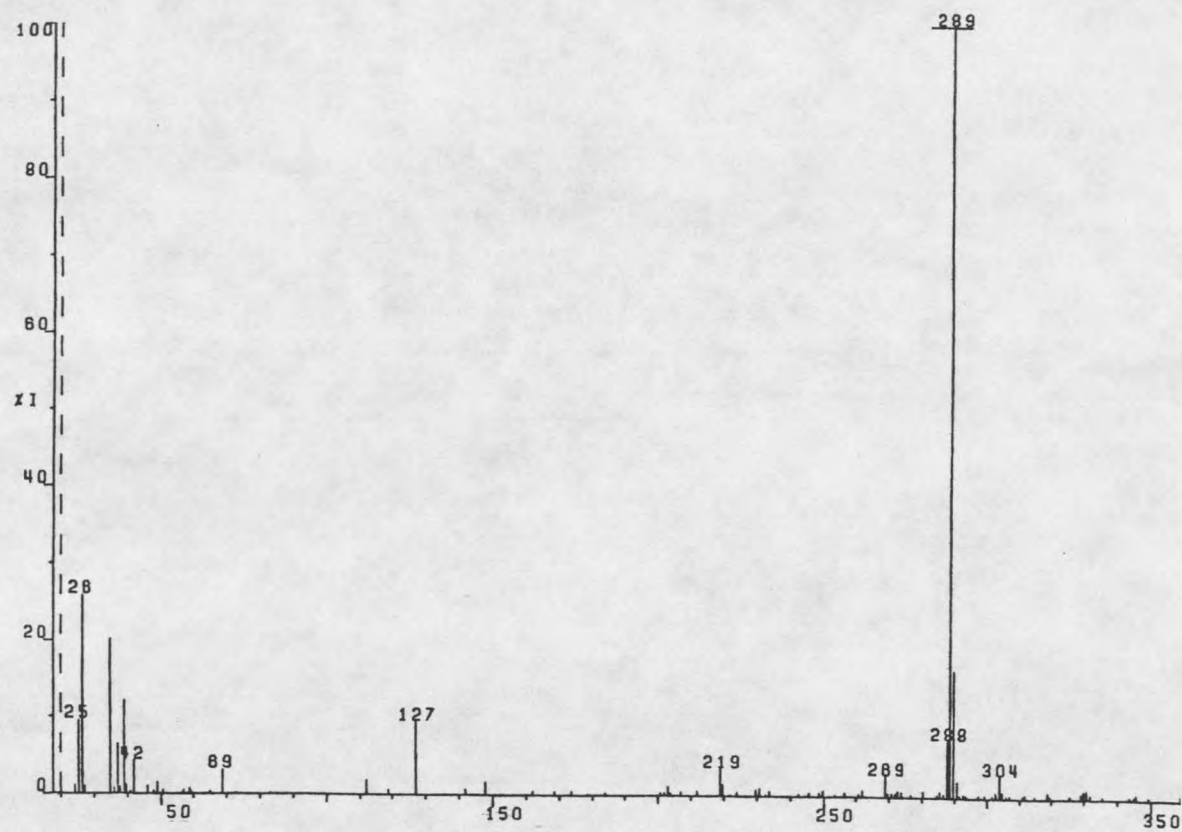


Figure 41. Isobutane negative chemical ionization mass spectrum of 1-aminoanthracene (TFAA).

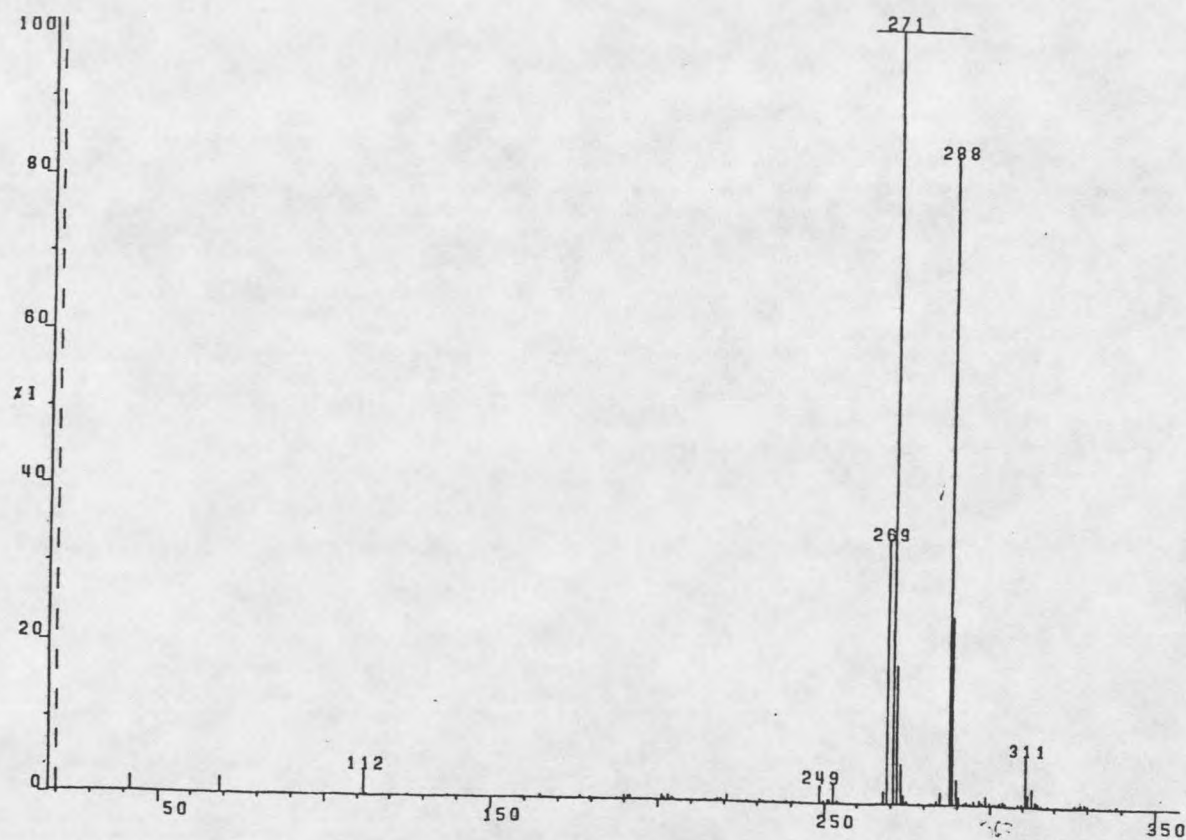


Figure 42. Isobutane negative chemical ionization mass spectrum of 4-aminophenanthrene (TFAA).

Table 10. Ion Intensities from the NCI (isobutane) Mass Spectra of the TFAA Derivatives of the Isomers of Aminoanthracene and Phenanthrene

|              | <u>M/E (% Abundance)</u> |            |            |            |            |            |            |            |
|--------------|--------------------------|------------|------------|------------|------------|------------|------------|------------|
| <u>Amine</u> | <u>289</u>               | <u>288</u> | <u>273</u> | <u>271</u> | <u>269</u> | <u>219</u> | <u>203</u> | <u>112</u> |
| 1A           | 100                      | 8          | 1          | 1          | 3          | 3          | 2          | 2          |
| 2A           | 100                      | 20         | 5          | 0          | 17         | 4          | 20         | 0          |
| 9A           | 100                      | 22         | 6          | 1          | 8          | 22         | 2          | 50         |
| 1P           | 20                       | 52         | 48         | 4          | 100        | 0          | 5          | 22         |
| 2P           | 13                       | 53         | 24         | 3          | 100        | 1          | 2          | 8          |
| 3P           | 8                        | 46         | 63         | 5          | 100        | 0          | 3          | 14         |
| 4P           | 25                       | 84         | 6          | 100        | 35         | 0          | 0          | 4          |
| 9P           | 21                       | 63         | 54         | 0          | 100        | 0          | 5          | 38         |

Table 11. Ion Intensities from the PCI (methane) Mass Spectra of the TFAA Derivatives of the Isomers of Aminoanthracene and Phenanthrene

|              | <u>M/E (% Abundance)</u> |            |            |            |            |            |            |            |
|--------------|--------------------------|------------|------------|------------|------------|------------|------------|------------|
| <u>Amine</u> | <u>292</u>               | <u>291</u> | <u>290</u> | <u>289</u> | <u>272</u> | <u>220</u> | <u>219</u> | <u>194</u> |
| 1A           | 20                       | 23         | 100        | 42         | 1          | 7          | 8          | 5          |
| 2A           | 25                       | 24         | 100        | 39         | 0          | 20         | 8          | 21         |
| 9A           | 5                        | 20         | 100        | 38         | 0          | 30         | 24         | 18         |
| 1P           | 5                        | 23         | 100        | 18         | 5          | 13         | 8          | 13         |
| 2P           | 2                        | 12         | 100        | 23         | 0          | 10         | 10         | 25         |
| 3P           | 2                        | 14         | 100        | 29         | 4          | 14         | 13         | 35         |
| 4P           | 1                        | 21         | 100        | 32         | 44         | 21         | 0          | 2          |
| 9P           | 2                        | 15         | 100        | 18         | 1          | 15         | 8          | 15         |

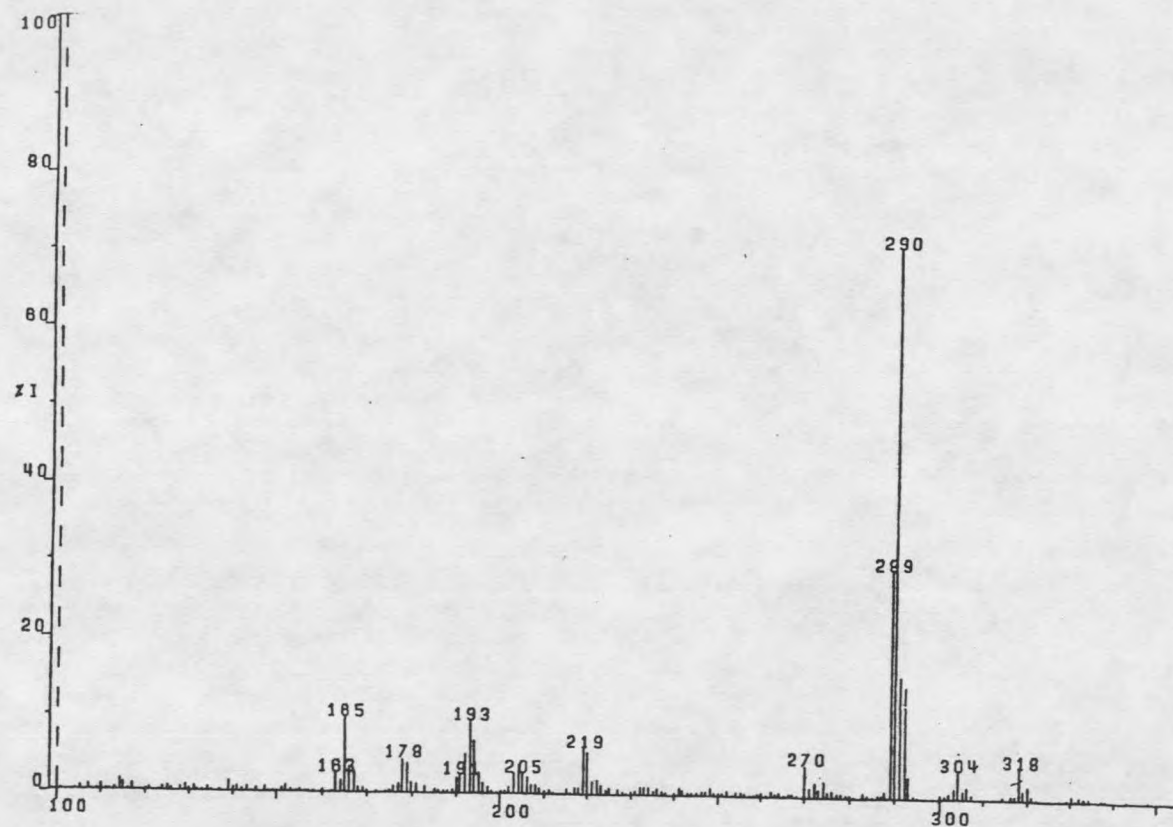


Figure 43. Methane positive chemical ionization mass spectrum of 1-aminoanthracene (TFAA).

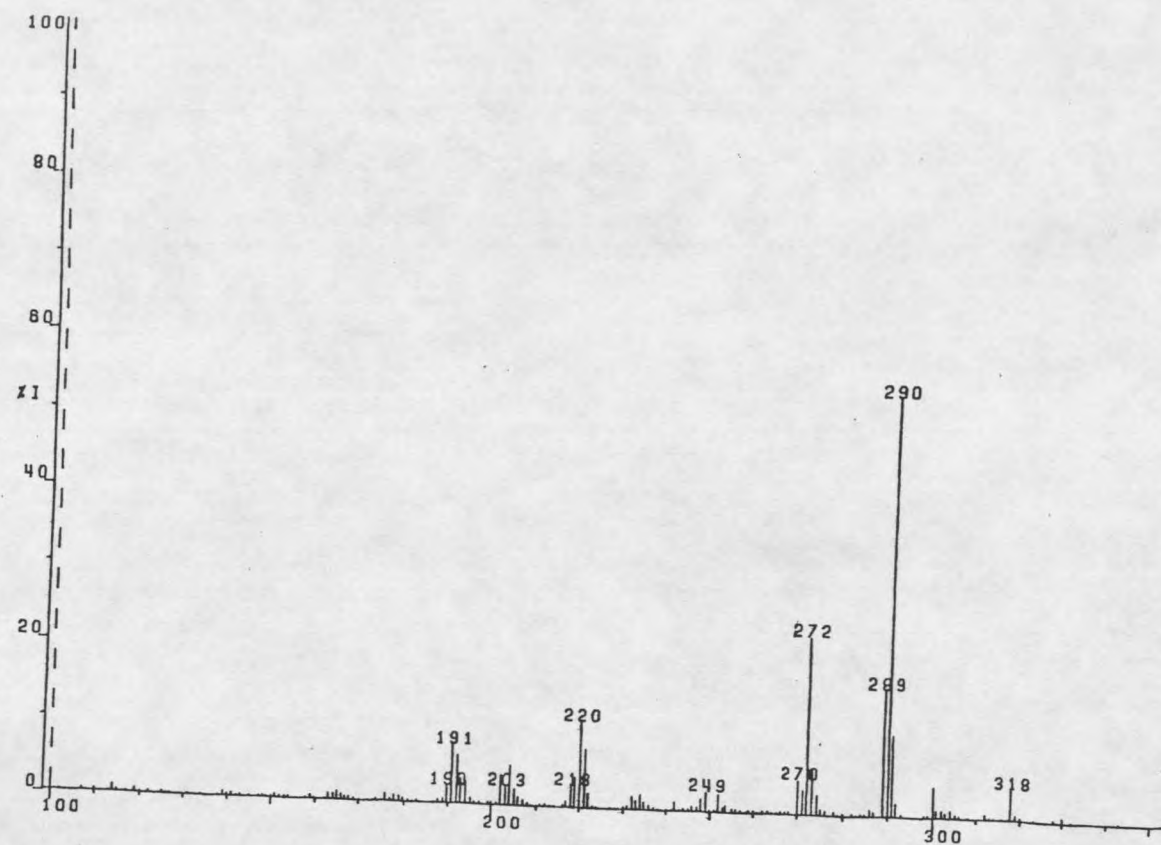


Figure 44. Methane positive chemical ionization mass spectrum of 4-aminophenanthrene (TFAA).

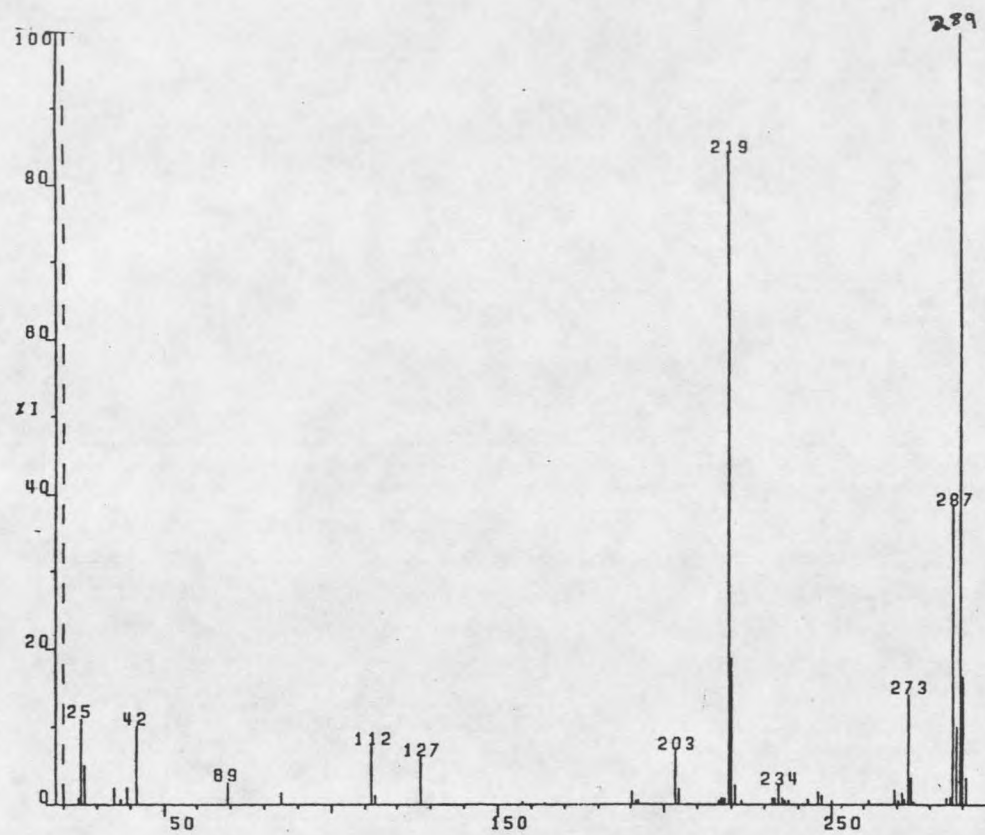


Figure 45. Methane negative chemical ionization mass spectrum of 1-aminoanthracene (TFAA).

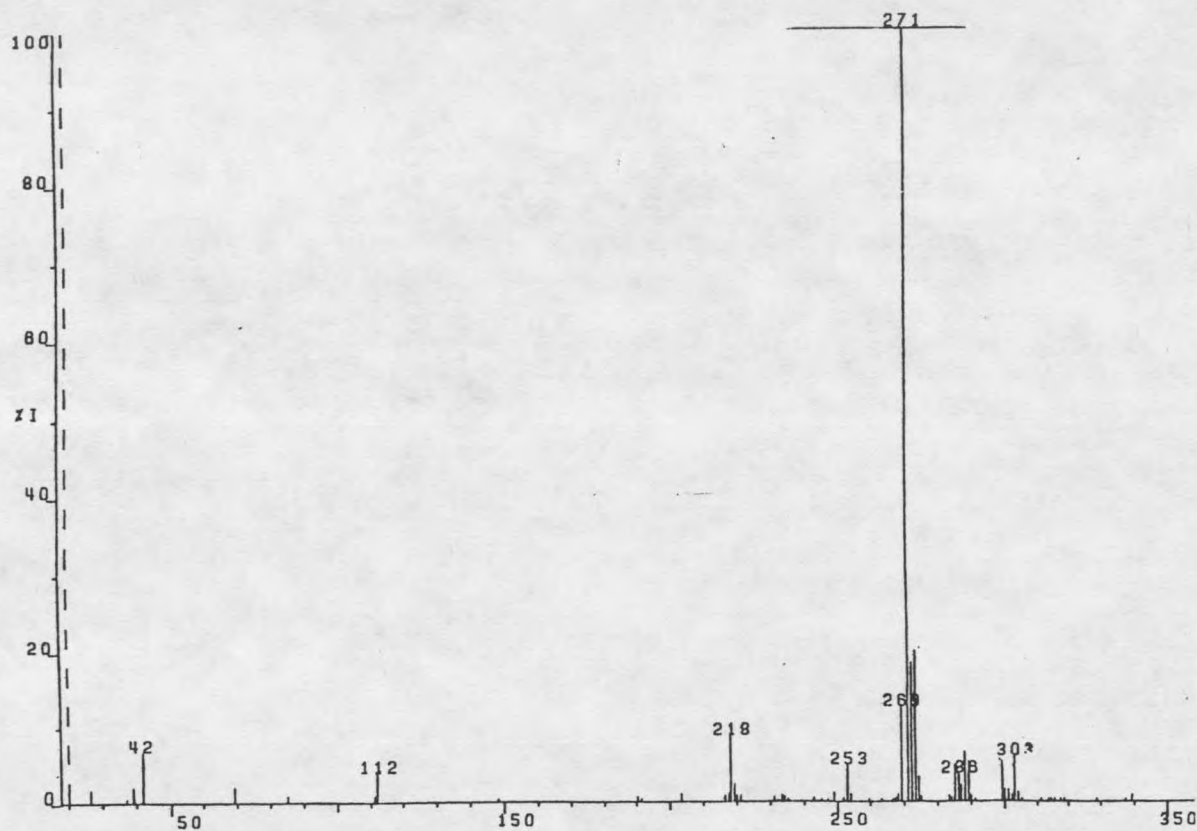


Figure 46. Methane negative chemical ionization mass spectrum of 4-aminophenanthrene (TFAA).

Table 12. Ion Intensities from the NCI (methane) Mass Spectra of the TFAA Derivatives of the Isomers of Aminoanthracene and Phenanthrene

|              | <u>M/E (% Abundance)</u> |            |            |            |            |            |            |            |            |            |
|--------------|--------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| <u>Amine</u> | <u>289</u>               | <u>288</u> | <u>287</u> | <u>273</u> | <u>272</u> | <u>271</u> | <u>269</u> | <u>219</u> | <u>203</u> | <u>112</u> |
| 1A           | 100                      | 12         | 40         | 16         | 0          | 2          | 2          | 85         | 8          | 8          |
| 2A           | 100                      | 15         | 21         | 23         | 0          | 2          | 15         | 34         | 55         | 9          |
| 9A           | 6                        | 7          | 38         | 3          | 0          | 1          | 1          | 100        | 2          | 6          |
| 1P           | 8                        | 12         | 8          | 100        | 0          | 4          | 24         | 0          | 9          | 13         |
| 2P           | 15                       | 13         | 10         | 100        | 0          | 8          | 40         | 1          | 4          | 9          |
| 3P           | 9                        | 8          | 5          | 100        | 0          | 3          | 25         | 0          | 6          | 8          |
| 4P           | 6                        | 7          | 4          | 20         | 20         | 100        | 13         | 0          | 1          | 4          |
| 9P           | 15                       | 27         | 5          | 100        | 0          | 4          | 58         | 1          | 7          | 2          |

The electron impact mass spectra allows differentiation of only three of the eight isomers.

The positive ion isobutane CIMS for all eight isomers are all quite similar. The major ions formed include (M+1), (M+2), and (M+3). However, the 4-aminophenanthrene TFAA isomer can be easily differentiated from the others by a fragment ion in its PCI spectrum at m/e 272. The gas phase ion that gives rise to this fragment is unique to the 4-isomer because of its substitution position, termed the bay region of the molecule. B/E linked scans were done on m/e 290 and the fragment ions observed were m/e 272, 220, and 202. The spectrum is shown in Figure 47. Furthermore, B/E linked scans were done on m/e 272 and the major fragment ion observed was m/e 202 and the spectrum is illustrated in Figure 48. There are probably

several mechanisms that could account for the ions observed in the spectrum for 4-aminophenanthrene(TFAA) and one of them is shown as follows:

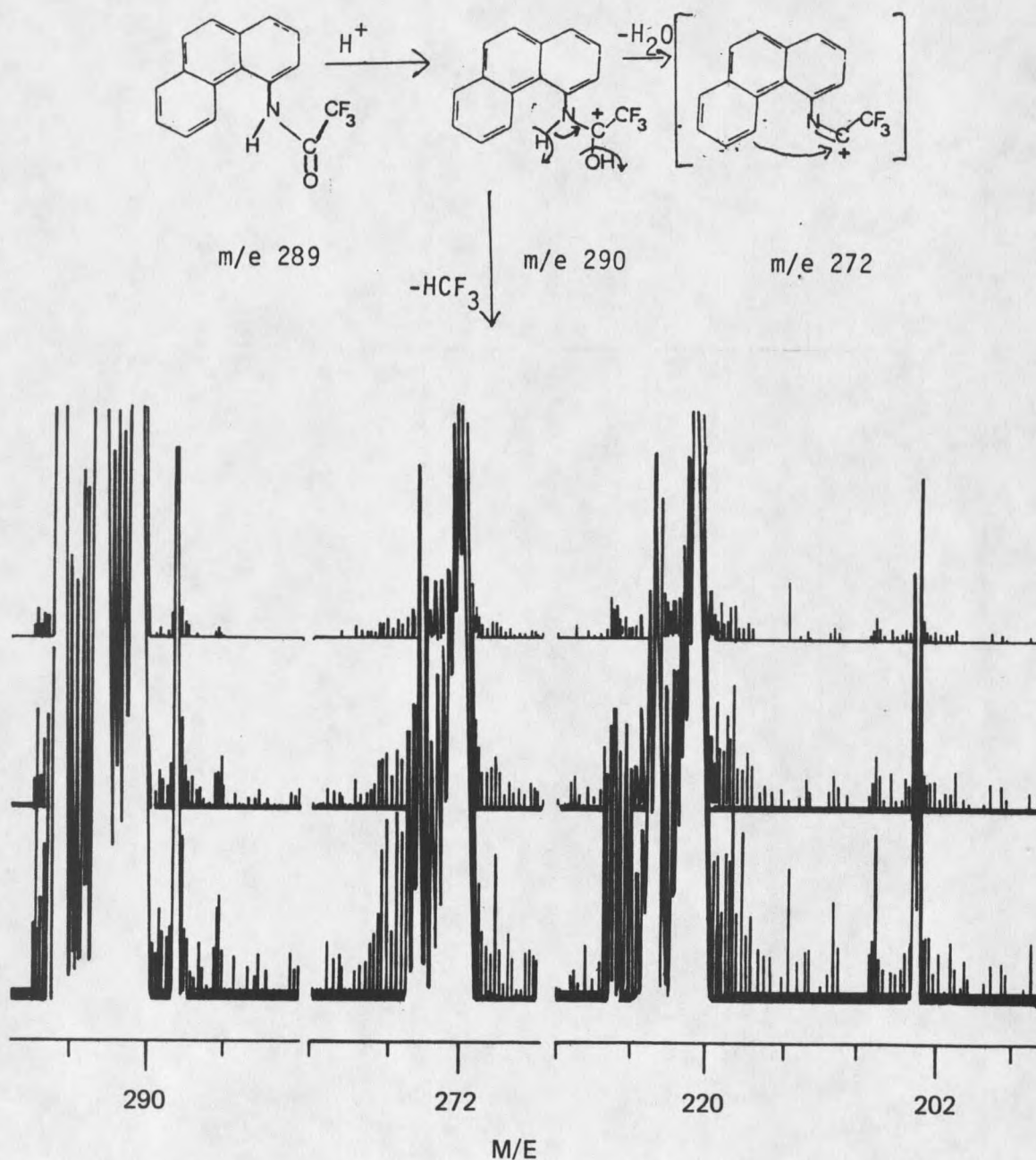


Figure 47. B/E scan on m/e 290 of 4-aminophenanthrene (TFAA).

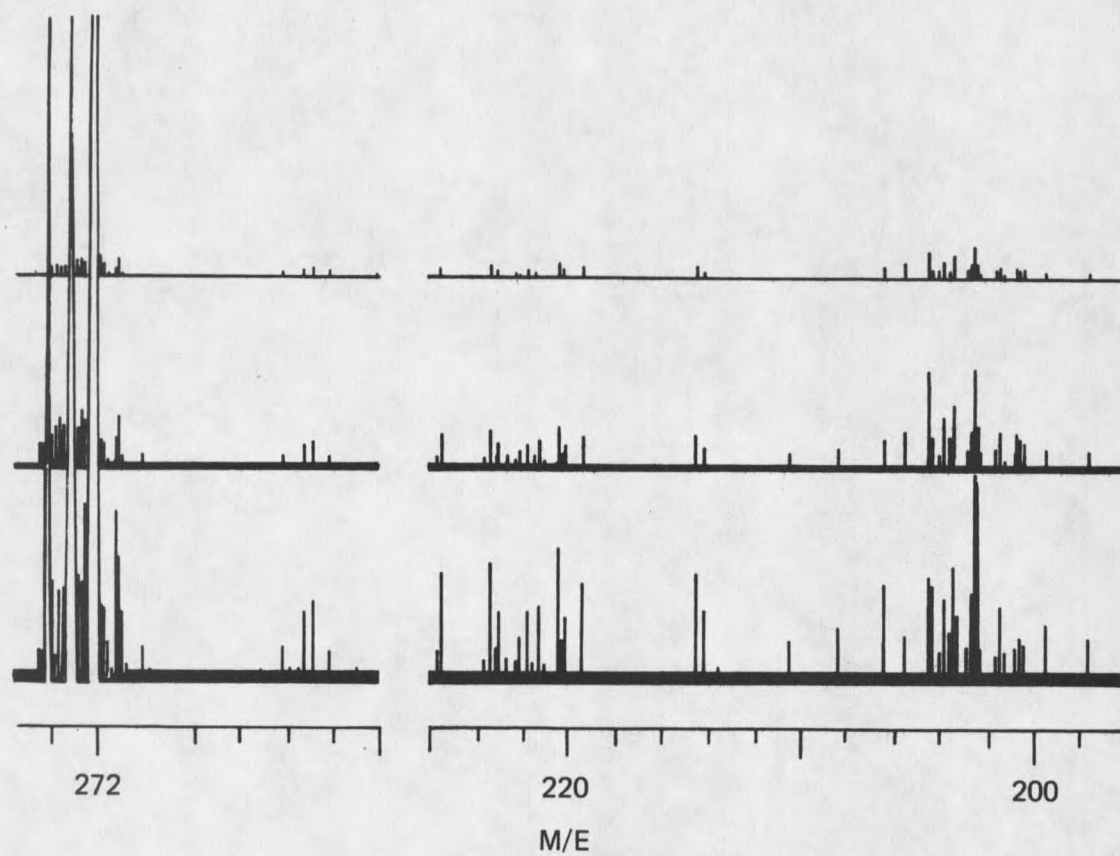
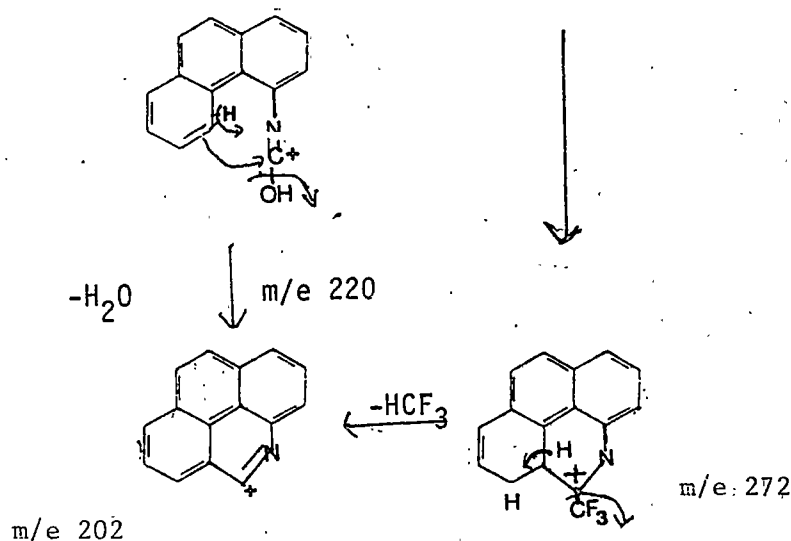


Figure 48. B/E scan on m/e 272 of 4-aminophenanthrene (TFAA).



Following the initial protonation of the molecule at the carbonyl oxygen, there is a loss of  $\text{H}_2\text{O}$  which leads to the formation of a six-membered ring bridging at the carbonyl carbon atom of the TFAA side chain. Subsequent loss of  $\text{HCF}_3$  gives rise to the observed fragment ion of m/e 202. Alternatively, the proposed structure of m/e 290 could lose the fragment  $\text{HCF}_3$  to form the ion m/e 220 and then lose the water molecule to again form the cyclized structure of m/e 202. Another indication of the formation of the cyclized structure of m/e 272 was obtained from the results of B/E linked scans with and without collisional activation with helium gas. As shown in Figure 49, m/e 272 seems to be a relatively stable ion. The CA spectrum shows loss of  $\text{HF}$  (m/e 252) and  $\text{HCF}_3$  (m/e 202). If the ion m/e 272 did not have the proposed cyclic structure, it might be expected that more daughter ions would result in the CA spectrum of this fragmentation. It should be emphasized that the proposed mechanism for fragmentation of the 4-isomer may be one of many possible to explain the observed fragmentation pattern.

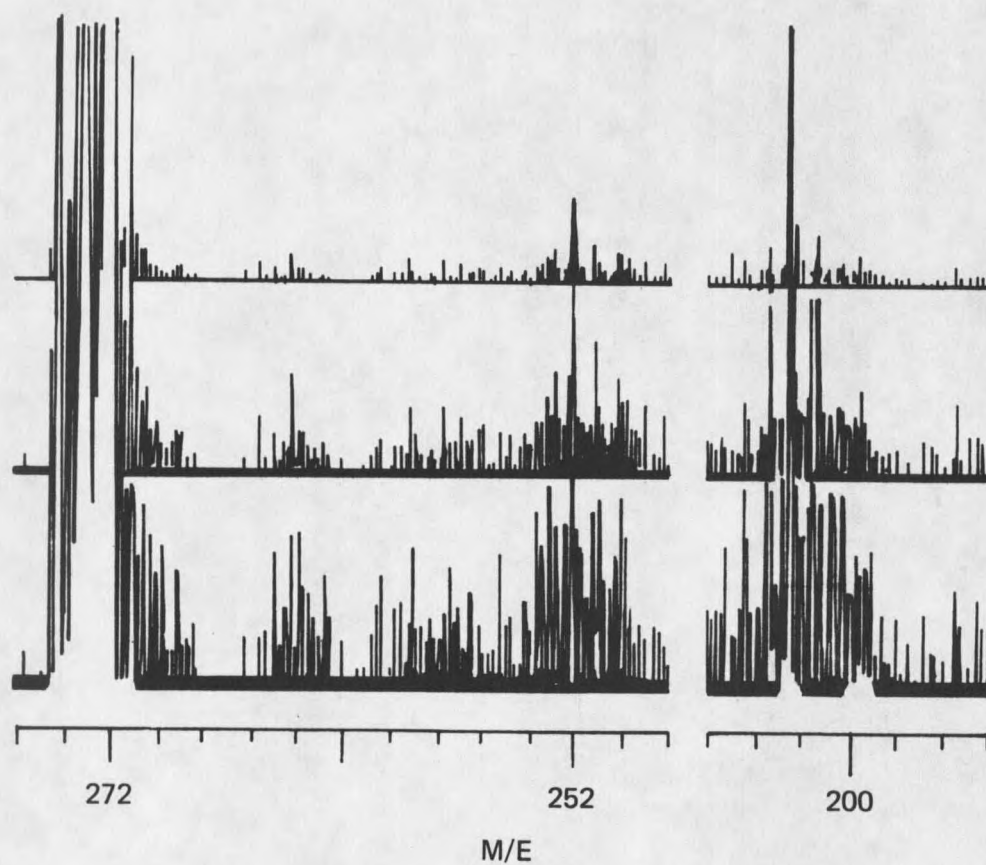
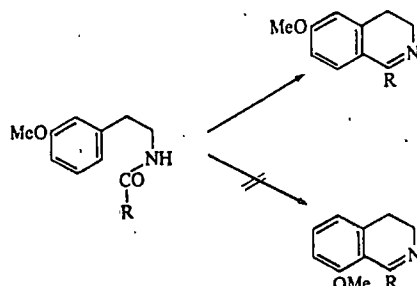
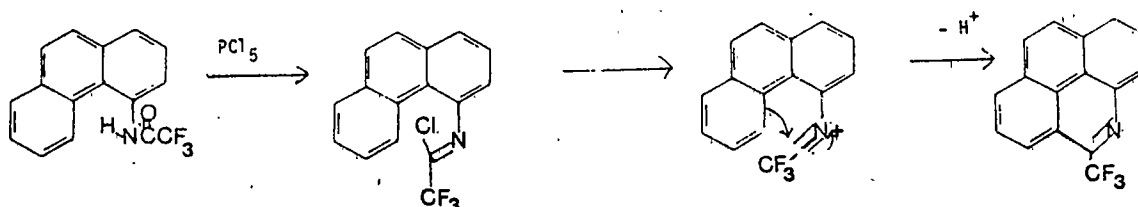


Figure 49. B/E scan on m/e 272 of 4-aminophenanthrene (TFAA) with He as the CAD gas.

The formation of the cyclic structure similar to m/e 272 is also found in solution chemistry. The following cyclization of m-methoxy-phenylamine occurs quite easily (133).



As a similar reaction, the origin of m/e 202 could be studied by preparing and isolating the proposed structure of m/e 272 by the following reaction.



This reaction is actually a modification of the Pictet-Gans synthesis (134,135). This compound could then be used as the starting point for further EI and CI studies. This synthesis has not been attempted in our lab because of the lack of adequate sample and in view of the carcinogenic and mutagenic properties of these derivatives. Our laboratory is simply not equipped for this type of procedure.

The positive ion methane CIMS indicates much more fragmentation and could be utilized to identify 9-aminoanthracene and 4-aminophenanthrene. Again, the propensity of the TFAA derivative of 4-aminophenanthrene to form the fragment ion at m/e 272 clearly differentiates that particular isomer. The TFAA derivative of

9-aminoanthracene can also be distinguished by the ions at  $m/e$  219 and 179. The ion at  $m/e$  179 corresponds simply to the protonated anthracene ion.

The negative ion CI (isobutane) spectra for the 1-, 2-, and 9-aminoanthracene(TFAA) derivatives are very similar, but based on the intensity of the fragment ion at  $m/e$  112 which corresponds to the actual charge remaining with the amide substituent, the 9-aminoanthracene can be distinguished from the other two. The 4-aminophenanthrene derivative is easily differentiated from the others based on the fragment ion at  $m/e$  271. This structure may be similar to the four-fused ring structure postulated for the PCI at  $m/e$  272. The NCI (methane) seems to be more informative. The 9-aminoanthracene can easily be distinguished from the others, due to the formation of the ion at  $m/e$  219 which corresponds to loss of  $HCF_3$  from the parent ion. The 4-aminophenanthrene can easily be differentiated by the fragment ion at  $m/e$  271. Also, the 9-aminophenanthrene derivative can be identified, primarily based on the intensities of  $m/e$  112 and 269.

The results obtained by negative ion CI in methane and isobutane appear to be more promising than those with either EI or PCI. The negative ion CI of these compounds indicate that the relative intensities of the negative fragment ions are dependent on the concentration of the analyte. Apparently reactions in addition to simple electron attachment are reasonable for the total negative ion CI spectra observed. An example of typical concentration dependence observed in the NCI of several of the derivatives is illustrated in

Figure 50. This phenomenon may be due in part to ion source chemistry or possible reaction with other reagent ions present in the methane or isobutane reagent gases. We have observed ions including  $C^-$ ,  $CH^-$ ,  $CH_2^-$ ,  $CH_3^-$ ,  $O^-$  and  $OH^-$  when either methane or isobutane were used as the reagent gases. Other researchers have found similar reagent ions (136) in the negative ion CIMS when methane was used as the reagent gas. The concentration dependence is presently under further study.

In summary, negative ion CI shows considerable promise for the differentiation of isomeric PAAs but appears to be complicated by presently unknown ionization processes. Positive ion EI and CI provide only partial differentiation of the isomers.

The EI spectrum for the PFPA derivatives of 3-aminophenanthrene and 4-aminophenanthrene are shown in Figures 51 and 52, respectively. The isobutane and methane PCI of 4-aminophenanthrene(PFPA) are shown in Figures 53 and 54. The PFPA derivative also forms the  $(M + 1)$ ,  $(M + 2)$ , and  $(M + 3)$ , similar to the TFAA derivatives. However, the PFPA derivative does not form the  $(M + 1)$  species as the major ion in the positive ion CI mass spectrum as does the TFAA compounds. In addition, there is evidence of the postulated ring structure  $m/e$  202 (similar to that observed for the TFAA derivative). The peak at  $m/e = 202$  might be formed as a result of the following proposed reaction scheme:

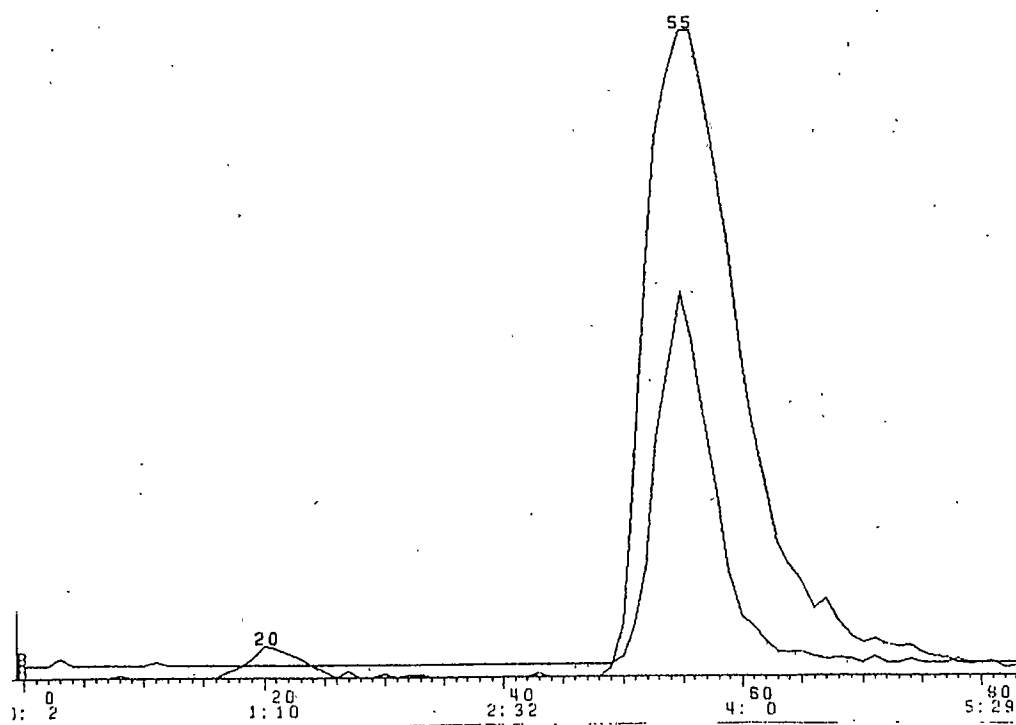


Figure 50. Single-ion traces of  $m/e$  289 and 112 for 9-aminoanthracene (TFAA) with isobutane negative chemical ionization mass spectrometry.

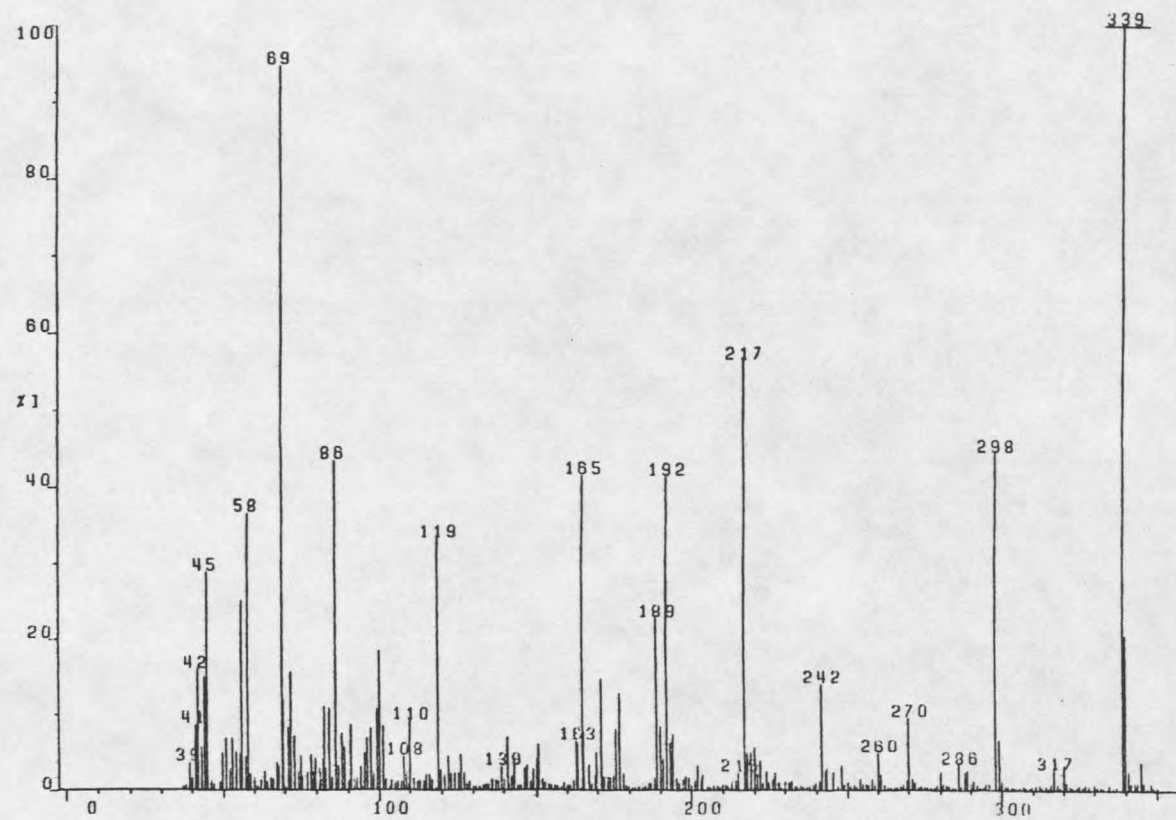


Figure 51. Electron impact mass spectrum of 3-aminophenanthrene (PFPA).

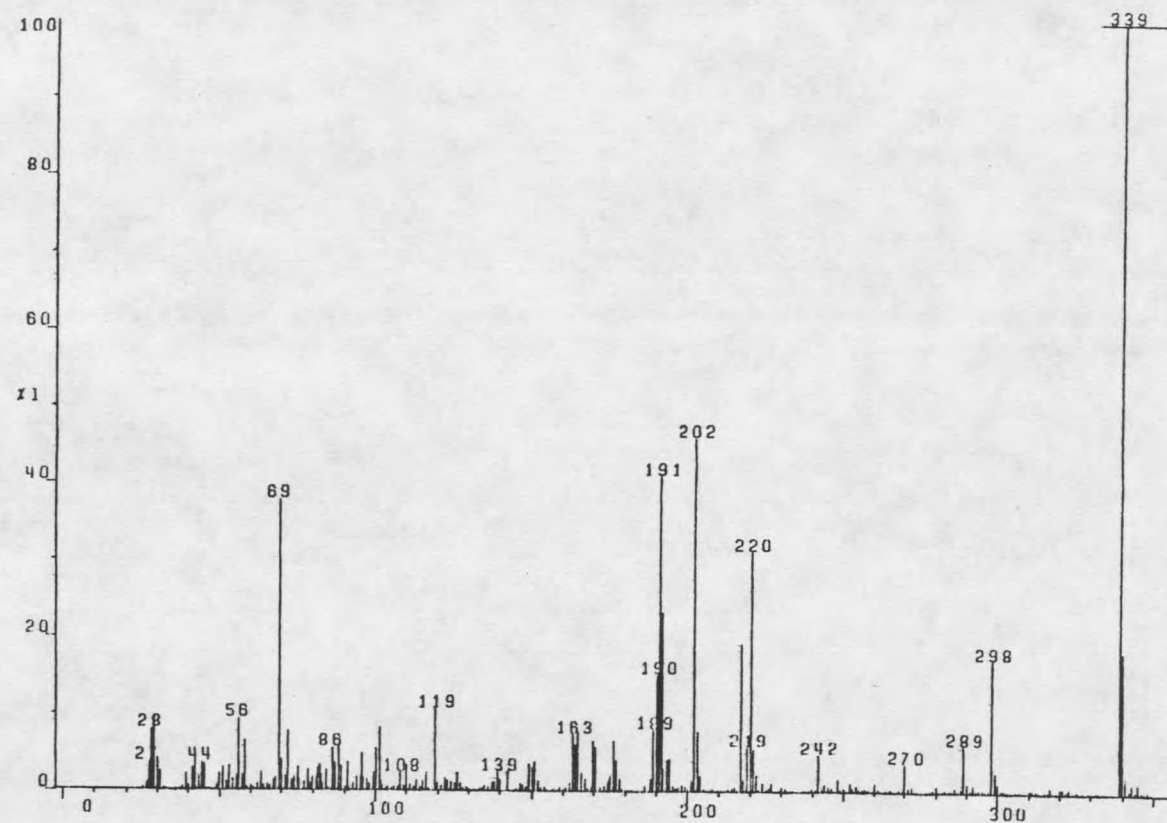


Figure 52. Electron impact mass spectrum of 4-aminophenanthrene (PFPA).

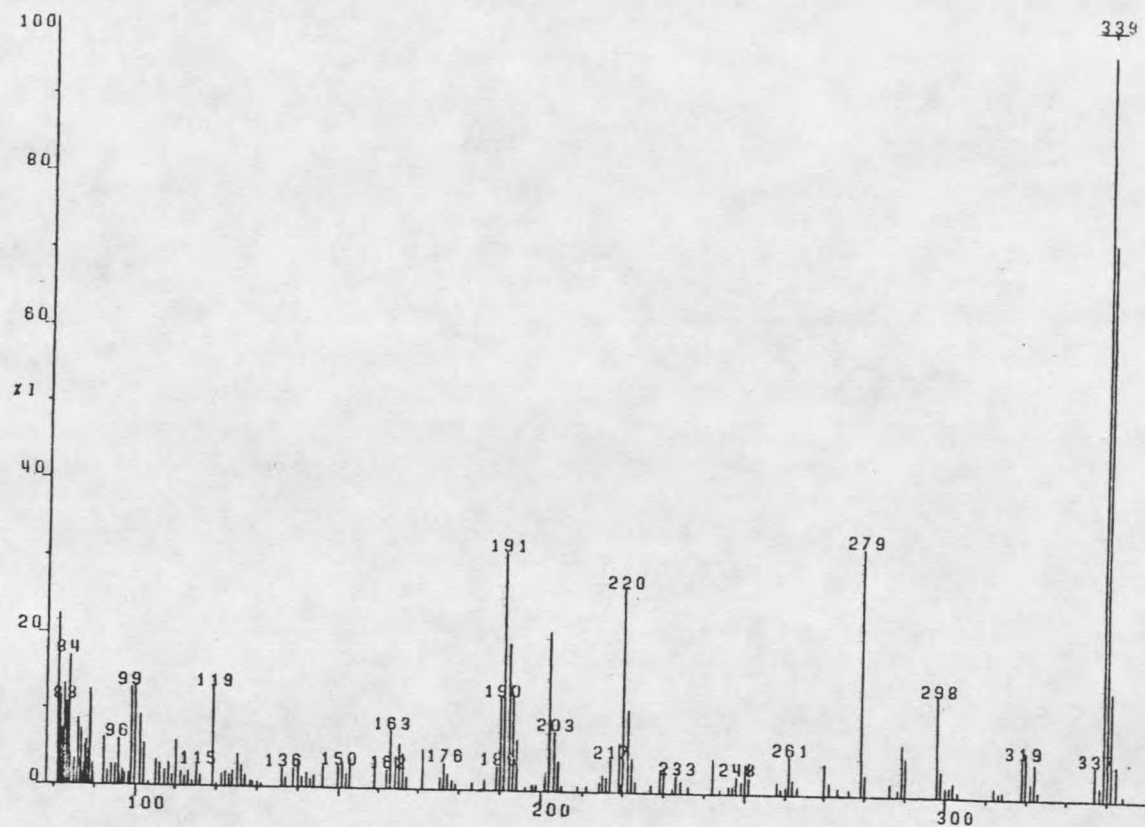


Figure 53. Isobutane positive chemical ionization mass spectrum of 4-aminophenanthrene (PFPA).

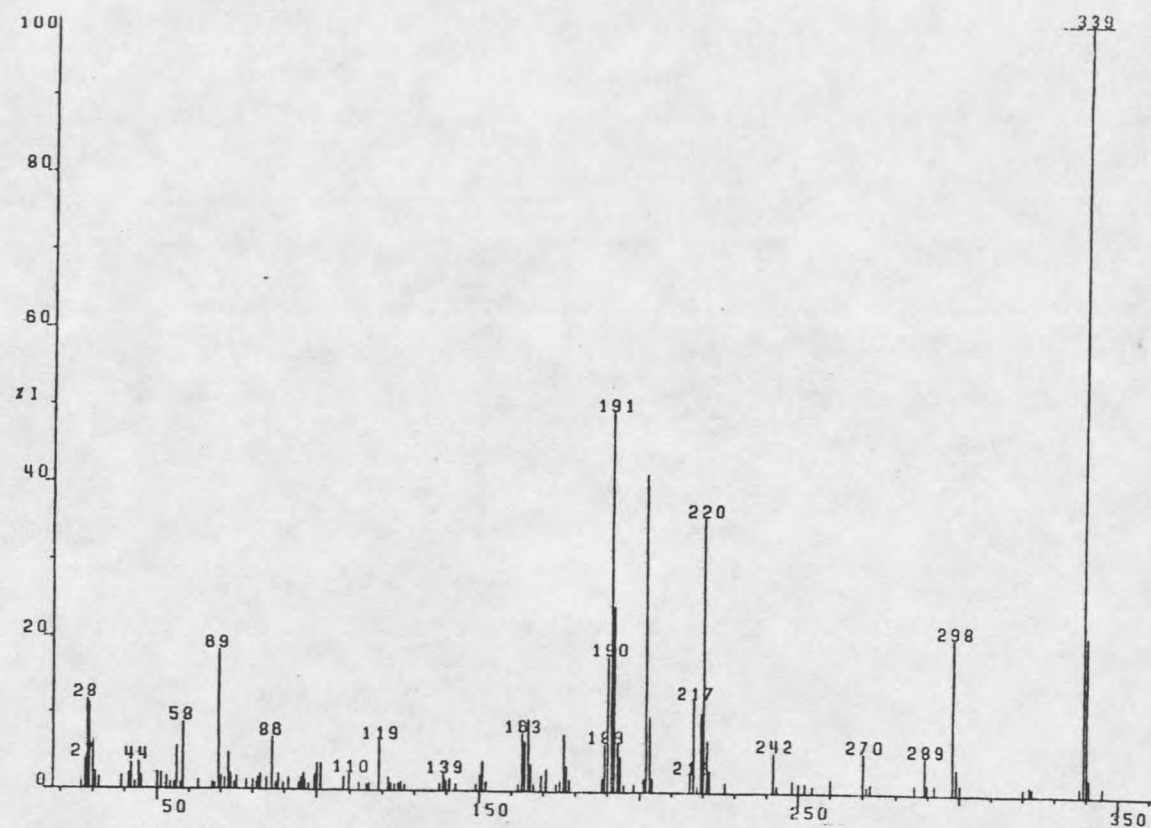
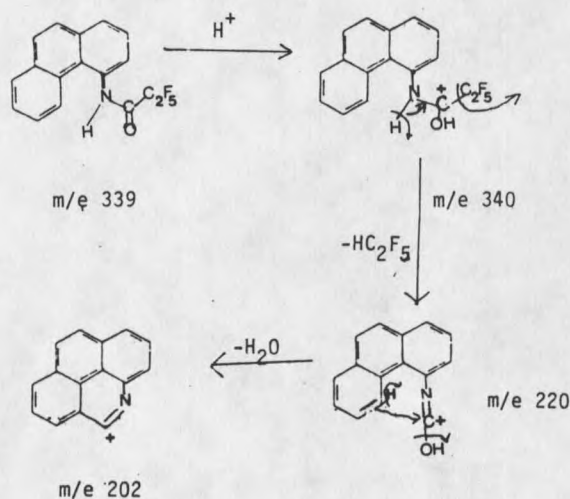


Figure 54. Methane positive chemical ionization mass spectrum of 4-aminophenanthrene (PFPA).



It would be interesting to do B/E scans on  $m/e = 220$ , 339, and 340 to see the formation of the ion at  $m/e = 202$ . In addition, it would be interesting to react the derivative with  $PCl_5$ , similar to that discussed for the TFAA derivative, analyze the mixture by mass spectrometry to see if the cyclized product can be made in solution.

The negative CI of the 4-aminophenanthrene (PFPA) derivative indicates fragment ions at  $m/e$  201 and 219, probably indicating the formation of the proposed ring structure discussed previously. The negative ion mass spectra (both methane and isobutane) show many other fragment ions of lower intensity that have not been identified.

#### Polycyclic Aromatic Hydroxides (124)

The hydroxy compounds were derivatized for the reasons described for the amine compounds as well as for increasing the thermal stability of the parent compound.

### Isomer Differentiation

Figure 55 indicates an example of the chromatograms from which the response enhancements for the hydroxy compounds were determined. For the methoxy derivatives listed in Table 13, the RE differences among members of isomer sets in most instances again exceed the  $\pm 6\%$  level for estimated uncertainty. The 1- and 2-methoxynaphthalene isomers can be distinguished with RE values of 81 and 62, respectively. The dimethoxy derivatives of naphthalene are also easily discerned with enhancement values ranging from 24 to 105. The only two methoxyphenanthrenes available for study here show great variation of their enhancements, as do the three isomers of dimethoxyphenanthrene. While the RE values of 6-methoxy-12-methylbenz(a)anthracene and 5-methoxy-7-methylbenz(a)anthracene are too similar to be distinguished, the other members of this isomer group can be differentiated. In the case of the six methoxychrysene isomers, an almost continuous range of enhancements from 3.6 to 11.1 are observed. The enhancement value of 9-amino-3-methoxyphenanthrene (TFAA) also included in Table 13 is 31. This compound was prepared by using the two derivatization methods sequentially with methylation of the hydroxy functional group performed first. This result enables one to stepwise derivatize groups on a single compound to make them more EC responsive and oxygen sensitive.

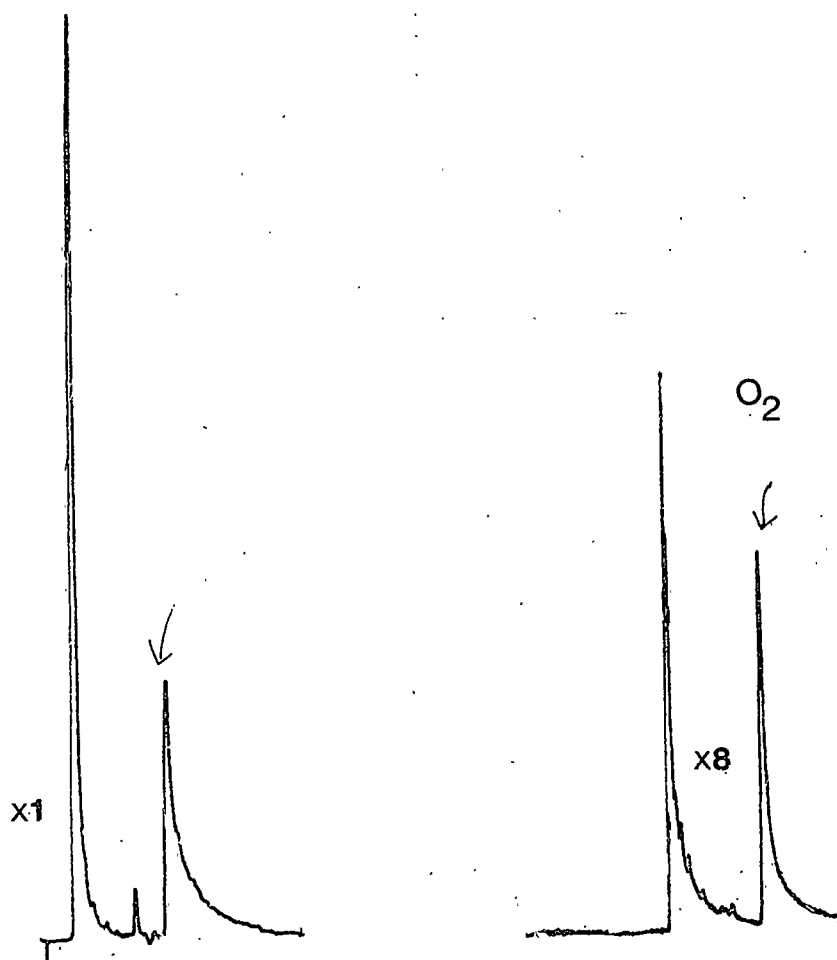


Figure 55. Capillary column gas chromatograms of 4-hydroxyphenanthrene (methoxy derivative). The chromatogram on the left is without oxygen and the one on the right is with 0.30% oxygen in the makeup gas. The detector temperature is 300°C.

Table 13. Oxygen Induced Response Enhancements for the Methoxy Derivatives for Several Polycyclic Aromatic Hydroxides

| <u>Hydroxide</u>                         | <u>Response<br/>Enhancement</u> |
|------------------------------------------|---------------------------------|
| 1-hydroxynaphthalene                     | 81                              |
| 2-                                       | 62                              |
| 1,4-dihydroxynaphthalene                 | 24                              |
| 1,5-                                     | 74                              |
| 1,7-                                     | 105                             |
| 4-hydroxyphenanthrene                    | 11.5                            |
| 9-                                       | 80                              |
| 4,5-dihydroxyphenanthrene                | 13.9                            |
| 1,9-                                     | 3.0                             |
| 2,7-                                     | 63                              |
| 1-hydroxychrysene                        | 3.6                             |
| 2-                                       | 8.0                             |
| 3-                                       | 9.2                             |
| 4-                                       | 3.8                             |
| 5-                                       | 6.8                             |
| 6-                                       | 11.1                            |
| 12-hydroxy-7-methyl<br>benz(a)anthracene | 16.0                            |
| 6-hydroxy-12-methyl<br>benz(a)anthracene | 22                              |
| 5-hydroxy-7-methyl                       |                                 |

TABLE 13 (cont'd.)

|                           |      |
|---------------------------|------|
| benz(a)anthracene         | 20   |
| 8-hydroxy-7-methyl        |      |
| benz(a)anthracene         | 11.1 |
| 9-amino-3-hydroxy         |      |
| phenanthrene <sup>b</sup> | 31   |

<sup>a</sup> EC detector temperature is 300°C. Oxygen concentration in the doped detector is 3.0 parts per thousand.

<sup>b</sup> Methoxy, TFAA derivative.

#### Atmospheric Pressure Ionization Mass Spectrometry

The only ions observed by APIMS for the methoxy derivatives of 2-hydroxynaphthalene and 9-hydroxyphenanthrene with and without oxygen was the  $(M-15)^-$  ion. The dimethoxy compounds of 1,7-dimethoxynaphthalene and 2,7-dimethoxyphenanthrene were also examined and ions observed included both the  $M^-$  and the  $(M-15)^-$  ion. Both of these were formed with and without the presence of added oxygen. Without oxygen the  $M^-$  ion is the predominant ion and with oxygen the  $(M-15)^-$  is the predominant ionic species.

#### Methylanthracenes and Methylphenanthrenes

##### Isomer Differentiation

The methyl isomers of anthracene and phenanthrene present another interesting set of isomeric compounds in which typical forms mass spectrometry fail to discern them. The electron impact mass spectra(EI) for 2-methylanthracene, 2-methylphenanthrene,

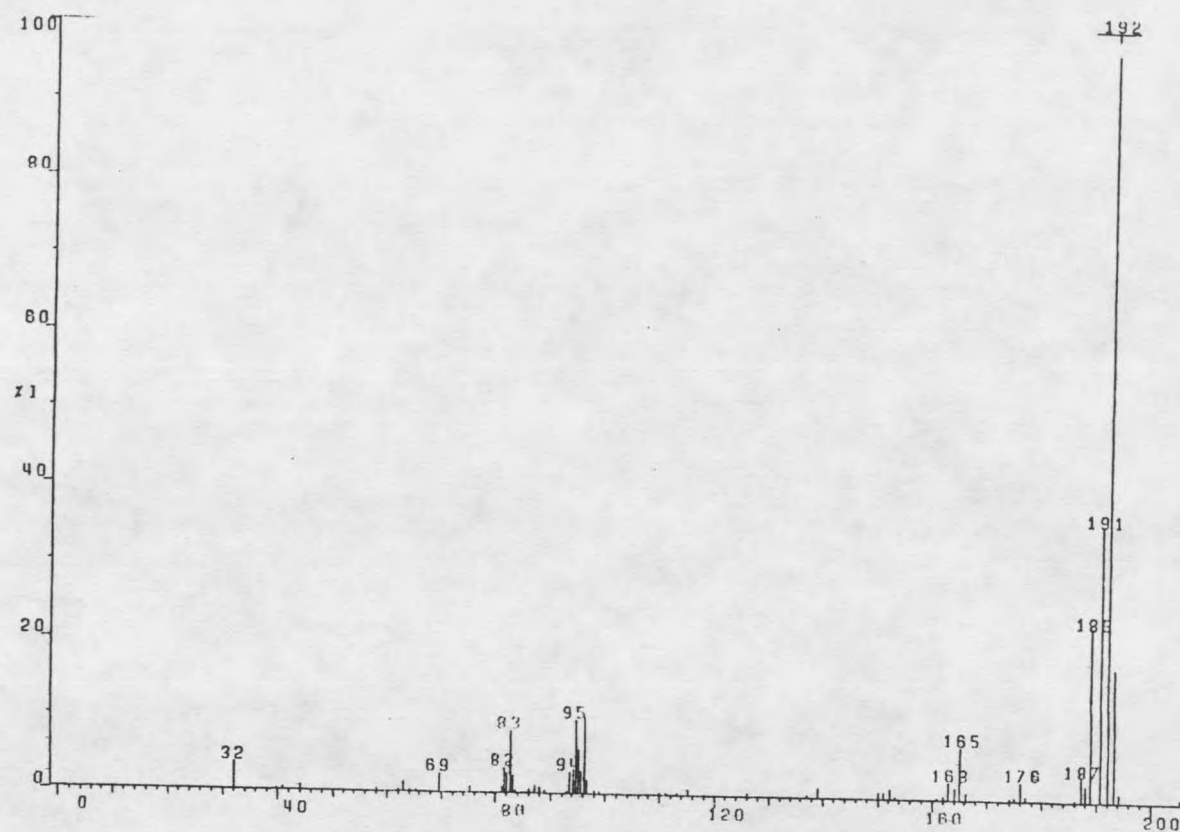


Figure 56. Electron impact mass spectrum of 2-methylantracene.

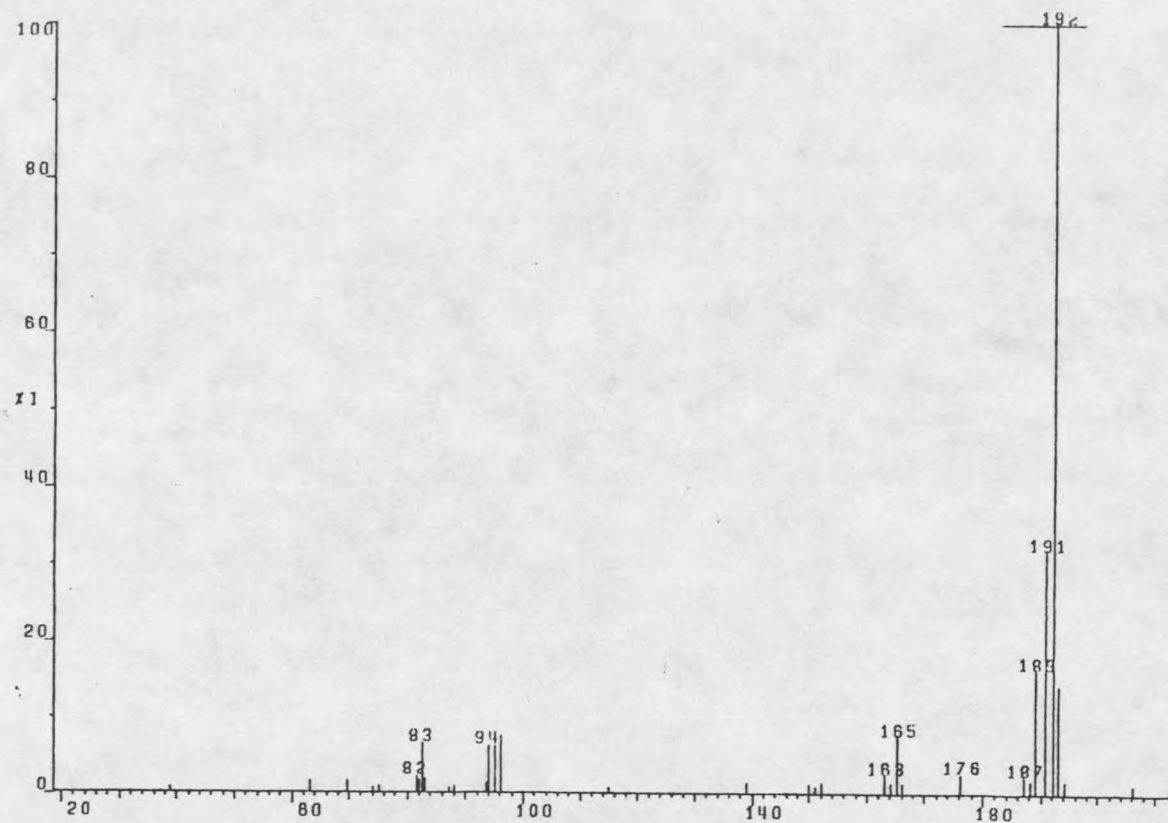


Figure 57. Electron impact mass spectrum of 2-methylphenanthrene.

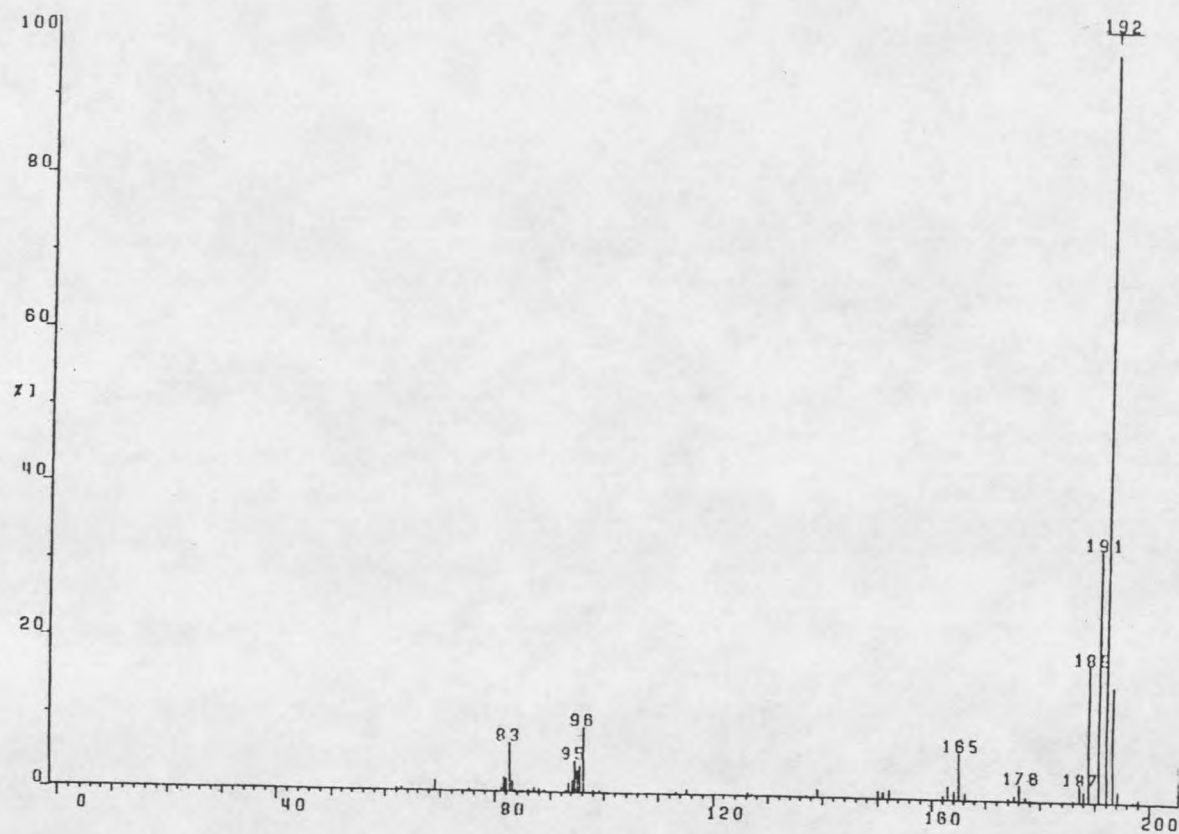


Figure 58. Electron impact mass spectrum of 1-methylphenanthrene.

and 1-methylphenanthrene are shown in Figures 56, 57, and 58, respectively, and for all practical purposes, are almost identical.

The response enhancements for these compounds are listed in Table 14. The oxygen concentration was 0.2% with a detector temperature of 250° C and column temperature of 180°C. The RE values for this isomeric group allow these compounds to be distinguished based solely on the oxygen-induced response. It should also be noted that the RE values were determined using the

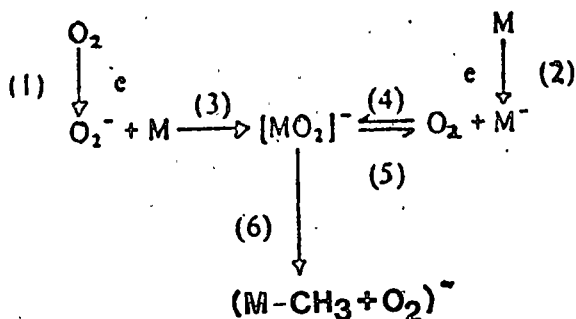
Table 14. Response Enhancements of the Methylantracenes and Methylphenanthrenes

| <u>Name</u>            | <u>R. E.</u> |
|------------------------|--------------|
| 1-methylantracene      | 3.4          |
| 2-                     | 5.7          |
| 9-                     | 13.6         |
| 9,10-dimethylantracene | 10.8         |
| 1-methylphenanthrene   | 14.1         |
| 2-                     | 20.2         |
| 3-                     | 1.0          |
| 4-                     | 11.0         |
| 9-                     | 3.5          |

series detector design that will be discussed in more detail later. An example is shown in Figure 59. Again, the values range from 3.4 for 1-methylantracene, 13.6 for 9-methylantracene, and 20.2 for 2-methylphenanthrene. The only two isomers that can not be differentiated are 9-methylphenanthrene(3.5) and 1-methylantracene(3.4), because their RE values are too similar.

#### Atmospheric Pressure Ionization Mass Spectrometry (APIMS)

In order to establish the ions formed with and without the presence of oxygen, the APIMS was again utilized. For the 9-methylantracene isomer, the major ion formed with and without added oxygen was the  $(M-CH_3+O_2)^-$  species. The results are quite similar to that obtained for the 9-chloroanthracene molecule. Without oxygen for the 9-methylantracene, the ions formed were  $(M+O_2)^-$  and  $(M-CH_3+O_2)^-$  in a ratio of about 1:4. With oxygen present, the major ion formed is the  $(M-CH_3+O_2)^-$ . For the 2-methylphenanthrene and without oxygen, the major ionic species present were  $M^-$  and  $(M+O_2)^-$  in a ratio of approximately 5:1. With the addition of oxygen, the major ion formed is the  $(M+O_2)^-$  with a small amount (<5%) of  $(M+O)^-$ . The reaction mechanism for 9-methylantracene is similar to that postulated for the 9-chloroanthracene and 9-chlorophenanthrene.



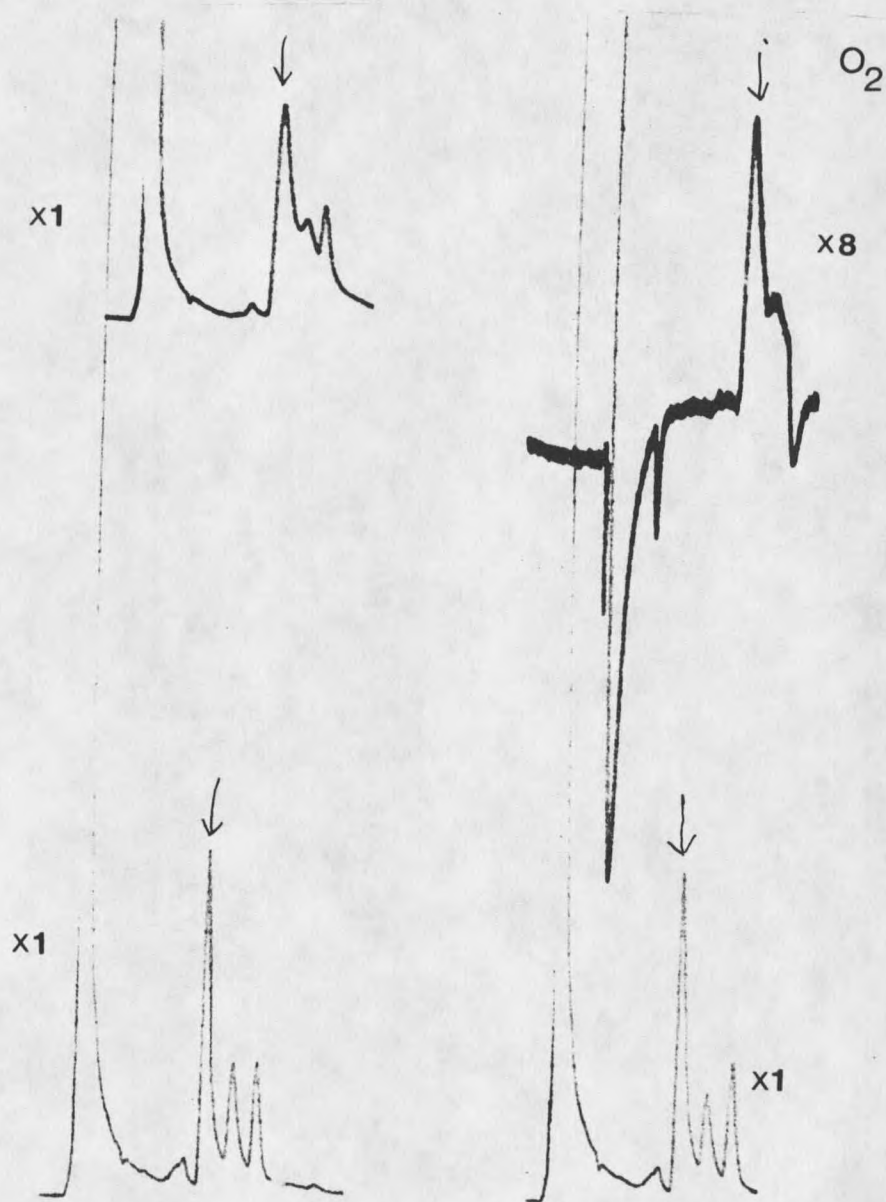
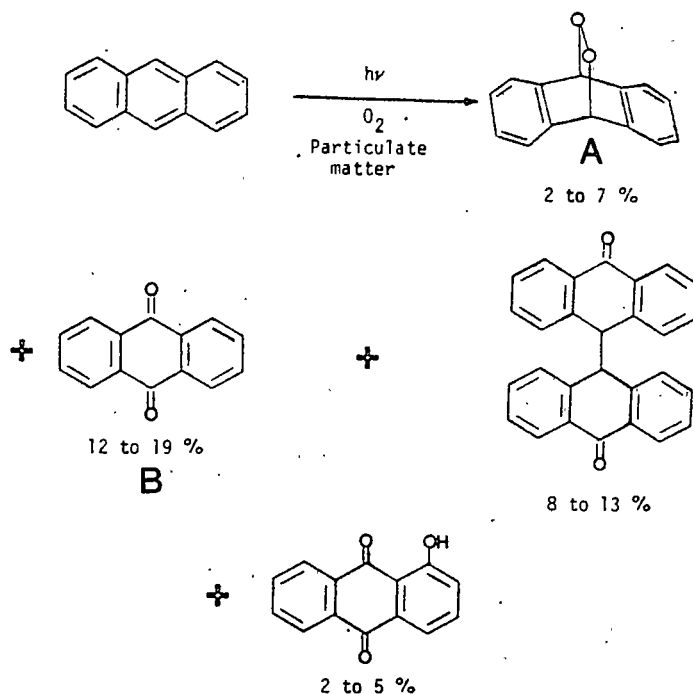


Figure 59. Response enhancement for 9, 10-dimethylantracene using series detectors. The chromatogram on the left is without oxygen and the one in the top right is with 0.20% oxygen in the detector at 250°C.

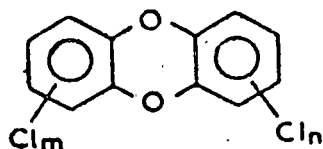
For 9-methylantracene, the intermediate  $(M+O_2)^-$  is formed by reactions 1 and 3 or 2 and 4. This intermediate dissociates through reaction 6 to form  $(M-CH_3+O_2)^-$ . In the case of 2-methylantracene, the intermediate again is formed through reactions 1 and 3 or 2 and 4, but remains intact. Another compound examined was the 9,10-dimethylantracene molecule, and the major ion formed both with and without oxygen was a species at  $m/e$  209 which corresponds to a species of the type  $(M-2CH_3+O_2)^-$ ,  $(M-2CH_3+H+O_2)^-$ , or possibly  $(M-2CH_3+2H+O_2)^-$ . In view of the resolution problem or inability to differentiate mass differences of 1-2, it is difficult to distinguish the differences between these postulated species. The structure and exact mass of the ionic species could possibly be an oxygen bridged system similar to that observed with the photooxidation of anthracene on atmospheric particulate matter (137). The following products have been identified



The species formed for the 9,10-dimethylantracene in the presence of oxygen in the APIMS might be similar to structure or product A or B. If one used (a) labelled oxygen the question might be resolved or (b) if species A could be isolated and then put in the source of the APIMS, one might be able to deduce the structure of the oxygenated species of this particular compound. Both of these experiments would be interesting to perform and be very informative at the same time. In addition, it might be informative to examine a molecule such as 9,10-dibromoanthracene with the APIMS and added oxygen to determine the species formed. If a ion of the form  $(M - 2Br + O_2)$  is produced in the presence of oxygen, there should be no trouble in resolving that from the parent ion.

### Dioxin

The structure for the dioxins is shown in the following illustration.



For the single dioxin compound examined, 2,3,7-trichlorodibenzo-p-dioxin, the response both with and without the presence of oxygen in the detector is shown in Figure 60. At a detector temperature of 250° C, column temperature of 180° C, and approximately 2 ppt oxygen in the detector, the response enhancement was determined to be 14.1. In addition, Miller *et al.* (105) determined the response enhancement

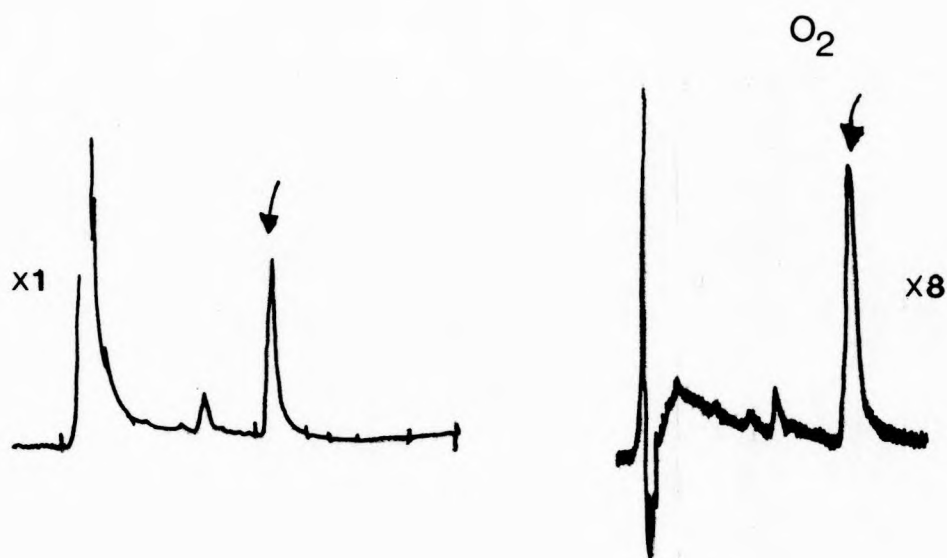


Figure 60. Capillary column gas chromatograms of 2,3,7-trichloro-dibenzo-p-dioxin. The chromatogram on the left is the normal ECD response and the one on the right is with 0.20% oxygen in the detector at a temperature of 250°C. Sample contains approximately 2 ng of dioxin.

of dibenzofuran and found it to be 175. From the analysis of these two compounds some interesting implications might be made. As an example, in using the series detector scheme which will be discussed in the next section, the uncertainty in determining response enhancement values was determined to about 2% and could be applied to the dioxin isomers for possible differentiation. Utilizing a HPLC for prior cleanup and other forms of extraction schemes, it would be interesting to see if the oxygen-doped ECD could be used with actual environmental samples containing trace quantities of dioxins. It should be noted that precautionary procedures for handling and disposal of the dioxin waste should be strictly adhered to. Handling the samples with gloves and venting the ECD effluent out of the laboratory are highly recommended safety precautions.

#### Simultaneous Electron Capture and Oxygen-Sensitized Electron Capture Detection

The ECD is used extensively for the trace analysis of organic compounds and frequently provides the only or best means of sensing pollutants at their environmental concentrations. The oxygen sensitized ECD may add to this detector's proven worth by also offering a means for compound verification in the trace analysis of environmental samples. It has been previously shown that the method is greatly assisted by the large variations of RE values among various sets of related compounds, but the precision with which an individual RE measurement needs to be improved. A decrease in the

uncertainty of individual RE measurements will correspondingly increase the discriminating power of the method.

Previously, all oxygen RE measurements have been made using a single ECD and a given chromatographic separation which was performed twice, once without oxygen and again with oxygen in the detector. With great care in reproducing manual, splitless injections to a capillary column, the relative standard deviation of previous RE measurements have typically been +7%. The precision of this technique was determined by analyzing one of the TFAA derivatives of the amines ten times both with and without oxygen. For these measurements, the relative standard deviation of the measured response enhancements was +7%. Miller's reproducibility was estimated at 10% for primarily packed column chromatography.

#### Parallel ECDs (138)

##### Dual Columns

Improved reproducibility as well as increased ease of measurement might be expected if two ECDs are simultaneously used for each analysis where one detector is operated normally and the other is doped with oxygen. The first new technique using two parallel ECDs that will be discussed involves the use of two identical capillary columns placed in the same injector port with one column going to one ECD and the other one going to ECD number two. In order to determine the split ratio which occurs in the injector port and to ensure that the split ratio is approximately 1:1, the chromatograms shown in Figure 61, were first obtained in

the normal, oxygen-free mode. The relative peak heights observed suggest that the split ratio to column A and B is 1.20. The possibility that the paired ECD responses may also differ due to differing sensitivities of the two detectors was tested by reversing the columns at the detectors. As shown in part b of Figure 61, an A to B response ratio of 0.82 is obtained. This result indicates that our two detectors have essentially identical sensitivities and the small difference in normal EC responses seen here, is entirely due to the split ratio of the sample at the detector and not due to any differences in the detector response. Also, it is noted that in this preliminary test that the retention times of 2-chloroanthracene in the two columns are essentially identical for all practical purposes.

In Figure 62, a single 2-chloroanthracene sample has been analyzed ten times in repetition. While the peak heights vary noticeably from one injection to the next (due to the difficulty in reproducibly delivering the 0.4  $\mu$ l sample by syringe), the ratio of the oxygen-sensitized to the normal responses remains very constant. The ratios of the ten dual responses shown are 6.2, 6.2, 6.2, 5.9, 5.8, 6.3, 5.9, 6.0, 6.1, and 6.1. The relative standard deviation of these values is 2.6%. The average of these values, 6.1, times the split ratio, 1.20, indicates that the oxygen-induced RE value for 2-chloroanthracene is 7.3. This value correlates well with the value of 6.9 previously observed in a study using 0.3% oxygen and a 300° C detector temperature, but by two separate, paired analyses with only one detector (119). In that study unusually great care

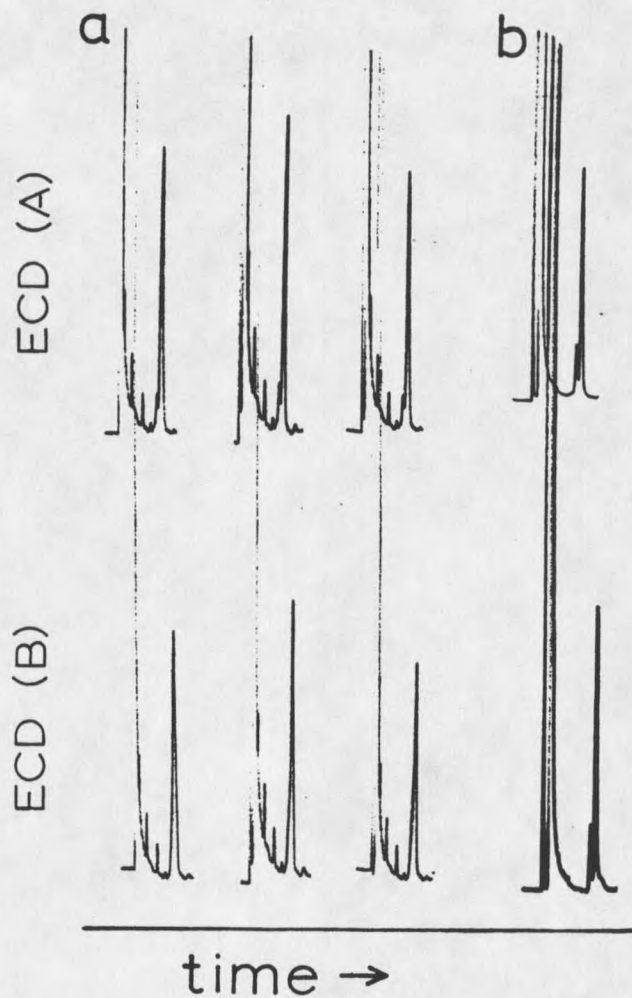


Figure 61. Dual ECD responses with dual columns of sample containing 2 ng of 2-chloroanthracene, repeated three times with both detectors operated in the normal, oxygen-free mode. The last chromatogram is repeated with column-to-detector connections reversed. Detector temperatures are 300°C.

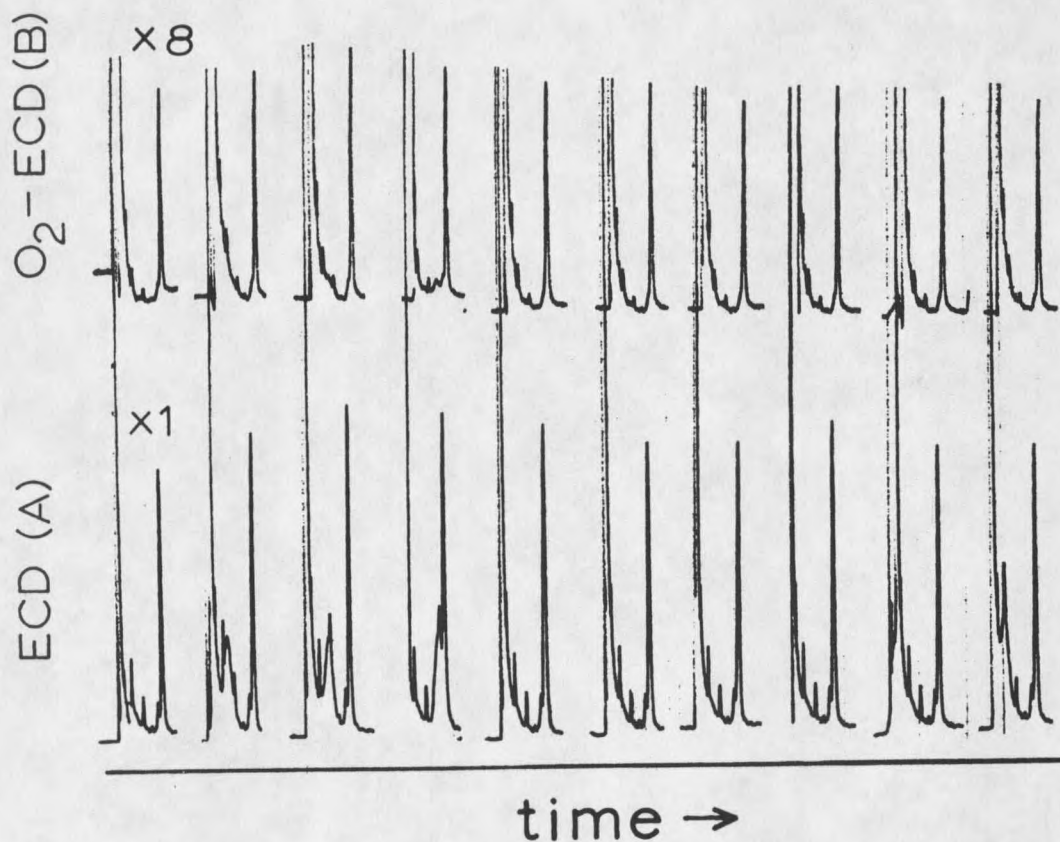


Figure 62. Dual ECD and oxygen-sensitized detection of sample containing 12 ng 2-chloroanthracene, repeated ten times. Detector temperature is 300°C and oxygen concentration in detector is .30%.

was taken to reproducibly inject samples and the uncertainty (relative standard deviation) was estimated to be +7%. The use of the two parallel detectors as described has reduced this uncertainty a factor of two and has greatly relaxed the requirement for precise injections.

In Figure 63 chromatograms are shown which indicate that the response ratios are quite constant over a range of different analyte concentrations. In these analyses, RE values of 6.9, 7.0, 7.0, and 7.4 are observed as the analyte concentration is repeatedly doubled. In a previous study (119), the RE values of this compound and its two isomers were found to be independent of concentrations over a change of approximately two orders of magnitude.

Also, in Figure 64, the simultaneous dual ECD responses to all three isomers of chloroanthracene are shown. From these analyses, the injection split ratio is again 1.20, and RE values for 1-, 2-, and 9-chloroanthracene are determined to be 3.4, 7.3, and 26.0. These values are in reasonable agreement with those previously observed under similar conditions by the single detector method (119). Since the mass spectra of the three chloroanthracenes are identical (See Figure 14), their ECD responses as shown in Figure 64 would seem to offer a particularly useful means for their identification. The improved precision accompanying the use of the two parallel ECDs is expected to proportionately increase the reliability of the method. In addition, another advantage of this method involves the time required for analyses. Using the previously described method, one analyzed the samples without

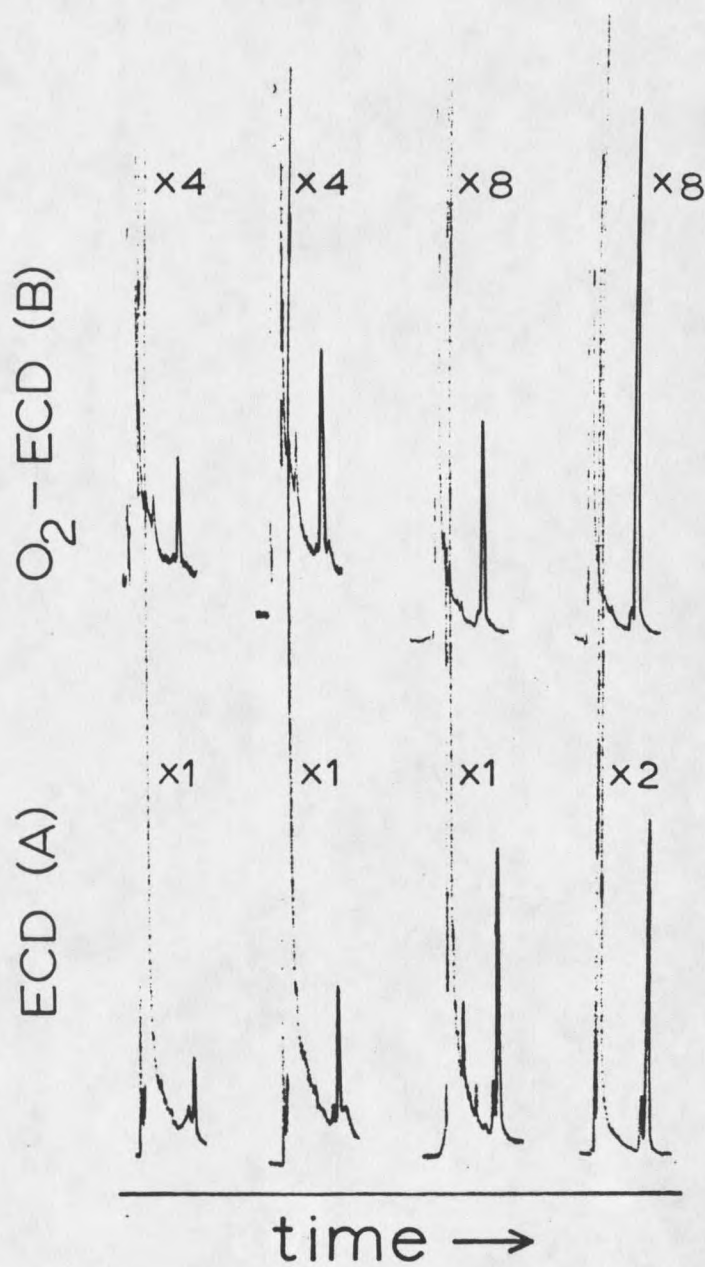


Figure 63. Dual ECD and  $O_2$ -sensitized ECD detection of four samples containing 1.5, 3.0, 6.0, and 12 ng 2-chloroanthracene.

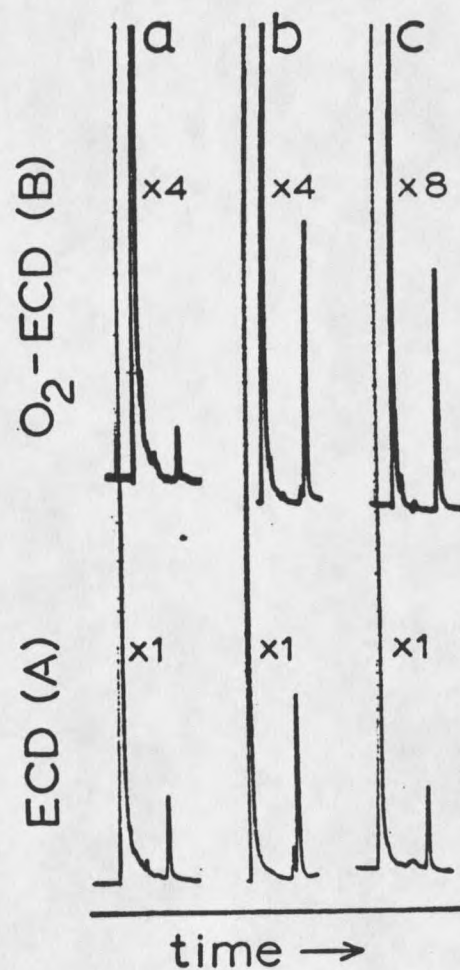


Figure 64. Dual ECD and oxygen-sensitized EC detection of samples containing 5 ng of 1-chloroanthracene (a), 12 ng of 2-chloroanthracene (b), and 6 ng 9-chloroanthracene (c).

oxygen, added oxygen to the detector and waited approximately 2-3 hours for equilibration, and then analyzed the samples again in the presence of oxygen. Using this technique with two parallel detectors the analysis time is reduced by a factor of two.

### Splitter

The response enhancements have been examined where the split was performed with a post-column effluent splitter. A Varian capillary column effluent splitter was utilized. As far as the detector performance is concerned, this scheme functions as well as when the split occurs in the injection port. Chromatograms are shown in Figure 65 which clearly indicates the only disadvantage of the effluent splitter is some deterioration of the chromatographic resolution. In addition, 9-chloroanthracene was analyzed ten times in repetition. The peak heights vary noticeably from one injection to the next, but again the reproducibility is still quite good. The relative standard deviation of these measurements is 5.4%, which is still an improvement over the old method of using single detector. The response enhancement as determined for the 9-chloroanthracene was 34, which is slightly higher than previously determined (119), but comparable with Miller's results (105). The response enhancements for the other isomers agree quite well with previous studies. The values obtained are 3.8 and 7.1 for the 1-chloroanthracene and 2-chloroanthracene molecules, respectively. The major factor contributing to the poor resolution is the effluent splitter itself. The major problem associated with this splitter is

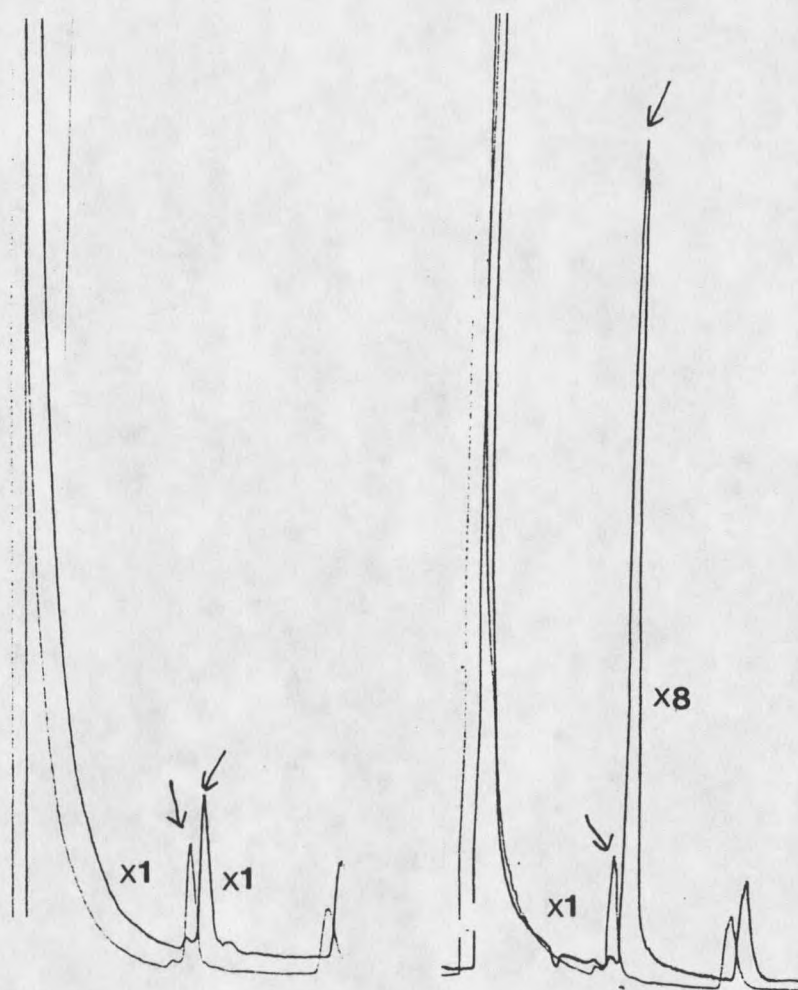


Figure 65. Dual ECD responses with a capillary column effluent splitter of sample containing 8 ng of 9-chloroanthracene. The chromatogram on the left is the normal ECD responses and the one on the right is with 0.30% oxygen in the second cell. Both detectors are at 300°C.

the fact that it has stainless steel tubing in places (this was not known at the time of the experiment). It has been shown that for some molecules that stainless steel will absorb some quantity of sample. A splitter constructed as to reduce the dead volume involved, as well as removing the stainless steel, would be very beneficial and probably solve the problem in resolution. An efficient fused silica capillary column effluent splitter has been reported by Later, Wright, and Lee (138). A schematic diagram of this splitter is illustrated in Figure 66, and would probably improve the peak broadening problems as experienced with the Varian splitter.

The use of either dual columns or a splitter could be used in a parallel combination of the  $O_2$ -doped ECD and a FID or nitrogen or phosphorous specific detectors. Other combinations of detectors could be possible with this type of arrangement.

#### Series Detectors (138)

In this experiment, the effluent from one undoped ECD is connected to the inlet part of the second detector with a section of glass-lined stainless steel tubing (1.5ft). The glass-lined tubing and the ECD exit line was connected by a small piece of Teflon tubing. Typical chromatograms indicating the difference in detector response is shown in Figure 67 for the chloroanthracenes and 9-chlorophenanthrene. It is interesting to note that the response in the two detectors is similar for all the compounds except 9-chlorophenanthrene. Figure 68 illustrates the enhancements obtained

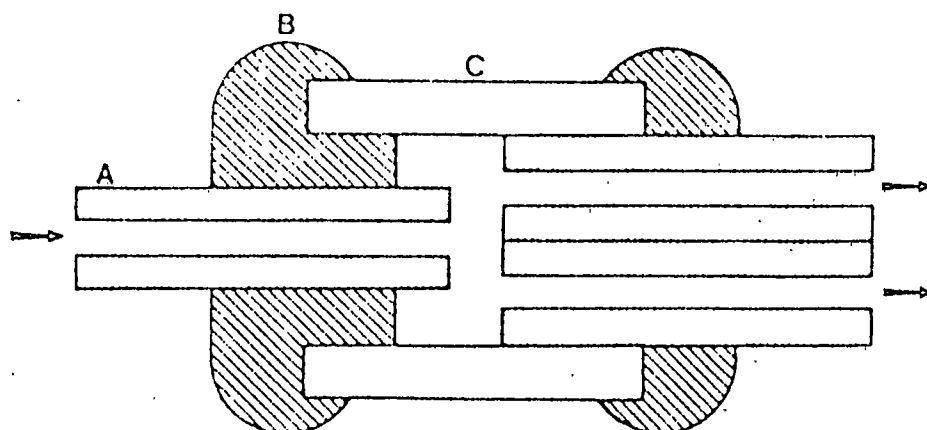


Figure 66. Schematic diagram of the fused silica capillary column effluent splitter. A: fused silica capillary column; B: AgCl cement; C: glass sleeve. (Reference 139).

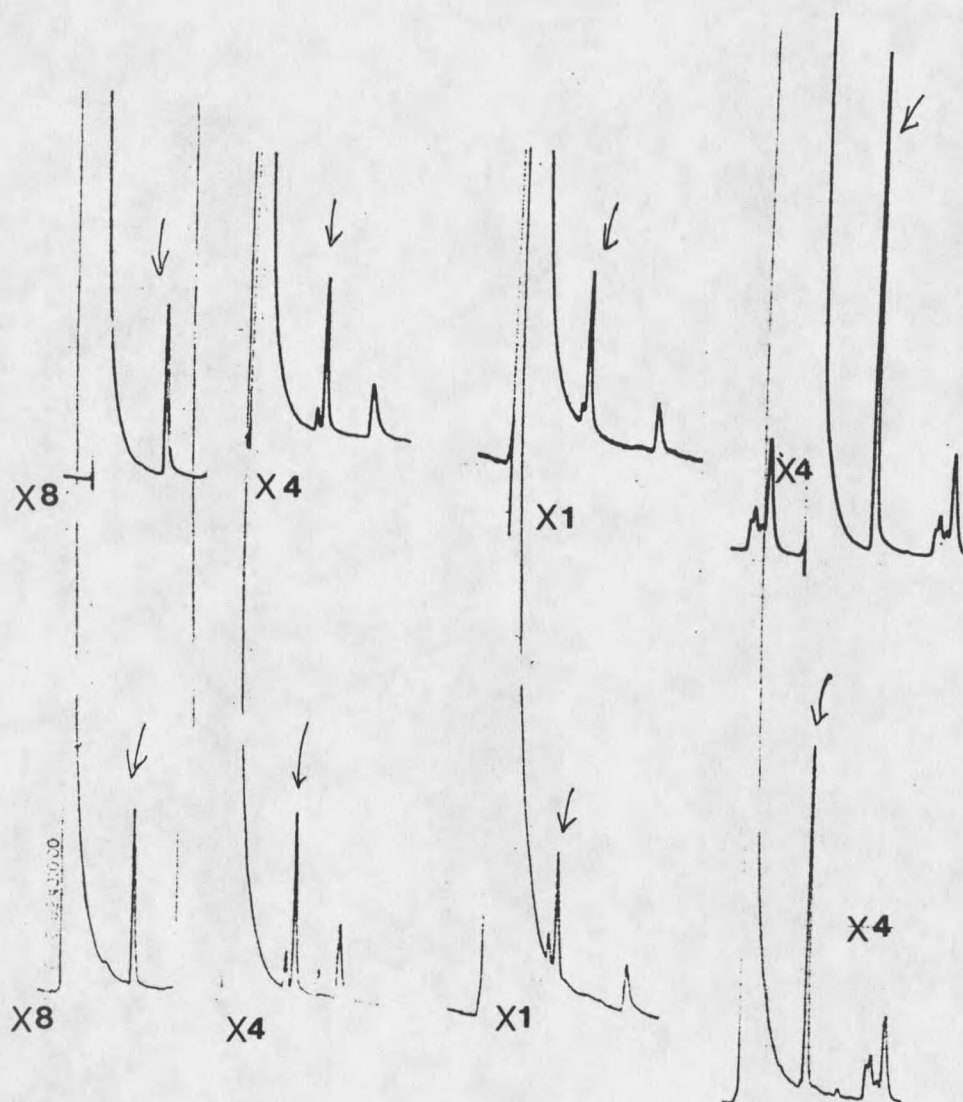


Figure 67. Dual ECD responses in series detection of 1-, 2-, 9-chloroanthracene and 9-chlorophenanthrene. Detector temperatures are 300°C.

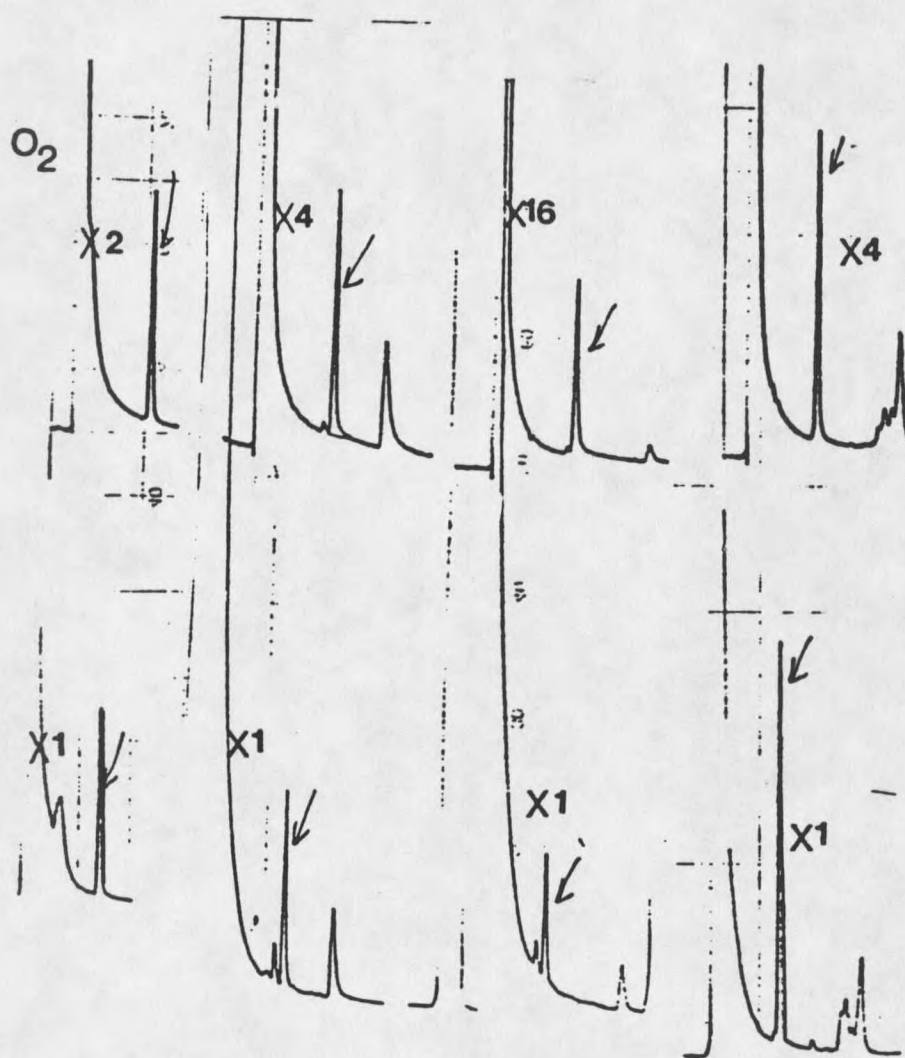


Figure 68. Dual ECD responses and oxygen-sensitized ECDs in series detection of 1-, 2-, and 9-chloroanthracene and 9-chlorophenanthrene. The bottom chromatograms are normal ECD responses and the upper ones are with 0.30% oxygen present in the second detector. Both detector temperatures are 300°C

with oxygen present in the second detector. The enhancements obtained are 2.5, 6.1, 16.6, and 1.8 for the 1-chloroanthracene, 2-chloroanthracene, 9-chloroanthracene, and 9-chlorophenanthrene. These values are somewhat lower than those obtained with a single detector (119). A sample of 9-chloroanthracene was analyzed in the same repetitive fashion as reported previously. The results of these analyses are shown in Figure 69. The response enhancements are 16.7, 16.7, 16.6, 17.2, 16.8, 17.0, 17.2, 17.4, 17.4, and 17.2. The results of the response enhancement measurement indicate that the relative standard deviation for repetitive analyses is 2.1%.

For those compounds which have large normal ECD responses, one would expect that the second undoped detector would see slightly less material, and as a result, the response in the second detector would be somewhat less. This is in fact what is observed in Figure 70 which is an example of the two undoped detector responses to 9-nitroanthracene and hexachlorobenzene. Both of these compounds are very strongly responding compounds (140).

Mixture analysis can be accomplished with little or no loss of resolution from one detector to the other. This is shown in Figure 71 and illustrates no loss of chromatographic resolution. In this illustration, it should be noted that the response of 9-chlorophenanthrene is larger in the second detector when both are undoped. This might simply reflect the second detector's increased sensitivity for that particular compound. Figure 72 shows the response enhancement as a function of concentration of the analyte molecule using the series detector system of analysis.

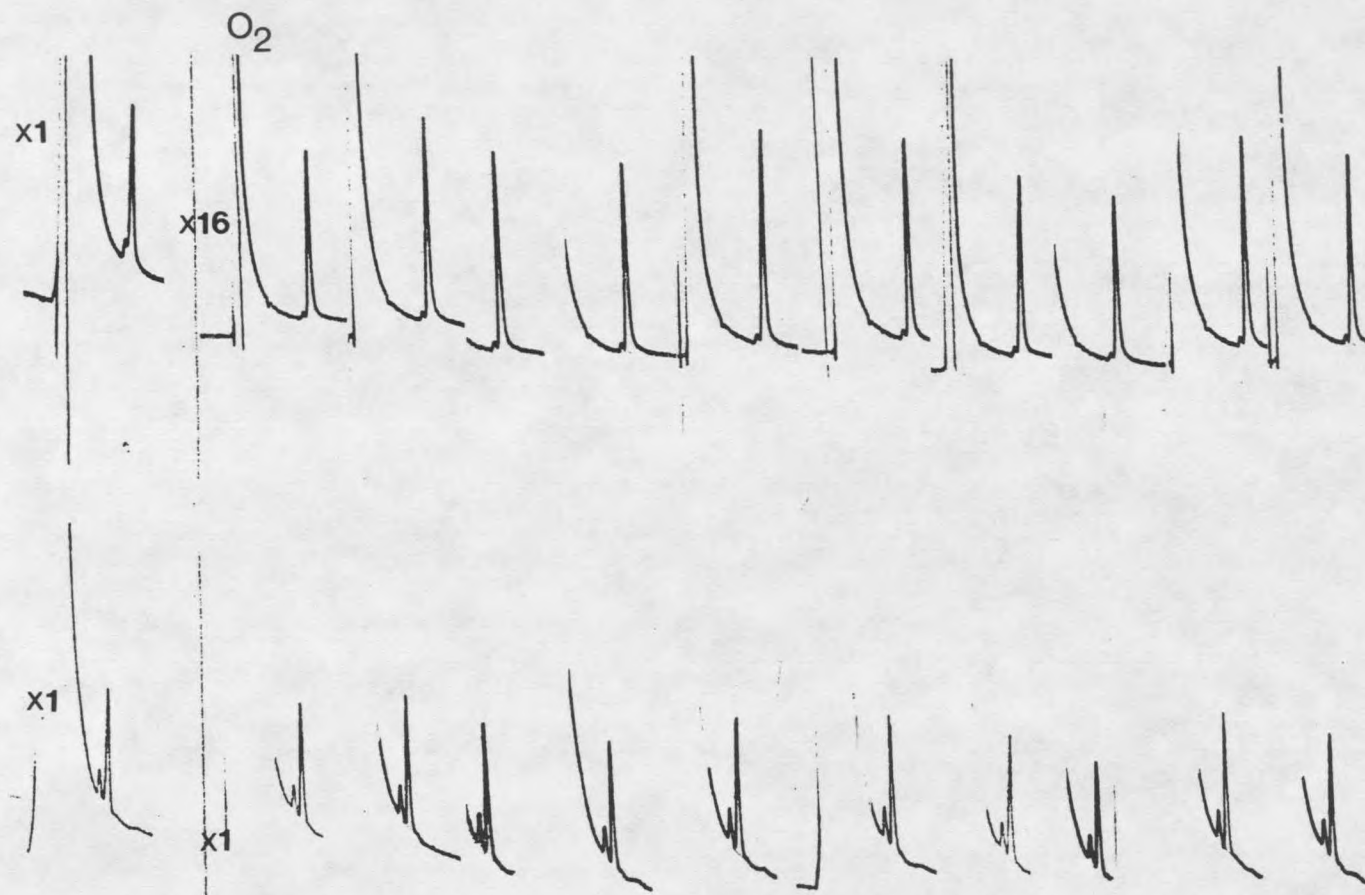


Figure 69. Dual ECD and  $O_2$ -sensitized ECD responses in series of sampling containing 9-chloroanthracene repeated ten times. The chromatogram on the left is the normal ECD response in both detectors. The concentration of oxygen is 0.30% and temperatures are 300°C.

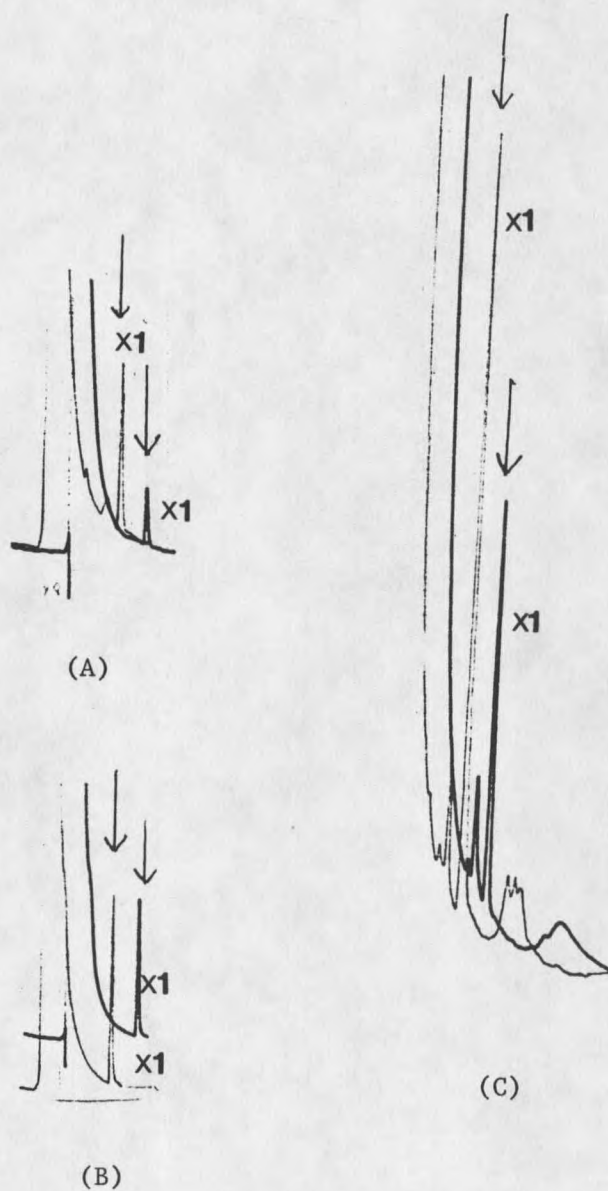


Figure 70. Dual ECD responses of series detectors of separate samples containing (A) hexachlorobenzene, (B) 9-nitrobenzene, and (C) 2,7-dinitrofluorene. The arrows indicate the peaks of interest in the two cells.

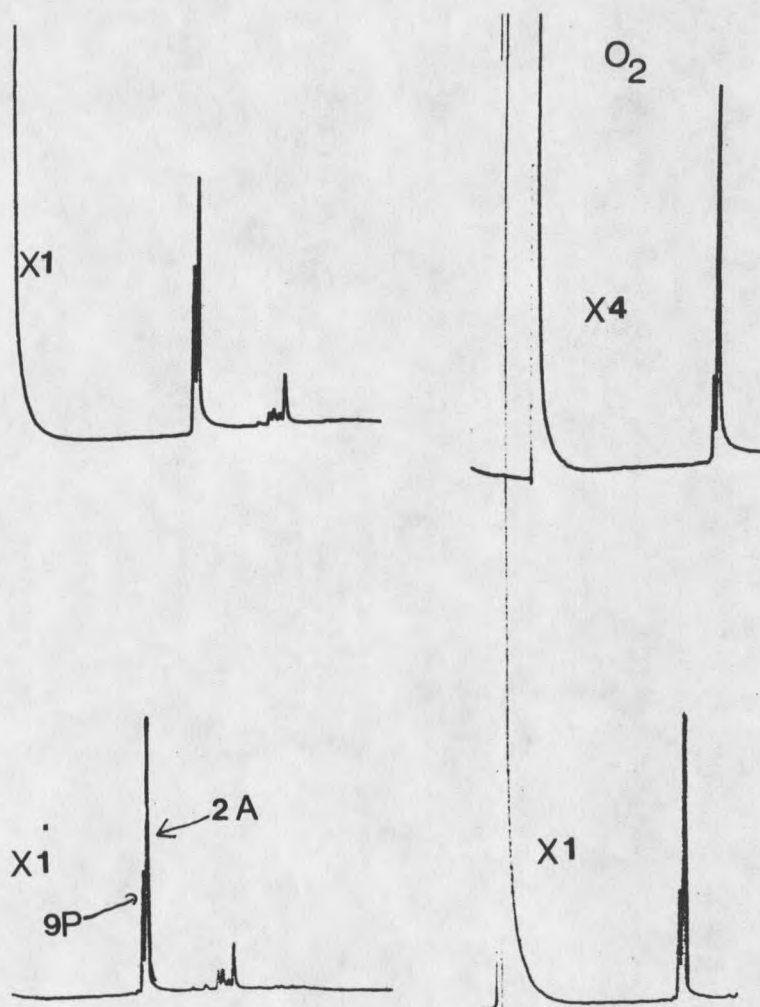


Figure 71. Dual ECD and oxygen-sensitized ECD responses of series detectors of a mixture of 9-chlorophenanthrene and 2-chloroanthracene. The chromatogram on the left is without oxygen and the upper right is with 0.30% oxygen in the second detector. Detector temperature is 300°C.

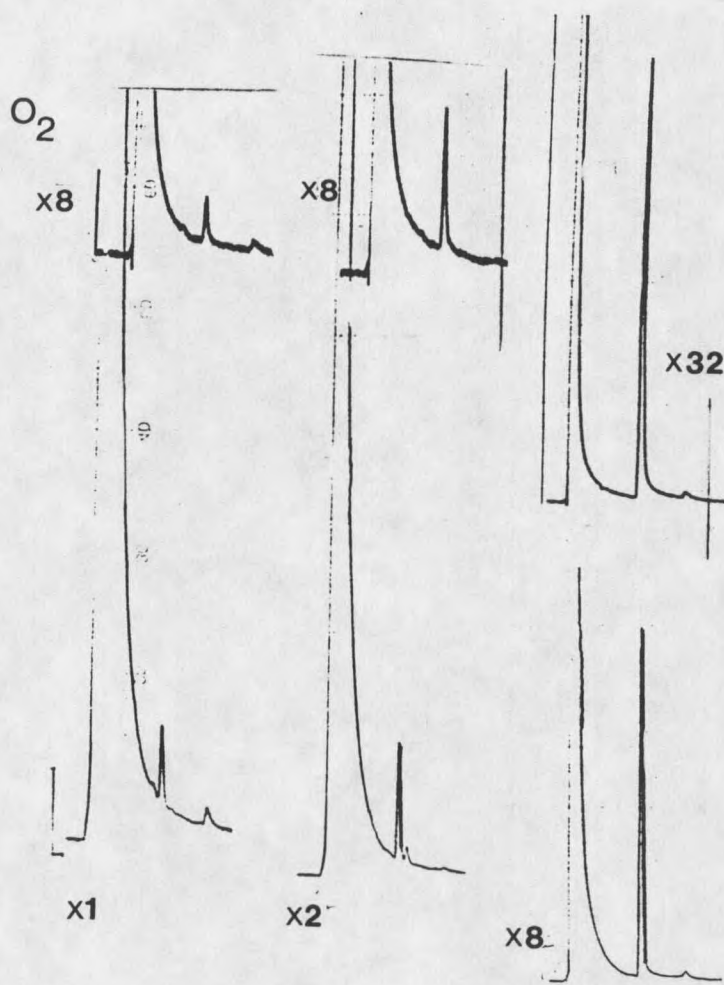


Figure 72. Series detectors in which the bottom chromatograms are normal ECD responses and the top chromatograms are with 0.30% oxygen in the second detector. The sample analyzed is 2-chloroanthracene with 100 ng, 8 ng, and 3 ng, respectively. Detector temperature is 300°C.

Also, this type of experimental design allows the opportunity to have oxygen present in both detectors, and the results are shown in Figure 73. The response enhancements from both detectors being doped for the 9-isomer are 24.6 and 19.8 for an average of 22.2. For the 2-isomer, the enhancements obtained are 6.4 and 8.1 for an average of 6.9. The 1-chloroanthracene exhibits response enhancements of 3.7 for detector 1 and 5.4 from detector 2 for an average of 4.5. These results compare quite favorably with results obtained previously with parallel detectors and a single detector. Another interesting aspect of doping both detectors is shown in Figure 74 in which the concentration is fairly large. For this particular instance, the second detector shows a larger enhancement than the first detector. A possible explanation is that several oxygenated species are formed in the first detector which in turn react with oxygen in the second detector. This type of system is again a much more precise method of determining response enhancements and allows for much faster analysis times.

In order to more accurately determine relative detector responses, a much better and shorter transfer line might be used. Part of the problem here might involve some absorption in the transfer line. This technique definitely has some interesting and varied applications.

#### Tandem Cells

Another example of series detectors is shown in Figure 11. This is a specialized dual detector in which two EC volumes are placed in

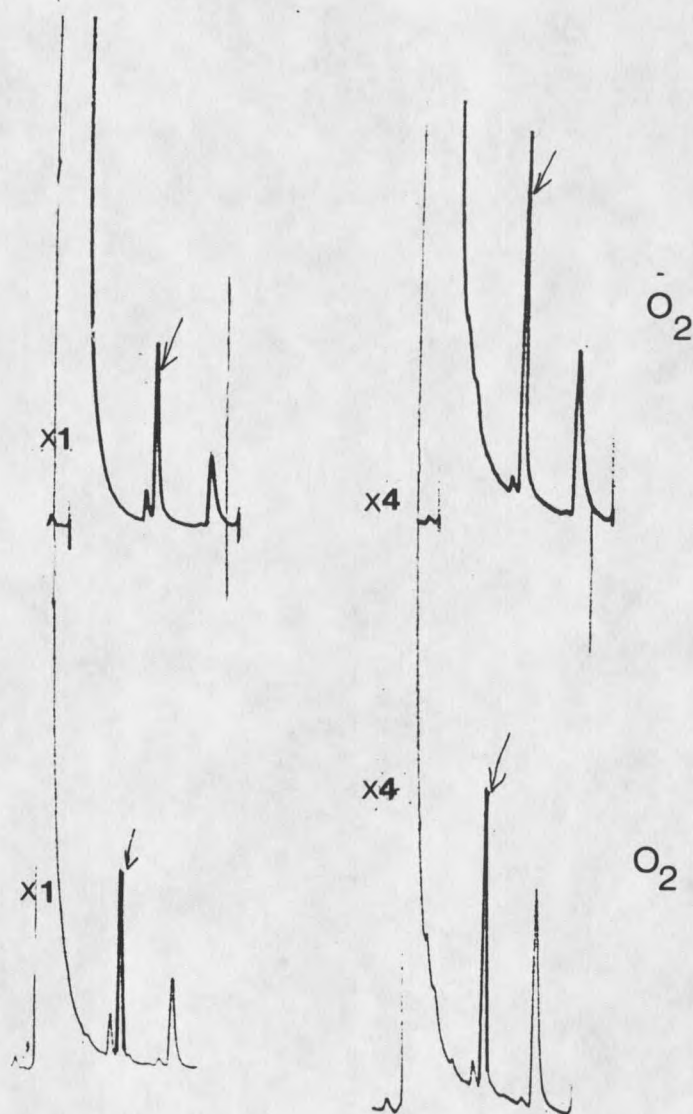


Figure 73. Series detectors in which the chromatograms on the left are with the normal ECD response and the ones on the right are with 0.30% oxygen present in both detectors. The sample is 2-chloroanthracene at a detector temperature of 300°C.

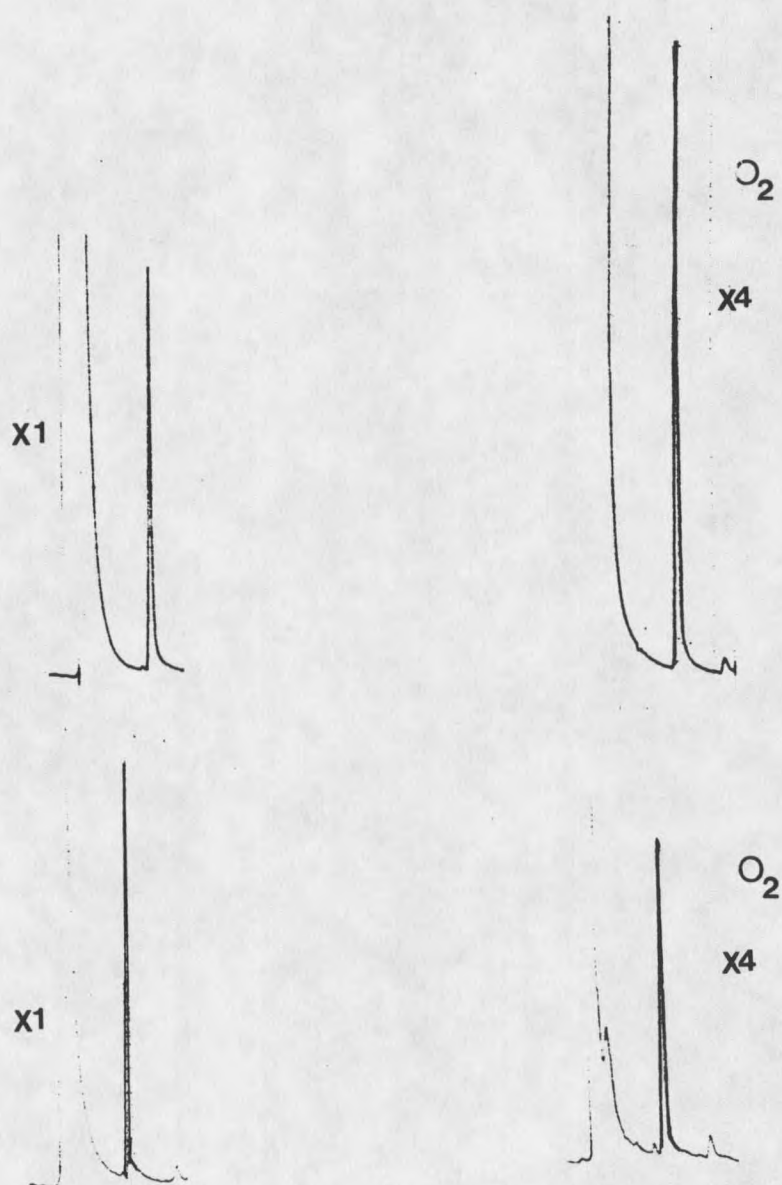


Figure 74. Dual ECD responses and oxygen-sensitized response of 50 ng sample of 2-chloroanthracene. The chromatograms on the left are with normal EC detection and the ones on the right are with oxygen present in both detectors.

series and the second volume contains added oxygen when applicable. Except for the most strongly responding molecules, the ECD can be considered a nondestructive detector. With this tandem arrangement, one can arrange conditions so that each cell receives the same quantity of analyte, and the reproducibility of oxygen-induced enhancement measurements should be significantly improved. At the time of this writing, the tandem cells are being characterized and evaluated for analysis capabilities. The tandem cell presents an interesting cell design (i.e. the anode pins in the side of the cell rather than coaxial as in the Varian ECD). This type of design would allow oxygen doping to take place in the second cell, and, in addition, studies of strongly responding compounds can be accomplished. For those strongly responding compounds, one should see a much smaller response in the second cell. Also, since the response enhancement measurements can be done with one injection, and thereby increasing the precision of measurements and at the same time, decreasing the amount of time for analysis. In addition, oxygen can be added to both cells by adding it as a portion of the total makeup gas prior to the first detector.

The best arrangement for reproducibility is the parallel detectors using dual columns in the same injector port. The series detector arrangement should be used with caution, in view of the fact that additional reactions seem to be occurring in the second detector, particularly when both are doped.

## SUMMARY

This study has clearly shown that oxygen-induced enhancements in the ECD analysis of various isomeric sets of compounds vary with the chemical structure of the molecule.

For the polychlorinated biphenyls, the response enhancements were small but several isomers could be differentiated in some instances. The response enhancements seem to be useful for isomer distinction for these compounds up to the tetrachloro series. For this particular set of isomers, the normal ECD response is high, and as a result, the enhancements were small and very similar. Most of the enhancement values were approximately 2, regardless of the number of chlorine atoms attached to the ring.

The chloroanthracenes and chlorophenanthrene isomers can easily be differentiated based solely on their response enhancement values. Binary mixtures of coeluting compounds can be quantitatively determined by utilizing the oxygen-doped ECD and the mole fraction of each component in the unresolved peak can be determined. For mixtures of three coeluting components, the response enhancement measurements must be repeated at another detector temperature. In cases where only partial resolution of the components is observed and where the retention times are much too close for distinction, the O<sub>2</sub>-doped ECD can be extremely beneficial for identification.

The APIMS was used to identify specific ionic species formed with and without the presence of added oxygen for the chloroanthracene and phenanthrene isomers. For these compounds, actual oxygen incorporation is observed and a reaction scheme has been proposed to account for the species observed in the APIMS. For the 1-chloroanthracene and 2-chloroanthracene molecules, the major ionic species observed without oxygen was the  $M^-$  parent ion and with oxygen present in the source, the major ion was  $(M+O_2)^-$ . The 9-chloroanthracene and 9-chlorophenanthrene form  $(M-Cl+O_2)^-$  species both with and without the presence of oxygen in the source. In addition, the results indicate that oxygen attack actually occurs at the 9-position in anthracene. Several of the isomers can be differentiated based on the ratios of observed ionic species.

The polycyclic aromatic amines and hydroxides provided an interesting set of isomers that were examined. Both of these are extremely important from an environmental standpoint, in view of their reported mutagenic and carcinogenic characteristics. Their normal ECD responses are very low; therefore, an electron enhancing tag is attached to the substituent (trifluoroacetic anhydride or perfluoropropionic anhydride for the amine and methyl for the hydroxy compounds). The response enhancements observed were determined for various sets of isomers including biphenyl, naphthalene, anthracene, phenanthrene, fluorene, pyrene, and chrysene. In most cases, isomers could be distinguished based solely on the enhancement values. In addition, stepwise derivatization can be done on two different substituents and the

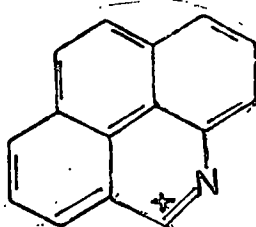
results indicate the enhancement values may be isomer dependent.

The APIMS was utilized to examine the negative ions of the TFAA and PFPA derivatives with and without the presence of oxygen. The salient feature of the API mass spectrometry of every TFAA derivative examined was that the only negative ion observed both with and without added oxygen was the M<sup>-</sup> ion. This suggests that the ionization of these molecules under oxygen free conditions occur by simple electron capture and with added oxygen occurs by charge transfer to form the parent negative ion in both cases. The APIMS results support a resonance type of electron capture mechanism for the TFAA derivatives which is substantiated by a temperature vs. response for this type of derivative with the normal ECD response. The PFPA derivatives enhance very little and the APIMS results indicate for dissociative type of electron capture mechanism which is again supported by ECD studies.

The TFAA derivatives of anthracene and phenanthrene were examined using the same experimental conditions in both the ECD and the APIMS. The response enhancement values obtained from the two methods correlate quite well. The relative order of the observed ECD and APIMS enhancements are the same, although the exact numbers determined are not the same.

Several of the TFAA and PFPA derivatives were examined by electron impact and chemical ionization mass spectrometry. For the TFAA derivatives of aminoanthracene and aminophenanthrene, negative CI shows considerable promise for isomer distinction. The 4-aminophenanthrene (both PFPA and TFAA) can easily be distinguished

from the other isomers based solely on the propensity of this derivative to form the following proposed ring structure:



The precision of the enhancement measurements was primarily determined by the ability to reproducibly inject a given volume of sample. Improved reproducibility as well as increased ease of measurement was accomplished by using two ECDs simultaneously where one detector is operated normally and the other is doped with oxygen. By using dual columns in the same injector port, the relative standard deviation in repetitive measurements was 2.6%. This was a tremendous improvement over the previous method of two separate, paired analyses with only one detector. The use of the parallel detectors also has reduced the uncertainty by a factor of three and has greatly relaxed the requirement for precise injections. In addition, series detectors were utilized in which the first ECD is connected to the second one with a transfer line. By doping the second detector the response enhancements can then be determined with one injection. The relative standard deviation for repetitive analyses was 2.1%. Both of these techniques represent a major improvement in determining response enhancements.

The O<sub>2</sub>-doped ECD has become a very powerful analytical for distinguishing isomers even in cases where mass spectrometry fails. In addition, the technique can be used in quantitative analysis of

coeluting components and in instances where only partial resolution is obtained.

## FUTURE APPLICATIONS

The next logical step in utilizing the O<sub>2</sub>-doped ECD would be to extend its application to actual environmental samples. An example of this would be to examine the amine fraction from a SRC II process. By the following separation procedure modeled after Later et al. (115), the enriched amine fraction can be isolated. The separation procedure is illustrated in Figure 75. After the derivatization procedure with either TFAA or PFPA and utilizing the oxygen-doped ECD, the derivatized amines could be identified based on their specific response enhancements. Using Figure 76 as an example of very good chromatographic separation of TFAA derivatives, the response enhancements would allow identification.

The application of the O<sub>2</sub>-doped ECD could also be extended to environmental samples such as dioxins or dibenzofurans. With the preliminary separation and clean up done by HPLC, the doped ECD should be very helpful in this area.

By using dual columns or a fused silica splitter, the oxygen-doped ECD can be used in parallel with other detectors such as the FID or with nitrogen, sulfur, or phosphorous specific detectors.

In addition, Andy Valkenburg in our laboratory has recently discovered that the addition of ethyl chloride to an electron capture detector increased the response for molecules similar to anthracene, molecules that have a low normal ECD response and

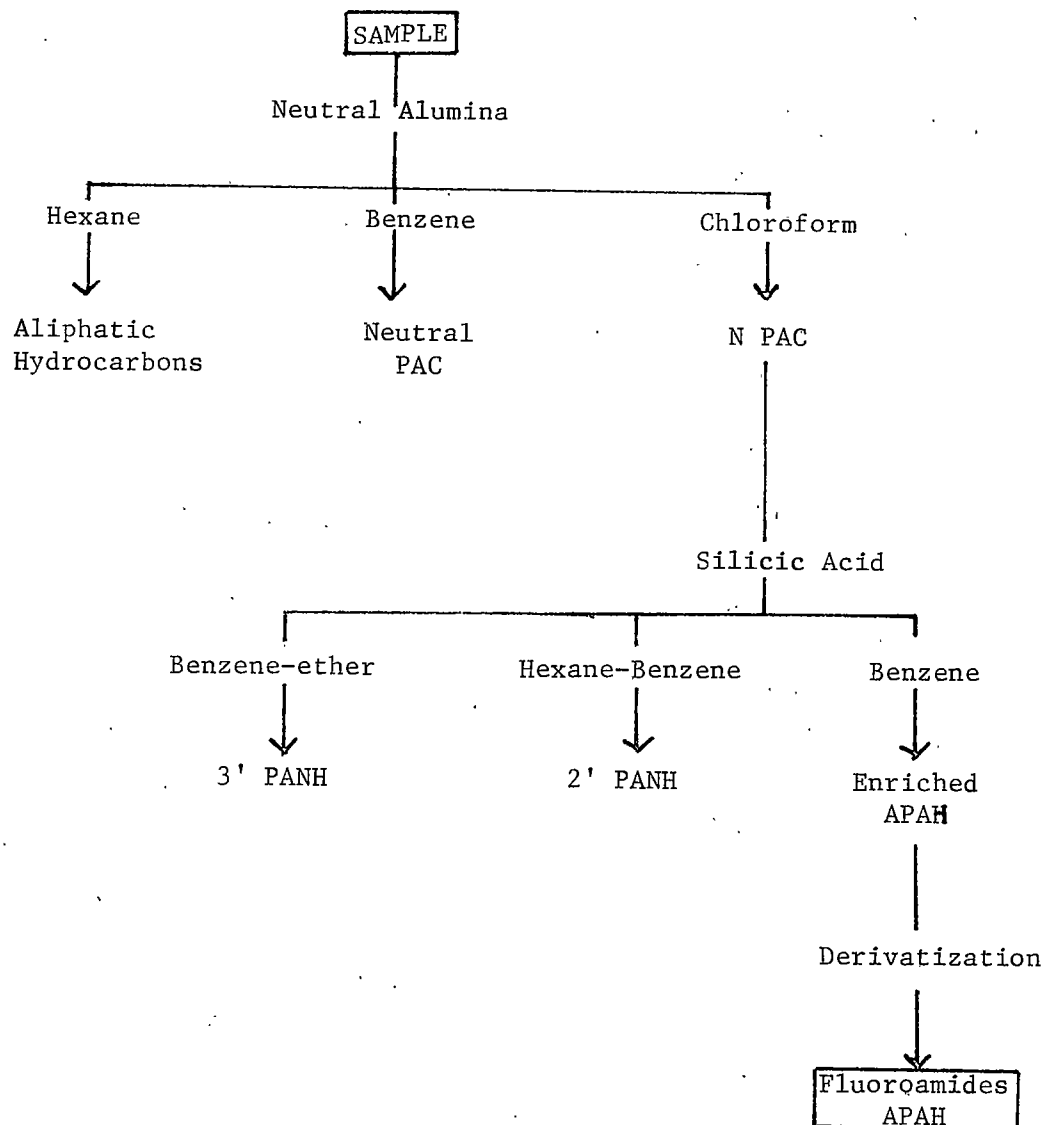


Figure 75. Chemical class separation scheme for synthetic fuel products. Key: polycyclic aromatic compounds (PAC), nitrogen polycyclic aromatic compounds (N-PAC), secondary nitrogen polycyclic aromatic heterocycles ( $2^\circ$  -PANH), amino polycyclic hydrocarbons (APAH), and tertiary nitrogen polycyclic aromatic heterocycles ( $3^\circ$  -PANH). (Reference 59).

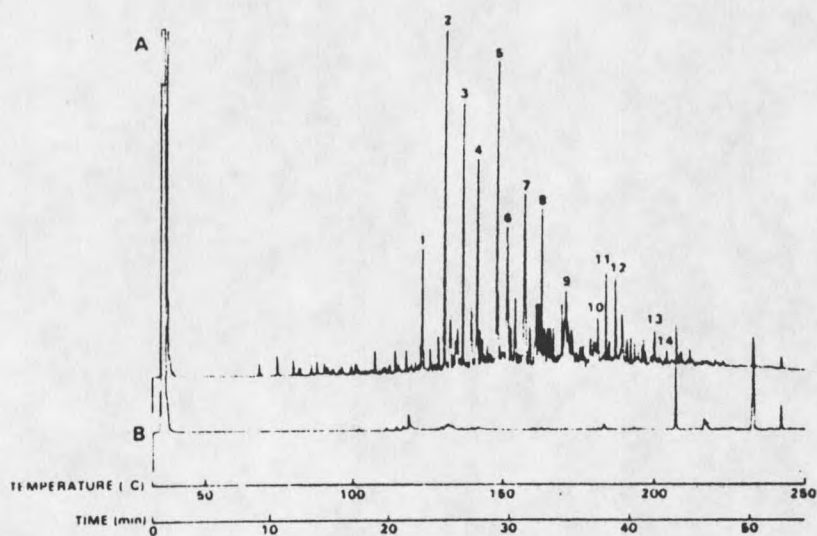


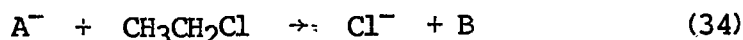
Figure 76. ECD capillary gas chromatogram of TFAA derivatized APAH fraction in SRC II HD. (1) aminoaphthalene, (2) 2-aminoaphthalene, (3) C<sub>1</sub>-aminoaphthalene, (4) C<sub>2</sub>-aminoaphthalenes, (5) 3-aminobiphenyl, (6) 4-aminobiphenyl, (7) C<sub>1</sub>-aminobiphenyl, (8) C<sub>2</sub>-aminobiphenyl, (9) aminofluorene, (10-12) aminoanthracenes, (13) aminofluoranthrene and (14) aminopyrene. (Reference 59).

capture electrons by a resonance type of mechanism. It should also be pointed out that the addition of ethyl chloride to the detector does not significantly effect the baseline frequency, in contrast to the presence of oxygen.

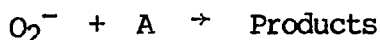
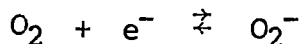
Figure 77 illustrates the normal ECD response for anthracene with and without the presence of ethyl chloride. The response to anthracene is enhanced by approximately 70.

In much the same way that the APIMS was utilized to determine the ions formed with and without the presence of oxygen, the API was also used to observe the negative ions formed in the presence of ethyl chloride in the source. The ions observed with ethyl chloride included  $\text{Cl}^-$  and  $m/e$  at 206. Both of these ions were not observed with the absence of ethyl chloride. The corresponding scanning mass spectra and single-ion monitoring is illustrated in Figure 78.

The following mechanism is proposed for the reaction of ethyl chloride with anthracene to produce an enhancement in the observed detector response.



where A is the anthracene molecule. This mechanism is similar to the mechanism proposed for the oxygen-induced response enhancement.



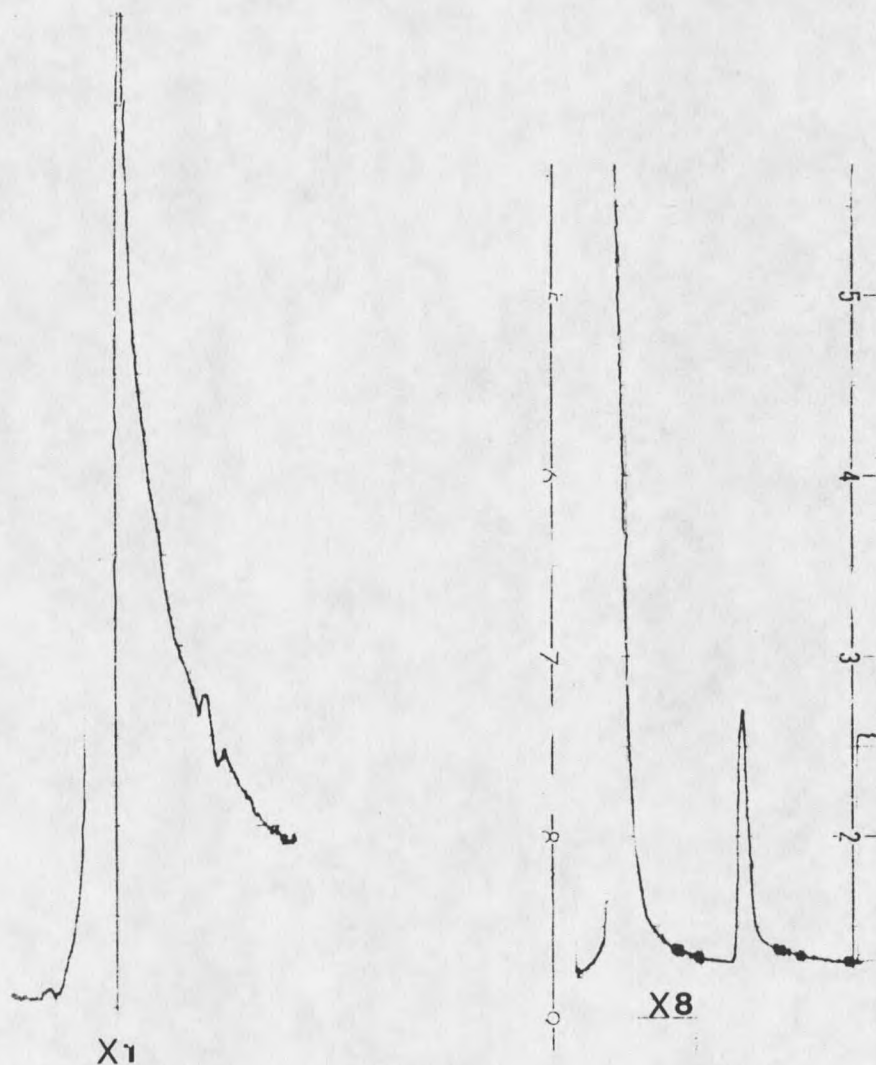


Figure 77. Capillary gas chromatograms of 7 ng sample of anthracene with ethyl chloride doping. The chromatogram on the left is with normal EC response and the one on the right is with 100 ppm ethyl chloride in the detector. Detector temperature is 250°C.

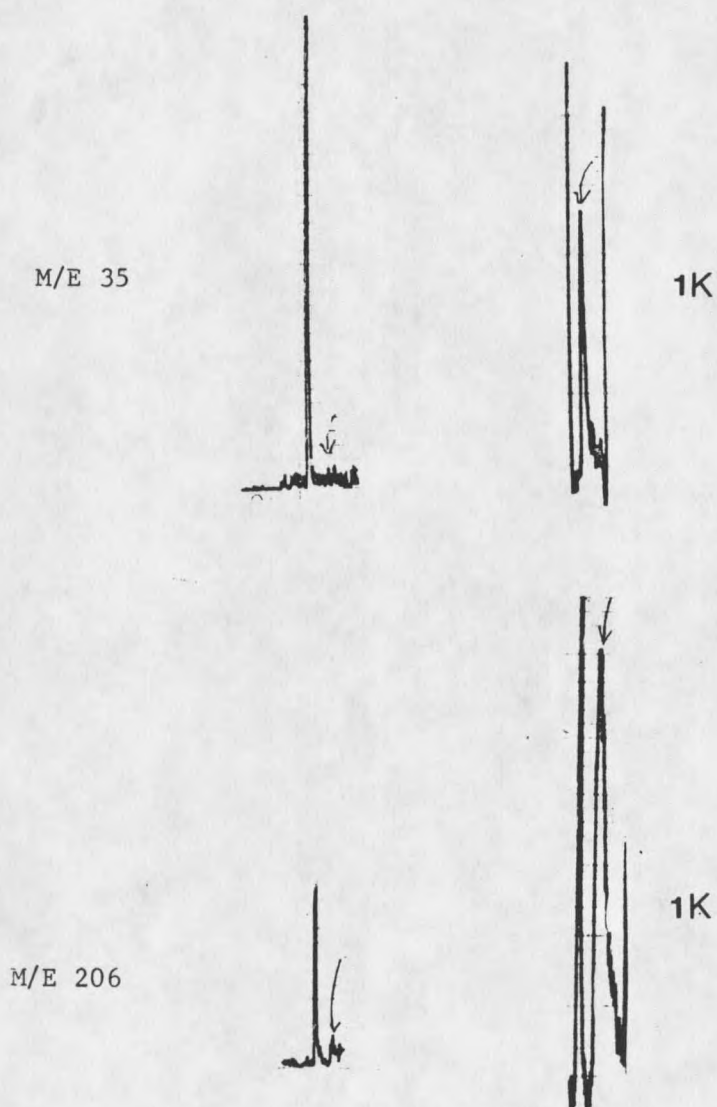


Figure 78. Single ion APIMS monitor of the negative ion intensity at m/e 35 (top) with a sample of anthracene with and without added ethyl chloride at a source temperature of 250°C. The bottom chromatograms are single ion APIMS monitor of the negative ion intensity at m/e 206 with a sample of anthracene with and without added ethyl chloride at source temperature of 250°C.

In the second case, the anthracene molecule is actually the substrate with the oxygen anion the catalyst. However, in the first example, the anthracene molecule actually substitutes for the oxygen an now becomes the catalyst.

In view of the fact that the addition of ethyl chloride actually decreases the baseline frequency in contrast to oxygen doping, there are many applications for this technique. Other compounds will be examined for response enhancements in the presence of ethyl chloride.

Another application with the addition of ethyl chloride doping and using parallel detectors, one could be doped with oxygen and the other with ethyl chloride. The ratio of responses might also be isomer dependent.

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