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A Review of Gas Chromatographic-Mass Spectrometric Methods of Analysis

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ABSTRACT

A literature survey of the gas chromatographic-mass spectrometric methods of analysis has been made which provides a comprehensive review of the past and present research efforts on the identification of gas chromatograph effluents with a mass spectrometer. The various types of instrumentation employed are described briefly, and critical assessments are made of the various techniques for tandem operation of a gas chromatograph and a mass spectrometer.

PROBLEM STATUS

This is an interim report; work on these problems is continuing.

AUTHORIZATION

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A REVIEW OF GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC METHODS OF ANALYSIS

INTRODUCTION

Identification of the organic contaminants found in the closed atmospheres of nuclear submarines or of space vehicles is of paramount importance for long-term habitability in these vessels. Pollutant mixtures are often so extraordinarily complex and the trace concentrations are frequently so minute that analysis by conventional methods is essentially useless. The effectiveness of a gas chromatograph in separating the constituents of a mixture and the efficiency of a mass spectrometer for identifying single compounds, or the components of simple mixtures, has focused increasing attention on the combination of these two powerful analytical instruments.

Coupling of the gas chromatograph with the mass spectrometer results in an analytical instrument far more powerful than the sum of the two components. The Naval Research Laboratory has installed such a tandem gas chromatograph-mass spectrometer system to aid in the analysis of the pollutant mixtures found in the nuclear submarines. It is anticipated that this system will be of the utmost importance in the analysis of atmospheric contaminants in general and of mixtures formed in the degradation of organic compounds or chemical reactions. It will also be useful as a monitor of materials for adherence to specifications, as a detector of extraneous compounds, and possibly to identify the source of deleterious compounds found in the atmosphere analysis.

The principal purpose of this review is to discuss the various techniques which have been applied for the identification of gas chromatographic peaks by mass spectrometry; however, for those not familiar with the two instruments the basic theory of their operation will be briefly described.

INSTRUMENTATION

Gas Chromatography

A gas chromatograph consists of three major parts: a sample inlet system; a column, where separation occurs; and a detector, which is used to sense the separated components as they emerge from the column.

The method used to introduce the sample into the chromatograph varies with the form of the sample. Liquid samples are most often studied and, fortunately, are the most easily handled. A hypodermic syringe is used to inject a sample through a rubber septum into a heated area immediately in front of the gas chromatograph column. The sample is immediately vaporized in this area and swept onto the column by the carrier gas (usually helium). The handling of gaseous samples is more complex. The sample container is connected to a U-tube; this tube and the volume of the connection between the tube and the sample valve are evacuated and the U-tube cooled to liquid nitrogen temperature. The gases are transferred into the cooled, evacuated U-tube by opening the sample valve; any noncondensable components of the mixture are thus removed by evacuation. The valve between the U-tube and the vacuum pump is closed; then the U-tube is warmed to room temperature and the mixture swept onto the gas chromatograph column with the carrier

gas. Solid samples are placed in an oven, through which the carrier gas is passing, and the temperature of the oven is increased rapidly to flash evaporate the sample so that it will be swept onto the column by the carrier gas as a single pulse.

The gas chromatograph column is the heart of the instrument. It is here that the mixture is separated into its components. The column is a tube which is either coated on the inside with a nonvolatile liquid (used only with capillary tubes) or filled with a porous granular solid, whose pores have been impregnated with a liquid which is not volatile at the operating temperature of the column. The nonvolatile liquid is known as the stationary phase, and the sample is called the moving phase.

It is not practical to discuss here the theory of gas chromatographic separations; suffice it to say that if a small volume of a mixture of volatile compounds enters the column, under favorable circumstances the components of the mixture will pass through the tube at a rate which varies inversely according to their affinities for the stationary phase and thus ideally emerge from the column separately. As each component passes down the column, it is alternately dissolved and vaporized from the stationary phase. With extremely complex mixtures, such as those found in the atmospheres of nuclear submarines, a complete separation is seldom achieved; however, the complexity of the mixture which finally emerges from the column is drastically reduced.

Three basic types of columns are used in gas chromatography: the packed column, the open-tubular column (also called a capillary column or a Golay column), and the support-coated open-tubular column. The packed columns used in analytical gas chromatographs are tubes with internal diameters varying from 1/8 to 1/4 in. which have been filled with inert solid support coated with the stationary phase. Packed columns are the most used type, therefore more information concerning the choice of the stationary phase, operation temperature, etc., is available. However, packed columns require large samples and copious amounts of carrier gas; this is a disadvantage when the chromatograph is combined with a mass spectrometer because the latter must be operated at vacuum pressures. Thus, some method must be employed to reduce the amount of material emerging from the packed column chromatograph prior to the introduction of the stream into the mass spectrometer. Another disadvantage of the packed columns is their low resolution (ability to separate components of a mixture).

Open-tubular columns, with internal diameters 0.02 to 0.01 in., on the other hand, have extremely high resolution and use small samples ($\sim 10^{-3}$ μl) and reduced amounts of carrier gas, so the total output from these columns can be fed into the mass spectrometer without damaging the instrument. There is, however, a dearth of experimental data for these columns so the optimum operating conditions must be determined for every column. Another handicap of open-tubular columns is their inability to handle gaseous samples containing trace contaminants.

A compromise between the open-tubular column and the packed column is the support-coated open-tubular column, in which the stationary phase is a thin film on a micron-sized inert solid support which has been deposited on the tube's wall. These columns retain the excellent resolution of the open-tubular columns but, due to increased surface area, can accept a larger sample charge thus facilitating analysis by effluent monitoring with a mass spectrometer.

Gas emerging from the column is passed through a device which senses each component as it arrives. While many types of gas chromatograph detectors have been developed, only a few of the most widely used ones will be discussed here.

Thermal conductivity detectors are probably the most common type of detector used in gas chromatography because of their uniform response to a variety of organic vapors, linearity of response over extensive concentration ranges, and rugged simplicity. However,

the development of the open-tubular columns, which use very small samples and have very narrow peaks, resulted in a need for detectors with greater sensitivity and speed. These needs are more nearly met by the ionization type detectors, such as (a) flame ionization, (b) β-ray ionization, or (c) the mass spectrometer. While the first two detectors are very sensitive, they do not have uniform response for all contaminants and do not meet one of the most improtant criteria for the analysis of complex mixtures, i.e., the positive identification of the substance emerging from the chromatograph column. The third type of ionization detector–the mass spectrometer–does meet this requirement. It is, therefore, the most useful and, unfortunately, the most costly of all gas chromatograph detectors.

Mass Spectrometer

Mass spectrometers have the unique ability to permit the unambiguous identification of minute quantities of any gaseous compound. Basically, the mass spectrometer is an instrument for sorting and identifying atoms and/or molecules. The neutral molecules and/or atoms are ionized by impact with a stream of electrons and then separated into individual ion beams containing only one specific mass. While most mass spectrometers separate the ions in a magnetic field, many other methods are used; e.g., the linear time-of-flight (TOF) spectrometer, the radio-frequency spectrometer, and the resonant spectrometer employ different physical principles for sorting the ions into mass-to-charge ratios (m/e). The most important of the nonmagnetic instruments is the TOF mass spectrometer, where the accelerating potential is applied intermittently, thus cutting the ion beam into pulses. Thus, the ions can be sorted according to their velocities, which is the same as mass sorting without a magnetic field. This discussion of mass spectrometers will deal principally with instruments which employ a magnetic field for the ion separation. These are called magnetic mass spectrometers and are in three general classes: the conventional single-focusing magnetic instrument; the dual ion source single-focusing mass spectrometer; and the double-focusing mass spectrometer.

In a conventional mass spectrometer, gas molecules are bombarded by controlled-energy electrons emitted from a heated filament (usually tungsten or rhenium metal). Since the filament would be seriously damaged if the pressure rose above 10^{-8} atmospheres in the ion source, high-vacuum pumps are used to maintain this pressure. The bombarding electrons ionize a fraction of the molecules, and the positive ions thus formed are pushed out of the ion source by a repeller electrode which operates at a potential of a few volts positive with respect to the ion source. The emerging ions are collimated and accelerated by a series of electrode slits, the final one being held at ground potential, usually about 3000 volts below the ion source potential. Ions so accelerated pass into a magnetic field where they are separated by direction focusing according to their mass-to-charge ratios (m/e). For example, in a Dempster mass spectrometer the ions are bent 180° by the magnetic field. In other instruments the ions may be bent 60° or 90°. These separated ions are then focused on a detector, either an electron multiplier or Faraday cup, by changing either the magnetic field strength or the accelerating potential. This operation is called scanning the mass spectrum. It is paramount that the mass spectrum be scanned very quickly if a complete spectrum is to be obtained for every eluted chromatographic peak as it passes through the ion source. Since this transit time may be as short as 2 to 4 seconds, the spectra must be recorded either on a direct writing galvanometer oscillograph or on magnetic tape which can record a mass spectrum from m/e 20 to 220 in less than 3 seconds. This m/e range permits the contaminant compounds to be identified but prevents the copious amounts of the carrier gas, helium m/e = 4, from saturating and damaging the electron multiplier.

Conventional magnetic mass spectrometers normally employ total ion current monitoring as a chromatographic detector. In this method a portion of the total ions formed in the ion source (including those produced from the carrier gas) are intercepted at a

collector in the analyzer tube prior to mass separation and the electrical signal generated by these ions is amplified, and recorded. The major limitation of this method is that the large signal due to the carrier must be repressed and the observed chromatogram is the small difference between two large signals. Thus, this technique is not as efficient as the dual ion source mass spectrometer which will now be described.

One of the commercially available spectrometers has a special dual ion source which makes the instrument convenient to use as a gas chromatograph detector; it therefore merits special discussion. One of the ion sources serves as the gas chromatograph detector, while the second is used to obtain the analytical mass spectrum from which each eluted peak is identified. The effluent from the chromatograph is split into equal portions, and is introduced concurrently into each ion source. In the chromatographic ion source the gas is bombarded with 20-volt electrons. Ions produced by this bombardment are repelled to a collector inside the ion source (no m/e separation occurring) and the electrical signal produced is amplified and recorded. Since the ionization potential of helium is 24.58 volts, the carrier gas is not ionized; hence, the electrical signal recorded depends solely on the concentration and ionization characteristics of the eluted material. Therefore, the signal is similar to a conventional chromatogram. In addition, since the ionization potentials of most molecules do not vary by more than a factor of two, all compounds, including the fixed gases, give to a first approximation an equal response on this detector. Concurrently with the process just described, the second part of the effluent gas enters the analytical ion source and is ionized with electrons having an energy of 70 volts; the positive ions are extracted, accelerated, separated, and recorded in the manner described previously for a conventional single-focusing mass spectrometer. Seventy-volt electrons are used in order that the mass spectra obtained can be compared with those cited in the literature for identification of the eluted peaks.

In the production of ions by electron impact the ions have a small spread in their energy due to the contribution of the kinetic and thermal energy of the ions. This spread of energies causes the resolution (the separation between adjacent m/e peaks) to deteriorate. If this variation of ion energies could be eliminated or reduced, the mass spectral resolution would be enhanced considerably. The ion energy variation is essentially eliminated in a double-focusing mass spectrometer. Positive ions are produced in the manner described previously and are passed through a radial electrostatic field, where they undergo velocity focusing prior to their entrance into the magnetic field for direction focusing. Double focusing increases the resolution to a degree which permits the exact mass of a species to be determined; thus, the ion's elemental composition can be assigned unequivocally. For example, with exact mass measurements it is possible to identify three ions appearing at nominal m/e 28: CO, m/e = 27.994915; N_2, 28.006148; and C_2H_4, 28.031300. In this example all of the ion species would be positively identified by precise mass measurements. Because of the ease with which compounds can be identified by mass measurements alone, it is not surprising that these instruments were employed as gas chromatographic detectors when they became commercially available. The organic chemists, in particular, find this combination especially useful, as they can purify the substance under investigation and elucidate its structure in one operation. The main limitations of a double-focusing mass spectrometer are its high cost (> $100,000), its relatively slow scan speeds, and the tremendous amounts of data it produces, making computer computation necessary.

Molecular Separators

Whereas the combination of a gas chromatograph and a mass spectrometer was shown in 1959 (23) to be a powerful analytical instrument, it took four years before studies dealing with the interface of these two instruments were reported. The interface may include a molecular separator which can have many forms. The principle of a molecular

separator is to remove the carrier gas (usually helium or hydrogen) from the chromatographic effluent without removing any of the eluting component and to reduce the pressure to a level which is not deleterious to the mass spectrometer. Ryhage and his collaborators (52-54) reported the first separator which was an adaptation of the isotope separation jet described by Becker (4) for the separation of uranium isotopes. In Ryhage's jet separator the entrance and exit orifices of the stages (two stages are used for packed columns and one stage for open-tubular columns) have varying diameters in the order of a few thousandths of an inch. The dimensions of the orifices and the distance between the stages appear to be critical. The first stage vacuum is obtained with a mechanical pump, and a diffusion pump backed by a roughing pump is employed for the second stage. An efficiency increase of approximately 50% for this separator has recently been reported by Ryhage (56).

A second type of separator, developed by Watson and Biemann (7,76,77), is based on the effusion principle. In this device the effluent from the chromatograph is passed through a porous tube which is inside a vacuum jacket. The difference in the effusion between the carrier gas and the substrate determines the enrichment ratio of sample to helium. While the developers of this separator (77) claim an enrichment of "50-fold" for diethyl ether, a more realistic figure is probably the 13 to 20% efficiency (defined below) reported by Lipsky, Horvath, and McMurray (37). These latter authors have reviewed the available types of separators and described their own separator. The Lipsky separator is based on the diffusion of helium through Teflon FEP (a du Pont copolymer of tetrafluoroethylene and hexafluoropropylene). It was developed to eliminate the large sample losses encountered with the Ryhage and Watson and Biemann separators. The pertinent part of the system described by Lipsky, et al. (37), is a thin-walled Teflon capillary tubing surrounded by a vacuum jacket. Their excellent paper also describes an outstanding method for determining the efficiencies of the molecular separators, provided a direct insertion probe is available. Here, a prescribed amount of sample is evaporated from the probe directly into the ionizing beam of the mass spectrometer. The resulting ion beam of a particular molecular weight (e.g., m/e 298 for methyl stearate (37)) was observed as a function of time, and the area under this curve was given the value 100. The same amount of sample was then introduced into the gas chromatograph column, and the effluent was passed through the separator into the mass spectrometer, where the molecular weight peak was again monitored as a function of time. The area observed under this latter curve was compared with the area obtained with the direct insertion probe to find the efficiency of the separator. There are two major limitations to this procedure to determine efficiency: (a) the compound used to make the determination must be relatively nonvolatile and therefore moderately high in molecular weight which precludes a valid calibration for the low molecular weight compounds; and (b) not all mass spectrometers are equipped with direct insertion probes. However, the Lipsky, et al., method is the most valid method for evaluating molecular separators yet reported.

Llewellyn and Littlejohn (38) have reported the use of a silicone rubber diaphragm as a molecular separator. With this device, the eluted materials pass through the diaphragm and depend on the low permeability of helium through the silicone rubber. The reason for the low permeability of helium is its minute solubility in the rubber under the operating parameters. (Permeability = diffusiveness × solubility.)

TRAPPING TECHNIQUES

The major advantages of trapping chromatographic peaks prior to mass spectrometric introduction are: (a) rapid recording of the spectrum is not required, so that better accuracy may be obtained and a less elaborate mass spectrometer can be employed; (b) the sensitivity of the mass spectrometer is not reduced by dilution of the sample with carrier gas; and (c) compounds may be separated on several chromatographs using different columns and then identified with one mass spectrometer. On the other hand this approach has the disadvantages that trapping every member of a mixture containing a large number

of components is a horrendous task and the samples may be hydrolyzed or oxidized during the collection procedures. However, this method is still one of the most useful approaches for relatively simple mixtures and will be used extensively for some time.

In the first attempts to identify chromatographic peaks with a mass spectrometer the components were collected as they emerged from the chromatographic column and then were introduced into the mass spectrometer. This method was developed in the petroleum industry, and eventually it has been applied in most mass spectrometry laboratories. There are two general approaches to trapping techniques—one requires a special trapping inlet system on the mass spectrometer, to which a gas chromatograph is connected; the second uses a fraction collector which can be attached to any chromatograph, with the collected samples being subsequently introduced into the mass spectrometer through conventional gas inlet systems. The first method, reported by Beynon, Saunders, and Williams (5), Ebert (18,19), Eustache, Guillemin, and Auricourt (22), and Miller (47) has the advantage that the sample does not have to be manually transferred from the gas chromatograph to the mass spectrometer and can be conveniently introduced into the instrument. However, if a large number of samples are to be trapped, this technique is not practical because of the limited number of collection traps available on any one instrument.

The second approach permits more collection tubes to be used, but special skills must be developed to trap each peak in a mixture as it is eluted. Furthermore, the sample must be identified shortly after the collection, limiting the number of components which can be identified. A notable exception to this statement is the technique reported by Amy, et al. (1). These authors trap the eluted peak in a capillary melting point tube which has been filled with the inert solid material used to pack the chromatograph column. The tube is sealed after the collection and stored until the mass spectral identification can be made. However, with their procedures it would be difficult to trap highly volatile or air-sensitive compounds. Pichler, Herlan, and Schulz (49) and Saunders (59,60) have reported methods of trapping chromatographic peaks for spectral analysis which can be employed to identify volatile compounds. Saunders' method (59,60) has been used to analyze complex mixtures found in the atmospheres of nuclear submarines and spacecrafts. The trapped samples were introduced into a conventional Dempster-type mass spectrometer through a chromatographic inlet described by Saalfeld and Saunders (58). Ryhage, Ställberg-Stenhagen, and Stenhagen (51) have used trapping techniques to identify some of the chromatographic peaks of C_{11}-methoxy fraction obtained by the oxidation of phthiocerol.

DIRECT CHROMATOGRAPHIC PEAK MONITORING WITH A SINGLE-FOCUSING MASS SPECTROMETER

General Considerations of a Combination Gas Chromatograph-Mass Spectrometer

The disadvantages of the trapping of chromatographic peaks for mass spectral identification are eliminated when the two instruments are directly combined; however, some of the advantages of these techniques are also lost. Nonetheless, for the analysis of complex mixtures, direct effluent monitoring by a mass spectrometer is the most powerful method available, and it is to this area that attention is now focused.

The most important consideration in the tandem operation of a gas chromatograph and mass spectrometer is the interface between the two instruments. Brunnée, et al., have discussed this aspect of the operation in a series of papers (8-11). They have also pointed out some of the disadvantages of using flame ionization in parallel with the mass spectrometer as detectors for the gas chromatograph. In these papers Brunnée and his coworkers have described the use of a dual ion source as a qualitiative and quantitative

detector for the eluted gas chromatographic peaks. They also discuss fluctuations in the relative peak height of the ions caused by the nature of the ion collection process. Downer (17) has reviewed chromatographic peak monitoring by mass spectrometry, but unfortunately his paper deals in the main with only one instrument manufacturer's products and thus is limited in its scope. Teranishi, et al. (70), have described the extent of column bleed as detected with the hydrogen flame detector and with a mass spectrometer for various stationary liquids used in stainless-steel open-tubular columns. These authors (70) have also made a comparison of open-tubular column efficiencies with the hydrogen flame detector at atmospheric pressure to the efficiencies obtained with the mass spectrometer which operates at vacuum. They report no loss in efficiency when the columns are operating under a vacuum. This elegant paper should be studied by anyone entering the gas chromatographic-mass spectrometric analysis field; it is replete with pertinent experimental details seldom found in a journal article.

Packed Column Applications

The first gas chromatographic peak monitoring with a mass spectrometer was reported by Gohlke in 1959 (23). Since then this method of analysis has been employed at an increasing rate. Gohlke used a packed column gas chromatograph with a time-of-flight (TOF) mass spectrometer; then, in a subsequent paper (24), he reported modifications to his TOF instrument which greatly enhanced its ability to be used as a chromatographic detector. Widmer and Gäumann have also described the direct combination of a gas chromatograph with a TOF spectrometer (79). These authors point out that the advantages of this combination are high sensitivity, high chromatographic resolution, and rapid accumulation of data. Some of the disadvantages noted are the memory effect of their TOF instrument, low abundance sensitivity, and gas noise.

Henneberg and his collaborators (26-30) have discussed many aspects of gas chromatographic-mass spectrometric analysis. In the first of these papers (26,27), Henneberg describes the continuous mass spectrometric monitoring of chromatographic effluent after the gas has passed through a thermal conductivity gas chromatographic detector. Only one m/e ratio is observed for the entire run. He identifies the eluted peak by the ratio of the thermal conductivity peak height to the peak height of the observed m/e mass spectrometric peak. This procedure is compared by Henneberg and Schomburg in subsequent papers (28,29) to a method which uses the complete mass spectrum to identify the eluted gas chromatographic peaks. The method appears to be useful for mixtures which are not too diverse in their chemical nature.

Holmes and Morrell (31) have published circuitry which enables the mass spectrum of a gas chromatographic peak to be displayed on an oscilloscope and photographed. Their approach was one of the first attempts to identify gas chromatographic eluants directly with a Dempster-type mass spectrometer. Judson, et al. (33), have summarized the necessary modifications to a conventional mass spectrometer for gas chromatography monitoring. Their instrument is a compromise between the minimum modifications used by Lindeman and Annis (36) and the extensive alterations employed by Dorsey, et al. (16). Levy and his coworkers (34,35) have reported the use of TOF mass spectrometry and gas chromatography for the rapid qualitative and quantitative identification of the products of a complex chemical reaction. They discuss many of the instrumental problems encountered in such an analysis and state that their technique is applicable to any thermal, photochemical, or catalytic reaction which can be carried out in a flow system. Merritt, et al. (45) have described a method which enlarges the range of gas chromatographic temperature programming to include temperatures from -196°C to over +200°C. The increased efficacy of the packed column gas chromatograph for separating extremely volatile components and the reduced column bleed obtained by using subambient temperatures are excellent advances when a mass spectrometer is used as the gas chromatograph detector.

The problems arising in combining chromatography columns with a mass spectrometric detector have been described by Talroze and his associates (66). They have shown that the most useful combination of these instruments is one where all of the carrier gas flows from the chromatograph into the mass spectrometer. A detection sensitivity of 10^{-12} to 10^{-13} g/sec is reported.

Varadi (72) has developed a detector where both quantitative and qualitative measurements can be made simultaneously on the same sample. His device is similar to the dual ion source described by Brunnée (10), but the mass analyzer is not as sophisticated. Varadi's paper (72) is replete with experimental details so essential to successful usage of the quantitative-qualitative (QQ) detector. Varadi and Ettre (73) have reported the use of their QQ detector for the analysis of several mixtures and predicted that the sensitivity of this detector should be similar to that of a flame ionization detector. In a subsequent paper (74) Varadi and Ettre have reported experimental results that demonstrated the applicability of their QQ detector for the detection of peaks eluted from open-tubular columns. The mixture tested contained CH_4, C_2H_6, C_4H_{10}, CO_2, and N_2. They showed that the separating qualities of the chromatograph whose output is under a vacuum are comparable to or better than those of a gas chromatograph whose output is at atmospheric pressures; furthermore, with the vacuum output chromatographic system the retention times for the respective compounds are almost half of the values obtained when the separations are carried out on a conventional chromatograph.

The advantages of combined gas chromatographic-mass spectrometric analysis of coke gas compared to the analysis by mass spectrometry alone has been discussed by Pichler, et al. (49). These authors developed a double valve system for the introduction of the gas into the mass spectrometer. An analysis of a monoterpene hydrocarbon mixture has been carried out by Ryhage and von Sydow (52) with considerable success. They used a molecular separator as part of the interfacing between their chromatograph and their mass spectrometer. Ryhage (53) has also applied his method to the analysis of a mixture of fatty acid methyl esters and in a note coauthored by Sjövall (54) discussed the analysis of steroids by the gas chromatographic-mass spectrometric method. Selke, et al. (61) have used the gas chromatographic-mass spectrometric technique in lipid research and report that when used as a chromatographic detector, the mass spectrometer is 1000 times more sensitive than the thermal conductivity detector. They further note that the rapid clearance of successive components from the ion source of the mass spectrometer have enabled the analysis of complex mixtures of fatty acid methyl esters to be performed successfully. Eneroth, et al. (21) have employed the gas chromatograph-mass spectrometer combination to analyze fecal steroids in their studies of human excretions during two dietary regimens.

Struck and his collaborators have reported (63,64) the use of a gas chromatograph-mass spectrometric system to analyze high-molecular-weight compounds stressing the versatility of the connection between the gas chromatograph and mass spectrometer. They employed total ion current monitoring as a chromatographic effluent detector. Sweeley, et al. (65), have developed a technique for the identification of unresolved gas chromatographic peaks by monitoring the intensities of m/e values characteristic of each species and then plotting these intensities as a function of time. Individual curves are obtained and their areas are related to the composition of the mixture. This method has been extended and automated so that it is applicable for the determination of isotopic abundances in volatiles at the submicrogram level for a two-component mixture. The technique, when used with stable isotopes, should be a very powerful tool in biochemical studies as well as in other studies which use isotope tracers. Teeter, et al. (67), have employed the gas chromatograph-mass spectrometer combination, both with and without catalytic hydrogenation to analyze commercial alpha olefin mixtures. They have extended their technique to include alpha olefins to C_{20} and demonstrated the analysis with a C_{11}-C_{14} alpha olefin mixture.

von Sydow and his coauthors have reported the analysis of the esters of fifteen monoterpene alcohols (75) and the composition of the essential oil of black currant leaves (2) with a combined gas chromatograph-mass spectrometer. Weygand, Prox, König, and Fessel have used the combination of gas chromatograph-mass spectrometer for the analysis of peptides (78) with considerable success.

Open-Tubular Column Applications

One of the most desirable features of an open-tubular column separation is that the amount of carrier gas flowing from the column exit can be made small enough, without degrading the resolution of the column, to be handled by the high-vacuum pumps available in today's modern mass spectrometers. The entire output of a chromatograph using such columns can be directed into the mass spectrometer without the pressure in the ion source rising above the limit for satisfactory operation of the mass spectrometer. To be certain, the amount of sample entering the mass spectrometer is smaller with a capillary column gas chromatograph than with one using a packed column, but the mass spectrometer has ample sensitivity to detect these small peaks.

Banner, Elliott, and Kelly (3) and Elliott and Fitches (20) have described in detail a single-focusing mass spectrometer designed primarily for the chromatographic application and have reported some preliminary results with their instrument coupled to an open-tubular column. The major hindrance to their instrument is the lack of a dual ion source for qualitative and quantitative detection. Gohlke (25) has extended the application of TOF mass spectrometer chromatographic peak monitoring to include chromatographs employing open-tubular columns.

Buttery, et al., have used an open-tubular column chromatograph coupled to a time-of-flight mass spectrometer for the analysis of hop oils (12) and oxygenated constituents of hops (13). This technique was developed by Teranishi, et al. for the analysis of strawberry oils (68) and the volatile hydrocarbons from oranges (69). In the latter study (69) Teranishi and his coworkers take one-half to one-quarter of the effluent from the capillary column into the mass spectrometer without an intervening detector for the chromatograph. The mass spectrum is monitored on an oscilloscope and, in addition, m/e 15 is also continuously recorded to obtain a chromatogram record. When a compound enters the ion source from the chromatograph the complete mass spectrum is recorded from m/e 24 to m/e 200 in 6 sec. In a succeeding paper (70) this group at The Western Regional Research Laboratory reported the open-tubular column efficiencies in their instruments. They show that there is no significant loss in efficiency when one end of the column is operated at the reduced pressure of a mass spectrometer ion source. They also discuss the limitations of various stationary phases in combined chromatograph mass spectral analysis and compare the temperature range and extent of stationary phase bleed for the various columns. Teranishi, et al. (71) have reviewed their work in aroma research through 1963 and have reemphasized the advantages of using the combined gas chromatograph-mass spectrometer for analyses.

McFadden, et al. (39), have reported in greater detail on the instrumentation used by the excellent research team at The Western Research Regional Research Laboratory. These authors point out the simplicity with which an open-tubular chromatograph can be coupled to a mass spectrometer. McFadden and his coworkers reported the application of their technique for the analysis of several flavor extracts (40), fruit volatiles (41), and other complex mixtures (43). In these papers the authors also bring to light some limitations of the technique.

McFadden and Day (42) have reported a study on scan rate considerations in combined gas chromatography-mass spectrometry. They state that scan rate limits the precision and that at very fast scans the collected signal may have a 10% counting error; thus a scan

rate greater or a mass spectrometric resolution higher than essential should not be employed. They conclude that use of a fast-scan double-focusing mass spectrometer for this application is impractical because of the statistical limitations. This conclusion has been disputed by McMurray, Greene, and Lipsky (44), who describe an electrical scan system where a mass spectrum of a chromatographic effluent containing 1 μg of sample can be scanned at the rate of 8 seconds per mass decade with a mass spectrometric resolving power of 10,000 to 12,000. This feat was accomplished by recording the spectra on analog magnetic tape; their system is designed so the data are readily amenable to computer calculations.

Day and his collaborators have reported the identification of the neutral components of the aroma fraction of cheddar cheese (14) and blue cheese (15), using the techniques developed by the group at The Western Regional Research Laboratory. Ralls, et al. have also applied the same techniques to the analysis of the volatiles from a commercial pea blancher (50).

Olfky and Saalfeld (48) have reported the use of an open-tubular column chromatograph coupled to a mass spectrometer for the analysis of the complex organic contaminants found in the atmosphere of nuclear submarines. Saalfeld (57) has described the experimental arrangement of a gas chromatograph-mass spectrometer and discussed its usage for the analysis of complex mixtures. Ryhage, Wikstrom, and Waller (55) have discussed the use of an open-tubular column gas chromatograph coupled to a mass spectrometer by means of a molecular separator. The principal difference in the separator used for capillary columns and the one used previously for packed columns (53,54) is the number of stages employed. These authors reported that they can detect as little as 0.5 nanogram of a substance.

Struck and his coworkers (63,64) have employed support-coated open-tubular columns for the separation of complex mixtures prior to mass spectral identification. This type of column has also been used by Lipsky, McMurray, and their coworkers (37,44) at Yale and appears to be an excellent type of chromatograph column for combination with the mass spectrometer.

DIRECT INTRODUCTION OF A GAS CHROMATOGRAPH EFFLUENT INTO A DOUBLE-FOCUSING MASS SPECTROMETER

Packed Column Applications

Elliott and Fitches (20) have described a fast-scanning high-resolution mass spectrometer of the Nier-Roberts geometry. They point out that the major disadvantage of using a conventional high-speed light galvanometer to record a high-resolution mass spectrum is that a chart speed of 120 ips is required; thus, a single 5-second scan consumes 50 feet of chart paper! By using magnetic tape recording, Elliott and Fitches (20) have in ten seconds scanned a factor of 10 in m/e with a resolving power of 10,000 and a sensitivity sufficient to produce an identifiable mass spectrum from 1 μg of sample. They state that the data can then be recovered by either playing the tape back into a strip chart recorder at slow speeds and then making the mass measurements on the chart or, preferably, feeding the data into an automatic digitizer which converts the data to a form amenable to computer computation. They point out that approximately 10^{-7} g/sec of material is required now to use a double-focusing mass spectrometer as a monitor of a gas chromatograph, but the development of molecular separators to effectively enrich the sample concentration relative to the carrier gas should permit improved accuracy and greater sensitivity on a much smaller sample.

Stafford and Morgan (62) have discussed an all-glass heated inlet for a high-resolution mass spectrometer of the Mattauch-Herzog geometry which can be operated at 455°C and

temperature programmed. The authors state that the inlet is useful in the analysis of gas chromatographic fractions.

High-resolution mass spectrometry has been applied with a great deal of success for the analysis of gas chromatographic peaks by workers at the Massachusetts Institute of Technology. This team has reported using the combination to obtain high-resolution mass spectra of several organic compounds (7,76,77). Watson and Biemann (77) present arguments for using a Mattauch-Herzog high-resolution mass spectrometer employing a photoplate as the ion detector. While the authors have stated their case well, they have failed to point out any of the photoplate's faults–and there are many! This review is not the place for a discussion on the pros and cons of ion detection; suffice it to say that the photoplate is not very accurate for recording ion abundances. Beynon (6) has adequately discussed this point.

Open-Tubular Column Applications

Although tremendous advances in the art of rapid scanning a high-resolution mass spectrum have been made, it is still a very difficult task, and the copious amounts of data which are obtained from double-focusing mass spectrometers can be handled routinely only with computer techniques. Only a few laboratories have combined gas chromatographs which use open-tubular columns with a double-focusing mass spectrometer, because the narrow peak eluted from these columns accentuates the scanning problems present in the double-focusing mass spectrometer. However, there has recently become available a compromise between the packed column and the capillary column–the support-coated capillary column–in which the peaks are not as narrow, contain more sample, but retain the resolution observed with the regular capillary columns. McMurray, Greene, and Lipsky (44) have reported using an 8-second-per-mass-decade magnetic scan with a mass spectrometric resolution between 10,000 and 12,000 to monitor the fatty acid effluents emerging from a 50-foot, 0.02-inch-I.D., support-coated (Apiezon L) capillary column. The problem of rapidly scanning the mass spectrum and still retaining high resolution was discussed by Henneberg (30), who employed a Mattauch-Herzog-type mass spectrometer in his investigations. Although Henneberg's results are excellent, his technique is not applicable for the analysis of a 60-70 component mixture, especially when the adjacent peaks are eluted at very short intervals. Merritt and his coworkers (32,46) have reported the use of magnetic tape for the recording of mass spectral data and have shown their technique applicable to high-resolution mass spectrometry studies.

THE NAVY'S FUTURE IN GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS

As has been mentioned earlier, the combination of the techniques of gas chromatography and mass spectrometry is much more powerful than either technique alone. With this combination, not only will a much larger number of the atmospheric contaminants of nuclear submarines and spacecrafts be identifiable, but many materials will be able to be checked for outgassing properties to ascertain whether or not the materials will release any deleterious compounds into the atmosphere. In addition, the volatiles released from paints upon exposure to ultraviolet light and the rate at which they are produced could be investigated. In this field, the gas chromatograph-mass spectrometer combination will be particularly useful since the effect of oxygen on the degradation could be studied. The combination will be a tremendous aid to organic chemists for preparation studies as it will be possible to determine not only the purity of the final product but also the identity of the impurities. Compounds formed from competition reactions will also be readily identified with this instrument. The list of possible applications is endless. A judicious choice of a gas chromatographic column will, in theory, permit any mixture to be separated and identified regardless of its complexity.

In the future, it is expected that the output of the mass spectrometer will be recorded on magnetic tape and then a computer will be used for automatic data processing. Such data-handling procedures will enable laboratory personnel to successfully analyze the atmospheres and materials problems for the entire submarine fleet with ease and to increase the data output of the gas chromatograph-mass spectrometer combination by at least 300 percent. The use of tape recording is less expensive than the light galvanometer recording because the tape can be reused after the data has been interpreted.

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13. ABSTRACT

A literature survey of the gas chromatographic-mass spectrometric methods of analysis has been made which provides a comprehensive review of the past and present research efforts on the identification of gas chromatograph effluents with a mass spectrometer. The various types of instrumentation employed are described briefly, and critical assessments are made of the various techniques for tandem operation of a gas chromatograph and a mass spectrometer.

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