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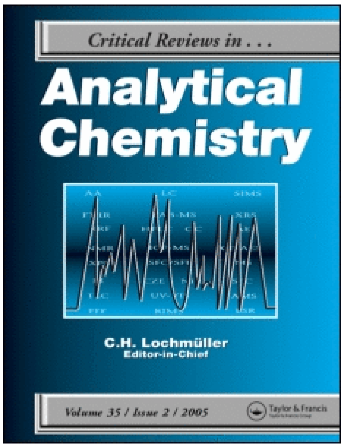

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Microwave Induced Electrical Discharge Detectors for Gas Chromatography

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MICROWAVE INDUCED ELECTRICAL DISCHARGE DETECTORS FOR GAS CHROMATOGRAPHY

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I. INTRODUCTION

A. General

Gas chromatography has the unique characteristic of separation based on the interaction of molecules in the vapor state with a stationary liquid or solid phase. As a result of these interactive forces, gas chromatography can separate groups of compounds providing these molecules exhibit vapor pressures of at least 1 torr and have thermal stability at the column operating temperature. There are many applications of gas chromatography reported in the literature which span the fields of chemistry and biochemistry, and these separations are only limited by the imagination of the investigators. Indeed, gas chromatography is one of the most widely used analytical chemistry techniques.

There are three pieces of information which are obtained from a gas chromatographic separation: retention volume, peak area, and peak shape. The retention volume is related to the way the solute molecule interacts with the column packing material based on the partition coefficient, and has been used for qualitative analysis. The peak area is related to the quantity of the solute entering the detector and may, therefore, be used for quantitative analysis. The peak shape is related to the kinetics of the separation and any unswept volumes in the injection port or detector.

Qualitative analysis of gas chromatographic effluents is one of the major problems experienced by practicing chromatographers, since on a particular column, at a particular column temperature and flow-rate, there could be as many as 50 compounds which have identical retention volume. This makes qualitative analysis difficult unless there is prior knowledge of either the sample or of the separation. As a direct result of this difficulty of solute identification, there has been extensive work developing procedures for qualitative analysis based on multiple column plots. This is a procedure based on the use of columns containing packings or coatings which exhibit different retentive abilities (sometimes known as "polarities") on which separations are made. The retention data thus obtained are plotted as shown in Figure 1. The coordinates of such plots allow qualitative analyses to be made from retention data.

The major drawback of this procedure is that it is time-consuming. Another problem experienced in gas chromatography is the change in the sample integrity during its passage through the column. An example of this problem was experienced early in the development of metal analysis by gas chromatography using volatile metal chelates.[1a] It was shown in later studies that some of the earlier reported separations of metal acetylacetonates were due to decomposition products rather than the unchanged metal complexes. The analysis of complex mixtures compounds these difficulties although often the experimenter is interested in only one peak or a group of peaks. For such analyses it is much easier to interpret the resulting chromatogram if the detector responds to these individual compounds or groups of compounds. Qualitative analysis has become more difficult with the advent of the use of high efficiency capillary columns which

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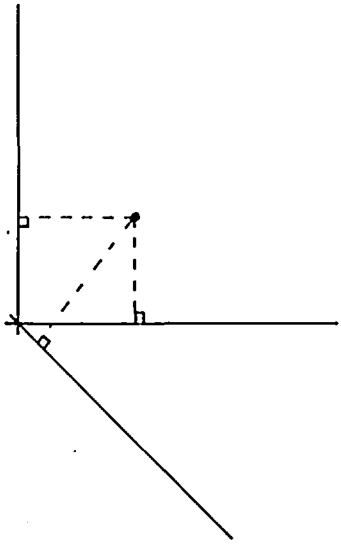

FIGURE 1. Multiple Column Plots.

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enable extremely complex samples such as natural products to be separated into hundreds of solutes.

B. Selective Detectors

As a result of these difficulties, and to enable rapid identification of eluting peaks, extensive research has been reported on the use of selective or specific detectors. This area of interest appears at first glance to be unusual, since prior separation by gas chromatography is unnecessary if a detector is specific or selective to a solute molecule. However, in spite of this apparent anomaly, this area has received considerable attention. Generally, the full benefit can be obtained from selective detectors when used in-parallel with nonselective detectors. This arrangement allows the maximum amount of information to be obtained for the sample, even though part of these data is not required.

The field of selective or specific detection systems is based on two approaches. The first group of detectors is selective to molecules, for example: Fourier Transform Infra Red Spectrometry (FTIR) and Mass Spectrometry (MS).

The second approach involves detectors which are selective to elements, for example: Thermionic Detector (TSD), Microcoulometric Detector (MCD), Coulson Conductivity Detector (CCD), Radiochemical Detector (RD), Electron Capture Detector (ECD), Flame Photometric Detector (FPD), and Microwave Induced Electrical Discharge Detector (MIEDD).

However, before discussing the microwave-induced electrical discharge detector, it is essential to give an overview of the requirements that are imperative for any gas chromatographic detector. A detector is a transducer which converts some physical or chemical property into an electrical signal, which is the most convenient way of displaying the progress of a gas chromatographic separation. Therefore, any device capable of acting as a transducer in the presence of a flowing carrier gas is theoretically suitable as a gas chromatographic detector. It should be obvious that such a general statement has drawbacks, and these limitations are related to the essential features of gas chromatography. Therefore, in the following discussion these limitations will be discussed.

Linearity — The most important requirement of a detector is that its response should be proportional to the quantity of samples entering it. As a general rule, with the exception of the response of the FPD to sulfur, most detectors respond linearly over two or more orders of magnitude with solute concentration.

Small detector volume — Ideally the volume of the detector (the volume between the end of the column packing and the sensing device in the detector) should be at least one order of magnitude smaller than the free gas volume of the column. This requirement is essential; otherwise, the resolution or resolving power of the column is degraded by the detector. This loss in efficiency is caused by kinetic processes such as diffusion and by "unswept" detector volumes which contribute extensively to peak broadening.

Rapid response — The detector and read-out system must be capable of responding at least one order of magnitude faster than the column is able to separate the components of a mixture; otherwise, the high efficiency separation effected by the column will be debased.

C. History of Microwave-Induced Electrical Discharge Detector

The major drawback of the flame photometric detector has been that the resulting emission spectra of the excited species produced in the hydrogen diffusion flame are extensive molecular band systems which lead to spectral interferences. Therefore, a number of atom reservoirs have been developed using electrical energy with the hope that the emission spectra would be from atoms rather than molecules. An atomic emission source could, thus, make this type of detection system selective. Also, if the eluting solute molecules were fragmented and excited completely to atomic species, then the empirical formula of the solutes would be obtained. The use of electrical discharges in analytical chemistry techniques is not new and the principles of operation are based on either detecting the ions produced or else monitoring the emission of photons that are emitted by excited species produced in the discharge. In argon ionization-type detectors, the electrical discharge produces metastable argon species which ionize the organic analyte compounds via Penning ionization reactions,[1-4] A commercial dc-ionization detector which uses a helium corona discharge[5] and a helium photoionization (PI) detector which utilizes a microwave discharge source[6-8] have also been reported. Since the photoionization detector is theoretically able to detect any sample which has an ionization potential less than that of the incident ultraviolet radiation, both argon and helium discharges have inherent advantages and disadvantages. The argon detector will not respond to any solute that has an ionization potential greater than 11.7 eV. Thus, the detector will respond to most organics but will have little or no response to inorganic gases. Consequently, a low background current and a stable baseline will be obtained. Conversely, helium detectors will behave as "universal detectors" since they will ionize any molecule with an ionization potential less than 24.6 eV, but considerable effort is required to purify the helium in order to reduce the background level and improve selectivity. Nevertheless, at high flow-rates, (*circa* 300 mℓ/min), a commercial helium ionization detector has been used successfully.[9]

Most photoionization detectors utilize a glow discharge and these electrical discharges require careful regulation and control of the following operational parameters: electrode gap, applied potential, and discharge current. The use of electrodes is complicated by electrode contamination, irreversible surface reactions, and other "aging" phenomena. In addition, the operating temperature of the detector is limited (~70°C) because of the thermal instability of these discharges.

Nevertheless, a glow discharge gas chromatographic detector with good sensitivity (10^{-2} μg/mℓ for *n*-octane) to organic compounds has been reported.[10] The response of this detector varied markedly depending on the type of compound introduced. Although the discharge was sensitive to pressure and voltage fluctuations, the signal output variations caused by these factors were small. Unfortunately, no precision and accuracy values

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were given to support this claim, and neither was the day-to-day performance of the system discussed.[10] The use of reduced pressure helium discharges sustained by microwave energy eliminates most of these operational problems. Excellent sensitivity (*circa* 10^{-11} g/sec) and dynamic range (*circa* 10^4) were reported for this type of photoionization detector.[6]

An electrodeless discharge in the annulus of an all-glass ozonizer has also been used as a gas chromatographic detector for both permanent gases and certain organic molecules.[11-14] The response of this detector is based on small changes in current ($\pm\Delta i$) in a constant background discharge current (i). Detection limits of 10^{-7} mol/sec were achieved without external amplification, but the signal response was linear only over a very narrow range (~ one order of magnitude).

Studies of the characteristics of emission spectra of organic vapors in electrical discharges started as early as 1920.[15] A very effective analytical use of such emission spectra could be for gas chromatographic detectors. However, the first emission spectrometric detectors specifically designed for gas chromatographic applications were based upon measurements of the total light emission from hydrocarbon fuel flames[16] and from a Tesla coil discharge.[17] In neither case was any valuable spectral information acquired. Nevertheless, some compound-class selectivity was achieved using response factors, RF, defined as:

$$RF = \frac{(Rx/Rbenzene)\ \text{emission detector}}{(Rx/Rbenzene)\ \text{thermal conductivity detector}}$$

where Rx = response for compound x; Rbenzene = response for benzene (used as a standard reference compound).

These RF values were indicative of classes of compounds and provide a means for the semiqualitative distinction between mixtures of aromatic hydrocarbons, cyclic paraffins, *n*-paraffins, and other compounds.

The work reported using the Tesla discharge[17] has revealed the effect of oxygen-doping on discharges. This dopant was found to remove free radical fragments and to prevent tailing faulty band shapes, which result from the contamination of the discharge tube and the electrodes by carbonaceous decomposition products. As will be discussed later, doping of a discharge with nitrogen or oxygen (scavangers) has a great effect on the degree of fragmentation and atomization of the sample molecule.

The first spectral emission detectors for gas chromatography used a hydrogen flame[18] to fragment and excite the transition metal, 2,4-pentanedionates and various organic compounds.[19] Also, in this same time period a rather elaborate study was reported which evaluated the feasibility of microwave-stimulated electrical discharges for gas chromatographic detectors.[20]

Although the main topic is microwave-powered discharge detectors, dc-discharge detectors also exhibit some very attractive features.[21] Basically, this early dc-discharge spectrometric detector was a quartz capillary (optical cell), with two platinum electrodes. The gap between the electrodes can be varied from approximately 0.3 to 2.5 cm, and the applied potential between 300 and 1100 V. Pure helium or argon-helium mixtures have been used as both the carrier and discharge gases. Examples of detection limits reported for this detector are 4×10^{-10} g.Br(734.8 nm) and 0.6 to 5×10^{-11} g.C at 516.5 nm (C_2) and 387.5 nm (CN), respectively. The main advantages of this dc-detector are simplicity of operation and construction, and relatively low cost. Researchers at the Oak Ridge National Laboratory[22] have optimized the dc-detector by redesigning the electrodes and the optical cell and, as a result, the reproducibility and reliability of the detector have been improved. The selection of the proper electrodes, the gap between them, and the geometry of the cell are critical parameters because contamination of the electrodes and

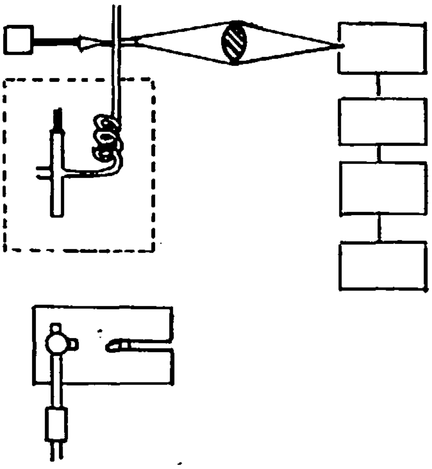

FIGURE 2. Block diagram of gas chromatograph — microwave induced electrical discharge detector system.

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irreversible reactions on their surface will limit the continuous use of the detector. A potential advantage of dc-detectors over low-power microwave-induced electrical discharge detectors is their ability to sustain a helium plasma at atmospheric pressure. Some of the problems of contamination have also been observed with microwave-induced electrical discharges and this will be discussed subsequently.

II. INSTRUMENTATION

A. Introduction

The microwave-induced electrical discharge detector, Figure 2, consists of a transparent quartz capillary (discharge cell) which conducts the effluent gas from the gas chromatographic column to the center of a microwave cavity. An argon or helium electrical discharge is maintained within this cavity by a low-power (100 to 200 W) microwave generator (typically, but not necessarily operating at 2.45 GHz), and by the boundaries of the quartz capillary. The separated solutes eluted from the gas chromatographic column are fragmented into excited molecular species (typically diatomics) and atoms by microwave-powered electrical discharge. The emitted spectrum, characteristic of the eluted compounds, is focused on the entrance slit of an optical spectrometer and the detector system typically consists of a photomultiplier tube with associated high voltage power supply, amplifier, and potentiometric recorder. The discharge is initiated by a Tesla coil spark and is sustained by coupling the microwave energy.

B. Microwave Generator

Various microwave generators have been used to supply the microwave energy and they include the Raytheon® PGM/10 series (100 W), Scintillonics HV-15A (120 W), Electromedical Supplies, Ltd., Microtron 200 (200 W), and Ito Chotampa, KTM-150 (100 W). All these generators operate with different ripple specifications at a frequency of 2450 ± 25 MHz. Usually, frequency modulation options are offered, although their use with the MIEDD is minimal. The power is produced by a magnetron tube, a diode in which a magnetic field is applied at right angles to the electric field between the cathode and anode. Magnetrons with power outputs of 0.05 to 2 kW (at 2.45 GHz) are available. These tubes are simple to operate, rugged, efficient, and relatively low-priced.

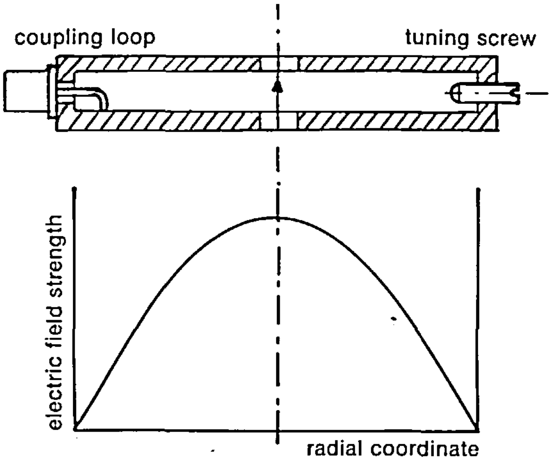

FIGURE 3. Resonant cavity.

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C. Microwave Discharge Cavities

The efficiency of a microwave power source is strongly dependent upon choice of discharge cavities or waveguides. Waveguides are metal tubes of rectangular or circular cross-section that are used to transfer power from the microwave generator to the gas. If a "short" is introduced into the waveguide at a position that causes total reflection of the energy traveling down the waveguide, then standing waves will be set up and, thus, a "resonant cavity" is formed. This cavity localizes the electric field at well-defined regions along the length of the waveguide such that the tube prevents loss due to radiation. To match the impedence of this structure to that of the coaxial line of the power supply, a coupling device is necessary (Figure 3).

The properties of the discharge and the efficiency of coupling (measured by the fraction of the reflected power) depend on the pressure and the nature of the support gases; therefore, the ability to make tuning and matching adjustments is necessary in order to optimize the energy coupling over a wide range of operating conditions.

Various cavity designs have been evaluated[23] according to two criteria: the pressure range (1 to 760 torr) over which the discharge with argon, helium, hydrogen, or air can be sustained; and the percent of power reflected from the cavity at different operating pressures. This study concluded that the cavity with the best overall design is the Evenson NBS Type 5, and the worst is the tapered NBS Type I. This evaluation, however, did not end the controversy concerning the analytical feasibility of the various cavities. As will be shown later, the unequivocal recommendation of one "panacean" design is unwise.

The tapered cavity provided higher sensitivity when operated at atmospheric pressure,[20] while the Evenson cavity was able to accommodate larger samples. In the pressure range 25 to 760 torr,[24] the tapered cavity was significantly easier to tune and has an overall lower spectral background compared to the Evenson cavity. In addition, the latter cavity was found to cause the appearance of hot spots in the quartz capillary and these results are contradictory to those obtained by McCormack et al.[20] Opposing views are given in another paper[25] which reports that the Evenson cavity was found to be easier to tune to minimum reflected power. Adding to the confusion is another study[26] in which the foreshortened ¼-wave radial cavity (211L EDT Supplies, Ltd.) was found to be superior because it caused less deposition of carbonaceous material on the silica capillary walls and could sustain a discharge over a relatively wide pressure range, e.g., 1 to 760 torr for air or argon and up to 65 torr with helium. Yet another study[27]

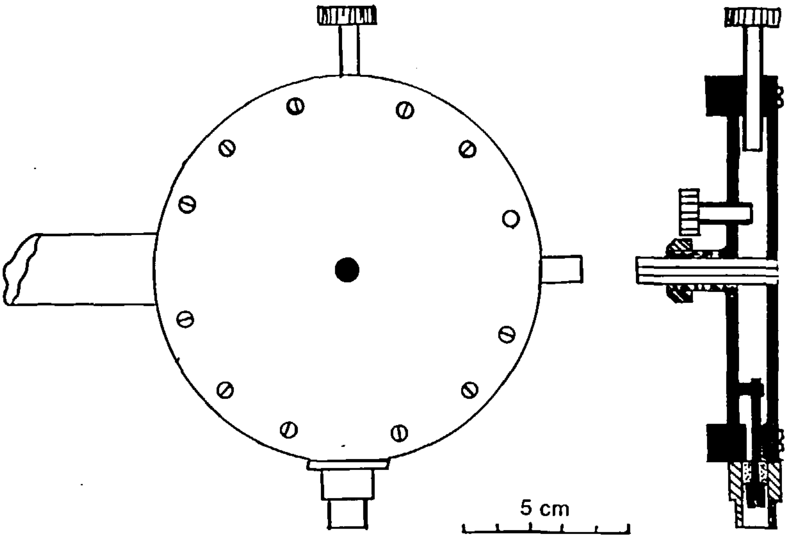

FIGURE 4. Beenakker cavity.

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concluded that the ¾-wave cavity was superior to all other cavities because it gave long (8-cm) stable atmospheric pressure discharges with negligible local overheating of the quartz tube. These conflicting opinions are not at all surprising, considering the wide range of equipment, operating conditions, applications, and evaluation criteria used by the different researchers. For instance, the study by the National Bureau of Standards[23] concluded that the tapered cavity has a very high reflector power value. However, later studies have shown that if very simple copper irises were mounted above the cavity slot, the reflected power was reduced to zero.

Nevertheless, it appears that a design most applicable to analytical problems is the tapered cavity, which has been successfully used for the determination of halogens, phosphorus, mercury, selenium, arsenic, antimony, bismuth, and silicon, and the Evenson cavity. The latter is probably more efficient at reduced pressures with a helium discharge, where superior determination of elements with high excitation-energy spectral lines from elements such as hydrogen, deuterium, oxygen, and sulfur can be performed.

A very promising cavity, Figure 4, has been designed[28,29] that is capable of sustaining both argon and helium atmospheric pressure discharges at low microwave power levels. Argon discharges have to be ignited with a Tesla coil, while helium discharges at power levels above 150 W are spontaneously initiated. The helium discharge allowed direct nebulization of aqueous solutions (1.7 mℓ/min into a support gas flow of 1.2ℓ /min), although a desolvation stage was necessary to achieve "analytically" stable operation.

The most important feature of the cavity is its efficient operation in the "axial viewing" mode where the discharge is monitored directly, in contrast to the "transverse viewing" mode where monitoring is performed through the capillary walls. With axial viewing, the discharge tube can be made of nontransparent material, e.g., aluminum oxide, and its cleanup or replacement is not required frequently. The results to date indicate that the detection limits for low-atomic number elements were improved by one or two orders of magnitude over those obtained with a reduced pressure helium discharge.[30] The first rigorous analytical gas chromatographic application of the Beenakker microwave cavity compared the detection limits and selectivities of this cavity with earlier studies for ten elements.[30a] Recently, a study has been reported in which the ¼-wave Evenson and the Beenakker cavities have been compared.[31] No definitive results were obtained since

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it was impossible on the basis of this study to find the cavity which provided consistently better results for different operating conditions.

D. Microwave Power Level

The microwave power level and the efficiency with which it is coupled to the gaseous discharge affect the nature and the degree of fragmentation and excitation occurring in this discharge, and, thus, the efficiency and response of the detector. Past studies concerning the effect of power were, unfortunately, rather superficial, incomplete, and demonstrate the complex nature of low-power microwave-induced discharge.

At atmospheric pressure[20] the response of the MIEDD was correlated to the power output in either a positive, negative, or a constant manner, depending, rather unpredictably, on the nature of the compound and the selection of the spectral line or molecular bandhead. Different power-response relationships have been observed for the determination of organo-phosphorous pesticides using the same tapered cavity but with different discharge pressures. At a pressure of 25 torr, the effect of power was found to be negligible.[24] Operation in argon at atmospheric pressure has shown[32] that for a specific column temperature and carrier-gas flow-rate, an optimum power setting exists which maximizes the signal-to-noise ratio for a given compound. However, this setting was found to be affected by the discharge cell geometry. In general, high column temperatures or flow-rates required high microwave power settings.

An increase in the microwave power causes elongation of the discharge and, therefore, optimization of the power setting requires a corresponding optimization of the region of the discharge which is monitored.[33] In other studies, the sensitivities of the MIEDD operating at atmospheric pressure, for the determination of volatile compounds of organic mercury, selenium, arsenic, antimony, bismuth, and tellurium,[34-37] were found to be independent of the power (in the range of 25 to 100 W).

The power-response relationships are complicated by the interrelationships with other operating parameters such as cavity design, capillary dimensions, and position relative to the spectrometer entrance slit, nature of the carrier gas and its flow-rate, discharge pressure, sample size, and emission spectra used for measurements. In addition, the coupling efficiency of the microwave power to the discharge must be controlled.

Whenever large samples are introduced at high gas flow-rates or, more generally, when the degree of fragmentation becomes the limiting factor, e.g., measurement of discharge-generated species such as Cl_2, Br_2, SO, and CS, control of the power setting becomes essential.

Excitation mechanisms appear to be only moderately affected by power settings. In fact, a high power discharge (250 to 800 W) will produce the same degree of fragmentation with a high discharge pressure that a lower power level (10 to 120 W) will produce with a low discharge pressure.[37] Also, the high power does not affect the characteristic emission of the discharge. Therefore, for GC applications in which small quantities of solutes enter the discharge, little, if any, advantage exists in using power outputs greater than 200 W. In general, the response seems less affected by power when operating at low pressures than at high pressures.

E. Microwave Radiation Exposure and Shielding

The effect of microwave exposure has yet to be precisely defined, but many accounts describing the various pathological effects have been published. The American Safety Standard for maximal permissible microwave radiation exposure level has been set at 10 mW/cm^2 while the Russian standard is significantly lower, 0.01 mW/cm^2. In a study published in 1973,[38] the actual radiation levels from various cavities have been shown to exceed these permissible levels. Fortunately, a very efficient shielding from microwave radiation can be obtained by enclosing the cavity inside a box made of 16-gauge expanded copper with 2.38-mm holes. In fact, any type of similar conducting box will prevent radiation escape as long as the diameters of the holes are substantially smaller than the radiation wavelength.

F. Discharge Tube

A low-power microwave discharge is confined typically in a silica capillary which is preferred over pyrex because of its high melting point. The stability of the discharge, its ability to accommodate large samples, and the sensitivity and reproducibility of the detector are all affected by the bore of the capillary. Diameters in the range 0.5 to 1.0 mm are preferred, at pressures of a few torr, but larger diameters of 2 to 10 mm are required to avoid discharge instability and overheating of the capillary. The capillary should be heated to avoid condensation of components with low vapor pressure along its cooler regions, i.e., prior to the discharge region. Also, the capillary must be placed in the center of the cavity to ensure an efficient coupling with the discharge.

Two capillary configurations can be used, transverse and axial. In the transverse configuration, the discharge is viewed through the capillary walls. This configuration is less attractive for the following reason: the deposition of carbonaceous, or inorganic materials, on the inner walls of the capillary which cause attenuation of the emission signals. Although carbonaceous films can be removed by oxidation (spiking of the carrier or auxiliary gas with oxygen or water), inorganic depositions require a more thorough cleanup of the capillary, usually with hydrofluoric acid. Devitrification of the capillary's inner walls also causes a gradual reduction in the transmitted emission signals, and eventually requires the replacement of the capillary. Increase in the microwave power levels produce elongation of the discharge with very little enhancement in the signal-to-noise ratios. In fact, the position of optimal viewing for a particular element moves along the capillary in accordance with the power level. Furthermore, with large samples, the shrinking of the discharge makes it rather difficult to maintain alignment and reduces accuracy and precision.

The axial configuration permits viewing through the open end of the capillary. This configuration has the following advantage: longer residence time of the fragmentations species in the discharge can be achieved and, thus, better signal-to-noise ratios, although self-adsorption may limit the dynamic range of the detector. The most important feature of axial detection is that it should extend the usable spectral range into the vacuum UV, assuming that the discharge can be interfaced to a vacuum UV spectrometer. Operation in the vacuum UV region will be useful for the detection of nonmetals. On the other hand, axial viewing may present major difficulties for the operation at reduced pressures.

It is worth noting that "cuvetteless" dc-jet plasmas should enjoy the same advantage as the axial cavity configurations. The characteristic emission intensity from the discharge can be measured through the transparent quartz wall or through the downstream open end if atmospheric discharges are being operated. Detection through the open end should extend the usable spectral range into the vacuum UV, assuming that the plasma can be interfaced to a vacuum UV spectrometer. Operation in the vacuum UV region may be useful for the detection of nonmetals.

G. Spectrometers

The selectivity of the detector to various elements is largely determined by the spectral region where the lines or bands are monitored. Although the discharge is an efficient excitation source and a large number of spectral lines or bands are produced for each element, only a few lines can provide the sensitivity required for trace analysis.

The sensitivities and detection limits of the detector towards a given element are often governed by spectral interferences of contaminants in the support gases, or by the elemental composition of the sample, rather than by noise originating from the discharge

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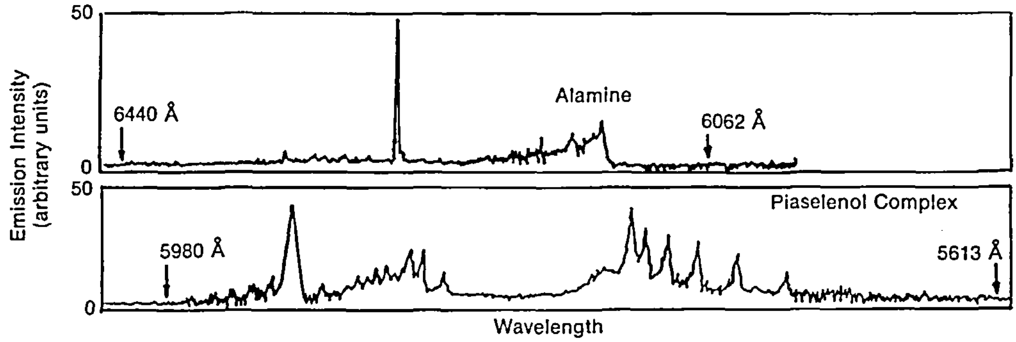

FIGURE 5. Real-time spectra of eluting peaks, obtained with a 1024-elements photodiodide array (Reticon® RL-1024C).

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or detector electronics. Typically, there is a compromise between selectivity and sensitivity. High selectivity usually requires smaller slits to reduce background noise; however, this causes a reduction in sensitivity. Thus, the detection limit is found by obtaining the optimum signal-to-noise ratio for a given elemental line while maintaining the desired degree of selectivity. Thus, the detection limit of the system is not discharge limited; neither is it directly discharge-noise limited. The presence of contaminants in the support gas that emit intense radiation will limit sensitivity and selectivity. Another way to express this limitation is that the shot noise from background species limits the detection. Thus, a high-performance general-purpose GC-MIEDD system requires a relatively high resolution (0.2 to 0.5 Å) spectrometer. On the other hand, systems utilized for preset routine applications, especially in cases where the spectral selectivity is very high (mercury, selenium, arsenic, etc.), could efficiently operate with low cost, low resolution, high optical aperture spectrometers. Some applications, such as the determination of the empirical formula of the eluted components, can be conveniently, rapidly, and accurately achieved with spectrometers that provide a simultaneous monitoring of a few wavelengths. A direct-reading spectrometer with secondary slits located on the Rowland circle of the grating, and positioned at the wavelengths of the most intense lines in the first order spectra of predetermined elements, has been the most popular method to date. Photomultipliers with required filters are used to quantify the radiation energy through each slit. Although this approach provides excellent sensitivity, wide dynamic range, and rapid response, it has a limited number of optical channels aligned for a predetermined specific application and, thus, lacks the ability and flexibility required of a "real" multichannel detector. A promising alternative involves TV multichannel detectors[39] which can provide several hundred independent optical channels. Figure 5 shows the characteristic molecular emission spectrum of an eluted tertiary amine as detected by a 1024-element self-scanned photodiode array (Reticon® RL-1024C).

H. Operating Temperature

The operating temperature of the GC-MIEDD system is limited by the thermal stability of the column packing material which causes the deposition of organic or inorganic residue along the capillary walls. This deposition increases the background emission, forms hot incandescent spots, or causes severe absorption of the light emitted from the discharge. Frequent cleaning of the capillary is required under such conditions.

The quartz capillary can be conveniently connected to the column outlet by standard compression fittings using ferrules which are stable up to 450° C.

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I. Gas Dopants

As will be discussed later, doping the carrier gas with small amounts of oxygen, hydrogen, or nitrogen can have the following advantageous effects:

1. Atomization efficiency is increased for solute molecules in gas-doped discharges compared to undoped discharges. This produces more accurate measurements of elemental ratios since they are less dependent on the chemical nature of the compounds.
2. The banded background emission from contaminant diatomic molecular species, such as N_2 and N_2^+, or from diatomic species produced by fragmentation of the sample, are reduced considerably.
3. Carbon deposition on the capillary walls is substantially reduced, thus allowing for larger samples and operation at higher temperatures.

Also, we have observed that when operating at reduced pressures, the carbonaceous deposition on the walls can be removed efficiently by consecutive injections of small amounts of water or oxygen into the column, when the stationary phase permits.

J. Miscellaneous

The following is a list of miscellaneous instructions and notes concerning the operation and use of the GC-MIEDD that may be useful to new operators.

1. Voltage regulation on the input to the microwave generator is necessary in order to maintain the discharge stability.
2. A good carrier-gas flow controller is essential since the detector is flow-rate sensitive.
3. When operating overnight, column temperature and carrier gas flow-rate should be reduced if the discharge is extinguished.
4. Molecular sieves should be used to remove most of the oxygen, nitrogen, and organic traces from the carrier gas. The outlet from the quartz capillary can be passed through a bubbler with dioctylphthalate to prevent back diffusion of air into the capillary.
5. The applicability of the detector to the determination of fluorine is limited because of the following reactions:[20,40]

$$SiO_2 + F \xrightarrow{\text{discharge}} SiF + 2O^* \text{ (oxygen emission)} \quad (1)$$

$$SiF \xrightarrow{\text{discharge}} Si + F^* \text{ (strong silicon emission)} \quad (2)$$

III. MECHANISMS

This section is concerned with the processes that are involved in the fragmentation and excitation of gas chromatographic effluents in order that the MIEDD may operate as a selective detector.

Electrical discharges are produced when an applied field causes a gas to change from an electrical insulator to an electrically conducting medium. This is the result of ionization of the gas which produces ions and electrons. The electrons are accelerated in the field until they have sufficient energy to cause further ionization in a chain reaction. In oscillating fields the electron gains energy from the field and, in addition, it receives further energy from the field as a result of elastic collisions. Without collisions, the electrons can only be accelerated to low energies since they are experiencing an alternating field; but with collisions, the electrons will have a vector in the opposite direction after collision, which will mean that the electron is not decelerated before it is accelerated by the field. The equation which describes the average kinetic energey $<\epsilon>$ (eV) of an electron over a cycle is as follows:[41]

$$<\epsilon> = \pi^2 \nu_F^2 \lambda^2 m \sqrt{(1 + \frac{e^2 E_o^2 M \cdot 10^{14}}{4\pi^4 \nu_F^4 \lambda^2 m^3}) - 1} \qquad (3)$$

where m is the mass of the electron (g); M is the mass of the discharge gas (g); E_o is the amplitude of the electric field (V cm^{-1}); ν_F is the frequency of the field (sec^{-1}); λ is mean free path of the electron between collisions (cm); and e is the charge, on the electron (coulombs).

In addition to elastic collisions, electrons will also experience inelastic collisions with other gaseous molecules which can result in the production of activated molecular species which deactivate by fragmentation or by the emission of photons. This latter process has been shown to have a low cross-section[42] as compared to the cross-section for ionization ($1:10^3$).[43]

In low energy fields the electrons are the active species and their kinetic energies follow a Maxwellian, or more correctly a Druyvesteyn, distribution, whereas the kinetic energies of the ions and neutrals are not significantly greater than ambient kinetic energies. Therefore, these discharges are not in thermodynamic equilibrium, and excitation or ionization of the discharge gas is caused by collisions of the gas molecules with energetic electrons.[44]

If we consider a simple helium-reduced pressure discharge it is reasonable to expect the following species will be present at pressures of $\simeq$ torr: He, He^+, He_2^+, and He_j^*, and the mechanisms which explain their production and destruction are discussed in detail subsequently. Other species such as the He^{+*}, He_2^{+*}, or He_2^* will not have appreciable concentrations. The number densities of He_2^* will be low even though a metastable state He_2 ($A^3\Sigma u^+$) exists, for it is superlastically converted to the He_2 ($A^1\Sigma u^+$) state by collision with an electron[45] for helium molecules having vibrational levels ≥ 2. The He_2 ($A^1\Sigma u^+$) molecules will rapidly deactivate since they are optically connected to the dissociative ground state (the ground state of He_2 is $He_2[X'\Sigma g^+]$ which is repulsive[46]). The number densities of He^{+*} will be low since the excitation energy for the helium ion corresponds to an energy greater than 54 eV,[47] which is typically higher than the average electron energy and, therefore, the probability of formation of He^{+*} is low. The number density of He_2^{+*} is low because, while no reference was found to the excitation energy of He_2^+ to He_2^{+*}, from consideration of two atoms the minimum activation energy must be of the order of 19.8 eV [$He_2^+ (1s) - (1s)^2 \rightarrow He_2^{+*} (1s) - (1s\, 2s)$]. As a result the probability of excitation is very low. The following Equations 4 to 17 show most of the important discharge reactions that are occurring in a reduced pressure helium discharge.

Excitation to the jth state (k_a cm^3 / sec)

$$He + e \xrightarrow{K_a} He_j^* + e \qquad (4)$$

Radiative deactivation to the ith state (A_{ij} sec^{-1})

$$He_j^* \xrightarrow{A_{ji}} He_i^* + h\nu_{ji} \qquad (5)$$

Radiative deactivation to the jth state (A_{kj} sec^{-1})

$$He_k^* \xrightarrow{A_{kj}} He_j^* + h\nu_{kj} \qquad (6)$$

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Associative ionization (Hornbeck-Molnar reaction $n > 2$) ($K_b\,cm^3/sec$)[48]

$$He_j^* + He \xrightarrow{K_b} He_2^+ + e \qquad (7)$$

Dissociative recombination (only occurs if He_2^+ is in highly excited state) ($K_c\,cm^3/sec$)[48-51]

$$He_2^+ + e \xrightarrow{K_c} He_j^* + He \qquad (8)$$

Electron impact ionization ($K_d\,cm^3/sec$)

$$He + e \xrightarrow{K_d} He^+ + 2e \qquad (9)$$

Three-body collisions (Ke, K_p, $K_q\,cm^3/sec$)[52]

$$He^+ + 2He \xrightarrow{K_e} He_2^+ + He \qquad (10)$$

$$He^+ + e + Wall \xrightarrow{K_p} He \qquad (10a)$$

$$He_2^+ + e + Wall \xrightarrow{K_q} 2He \qquad (10b)$$

Three-body collision ($K_f\,cm^3/sec$)[53]

$$He_j^* + 2He \xrightarrow{K_f} He_2^* + He \qquad (11)$$

Dissociative reaction ($K_g\,cm^3/sec$)[45]

$$He_2^* + He \xrightarrow{K_g} He_j^* + 2He \qquad (12)$$

Excited pair ionization ($K_h\,cm^3/sec$)[54]

$$He_j^* + He_j^* \xrightarrow{K_h} He^+ + He + e \qquad (13)$$

Excited pair ionization. ($K_i\,cm^3/sec$)[54]

$$He_j^* + He_j^* \xrightarrow{K_i} He_2^+ + e \qquad (14)$$

Excitation to jth state ($K_m\,cm^3/sec$)

$$He_m^* + e \xrightarrow{K_m} He_j^* + e \qquad (15)$$

Collisional deactivation ($K_n\,cm^3/sec$)

$$He_j^* + e \xrightarrow{K_n} He_m^* + e \qquad (16)$$

Electron impact ionization ($K_o\,cm^3/sec$)

$$He_m^* + e \xrightarrow{K_o} He^+ + 2e \qquad (17)$$

On the basis of this mechanistic scheme, the changes in the number densities of the species of interest with respect to time are

$$\frac{dn_{He_j^*}}{dt} = (K_a n_e n_{He}) + (\Sigma A_{kj} n_{He_k^*}) + (K_c n_{He_2^+} n_e)^+ (K_g n_{He_2^*} n_{He})^+$$

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$$(K_m n_{He_m^*} n_e) - (\Sigma A_{ji} n_{He_j^*}) - (K_b n_{He_j^*} n_{He}) - (K_f n_{He_j^*} (n_{He})^2)$$

$$-(K_h (n_{He_j^*})^2) - (K_i (n_{He_j^*})^2) - (K_n n_{He_j^*} n_e) \qquad (18)$$

$$\frac{dn_{He^+}}{dt} = (K_d n_{He} n_e) + K_h (n_{He_j^*})^2 + (K_o n_{He_m^*} n_e) - (K_e n_{He} + (n_{He})^2) -$$

$$(K_p n_{He^+} n_e) \qquad (19)$$

$$\frac{dn_{He_2}}{dt} = (K_b n_{He_j^*} n_e) + (K_e n_{H}^{+} (n_{He})^2) + (K_i (n_{He_j^*})^2) - (K_c n_{H_2^+} n_e) -$$

$$(k_q n_{He_2^+} + n_e) \qquad (20)$$

where n_x are the number densities of the various species (cm^{-3}), but

$$\tau_j(sec) = (\sum_{i<j} A_{ji})^{-1} \text{ and } \tau_k(sec) = (\sum_{k<j} A_{kj})^{-1}$$

At steady-state, $dn_x / dt = 0$ and, therefore, it is possible to produce an expression for the densities of the various species. Consider Equation 18:

$$0 = [(K_a n_e n_{He}) + (\tau_k^{-1} n_{He_k^*}) + (K_c n_e n_{He_2^+}) + (K_g n_{He} n_{He_2^*}) +$$

$$(K_m n_e n_{He_m^*})] - n_{He_j^*}[(\tau_j^{-1}) + (K_b n_{He}) + (K_f (n_{He})^2 + (K_n n_e)]$$

$$-(n_{He_j^*})^2 [k_n + k_e] \qquad (21)$$

But Equation 21 is the form $0 = ax^2 + bx + c$

$$\therefore n_{He_j^*} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad (22)$$

where $a = (K_n + K_e)$; $b = [(\tau_j^{-1}) + (K_b n_{He}) + (K_f (n_{He})^2) + (K_n n_e)]$; and $c = [(K_a n_e n_{He}) + (\tau_K^{-1} n_{He_K^*}) + (K_c n_e n_{He_2^+}) + (K_g n_{He} n_{He_m^*}) + (K_m n_e n_{He_m^*})]$.

Consider Equation 19:

$$0 = (K_d n_{He} n_e) + (K_n (n_{He_j^*})^2) + (K_o n_{He_m^*} n_e) - (K_e (n_{He})^2 n_{He^+}) -$$

$$(K_p n_{He} + n_e) \qquad (23)$$

$$\therefore n_{He^+} = \frac{(K_d n_{He} n_e) + (K_n (n_{He_j^*})^2) + (K_o n_{He_m^*} n_e)}{(K_e (n_{He})^2) + (K_p n_e)} \qquad (24)$$

Consider Equation 20:

$$0 = (K_b n_{He_j^*} n_{He}) + (K_e n_{He^+} (n_{He})^2) + (K_i (n_{He_j^*})^2) - (K_c n_{He_2^+} n_e) -$$

$$(K_q n_{He_2^+} n_e) \qquad (25)$$

$$n_{He_2^+} = \frac{(K_b n_{He_j^*} n_{He}) + (K_e n_{He^+} (n_{He})^2) + (K_i (n_{He_i^*})^2)}{(K_c n_e) + (K_q n_e)} \qquad (26)$$

These general expressions may be simplified for a number of reasons, which will be discussed in detail. Reaction 5, which is concerned with the population of the jth state by

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cascading from higher states, is only a few percent[42] of the rate of electron-impact excitation (Reaction 23). Reactions 13, 14, 15, 16, and 17 will only occur when He_j^* is the metastable state (2^3S or 2^1S) since, when n > 2, the probability for them occurring are low because they will be competing with radiative deactivation or the Hornbeck-Molnar Reaction 7 which has higher probability of occurring. The values for K_a, K_d, K_m, K_o, K_p, and K_q are dependent upon the energy of the electron, which means that they must be averaged over the electron energy distribution.

If a foreign species is then introduced into this helium discharge, the system is less easy to predict. However, it is probable that the only species which are sufficiently persistent so that they can collide with the foreign species are He_m^* (2^3S), He_2^+, and He^+. The density of He_m^* (2^1S) is low since it has been well established that He_m^* (2^1S) is rapidly converted to He_m^* (2^3S) by a superelastic collision with an electron.[55] The lifetimes of He_j^* in levels higher than He_m^* are such that the probability of collisions occurring between these species and the foreign species are low. The reaction between He_m^* and the foreign species will be a Penning ionization type[56-59] and the foreign species will be ionized.

$$He_m^* + AB \xrightarrow{K_1} He + AB^+ + e \qquad (27)$$

$$He_m^* + AB \xrightarrow{K_2} He + A^+ + B + e \qquad (28)$$

$$He_m^* + AB \xrightarrow{K_3} He + A + B^+ + e \qquad (29)$$

K_1, K_2, and K_3 are the rate constants (cm^3/sec) for Penning ionization. Reaction 27 is not likely to occur since the ionization potential for AB is probably much lower than 19.8 eV, which means AB^+ will be formed in an excited state and will subsequently dissociate.

Reactions 27, 28, and 29 have been investigated extensively by Cĕrmák,[60-64] Niehaus,[65] and Hotop,[66] and these researchers have developed Penning Ionization Electron Spectroscopy (PIES). This technique is similar to Photoelectron Spectroscopy in that it measures the energy distribution of the electrons released in ionization. The difference between the two techniques is that PIES shows changes in peak shape and peak position of the energy of the electron as a result of weak interactions in the collision state by the reactants. Also PIES shows differences in the population of the ionic states and their vibrational levels.

The reaction between He^+ or He_2^+ and the foreign species will be of the collision-induced ionization type.[59]

$$He^+ + AB \xrightarrow{K_4} AB^+ + He \qquad (30)$$

$$He^+ + AB \xrightarrow{K_5} A^+ + B + He \qquad (31)$$

$$He^+ + AB \xrightarrow{K_6} A + B^+ + He \qquad (32)$$

$$He_2^+ + AB \xrightarrow{K_7} AB^+ + 2He \qquad (33)$$

$$He_2^+ + AB \xrightarrow{K_8} A^+ + B + 2He \qquad (34)$$

$$He_2^+ + AB \xrightarrow{K_9} A^+ + B^+ + 2He \qquad (35)$$

K_4, K_5, K_6, K_7, K_8, and K_9 are the rate constants (cm^3/sec) for collision-induced ionization.

Reactions 30 and 33 are also unlikely to occur since the ionization potential for AB is probably much lower than 24.6 eV, which means AB^+ will subsequently dissociate.

The study of the excitation of substrate molecules by helium or other inert gas discharges has not received much attention apart from their empirical uses for gas chromatographic detectors and as atom reservoirs.[67-69] Although some inferences can be drawn to explain the processes involved in excitation and fragmentation based on previous studies which use flowing afterglow discharges, current information on reactions in the discharge region is severely limited. These prior studies of flowing afterglows have been concerned with studying ion-neutral reactions[70] and with chemical syntheses.[71-74]

However, it is possible to suggest some general mechanisms which may account for the fragmentation and excitation of foreign molecules in helium discharges. The first possible process is the direct fragmentation and excitation by the reactive discharge gas species

$$AB + He_m^* \xrightarrow{K_{10}} A^* + B + He \qquad (36)$$

$$AB + He_m^* \xrightarrow{K_{11}} A + B^* + He \qquad (37)$$

K_{10} and K_{11} are the rate constants (cm^3/sec) for direct fragmentation and excitation.

Reactions of this type are unlikely since they are far off resonance, although it has been suggested[45] as a possible explanation for the following two reactions:

$$C_2H_2 + He_m^*(2^3S) \longrightarrow C_2^* + 2H + He \qquad (38)$$

$$C_2H_2 + He_m^*(2^3S) \longrightarrow CH^* + CH + He \qquad (39)$$

A more reasonable mechanism involves the ion-electron recombination.

$$AB^+ + e \longrightarrow AB^* \qquad (40)$$

$$A^+ + e \longrightarrow A^* \qquad (41)$$

$$AB^+ + e \longrightarrow A^* + B \qquad (42)$$

This means that the excitation is at least a two-step process; the first is the ionization of the foreign molecules by reactions such as 27 to 35 and the second is the subsequent recombination of these ions by collisions with electrons. There are a number of ion-electron recombinations reported in the literature,[45-75] and the following reactions are examples of reactions 39 to 41.

$$OH^+ + e \longrightarrow OH^* \qquad (43)$$

$$H^+ + e \longrightarrow H^* \qquad (44)$$

$$O_2^+ + e \longrightarrow O^* + O \qquad (45)$$

There is also substantial information which can be drawn from electron impact mass spectrometry, for it is well-known that the collision between energetic electrons (≃70 eV) causes ionization and fragmentation,[75] although these processes occur at pressures less than 10^{-4} torr. However, once ionized, there is a low probability of ion-electron recombination before the ions leave the source region and are mass filtered. There is some evidence that excited species are produced and are subsequently ionized after the mass filter prior to the detection system. This type of process has been observed when the signal was mass independent.

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With chemical ionization sources the probability of ion-electron recombination is increased as a result of a larger density of electrons. This has been observed when large quantities of samples are introduced into the source.[76]

If Reaction 27, 28, 29, 36, or 37 is the dominant process in the fragmentation of substrate molecule AB, then the number density of He_m^* will be decreased with increased concentration of AB and concomitantly the discharge will show an increase in the number density of A^+, B^+, AB^+, A^*, or B^*.

Therefore, the change in the number density of He_m^* with respect to time will be

$$\begin{aligned}\frac{dn_{He_m^*}}{dt} = {} & (K_a n_e n_{He}) + (\textstyle\sum_{m<k} A_{km}\, n_{He_k^*}) + (k_n n_e n_{He_j^*}) - (K_o n_{He_m^*} n_e) \\ & - (K_m n_e n_{He_m^*}) - (K_i (n_{He_m^*})^2) - (K_h (n_{He_m^*})^2) - \\ & [(K_1 n_{He_m^*} n_{AB}) \text{ or } (K_2 n_{He_m^*} n_{AB}) \text{ or } K_3 n_{He_m^*} n_{AB}) \text{ or } \\ & (K_{10} n_{He_m^*}) \text{ or } (K_{11} n_{He_m^*} n_{AB})] \qquad (46)\end{aligned}$$

If Reaction 30, 31, 32, 33, 34, or 35 is the dominant process in the fragmentation of the substrate molecule, AB, then the number density of He^+ or He_2^+ will be decreased with increased concentration of AB and concomitantly the discharge will show an increase in the number density of AB^+, A^+, or B^+.

Therefore, the change in the number densities of He^+ or He_2^+ with respect to time will be

$$\begin{aligned}\frac{dn_{He^+}}{dt} = {} & (K_d n_{He} n_e) + (K_h (n_{He_j^*})^2) + (K_o n_{He_m^*}) - (K_e n_{He^+} (n_{He})^2) - \\ & (K_p n_{He^+} N_e) [(K_4 n_{He^+} n_{AB}) \text{ or } (K_5 n_{He^+} n_{AB}) \text{ or } \\ & (K_6 n_{He^+} n_{AB})] \qquad (47)\end{aligned}$$

$$\begin{aligned}\frac{dn_{He_2^+}}{dt} = {} & (K_6 n_{He_j^*} n_e) + (K_e n_{He^+} (n_{He})^2) + (K_i\ (n_{He_j^*})^2) - (K_c n_{He_2^+} n_e) - \\ & (k_q n_{He_2^+} n_e) [(K_7 n_{He_2^+} n_{AB}) \text{ or } (K_8 n_{He_2^+} n_{AB}) \text{ or } \\ & (K_g n_{He_2^+} n_{AB})] \qquad (48)\end{aligned}$$

Therefore, if the number densities of He_m^*, He^+, and He_2^+ are monitored as a function of increasing concentration of AB, then the dominant active species can be determined. Also, if the fragmentation products are monitored, then the dominant process can be ascertained. From this discussion it should be apparent that the exact processes that cause excitation are unknown and, therefore, it is difficult to base optimization studies on a theoretical basis.

At typical discharge pressures, 1 to 20 torr, a solute molecule will experience approximately 10^7 collisions and will be fragmented and excited further. Ideally, if this detector is to operate selectively, all the molecules must be fragmented to atoms and then be excited. To this end a number of studies have shown that the addition of small quantities of an easily ionized gas, e.g., nitrogen or oxygen, increases the production of excited atomic species.[40,77-82] Presently, the reasons why the addition of doping gases increase the production of excited atomic species are unknown. Various mechanisms have been suggested[79,81] which explain, in part, the effect of the addition of oxygen or nitrogen.

The presence of oxygen or nitrogen with organic molecules results in the production of species such as CN or CO which are known to be excellent chemical reducing agents. However, if hydrogen is used as a doping gas, then atomic hydrogen is produced which is

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also very good reducing agent; but it does not increase excitation to atomic species and, therefore, this explanation may not be valid.

The presence of a more easily ionized gas than helium, such as oxygen or nitrogen, increases the electron density as a result of Penning ionization and, consequently, fragmentation is caused by the presence of a more highly reducing environment. This mechanism would also explain the observed phenomenon. However, other gases which will undergo Penning ionization do not have the same effect. Currently, extensive research in this area to explain the mechanism of doping gas is being undertaken.[83,84] These studies involve monitoring both ground and excited states of the species in the discharge spectrometrically, and modeling the discharge in the source of a chemical ionization mass spectrometer, using helium as reagent gas. This latter study has been undertaken since both a discharge and a chemical ionization source involve excitation of a discharge or reagent gas by electrons, and the excited discharge or reagent gas causes fragmentation and excitation of the solute molecules. Also, the chemical ionization source and the discharge have similar pressures which means that similar collision frequencies are obtained. The study in the mass spectrometer provides the typical ions observed in discharges without suffering from the problems experienced with sampling discharges by mass spectrometers. This area of research is essential in order that the full potential of the MIEDD may be achieved.

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IV. OPERATION

The major advantage of the MIEDD is its ability to excite gas chromatographic effluents to atomic species. Theoretically, it can be operated in a number of modes: it can be selective to a heteroatom, universal by monitoring carbon; or it can be used to determine empirical formulas by monitoring emission from all the various atoms in the molecule. In the first mode, the MIEDD can respond with selectivity ratios which far exceed all other selective detectors, unless spectral overlap occurs. Also, this detector will respond linearly with concentration although its response will be dependent upon the solute detected. In the universal mode, the MIEDD is the most sensitive gas chromatographic detector since solute molecules generally contain more carbon atoms than heteroatoms. If the MIEDD is used for the determination of empirical formulas, then the extent of its use is dependant directly upon the number of channels that can be monitored. With current technology, this could conceivably be almost limitless. The detection limits obtained with this detector have been as low as 1×10^{-13} g in the selective mode and 1×10^{-16} g in the universal mode.[20] These limits of detection could be achieved routinely by the production of very stable plasmas and with the use of very sensitive photodetection devices providing that the background radiation from contaminants could be reduced.

The MIEDD can be operated at either reduced pressure or atmospheric pressure, and the disadvantages of the use of vacuum systems can be counteracted by increases in sensitivities. The advantages of reduced-pressure-doped plasmas have still to be fully exploited, especially since these discharges can allow the solvent to enter the detector without extinguishing the discharge or reducing the transparency of the discharge cell.[79,81] Theoretically, any heteroatom can be monitored with the MIEDD, providing that atomic emission can be monitored in a measurable part of the electromagnetic spectrum (ultraviolet or visible).

V. APPLICATIONS

A number of reviews have been presented which have discussed the general applications and uses of the GC-MIEDD system,[85-91] and one review has discussed its application for monitoring organic solutes.[88] Also, radiofrequency energy has been used to support an electrical discharge detector for gas chromatography.[92]

A. Nonselective Detection

The emission spectra of all organic compounds consist of many complex banded systems, particularly in the 350 to 560-nm spectral region.[20] The most prominent spectral features are the 388.3-nm CN band, various C_2 bands such as those at 385.2 and 785.2 nm, and the CH bands in the 431.4-nm region. To prevent the introduction of traces of nitrogen and oxygen into the discharge is practically impossible. These traces are present as contaminants in the carrier gas and can diffuse into the system through leaks or are continuously bled from the gas chromatographic column. Consequently, CN emission bands are always detectable and can actually become the most intense carbon emission spectral system.[20]

A detection limit of 2×10^{-16} g carbon per second was obtained at an argon flow rate of 20 mℓ/sec by monitoring the band head at 388.3 nm (CN). Any of the CH, C_2, or CN molecular bands can be used for high sensitivity, nonselective detection of organic eluents. Other workers have found that the relative emission intensities of various carbon species, e.g., C, CN, C_2, and CH, from an argon (atmospheric) discharge[93] were dependent on the molecular formula of the parent molecule. The applicability of a reduced pressure helium discharge to the determination of carbon dioxide, carbon monoxide, as well as nitrous oxide and sulfur dioxide in air, represents another example of the broad application of this detection system.[94] Although the absolute sensitivity of the detector to carbon dioxide and carbon monoxide (at 247.9-nm C line) was considerably improved (about 15 to 20 times better than a comparable atmospheric system), the size of the sample permitted was rather small (~50 μℓ of air) and, consequently, the relative sensitivity was also poor (50 ppm). No specific selectivity factors or description of the effect of spectral interferences were given, however, and the optimal operating conditions for the determination of each species were different.

A systematic attempt[27] to study the effect of the various operating parameters on the nonselective performance of an atmospheric pressure argon discharge has involved the determination of various organic compounds at a relatively high concentration level of a few hundred parts per million. Generally, an increase in the emission intensity was observed upon increasing the microwave power, and the quantitative relationship between these two parameters was determined by the structure of the compound and the selected spectral line or band. Similarly, an increase in flow-rate resulted in an increase in the emission intensity but again in a fashion dictated by the nature of the compound. The system was applied to the determination of hydrocarbon gases as well as carbon monoxide. Relatively linear working curves (1 to 180 ng) were obtained for the various gases with a maximum difference of 8.5% between the slopes. The average detection limit was 7.6×10^{-11} g carbon per second, and the dynamic range varied from 10^2 to 10^3 for the various compounds. Although this work has clearly shown the potential feasibility of the MIEDD as a nonselective detector, it has failed to demonstrate its use in routine analytical work. However, some recent studies have used the GC-MIEDD system to identify and quantify trace organic pollutants in water.[95]

Finally, it has been claimed that under reduced pressure an oxygen- (or nitrogen-) doped helium discharge will produce an identical universal calibration curve for all organic compounds at 247.9-nm C line.[40] These curves can be correlated directly to the carbon content of the chemical components, regardless of their molecular structure.

B. Element-Selective Detection

The unique separation capability of gas chromatography and the excellent sensitivity

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and selectivity of the MIEDD make the combined GC-MIEDD system a valuable analytical tool for the determination of volatile species in a large variety of samples. Samples with a complex matrix, e.g., environmental and biological, contain many constituent compounds that greatly complicate the interpretation of their corresponding chromatograms. Interferences from overlapping or obscuring peaks make it, at times, impossible to identify the analytes, let alone quantify their concentration in the samples.

The MIEDD is able to reduce, and in many cases eliminate, these interferences. The MIEDD is very sensitive because of the high excitation efficiency of microwave discharges. It is quantitative, has a very rapid response owing to its low volume, low "memory" effect, and a spectrometric selectivity characteristic of atom reservoirs. However, by its very nature, the selectivity is not uniform across the entire useful spectral region of 190 to 800 nm. Many parameters affect the selectivity of the detector; the most important are the spectral interferences from continuum, molecular, and atomic emissions, which are generally more significant in the visible than in the ultraviolet region. In fact, the spectrometric selectivity of the MIEDD is generally inferior to that of the flame photometric detector because of spectral interferences, although this is generally more than compensated for by the superior sensitivity of the former. The selectivity of the detector is also affected by the resolving power of the spectrometer determined by its linear dispersion, slit system, optical abberations, external optics, selection of helium or argon carrier gas, operating pressure inside the capillary, microwave power level, and especially by the selection of the discharge region which is monitored. Injections of oversized samples either extinguish the discharge or reduce the spectral selectivity owing to the increase in the interfering background emissions. In addition, large samples frequently produce hot spots on the capillary walls. These intense incandescent hot spots reduce the selectivity of the detector and shorten the lifetime of the capillary.

The rather complex, and as yet largely ambiguous, dependence of the sensitivity and selectivity of the detector on many interrelated experimental parameters requires a delicate optimization procedure for the determination of each element. Thus, the applicability of the MIEDD to multielemental analysis is more restricted, and a compromised set of operating conditions must be chosen for each sample. However, taking advantage of the efficient separation capability of gas chromatography, it should be possible to reoptimize automatically the experimental conditions for each solute as it is eluted. A preprogrammed, on-line laboratory computer should be capable of dynamically controlling the most important operating conditions, i.e., composition and flow-rate of the carrier gas, pressure, microwave power level, and region of the discharge to be monitored.

The element-selective analytical uses of the GC-MIEDD can be divided into two separate categories:

1. Quantitative determination of volatile contaminants, e.g., organics, pesticides, alkyl mercury, arsenic, and selenium compounds. In this capacity the system is most useful since it furnished information concerning the molecular form as well as the quantity of various trace contaminants.
2. Nonvolatile contaminants can be chemically transformed into volatile compounds amenable to analysis. A few examples of these complexes are the reaction of alkylarsenic acids into their corresponding volatile arsines and the chelation of metals, e.g., chromium, beryllium, aluminum, and copper, with β-diketones to form volatile and thermally stable complexes.

In the following sections these applications will be discussed.

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1. Nonmetals

a. Halogens

An atmospheric pressure argon discharge has been used to analyze iodine-, bromine-, chlorine-, and fluorine-containing compounds by monitoring the iodine atomic line (206.2 nm), bromine by an unidentified band (298.5 nm), CCl molecular band (278.8 nm), and fluorine indirectly by Si atomic emission (251.6 nm) resulting from SiF formation[20] (Equations 1 and 2). Sensitivies and selectivities are shown in Table 3. Substantial improvement in both selectivity and sensitivity have been achieved with the use of a reduced pressure (5 to 10 torr) helium discharge.[96] Halogenated pesticides as well as phosphorus- and sulfur-containing pesticides at the "sub-ppm" concentration level spiked into various agricultural products have been extracted and determined by the GC-MIEDD with recovery efficiencies better than 74 to 91%. Similarly, good recoveries and excellent sensitivities were obtained for iodinated herbicides.[97] The 206.2-nm iodine atomic line was used in these studies. Another study, to be discussed in more detail in Section V.C., measured the ratios of the emission intensities due to chlorine, iodine, or bromine as well as sulfur or phosphorus to the emission intensity due to carbon for a range of simple compounds. This study determined those factors which affect the intensity ratios and evaluated the potential of the MIEDD to determine interelement ratios. The analytical utility of this technique was found to be limited mainly by the spectral interferences at the wavelengths selected.

As with the carbon detection, the oxygen-doped helium discharge[37] MIEDD apparently produced universal calibration curves for each halogen. Each of these curves could be used for any compound containing the halogen, regardless of its molecular structure. The reason for this alleged universality is the complete atomization occurring in the discharge. Table 1 compares the sensitivity and selectivity values obtained with a few different GC-MIEDD systems. Recent applications have used the GC-MIEDD to determine chlorinated products in humic substances,[98] trihalomethanes in drinking water,[99] and to determine trace quantities of polybrominated biphenyls.[100] Two of these studies used the Beenakker cavity.[98,99]

b. Phosphorus

The emission spectra of phosphorus-containing compounds typically include four atomic lines: 243.4, 253.6, 244.3, and 255.5 nm; of these lines, the 253.6-nm line is the most intense.[20] Molecular bands from PO fragments are very intense and are superimposed on CN bands at the 324.6- and 327.1-nm regions. Various studies have evaluated the applicability of the MIEDD to the determination of phosphorus-containing pesticide residues in agricultural samples. Using an argon discharge,[32] untreated solvent extracts of agricultural samples were directly injected into the gas chromatographic column. Despite the relatively large concentration of impurities in these extracts, the chromatograms were practically clean and contained only the pesticide peaks. Satisfactory recoveries, 72 to 115% of phosphorus-containing insecticides, at the 0.03- to 0.6-ppm concentration range, have been achieved. By operating the argon discharge at reduced pressures, the sensitivity and selectivity were improved by a fractor of 10.[101] The superior selectivity of the MIEDD over the ECD is demonstrated in Figure 6[37]. by the absence of extraneous peaks in the MIEDD chromatogram. A scheme was developed[101] to determine the most analytically appropriate emission lines or bands for each individual phosphorus compound.

c. Sulfur

With an atmospheric pressure argon discharge,[20] CS_2 emission bands were detected for all the sulfur compounds studied. The detection limit was approximately 10^{-9} g-sulfur per

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Table 1
DETECTION LIMITS WITH GC-MIEDD

Element	Detection limit ng	Detection limit ng-sec^{-1}	Selectivity ratio	Species detected	Ref.
C		0.08		C	37
		0.0000002		C_2	20
		0.00003		CN	20
		0.2		CN	30
		0.012		C	113
H		0.03		H	37
		0.016	74[a]	H	113
D		0.09	880[b]	D	37
		0.020	194[c]	D	113
F		0.06	2,300[b]	F	37
		0.5		Si	20
		0.064	573[c]	F	113
Cl		0.06	510[b]	Cl	37
		0.8	20[d]	CCl	20
		4.5	150	Cl_2	30
		0.5		Cl II	99
		0.115	610[c]	Cl II	113
Br		0.09	1,300[b]	Br	37
		0.06	44	Br	91
		200	10	?	20
		2.5		Br_2	30
		0.02	38	Br_2	91
		0.3		Br II	99
		0.106	274[c]	Br II	113
I		0.05	400[b]	I	37
		0.00007	10^4—10^7[d]	I	20
		0.05	38	I	41
		0.1	—	I	30
	0.05		—	I	24
		1.0		I	99
		0.056	5,010[c]	I	113
S		0.09	390	S	37
		0.05	22	S	91
		1	100	CS	20
		0.04	1,000	S	30
		0.052	4,590[c]	S II	113
P		0.009	1,000	P	91
		0.01	100	P	20
		0.3	460	P	30
	0.07—0.65			P	24
		0.056	10,000[c]	P	113
N		2.9		N	37
Al	100			Al	104
		0.02		Al	105
		0.019	3,900[c]	Al II	113
Be	0.01			Be	104
Cr	1			Cr	104
		0.003	990	Cr	105
		0.019	10,800[c]	Cr II	113
Cu		0.008	2,250	Cu	105
Ga		0.0027	1,170	Ga	105
Fe		0.013	1,610	Fe	105
		0.00089	280,000	Fe II	113
Sc		0.0021	1,620	Sc	105

Table 1 (continued)
DETECTION LIMITS WITH GC-MIEDD

Element	Detection limit ng	Detection limit ng-sec^{-1}	Selectivity ratio	Species detected	Ref.
V		0.0085	1,400	V	105
		0.026	56,900^{c}	V II	113
Hg	0.6		10^4	Hg	102
	0.0005—0.002		10^4	Hg	32
		0.060	76,900	Hg	113
Se	0.04		10^4	Se	31
		0.062	10,900^{c}	Se	113
As	0.02		2×10^{4c}	As	33
		0.155	47,000^{c}	As	113
Sb	0.05		2,000^{c}	Sb	33
Si	0.2		200	Si	34
		0.018	15,800^{c}		113
B	—	0.027	9,250^{c}	B_g	105
Pb				Pb	119
		0.0007	246,000^{c}	Pb	113
Nb		0.335	32,100	Nb II	113
Mo		0.025	24,200	Mo II	113
W		0.646	54,500	W II	113
Ru		0.035	134,000	Ru II	113
Os		0.036	50,000	Os II	113
Co		0.018	182,000	Co	113
Ni		0.006	6,470	Ni II	113
Ge		0.004	75,000	Ge	113
Sn		0.006	358,000	Sn	113

[a] Selectivity ratio determined by comparison with triphenylarsine.

[b] Selectivity ratio determined by comparison with phenanthrene.

[c] Selectivity ratio determined by comparison with toluene, *n*-hexane, or *n*-heptane.

[d] Selectivity ratio determined by comparison with triphenylarsine and triphenyl stibine.

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second. At reduced pressure[26] an argon discharge produced more intense molecular band emissions that atomic line emissions and was also more restricted in its sample load capabilities compared to a helium discharge. The helium discharge produced simpler spectra, with sulfur lines (190 and 191.5 nm), a CS band (257.6 nm), and a C_2 band (516 nm) being the most prominent spectral features. But even with the helium discharge, the calibration curves were found to be dependent upon the sulfur compounds, and the detection limits varied from 0.2 ng to 7.5 ppm. Additionally, the working curves frequently deviated from linearity.

Quantitative determination of various sulfur-based pesticides, either by atomic emission or atomic absorption spectrometry, have been also performed using the 216.7-nm sulfur line.[103] The degree of dissociation and efficiency of excitation was found to vary with different compounds and was also affected by the carrier gas. These variations, it was speculated, originate from differences in the residence time of the species in the discharges sustained by gases of different densities (air, helium, or argon), as well as from differences in the quenching mechanisms in each discharge. However, the energy levels of the metastable state species, e.g., 11.6 and 21.3 eV for argon and helium, respectively, probably account for these differences in the degrees of fragmentation and excitation. These phenomena are not yet fully understood and should be addressed more seriously in future studies.

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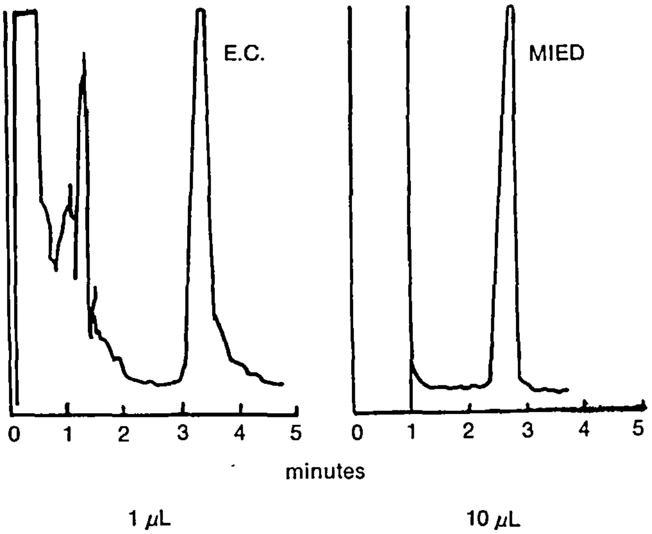

FIGURE 6. Comparison of electron capture and microwave emission responses for celery extract containing 10 ppb parathion.

Three sulfur-based pesticides have been determined utilizing a single universal analytical working curve, and the background emission intensity from carbon species in the discharge produced during the fragmentation of the pesticide were subtracted. However, in order to compensate for the carbon contributions, this procedure required an *a priori* knowledge of the identity of each compound. A more practical alternative would have been to determine an analytical curve for each compound separated by gas chromatography. In spite of the need to correct for background signals from carbon, detection limits of 0.02 μg sulfur were obtained.

As with carbon and halogens, the reduced pressure oxygen-doped helium discharge[40] has been claimed to produce a single calibration curve for all sulfur compounds with detection limits of 0.09 ng. This approach is rather oversimplistic since it fails to recognize the reduction in the signal-to-noise ratio caused by spectral interferences from species originating from the eluted solutes.

d. Silicon and Boron

Dimethylsilyl- and trimethylsilyl- ether groups have been introduced into various polar and nonvolatile compounds which contain active hydrogen groups by the reaction with various silylation reagents. The resulting silylated derivatives are amenable to gas chromatographic separation because they are often thermally stable and volatile. Studies which are interested in measuring the reaction kinetics or quantifying these silylation reactions could benefit from the use of the MIEDD in a silicon selective mode.

A feasibility study of the MIEDD as a silicon selective detector has been published using tributylsilane with dichlorobenzene as the nonsilicon reference compound. A low pressure (5 to 10 torr) argon discharge with the tapered (NBS type 1) cavity was found to be superior to an equivalent helium discharge since the argon background emission was lower and the stability and selectivity were higher. The argon discharge was also superior to helium doped with oxygen. Reduced pressure operation of the argon discharge was preferred over atmospheric pressure operation because larger samples could be introduced and higher sensitivities, selectivities, and discharge stability were obtained.

The silane molecules were found to be instantly fragmented when introduced into the discharge and the lifetime of the free silicon atoms is short. Although this phenomenon was previously observed with other elements, e.g., antimony, bismuth, aluminum, and copper, its effect was more pronounced for silicon.

Linear analytical curves at the 251.6-nm silicon line were obtained for tributylsilane in methylene chloride solutions over the 0.5 to 100 ppm concentration range with a detection limit of 0.1 ppm. Samples containing three carboxylic acids and three paraffins in pyridine were reacted with the silylation reagent, bis (trimethylsilyl) trifluoroacetamide. After silylation was completed, aliquots of these samples were separated on a gas chromatographic column and detected by both FID and MIEDD (Figure 7). In contrast to the FID, the silicon-selective MIEDD was insensitive to the unreacted paraffins. Thus, a simultaneous detection by an FID and an MIEDD should simplify the analysis of silylated samples by classifying the eluted compounds into volatile and silylated fractions. Capillary GC-MIEDD in the boron-selective mode has been used to study the pyrolysis of various carborane silicone polymers.[105] This investigation used the Beenakker cavity and an atmospheric pressure helium discharge and respresents the first determination of boron-containing compounds.

e. Selenium, Tellurium, Arsenic, Antimony, and Bismuth

Arsenic and antimony have been determined in various environmental samples,[36] and the analytical procedure was based on the cocrystallization of As^{+3} and Sb^{+3} with thionalide (α-mercapto-*N*, 2-naphtylacetamide) followed by reaction of the precipitate with phenylmagnesium bromide. The thermally stable and volatile triphenylarsine and stibine formed were extracted into ether and separated by gas chromatography. Linear working curves were obtained for arsenic (228.8-nm line) and antimony (259.8-nm line). Detection limits for arsenic and antimony were 20 and 50 pg, respectively. These results translated into relative sensitivities of 50 and 125 ng/ℓ for water samples and 30 and 75 ng/g for solid samples. This procedure was used to determine arsenic and antimony in mammalian and plant tissues, coal and fly-ash, and fresh and salt water samples. The relative error was found to range from 1.7 to 10% and the relative standard deviation from 2.6 to 7.1%.

Preliminary studies with selenium, tellurium, and bismuth have suggested that it should be possible to determine all these elements simultaneously with arsenic and antimony by temperature programming the gas chromatographic column. Additionally, a computer-interfaced scanning spectrometer or image device multichannel spectrometric detector should enable the emission intensity of each solute to be monitored at its optimum wavelength. Because of the excellent selectivities for these elements, e.g., $>10^4$ for arsenic $>2 \times 10^3$ for antimony, interferences due to overlapping peaks are negligible.

The GC-MIEDD has also been applied to the determination of alkylarsenic acids in commercial pesticides and in environmental samples.[37] The analytical procedure consisted of sodium borohydride reduction of the arsenic acids to their corresponding arsines followed by either solvent extraction or by flushing them into cold traps containing toluene at −5° C. Good gas chromatographic separation was obtained for various alkyl-arsines and there positive identification was performed by mass spectrometry. The excellent selectivity of the MIEDD to arsenic is due to its efficient sample fragmentation and atomic excitation. Consequently, its response to arsines is less dependent on molecular structure, and, therefore, universal analytical working curves based on peak areas could be constructed. The relative sensitivity for various alkylarsines in water samples was 0.25 μg/ℓ.

The GC-MIEDD has been applied successfully to the determination of selenium in

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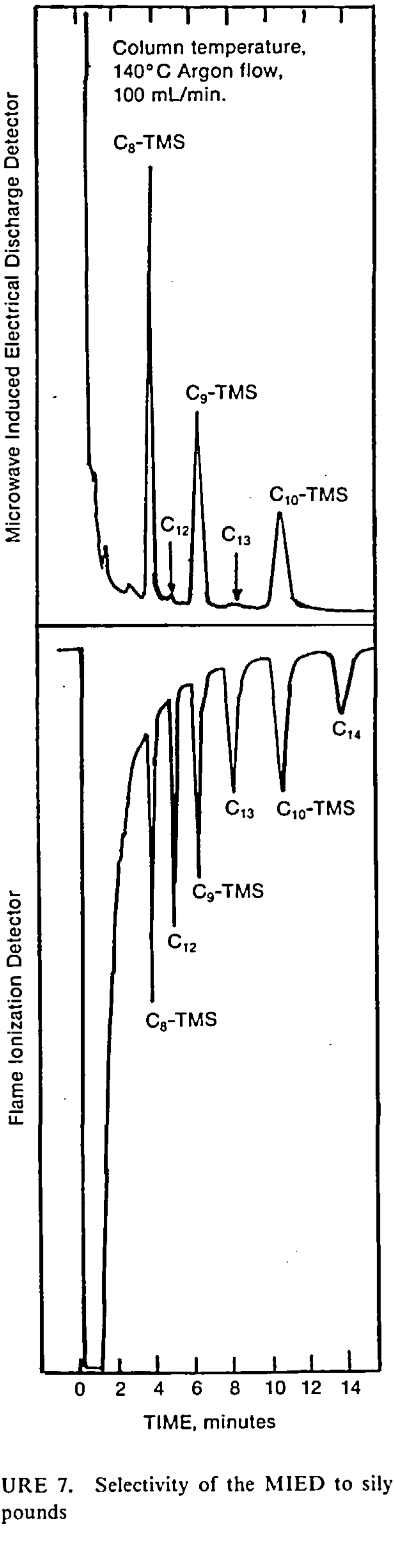

FIGURE 7. Selectivity of the MIED to silylated compounds

various environmental samples.[37] The analytical procedure which was developed involved chelating selenium with 5-nitro-*o*-phenylene diamine (PD) to form the thermally stable and volatile piaselenol complex which can be extracted into toluene. Aliquots of this extract can be injected directly onto the gas chromatographic column, and the selenium can be determined by monitoring the intensity at the 204-nm selenium line. The selectivity of the detector to selenium was greater than 10^4 when using triphenyl arsine as a reference compound. The samples which were analyzed included biological and plant tissues, coal, fly-ash, and scrubber solutions. The relative errors were in the 0 to 17.5% range and the relative standard deviations were in the range 2.2 to 9.5%. This analytical procedure was used successfully to determine selenium in coal, slag, and flue gas at the Allan Steam Plant in Memphis, Tennessee.[106] Additional valuable information concerning the emission of selenium in coal-fired steam plants and its fate in the environment was also obtained from this study.

The use of 5-nitro-*o*-phenylene diamine to determine antimony and bismuth was less successfull since these species could not be monitored in downstream regions of the discharge due to erratic fluctuations in their emission intensities. This problem seemed to increase with the metallic nature of the heteroatoms from arsenic to bismuth. This behavior suggests that the fragmentation of the phenyl complexes and the subsequent excitation of the heteroatoms, arsenic, antimony, and bismuth occurs at their very first contact with the discharge. The signal fluctuations and the loss in sensitivity observed in downstream regions are caused by condensation of the metalloid atoms on the relatively cool quartz walls, which leads to their eventual removal from the gaseous discharge. This behavior has been observed previously for copper and aluminum chelates[107] and may limit the applicability of the GC-MIEDD to trace metal analysis

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2. Metals

a. Volatile Organo-Mercury Compounds

The determination of trace amounts of methyl mercury, as well as other volatile organo-mercury compounds by GC-MIEDD, was demonstrated initially with a low pressure helium discharge.[108] A subsequent study showed that an atmospheric pressure argon discharge[35] had unequivocal superiority over the electron capture detector for the determination of methyl mercury in complex environmental samples. These results are shown in Table 2. The selectivity of the MIEDD to mercury (at the 253.7 nm) as compared to hexadecane or chloroform was greater than 10^4, and a detection limit of 0.5 pg with the relative sensitivity for fish samples of 1 ng/g was obtained. Figure 8 demonstrates the excellent sensitivity of this detector.

During the last 6 years the GC-MIEDD system has been routinely utilized at Oak Ridge National Laboratory for the determination of methyl mercury in various environmental samples. The system has clearly demonstrated its day-to-day reliability, sensitivity, and ruggedness. Also, the unique features of the GC-MIEDD were found to be essential for various studies on the vaporization and halogen decomposition of methyl mercury compounds.[109]

b. Metal Chelates

The use of metal chelates with sufficient volatility and thermal stability to enable them to be separated by gas chromatography is an area which has received extensive attention during the past 15 years. These studies showed that the best complexing ligands were 2,4-pentanedione and its analogs. Also, it was found that volatility was enhanced as the substitution of fluorine atoms increased. This desirable increased volatility displayed another major advantage. The increase in fluorine substitution increased the electron capture cross-section, with the result that detection limits in the range of 1×10^{-13} g/sec

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Table 2
THE APPLICABILITY OF EC AND MIED DETECTORS TO THE DETERMINATION OF VOLATILE ORGANO-MERCURY COMPOUNDS

	ECD	MIEDD
Selectivity	Poor, restricted to RHgX compounds	Highly selective to all Hg compounds
Sensitivity	Subnanogram for CH_3HgX; poor for $(CH_3)_2Hg$	Picogram level for all Hg compounds regardless of chemical form
Solvent	Highly polar solvents are generally avoided	Any solvent can be used
Stability	Detectors are readily fouled by contaminants from bleeding columns; frequent cleaning of detector is required	Stable over long periods of time; detectors relatively unaffected by column bleeding; cleaning procedures seldom required
Service and repairs	Usually by the manufacturer only	Very simple; usually by the user (except for the microwave generator)
Sample preparation	CH_3HgX: digestion; extraction into benzene; partitioning to aqueous thiosulfate solution; reextraction into benzene	CH_3HgX; digestion; extraction into benzene
Rate of sample injection	Usually 2—5/hr due to interferences from eluted substances	Up to 40/hr

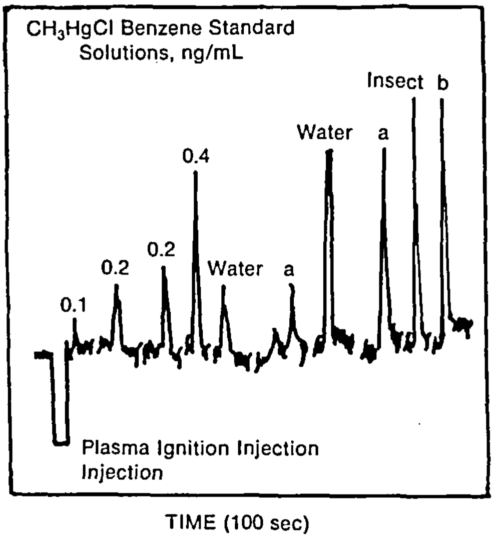

FIGURE 8. Detection of CH_3HgCl at the detection limit level. (*a*) water samples, 50 mℓ were extracted with 2 mℓ benzene following the addition of NaI. (*b*) 0.2 gm of ground insect were treated as described above and extracted into a 2 mℓ benzene. Benzene aliquots 5 μℓ were injected. (From Talmi, Y. and Norvell, V. E., *Anal. Chem.*, 47, 1510, 1975).

were obtained. Consequently, the use of the MIEDD for monitoring metal chelates was not investigated as early as would otherwise have been expected.

The first reported studies have used an atmospheric pressure argon MIEDD to monitor the 2,4-pentanedionates or 1,1,1,-trifluoro-2,4-pentanedionates of aluminum, beryllium, chromium, iron, copper, scandium, gallium, and vanadium (VO).[110,111] The detection limits obtained were in the range of 1 × 10^{-7} to 1 × 10^{-12} g/sec. Operation consisted of monitoring the atomic emission from the metal atom, and selectivity ratios of the order of 10^3 as compared to a hydrocarbon were obtained. One of the major problems experienced with this detection system, after continual use, was the loss of the transparency of the discharge tube due to metal deposition. To avoid this problem, it was necessary to ignite the discharge after the solvent had eluted and to limit the sample size. However, despite these difficulties this system was used for analyses of chromium (as chromium tris-[1,1,1-trifluoro-2,4-pentanedionate]) in blood plasma with excellent quantitation and precision.[112]

Other studies[80,81] have found that a reduced pressure (1 to 3 torr) helium MIEDD doped with oxygen gave much better fragmentation and excitation. As a result, the emission spectra from chromium tris-(2,4-pentanedionate), tris-(1,1,1-trifluoro-2,4-pentanedionate), or tris-(1,1,1,5,5,5,-hexafluoro-2,4-pentanedionate) was predominantly atomic in nature. These results were more satisfactory than earlier studies which were based on atomic and molecular emission spectra. Detection limits of 1 × 10^{-11} g/sec with selectivity ratios of around 3000, as compared to benzene, were obtained. These preliminary studies have been recently extended and the results have been extremely encouraging.[113,114] These data were obtained with the Beenakker cavity and in addition emissions from excited ions were observed, which demonstrates that this cavity produces a more energetic species. These studies have also demonstrated that the MIEDD is suitable for use with high resolution capillary columns. Also, other workers have used the GC-MIEDD system to determine trace levels of beryllium[115] as well as trace levels of copper and aluminum in zinc.[116]

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c. Other Volatile Metal Complexes

There was an unsuccessful attempt[117] to use a reduced-pressure (5 torr) helium MIEDD to monitor the volatile fluorides of molybdenum, tungsten, rhenium, arsenic, antimony, boron, sulfur, selenium, and tellurium. The problem experienced was that the quartz discharge tube had to be replaced after every analysis because it was rapidly attacked by the fluorine atoms, and consequently the emission was predominantly due to silicon species.

In some other studies, various metal carbonyls and metal alkyls[118] were detected using a reduced-pressure (1 to 2 torr) helium doped with oxygen discharge with excellent success. Recently, a helium discharge has been used with high resolution gas chromatography to determine various trialkyl lead chlorides. The solvent was vented prior to the discharge tube to prevent contamination of the discharge, and the Beenakker cavity was used to couple the microwave energy.[119]

C. Interelement Ratios

With the exception of mass spectrometers, most gas chromatographic detectors are incapable of providing information concerning the quantitative ratios between elements present in the eluent. Theoretically, emission spectrometric detectors are well suited for the simultaneous determination of several elements, with response that is molecular-structure independent. Success in this study requires that the emission intensity for each element is proportional to the elemental content in the solute. A study to measure the ratios of chlorine, iodine, bromine, sulfur, and phosphorus emission to carbon emission for a range of simple compounds was performed[40] in order to determine the factors which affect these ratios and the potential of this technique for the determination of interelement ratios.

For sulfur, iodine, and phosphorus, the simultaneous measurements of the emission from two atomic lines, hetero and carbon atoms, were sufficient for the determination of the quantitative relationship between the heteroatom and the number of carbon atoms in the eluted compound. For these elements, emission ratios and the elemental ratios were found to be independent of the flow-rate of the carrier gas and of the eluent concentration. The ratios of chlorine and bromine emissions to atomic carbon were, however, both flow-rate and eluent-concentration dependent. This behavior was explained on the basis of the assumption that the emitting species in the atmospheric argon discharge were diatomic, i.e., Cl_2 and Br_2. Thus, in the case of chlorine- and bromine-containing compounds, a series of peak ratios for a range of concentration of the sample sought are required, along with a standard sample in a similar range for analytical purpose. The practical use of this technique is limited by the relative sensitivity of the detector to each element and by the interelemental interferences. However, the most important interferences are either the physical interferences, when large amounts ($>10^{-6}$ g/sec) of another eluent overloads this discharge, or specific spectral interferences, primarily from C_2, CN, and C emissions.

Problems originating from the association of atoms into pairs, causing the production of complex band-emission spectra, were overcome with the use of a low-pressure helium discharge spiked with oxygen or nitrogen (0.1 to 1.0% V/V) as scavangers.[9] Under these conditions, atomization of all molecules was found to be practically complete. High detector selectivities and linear analytical curves were obtained for carbon, hydrogen, deuterium, oxygen, nitrogen, fluorine, chlorine, bromine, iodine, sulfur, and phosphorus.

In these studies the experimental H/C ratios for a large number of hydrocarbons were shown to be in agreement with the theoretical values. Although no similar data were shown for any other elemental ratios, it was claimed that the method provides the means to obtain the empirical formulas for practically any organic eluent.

The lower end of the dynamic range was fixed by the noise level of the backgound signal at the various element-selective wavelengths. The detectability of nitrogen and oxygen is limited due to high background at these wavelengths.

Sealing all the leaks, purifying the helium gas and preconditioning the columns will substantially reduce the background. In reality, no general method to stop species of the column packing material exists; consequently, column-based eluents will always increase the background level. These factors will have a diminishing effect on the sensitivities of all elements, and a multichannel spectrometer with simultaneous determination of a few elements of a few wavelengths is required to simplify the procedure for obtaining element ratios. The Beenakker cavity with its increased efficiency of fragmentation should be extremely useful for the determination of interelement ratios. Some preliminary studies[31] have compared interelement ratios for various *n*-alkanes by monitoring the emissions from C*, H*, C_2^*, and CH* and the results showed that the Beenakker cavity provided slightly superior interelement ratios.

D. Liquid Chromatography (LC)-MIEDD

Low-powered MIEDD cannot be directly interfaced to a high performance liquid chromatograph, since with normal operation large amounts of mobile phase (~ML/min) continuously introduced into the discharge will quench it. A few possible solutions to overcome this problem have been evaluated. One approach has employed high-power (1 to 10 kW) discharges, operating in the radio frequency range (10 to 40 MHz) or microwave range (0.8 to 3 GHz). These high-power discharges should accommodate the continuous solvent-flow, as long as the solvent is efficiently nebulized prior to its introduction. DC discharges have also been used to monitor liquid chromatographic effluents. The direct sample-introduction approach has one severe

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Table 3
COMPARISON OF THE PERFORMANCE OF VARIOUS GAS CHROMATOGRAPHIC DETECTORS[113-115]

Detector	Principle of operation	Response	Minimum detectable quantity (g/sec)	Linearity	Selectivity ratio	Remarks
Flame ionization	Measures the ion current produced by combustion in hydrogen diffusion flame	Universal except to fixed gases and water	2×10^{-11}	10^7	0	Simple, easy to use, stable and cheap detector, requires little maintenance
Mass-spectrometry	Monitors mass-to-charge ratio of parent ion	Tunably selective by molecular wt	1×10^{-10}	10^6	No data	Requires special GC-MS interface; expensive, difficult to operate, large downtime
Infrared spectrometry	Monitors absorption by a functional group	Tunably selective by functional group	1×10^{-8}	Log response	No data	Requires special GC-IR interface; expensive
Thermionic	Measures the selective release of electrons or ions	Selective to either sulfur or phosphorus; nitrogen-or chlorine-containing compounds	1×10^{-13}	10^3	10^5	Requires flow controllers for hydrogen and air; uses same equipment as FID; inexpensive
Micro-coulometric	Measures concentration of ions by titration	Selective to chlorine-, sulfur- and nitrogen-containing compounds	1×10^{-9}	10^4	10^2	Response can be related directly by theory to concentration; inexpensive
Coulson conductiometric	Measures concentration of ions by conductivity	Selective to chlorine-, sulfur-, and nitrogen-containing compounds	1×10^{-9}	10^3	10^2	Requires simple equipment; inexpensive
Electron capture	Measures the capture of electrons by solute molecules	Selective to electrophilic groups	1×10^{-13}	5×10^2	10^7	Limited to 225°C if ^3H is used or 350°C if ^{63}Ni is used, easily contaminated by solutes
Flame photometric	Measures the emission of diatomic species in hydrogen diffusion flame	Selective to sulfur, phosphorus, and other nonmetals	1×10^{-12}	10^3 except sulfur	10^4	Easy to use and operate, rugged, and inexpensive
Microwave-induced electrical discharge	Measures the atomic emission produced by molecules excited by electrical discharge	Tunably selective to any atomic emission	1×10^{-14}	10^4	10^6	Can require vacuum equipment, requires routine changing of plasma cell; moderately expensive

drawback: the background emission produced by the solvent will interfere spectrally with the solute-characteristic emission, thus reducing the overall selectivity and sensitivity of the detector. Furthermore, this approach does not allow for the use of the detector in the nonselective carbon detection mode of operation. These problems can be largely alleviated by the use of either pneumatic or ultrasonic nebulizers. Flow chambers or desolvation apparatus in conjunction with those nebulizers reduce the fraction of solvent that enters the discharge and, therefore, greatly improve its stability and dynamic range. The sample nebulization efficiency (fraction of analyte introduced into the discharge) of these sampling devices is approximately 10 to 15%.

A more elegant approach will require the removal of the solvent, e.g., using a moving wire device, followed by pyrolysis of the sample and flushing of the pyrolysis products with a carrier gas into a low power MIEDD. With this scheme the most attractive characteristics of the MIEDD, i.e., sensitivity and its operation in either the selective or the nonselective spectrometric modes, will be preserved.

Unfortunately, all these sampling techniques are rather complex and cause broadening of the chromatographic peaks and consequently a reduction in the resolution of the LC chromatographic system.

VI. CONCLUSIONS

The MIEDD has been widely investigated by a number of workers for its ability to detect a range of compounds. All these studies and other studies on selective detection systems have suggested that until the mechanisms of these detection systems are completely understood and the relative response factors are predicated, the full potential of these detectors will not be realized. However, even with these preliminary results the MIEDD is probably the most sensitive selective and nonselective GC detector available. This single feature will become more important as the studies of long-term effects of ultratrace quantities of chemicals on the environment and on biological systems are performed. Table 3 gives a comparison of some selective detectors with some universal detectors.

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