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Trace Analysis and Fundamental Studies by Plasma Chromatography[†]

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KEY WORDS: trace analysis, plasma chromatography, ion-molecule reaction, electron-capture detector

The plasma chromatograph uses an ion-molecule reactor coupled with an ion-drift spectrometer to produce plasmagram patterns of positive and negative ionic complexes of a trace constituent in a gas. Using an air carrier gas the reactant ions $(\text{H}_2\text{O})_n\text{H}^+$ and $(\text{H}_2\text{O})_n\text{O}_2^-$ are created to undergo ion-molecule reactions with trace organic molecules. The resulting plasmagrams are characteristic of the organic molecules, their concentration and reactivity. Organic compounds studied include salicylaldehyde, benzoic acid, acetophenone, naphthalene, and the polychlorinated biphenyls. Using a nitrogen carrier gas, thermal electrons are the only negative reactant species present, and a trace sample compound will undergo reactions such as occur in the gas chromatographic electron-capture detector, permitting a study of basic characteristics of this detector. Negative plasmagrams show only a strong halogen ion peak for many halogenated benzene compounds, providing experimental evidence of dissociative electron capture. The effect of the simultaneous presence of other electron-capturing species such as air in the carrier gas for the electron-capture detector on sensitivity and linearity is shown by plasmagrams.

INTRODUCTION

The plasma chromatograph couples an ion-molecule reactor with an ion-drift spectrometer and produces both positive and negative plasmagrams of organic compounds present in trace amounts in gases at atmospheric pressure. The method and instrumentation, conceived and developed over the past five years by scientists at the Franklin GNO Laboratories, were first described¹

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early in 1970. There are now five plasma chromatographs in different laboratories being applied to a wide range of exploratory studies of a fundamental and analytical nature. Upper atmospheric ion-molecule reactions have been studied as well as many aspects of chemical analysis such as the identification of specific organic molecules, biomedical analysis of large molecules, and pesticide analysis.

PRINCIPLE OF THE METHOD

The plasma chromatography technique is analytical in the sense that trace molecules in a gas are detected by subjecting them to an ion-molecule reaction and measuring the ion-molecules produced. Trace constituents must

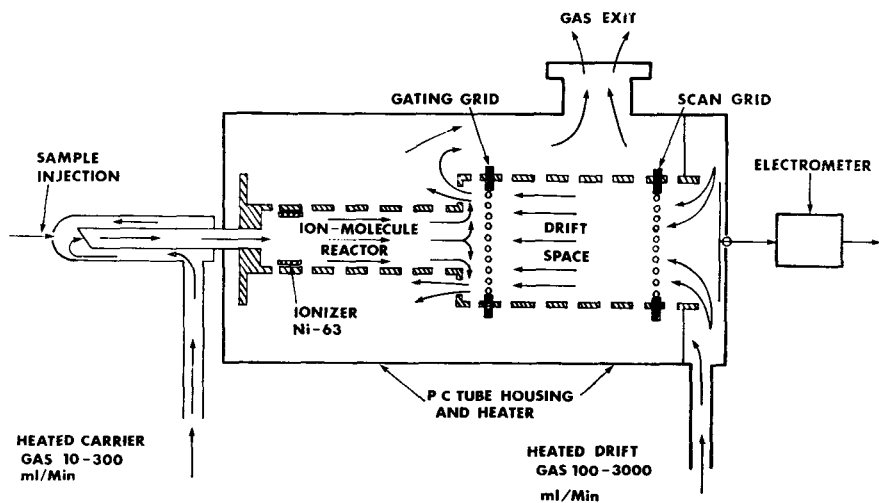


FIGURE 1 Schematic diagram of the plasma chromatograph.

be present in concentrations below parts-per-million so as not to saturate the instrument. Quantities as low as 10^{-12} g produce strong signals. The great sensitivity of the method to trace compounds arises because the ion-molecule reaction occurs at atmospheric pressure, where millions of collisions of reactant ions with trace molecules are possible. In the plasma chromatograph reactant ions are created in a carrier gas (air) by a radioactive ^{63}Ni source. These ions are reacted with trace molecules in a reactor where ion-molecules are created and then separated by being drifted through an electrical field toward a detector. The detector output of ion current versus time presents a plasmagram of the reactant ion and the different ion-molecules formed. Plasmagrams, both positive and negative, resemble chromatograms with a millisecond time scale. Illustrated in Figure 1, this technique uses a

shutter grid to inject a discrete ion-molecule pulse into the drift region and a variable delay gating grid that permits recording of the millisecond plasmagram scan in 1 to 10 min time spans. Formation of reactant ions and details of the instrumentation have been described by Cohen and Karasek.²

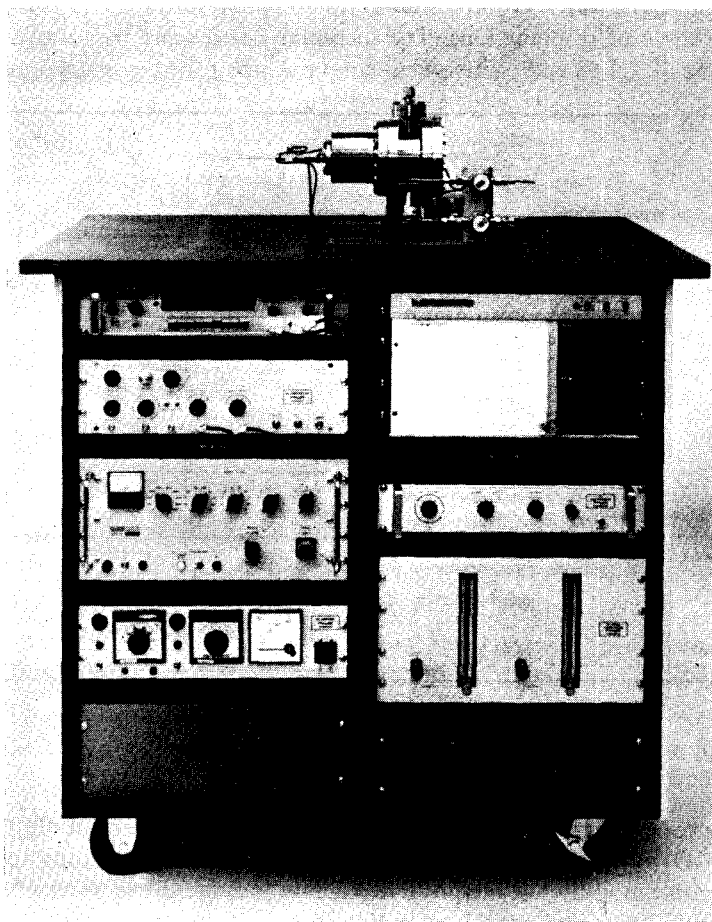


FIGURE 2 The BETA-VII plasma chromatograph.

In early work the individual ion-molecule peaks of a plasmagram were injected into a mass spectrometer for identification. It was soon found that there was a correlation between plasmagram time and molecular weight of the ion-molecule, a discovery which led to the simpler instrumentation of the BETA models that do not have a coupled mass spectrometer (Figure 2).

Studies by the author using this simpler instrumentation have produced characteristic "fingerprint" patterns of compounds and have led to detection of specific trace constituents in gaseous mixtures.

Reactant ions are formed from the direct, primary ionization of components in the air used as a carrier for introducing the sample. A drying procedure leaves sufficient water vapor, about 10 to 100 ppm, in the air to provide the major source of reactant ions. The incoming carrier gas passes over a 10-millicurie nickel-63 radioactive beta source which forms primary ions, that,

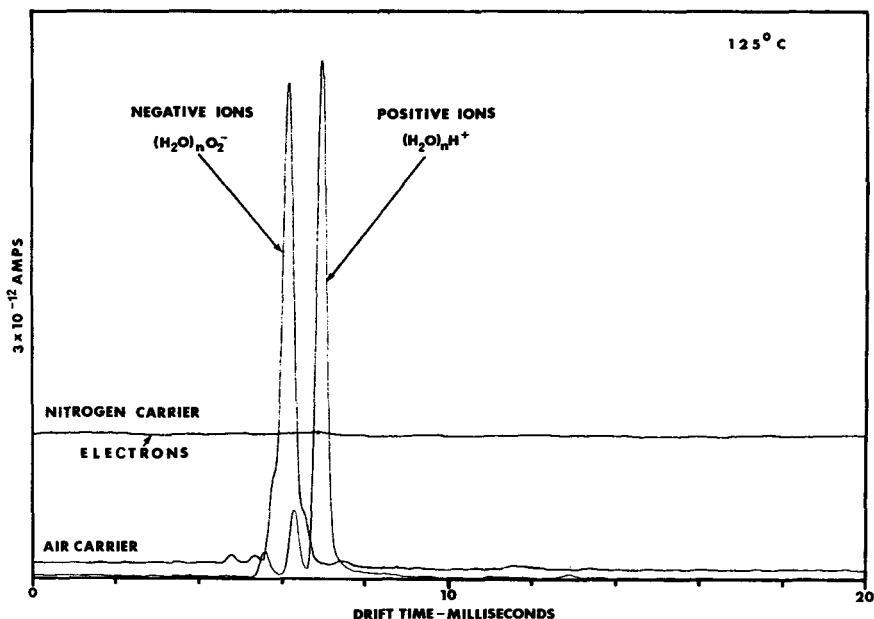


FIGURE 3 Reactant ions formed with N_2 carrier. When air carrier is used the negative species differ; the positive ones remain the same.

by a series of steps, evolve into stable reactant ions of the type $(H_2O)_nO_2^-$ and $(H_2O)_nH^+$. When nitrogen carrier gas is used, only electrons appear in the negative mode, while the positive reactant ions are the same as when air is the carrier. These ions are shown in Figure 3.

Separation of the ion-molecule complexes is brought about by their different mobilities as they move through an inert gas at 760 Torr under the influence of an electrical field. The ion-drift region, where separation occurs, is filled with a flowing inert gas, usually nitrogen, whose flow is countercurrent to that of the carrier gas. Temperature is an important variable in the instrument. It affects the composition and reactivity of reactant ions and mobility of ion-molecules in the separation step.

EXPLORATORY ANALYTICAL STUDIES

An early study was made by Karasek to determine the qualitative aspects of the plasmagrams obtained for a series of compounds of very similar molecular weights but different molecular structures.³ The positive plasmagrams of salicylaldehyde, benzoic acid, naphthalene, acetophenone, and phenethyl alcohol show that when concentrations are low, as indicated by the continued presence of a strong reactant-ion peak, a single peak of the ion-

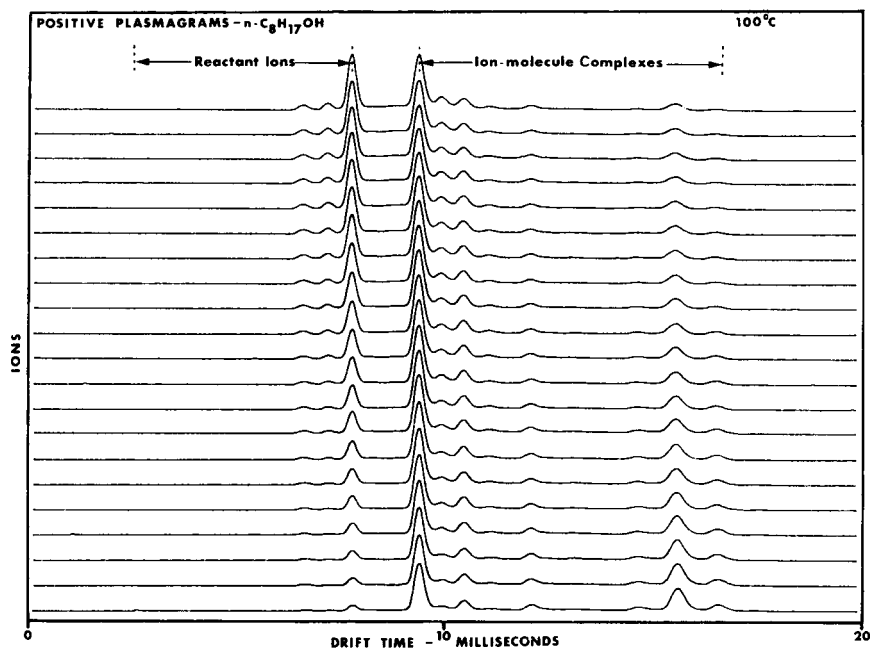


FIGURE 4 Positive plasmagrams obtained after injection of 10^{-9} g sample of *n*-octanol. Scans are 5 min apart, with the zero level offset.

molecule complex is formed. This ion-molecule complex is formed by the addition to the organic molecule of the $(\text{H}_2\text{O})_n\text{H}^+$ reactant. As either the concentration or reactivity of the organic molecule increases, the reactant ion will decrease and even disappear, with the resultant formation of higher molecular weight ion-molecule complexes containing multiples of the organic trace molecules. The appearance of dimer and trimer complexes at higher concentrations is characteristic of the plasma chromatographic (PC) technique. Negative plasmagrams occur only for the salicylaldehyde, benzoic acid, and phenethyl alcohol, and mainly by transfer of an electron to nega-

tively charge the trace molecule. Similar results have also been obtained for the alkyl alcohols ethanol, butanol, hexanol, and octanol.⁴ These alcohols were studied over a temperature range of 22° to 100°C. The data in the positive mode showed protonated molecules containing up to five molecules of alcohols. This is illustrated for octanol in Figure 4, which also reveals the unusually strong positive ion response obtained. Negative plasmagrams show no response with thermal electrons at any temperature, and very slight response with negative reactant ions.

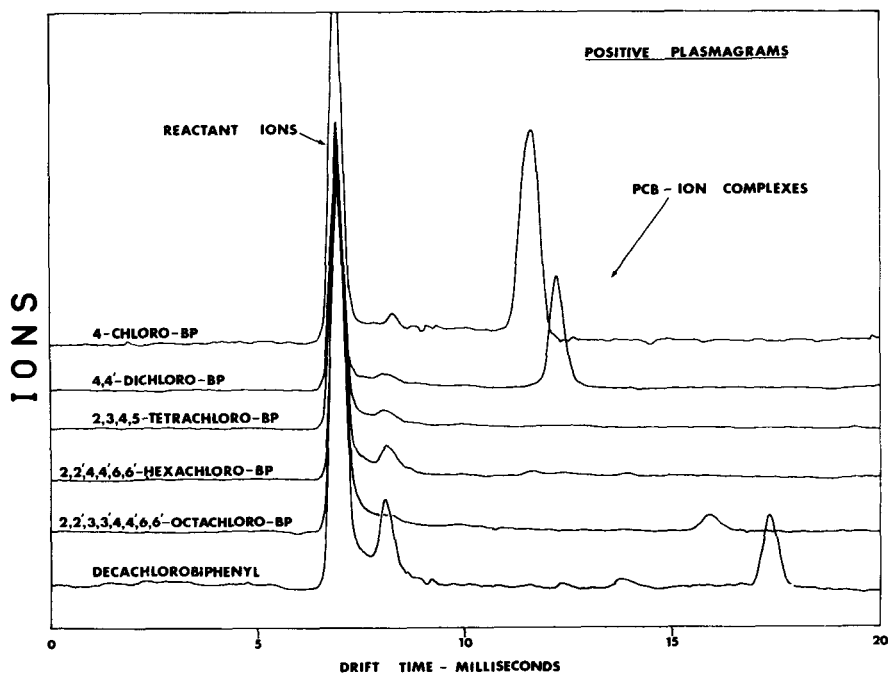


FIGURE 5 Composite of positive plasmagrams for PCB compounds.

These studies show that such compounds display characteristic, identifying positive and negative plasmagram patterns. By continuing such studies one can expect to develop "fingerprint" plasmagrams for all the different classes of organic compounds to provide identification data similar to those given by spectra such as infrared, mass and nmr.

The polychlorinated biphenyls (PCB) represent a type of compound that has assumed a prominent position in environmental studies because of their high toxicity and mounting evidence of their gross contamination of the global ecosystem. Because of their similarity to the common pesticides such

as DDT and their many possible isomers, analysis for traces is usually a difficult and lengthy procedure, involving largely mass spectrometric and gas chromatographic methods. It has been demonstrated that the plasma chromatograph can give a distinct set of positive and negative plasmagrams for these compounds.⁵ In the series of PCB compounds shown in Figure 5, those with the least chlorine substitution give the strongest positive plasmagrams. Those that give weak or no positive plasmagrams, give strong negative ones. This information, obtained for trace concentrations below the part-per-billion level, is a valuable aid in detecting and identifying such compounds in the environment.

FUNDAMENTAL STUDIES OF THE ELECTRON CAPTURE DETECTOR

The reactivity of the PCB compounds as evidenced in their negative plasmagrams has a general correspondence to their response in the gas chromatographic electron-capture (EC) detector. Since its inception the EC detector has occupied a unique position in gas chromatographic analysis because of its sensitivity and selectivity. Its importance has led to many studies of its characteristics and mechanisms by which it functions. The studies of electron attachment phenomena and the mechanisms advanced have done much to further our understanding of the capabilities of this detector. The data obtained with plasma chromatography can contribute considerably to our knowledge of the fundamental physical processes involved in the EC detector. The PC instrument essentially draws out a group of charged particles from a plasma such as found between the electrodes of the EC detector and subjects these charged species to a separation and identification step. Both the positive and negative particles can be examined separately and individually. The plasmagrams indicate the nature and relative quantities of these charged particles. By studying the plasmagrams of a series of halogenated aromatic compounds, Karasek and Tatone⁶ were able to experimentally verify the dissociative EC mechanism advanced for the EC detector by Wentworth. Using nitrogen gas as the carrier to form reactant ions, only electrons are produced in the negative mode. Upon the addition of trace amounts of halogenated benzene compounds, the plasmagrams reveal the loss of electrons by capture followed by the appearance of the halide ion from the subsequent dissociation. This phenomenon is shown in Figure 6, where one can see the chloride, bromide, and iodide ions formed. These data also reveal that the dissociative capture reaction does not occur in the case of fluorobenzene.

Recent studies⁷ with the plasma chromatograph add to a knowledge of the phenomena occurring in the EC detector. It is well known that traces of air in the carrier gas to the EC detector have a deleterious effect on sensitivity

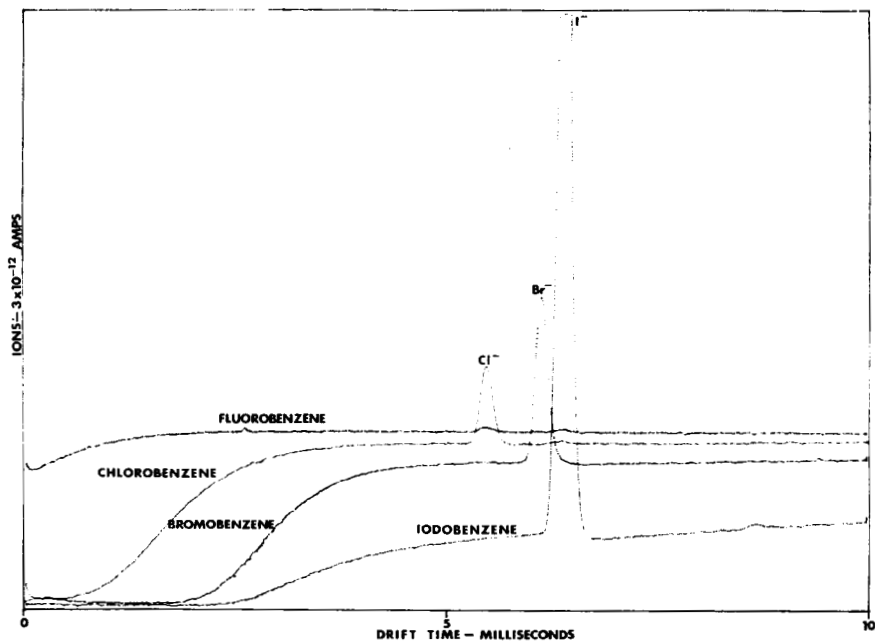


FIGURE 6 Negative plasmagrams of halogenated benzenes.

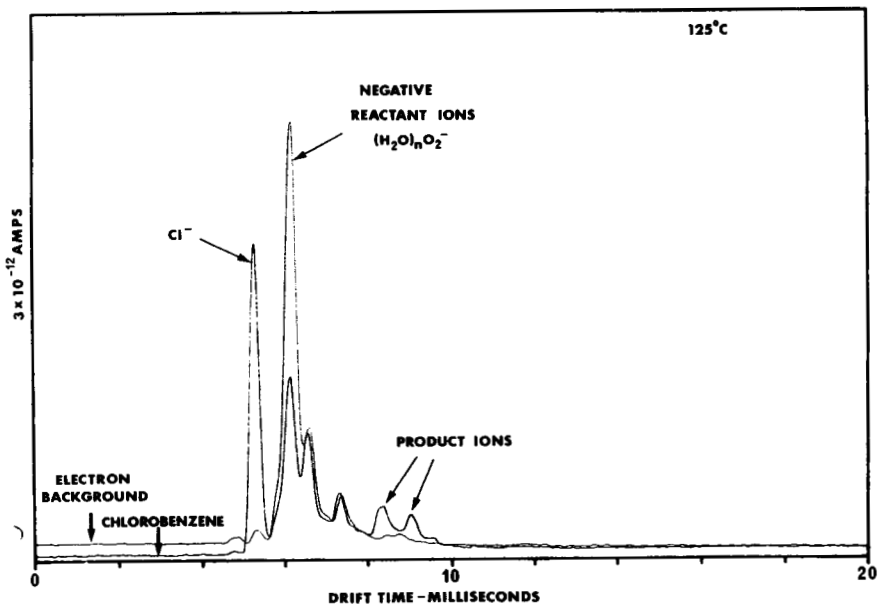


FIGURE 7 Negative plasmagrams showing both electron-capture and ion-molecule reaction of chlorobenzene when air is used as a carrier gas.

and linearity. The effect appears to be due to depletion of the reactive electrons by formation of $(\text{H}_2\text{O})_n\text{O}_2^-$ complexes. Not only are there fewer electrons now available to provide response for an electron-capturing compound entering the detector, but this compound will undergo a competing ion-molecule reaction with the $(\text{H}_2\text{O})_n\text{O}_2^-$ ions present. This is shown by the data in Figure 7. Other work in progress is identifying the ionic species formed as a result of electron-capture for many types of compounds. For example, with disubstituted halogenated benzenes, only a single halogen ion appears by dissociation: chlorobromobenzene forms the Br^- ion; bromiodobenzene forms the I^- ion.

INTERFACING THE PLASMA CHROMATOGRAPH WITH OTHER INSTRUMENTS

Much of the exploratory work in plasma chromatography was done with a directly interfaced mass spectrometer so that each ion-molecule peak in a plasmagram could be mass-identified. Since the particles are already charged they can be directed from the drift spectrometer through a single aperture and ion lens into the mass analyzer section of a quadrupole mass spectrometer. From this work it was observed that there was an empirical relation-

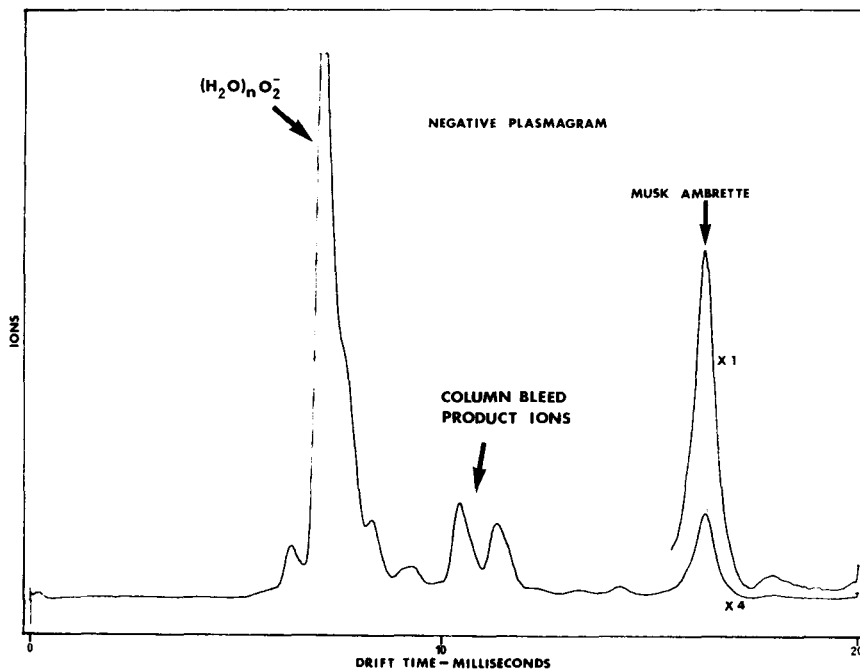


FIGURE 8 Plasmagram obtained from a GC peak for musk ambrette.

ship between the plasmagram time of an ion-molecule complex and its mass.⁸ This led to the simpler Beta VI and Beta VII PC instruments that have been used for qualitative studies without the use of a mass spectrometer.

Like a mass spectrometer, the plasma chromatograph functions best with only a single component being observed. An obvious sample source is the peaks from a gas chromatograph. Using a splitting technique which delivers only a fraction of a GC peak to the plasma chromatograph this has been successfully accomplished for a number of compounds such as halogenated aromatics and musk ambrette.⁹ Combining the gas chromatographic data with those of the plasmagram provides a very unique set of qualitative information, as shown in Figure 8 for musk ambrette.

FUTURE POTENTIAL

Only the surface of the potential of this method has been explored. The great promise of plasma chromatography lies in ultratrace analysis. Compounds showing high sensitivity in the EC detector give a strong negative mode response, but give an even greater response in the positive mode. Moreover, those with little response in the EC detector give a strong positive response in the plasma chromatograph. As more knowledge about the technique is accumulated and the instrumentation becomes more developed it can be expected that the analytical capabilities will be extensive. As a tool for fundamental studies of ion-molecule reactions, plasma chromatography is unique and will greatly extend our knowledge of these very important reactions.

Acknowledgments

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