

alyzed, only five compounds appeared: carbon dioxide, nitrogen, sulfur dioxide, argon, and oxygen. Where oxygen was reported, the amount was so small as to be of doubtful significance. Carbon monoxide and water might be expected to occur in glass bubbles; however, neither was positively identified. Because carbon monoxide is partially masked by the presence of nitrogen and carbon dioxide, small amounts might escape detection. Adsorption effects might alter the apparent concentration of water, but would not be likely to remove completely any appreciable amount.

Quantitative. The bubbles analyzed ranged from 0.015 to 1.2 $\mu\text{l.}$ -atm. (at 25° C.) total gas content. Because the gas pressure found in the bubbles is about 0.2 to 0.3 atm. (at 25° C.), a spherical bubble 1 mm. in diameter with a volume of 0.5 $\mu\text{l.}$ would contain about 0.1 $\mu\text{l.}$ -atm. of gas. The composition of this gas can be determined within 5% of the total sample. With smaller bubbles, the error would be proportionately greater. The smallest detectable amount of a gas depends on the particular gas; in the case of sulfur dioxide, 0.001 $\mu\text{l.}$ -atm. (25° C.) can

be detected readily. This amounts to less than 10^{-10} gram mole.

The principal limitation on the minimum size of bubbles that can be accurately analyzed is the blank: mainly air which desorbs from the walls of the bubble-breaker chamber even when no bubble has been broken. The quantity of a given component is not significant unless it is at least equal to the corresponding blank. Therefore, the blank (expressed in microliter-atmosphere at 25° C.) is numerically equal to the minimum detectable amount and to the minimum significant increment of the same component.

The figures listed in Table II represent a conservative estimate of the uncertainty due to the blank, which dominates when the amount of gas is small. When the amount of a given component is much larger (>50 times) than the blank, the accuracy is limited primarily by the instrumental reproducibility which is 1 or 2% of the amount present.

Expression of the analyses in microliter-atmosphere is subject to a possible consistent error, because it involves the absolute calibration of the micro-manometer used to measure the pressure of pure calibrating gases, and the

Table II. Uncertainty Due to Blank and Minimum Detectable Amounts

Component	Typical Blank, $\mu\text{l.}$ -atm.	Typical Blank, as % of Entire Gas Sample	
		Bubble content, 0.1 $\mu\text{l.}$ -atm.	Bubble content, 1.0 $\mu\text{l.}$ -atm.
N ₂	0.01	10	1.0
O ₂	0.005	5	0.5
SO ₂	0.001	1	0.1
CO ₂	0.001	1	0.1
Ar	0.001	1	0.1

calibration of the internal volume of the bubble-breaking manifold. This error in the absolute quantities probably does not exceed 10%, and does not affect the relative amounts or volume percentages.

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Time-of-Flight Mass Spectrometry and Gas-Liquid Partition Chromatography

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► The direct combination of a time-of-flight mass spectrometer, which scans a mass range from $m/e = 1$ to $m/e = 6000$ at the rate of 2000 times per second, with a gas-liquid partition chromatographic apparatus results in an instrument capable of rapidly and completely characterizing organic chemical mixtures boiling below 350° C.

MASS SPECTROMETRY, long used in the petroleum and more recently in the chemical industry (11, 12, 20), is one of the finest single tools available for the analysis of volatile chemical mixtures. It is a rapid, precise method, uses sample sizes on the order of a few milligrams, and is often capable of identifying single components even if previously obtained standard mass spectra are not available for comparison purposes.

Because mass spectra result from the rupture of the chemical bonds in a

molecule, the presence of various functional groups in the molecule usually will produce predictably distinctive mass spectra. Moreover, differences between the mass spectra of various types of chemical compounds are of such a magnitude that unknown spectra can be identified from correlations of the known behavior of similar compounds. These correlations of mass spectra, which are based on empirical evidence, have been made for the substituted aromatic hydrocarbons (14), halogenated compounds (10), alcohols (4), acids (13), esters (13), aldehydes (5), and a number of other compound types [for a complete list see (12)]. They are very valuable in the identification and analysis of unknown components for which detailed reference spectra are unavailable.

The interpretation and calculations involved in the analysis of mixtures containing more than 10 to 15 components are either rather laborious and time-consuming or impossible by mass

spectrometry, unless high speed computers are available to perform the necessary mathematical operations.

This disadvantage of the use of mass spectrometry for the analysis of complex mixtures is not shared by gas-liquid partition chromatography. In addition to the usual ability of gas-liquid partition chromatography to separate complex mixtures completely into their component parts, it also is a rapid, precise method, and the instrumentation cost is low (usually between \$1500 and \$4000 per complete installation).

Several books discuss the theory and practices of gas-liquid partition chromatography (2, 8, 16).

The applications to which this technique has been applied are rather diverse—analysis of petroleum hydrocarbons (3, 9, 19), determination of allyl sulfides in onion juice (1), fluorocarbon separations (15, 13), and rare gas separations (6), to mention only a few.

The major deterrent to the use of gas-

liquid partition chromatography as an aid in the analysis of nonroutine samples is the fact that the separated components cannot be absolutely identified from the chromatogram itself. There are two common means of overcoming this difficulty: to compare the retention volume of the unknown component with that of known compounds on two or more chromatographic columns containing different liquid substrates (17), or to collect the component as it leaves the column and subsequently identify the collected material by another method.

If the first method is to be effective, one must have data available regarding the behavior of the members of various homologous series on columns of different liquid substrates, at various operating temperatures. The experience of this laboratory has been that for identification of the components present in nonroutine samples, the data which must be obtained to use the comparative retention volume system of identification are so extensive as essentially to preclude use of this method.

The techniques of infrared spectrometry and mass spectrometry have been widely used for the second identification procedure, but several difficulties are attendant on these or any other subsequently applied identification procedures. The devices generally used for the collection of the chromatographic samples for infrared use involve bubbling the effluent gas from the column through a suitable solvent, or passing the effluent gas through a trap cooled in liquid air, with subsequent sample transfer to an infrared microcell for identification. These techniques always demand constant supervision of the fraction collection device and often involve the use of toxic, flammable solvents or fragile cold traps of diminutive size.

The chromatographic samples for mass spectrometry are invariably collected in liquid air-cooled cold traps. The use of cold traps for sample collection involves a high degree of skill, if samples free of atmospheric contaminants and previously eluted components from the chromatographic column are desired. It is almost always desirable to use the samples as soon after collection as possible, to avoid the difficulties encountered in the storage of minute samples for any length of time.

The greatest disadvantage to fraction collection is the time required to identify the collected fractions subsequently, particularly when mass spectrometers of conventional design are used, as it requires 20 to 40 minutes to obtain the spectrum and prepare the instrument for the next sample. This would mean that if one had a chromatogram containing 10 peaks whose identity was desired, it would require 3 to 8 hours of mass spectrometer instrument

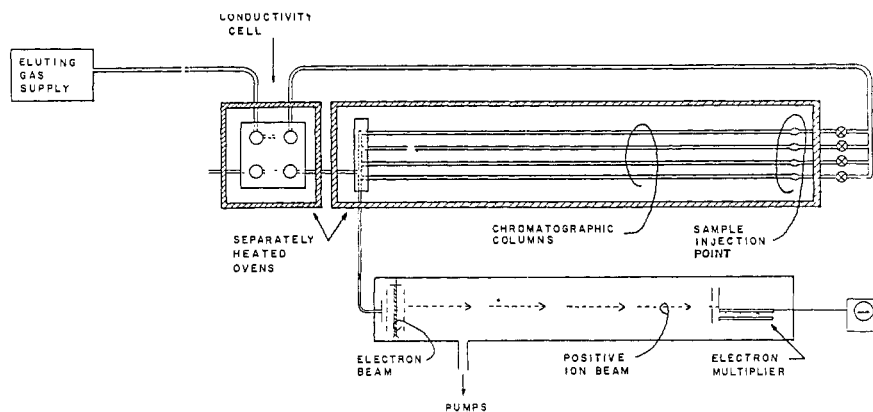


Figure 1. Schematic view of method of attachment of time-of-flight mass spectrometer to gas chromatographic apparatus

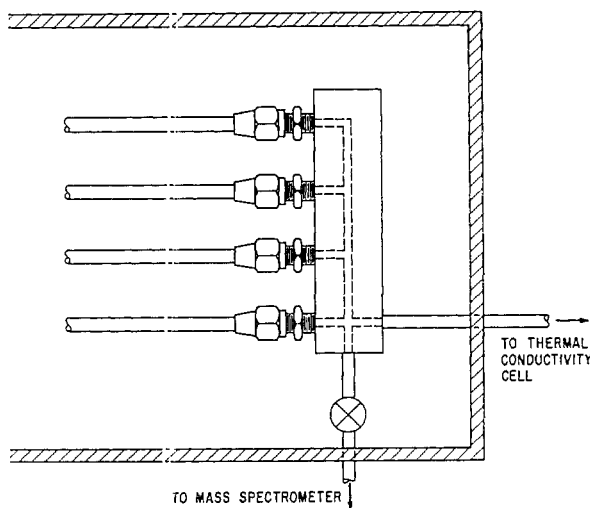


Figure 2. Chromatographic column recombination block

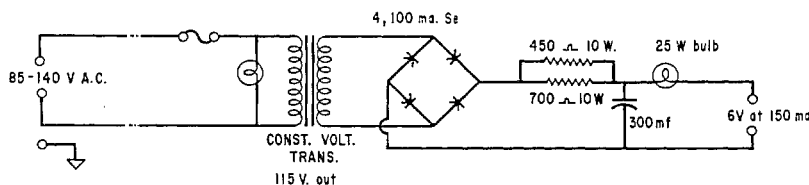


Figure 3. Constant current power supply for thermal conductivity cell

time to obtain the mass spectra of the fractions, in addition to the time required to collect them.

Infrared spectrometry for the identification is not significantly superior to conventional mass spectrometry. The time required to scan the infrared spectrum is somewhat less (12 to 15 minutes) than for mass spectrometry, but the small size of the chromatographic fractions usually requires the use of a liquid microcell (volume less than 1 drop) as a sample container. The proper use of a microcell makes the adjustment of certain instrument operating conditions (amplifier gain, slit width) desirable—and these adjustments often cannot be reliably performed by the personnel operating the instrument. A recent promising de-

velopment for component identification by infrared involves collection of the gaseous samples, directly in micro gas absorption cells of the multiple traversal type (21).

Application of infrared spectrometry for direct qualitative analysis of the effluent stream, however, suffers the disadvantages that the absorption spectra of heated gaseous samples are less sharp than those of solutions at room temperature and the very fast scanning required results in loss of detail.

The problem of chromatogram component identity was solved with the recent marketing of a mass spectrometer manufactured by the Bendix Aviation Corp., which is capable of directly and continuously monitoring the effluent stream from the chromatographic

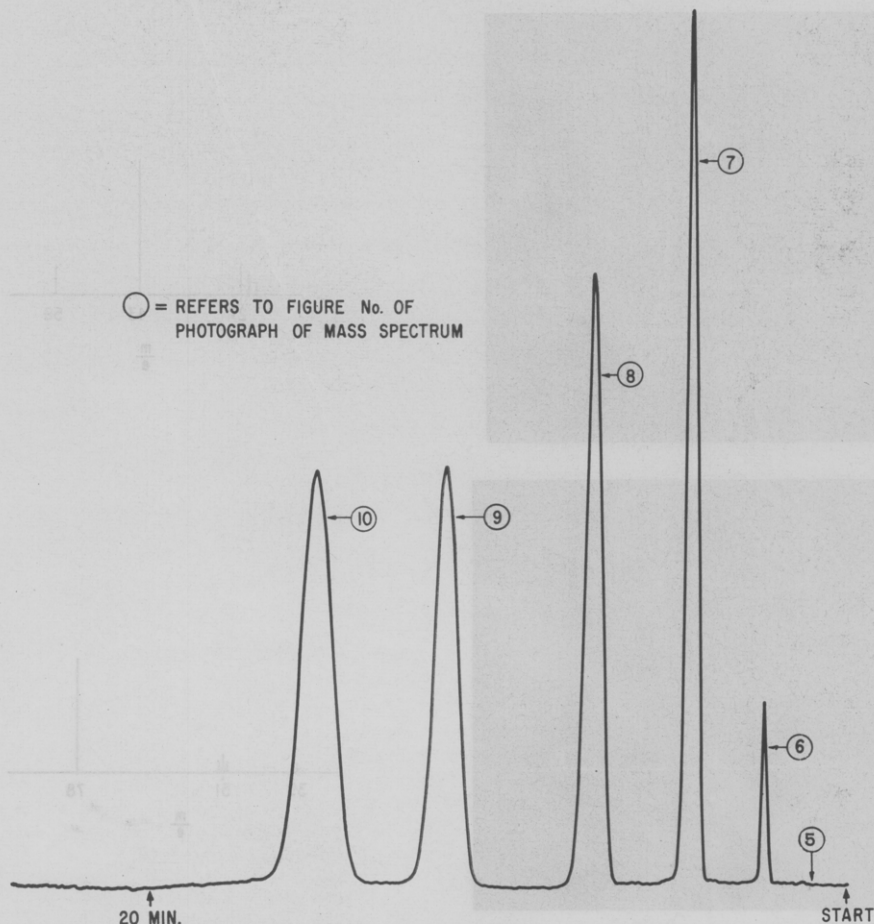


Figure 4. Sample chromatogram of acetone, benzene, toluene, ethylbenzene, and styrene

The sample was chromatographed on a 10 foot \times $\frac{1}{4}$ inch column of Tide detergent at a temperature of 138° C. with a helium inlet pressure of 10 p.s.i.g.

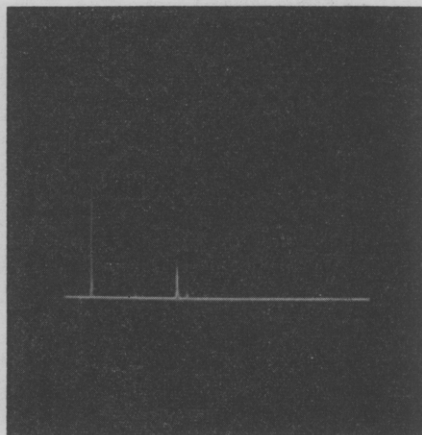


Figure 5. The mass spectrum of helium with a small amount of nitrogen (m/e 28) and oxygen (m/e 32) impurity present

column. The mass spectrum of the effluent vapor is presented on an oscilloscope 2000 times per second, thus completely eliminating the need for collection, or any other manipulation, of the components represented by the peaks on a chromatogram.

EXPERIMENTAL APPARATUS

Gas-Liquid Partition Chromatog-

raphy. The apparatus consists of a gas-liquid partition chromatography apparatus which has a time-of-flight mass spectrometer connected to the system at a point between the column exit and the thermal conductivity cell, as shown schematically in Figure 1.

The gas chromatography portion of the instrument is of essentially conventional design, except that four chromatographic columns are enclosed

in an insulated oven instead of the more widely used single column. The use of four columns connected in parallel, each complete with sample injection port, permits the separation of samples requiring different chromatographic columns without requiring the time-consuming act of physically changing columns every time this is desired. The exit ends of the four columns terminate in a block shown in detail in Figure 2. From this block a single line leads to the mass spectrometer and another single line leads to the separately enclosed Gow-Mac thermal conductivity cell used as the detector. The use of separately enclosed and heated column and conductivity cell chambers permits operation of the conductivity cell at a temperature independent of the column temperature. The temperature of the thermal conductivity cell is usually kept somewhat higher than the temperature of the columns, to minimize the tendency for high boiling components of a sample to condense in the cell.

The design details of gas chromatography equipment appear to be somewhat a matter of personal preference, and only the barest description is given here.

The chromatographic oven is a double-walled 17 \times 17 \times 6 inch box built of magnesium, with the 1-inch interstice between the double walls packed with glass wool for insulating purposes. A 600-watt cartridge-type heater is sufficient to raise the temperature of the oven interior to approximately 200° C. Because accurate reproduction of component residence time was not necessary for the application, no attempt was made to regulate the temperature of the oven carefully. In use, the 600-watt heater is connected to a variable autotransformer, which is supplied with a constant voltage input. The temperature of the oven interior is therefore a balance between the heat input from the heater and the radiated heat loss of the oven exterior and, in practice, may vary as much as $\pm 5^\circ$ C. from a constant value.

One arm of each of four copper tubing T fittings extends through the oven wall, is sealed with a silicone rubber disk, and is the point at which samples are introduced via a hypodermic syringe. Each column is equipped with an eluting gas shutoff valve mounted outside the oven (Figure 1).

The oven enclosing the thermal conductivity cell is identical to the column oven, except for somewhat smaller dimensions and a 300-watt heater. The thermal conductivity cell is mounted with the filaments vertical, the 300-watt heater is strapped directly to the cell block, and the temperature of the cell is measured by an iron-constantan couple inserted into a hole drilled into the cell block. The thermal conductivity cell used is a Gow-Mac Instrument Co. product (TE-III geometry, stainless steel block, 9225 filaments). The thermal conductivity cell is wired as a conventional Wheatstone

Figure 6. Mass spectrum of acetone (first chromatographic peak)

bridge and is supplied by a 150-ma. constant current power supply shown schematically in Figure 3.

Drifts in cell balance as observed by recorder base line due to temperature variations are on the order of 0.05 to 0.10 mv. over a 24-hour period at 200° C. Again, no attempt at precise thermostatic regulation was made.

Mass Spectrometry. The spectrometer used to monitor the effluent vapor of the chromatographic column is a time-of-flight mass spectrometer manufactured by the Bendix Aviation Corp., 3130 Wasson Road, Cincinnati, Ohio, Type 12-100. The theory of operation of time-of-flight mass spectrometry has been adequately described (22). The instrument was modified by replacing the supplied oil diffusion pump and water cooled baffle with a mercury diffusion pump, a Freon 22 refrigerated baffle (about -20° C. baffle interior temperature), and a liquid air trap. These modifications reduced the instrument background spectrum to an unobjectionable level for even the most critical work. The following features make this instrument admirably suited to a gas chromatographic application.

High rate of scan—2000 (or 10,000 to 20,000, optionally) new complete mass spectra per second are produced.

Resolution of adjacent mass units is complete to about mass 200 and adjacent mass resolution is usable to about mass 450.

The sensitivity of the mass spectrometer is such that spectra of perfect quality are presented if the maximum concentration of the chromatographic peak exceeds 0.2 mv., with the thermal conductivity detector and power supply described. The absolute sensitivity of the instrument is such that a partial pressure of 1×10^{-8} mm. of mercury of argon in the ion source will produce one recorded argon ion per instrument cycle (operating at 10,000 cycles per second) (7).

The mass spectra are presented on a Tektronix Type 541 oscilloscope equipped with a Tektronix Type 53154K plug-in preamplifier. The mass range presented on the oscilloscope screen is easily and continuously variable from a single mass unit to 6000 mass units.

EXPERIMENTAL

The mass spectra produced by the

Figure 9. Mass spectrum of ethylbenzene (fourth chromatographic peak)

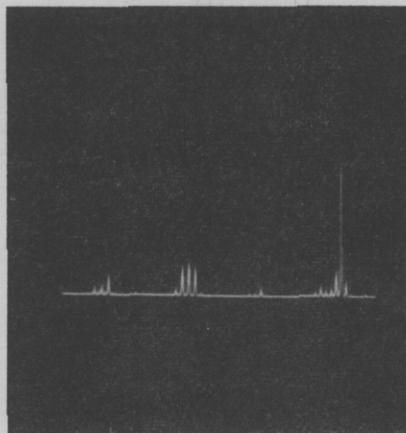
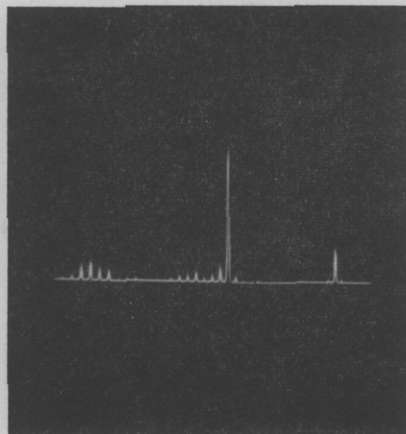


Figure 7. Mass spectrum of benzene (second chromatographic peak)

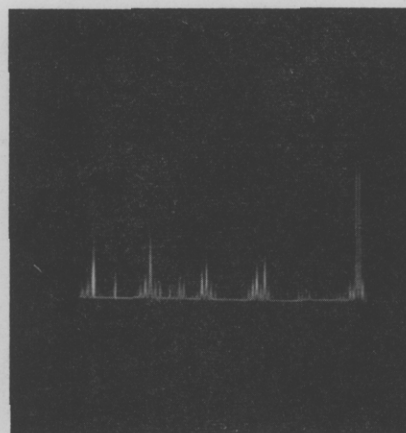
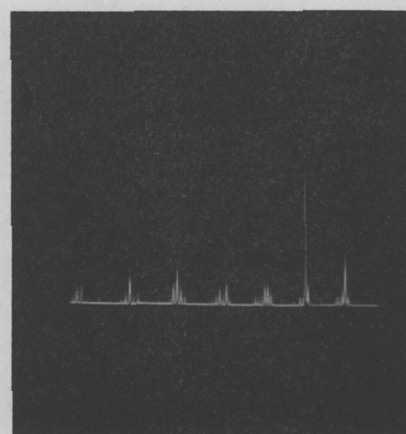


Figure 8. Mass spectrum of toluene (third chromatographic peak)



time-of-flight mass spectrometer can be made directly comparable to spectra produced by mass spectrometers of the conventional electrostatic or electromagnetic scanning design.

Thus, existing files of mass spectra can be directly compared to the time-of-flight spectra for identification purposes.

Table I compares portions of the mass spectrum of vinyl chloride as obtained on the time-of-flight mass spectrometer and on a Consolidated Electrodynamics Corp. 21-103 mass spectrometer. The difference in the relative intensity of the peaks in the time-of-flight spectra is due to the fact that it is difficult to measure the height of the ion peaks precisely in the time-of-flight mass spectrometer and is of no concern when the spectra are used solely for identification purposes.

If necessary, however, peak heights

can be accurately determined by the use of pulse-counting equipment (at a scanning rate of 10,000 spectra per second), but this has been found unnecessary for the gas chromatography applications of the instrument in this laboratory. An analog output system has become available recently, which provides meter indications and recordings of several peaks simultaneously, either directly or as ratios of each other, plus the ability to record spectra in the conventional manner on strip charts (7).

As it would serve no useful purpose to present a chromatogram containing 30 peaks and the corresponding photographs of the mass spectra the chromatogram of a simple synthetic mixture is used to illustrate the manner in which the combined gas-liquid chromatography-mass spectrometry technique is used.

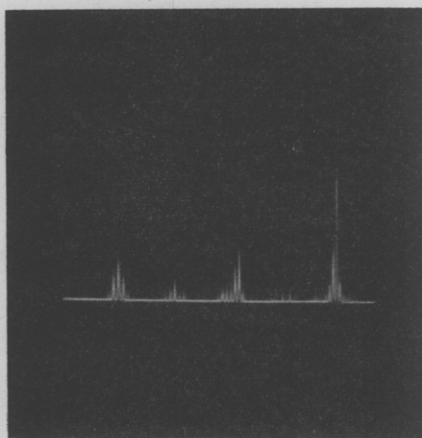


Figure 10. Mass spectrum of styrene (fifth chromatographic peak)

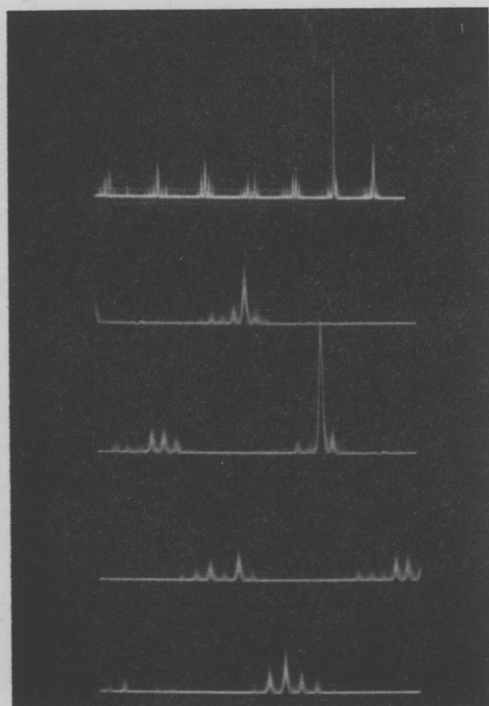


Figure 11. Mass spectrum of ethylbenzene

The top trace is the complete spectrum and the four lower traces are expanded portions of the top trace. The tap switch used for the lower traces has an additional seven mass ranges not used here

Table I. Relative Ion Intensity

m/e	CEC No. 21-103	Bendix TOF No. 12-100
12	4.66	5
25	17.4	18
26	43.3	42
27	132	140
35	8.97	10
47	4.74	5
48	2.06	2
59	1.89	2
60	6.26	6
61	9.00	9
62	100	100
63	4.82	5
64	31.61	32
65	0.67	...

The chromatogram of a mixture of acetone, benzene, toluene, ethylbenzene, and styrene is shown in Figure 4. Photographs of the mass spectrum appearing on the oscilloscope screen at the points indicated are shown in Figures 5 to 10.

The lag between the appearance of the peak on the chromatographic recorder and its mass spectrum on the oscilloscope screen is on the order of 1 second. The height of ion peaks in the mass spectrum rise and fall in intensity at the same rate as the component peak rises and falls in concentration, as indicated by the conductivity cell recorder. Single chromatographic peaks containing two or three components can usually be successfully resolved by a careful examination of several mass spectra obtained at various times during the development of the chromatographic peak.

In the photograph (Figure 11) of the complete ethylbenzene mass spectrum (trace 1) the ion peaks are so close together that accurate mass determination can be somewhat doubtful. The use of an auxiliary 10-position mass range switch makes it possible to present magnified overlapping portions of the complete spectrum as separate exposures in the same photograph. The ion mass position in traces 2, 3, and 4 is easily determined by placing a pre-calibrated mass ruler upon the photographed trace. The four traces comprising Figure 11 were photographed in a total of 3 seconds.

The tap switch has 10 positions, giving precisely controlled mass ranges from mass 10 to mass 300, in increments comprising about 36 mass units. About mass 300, the mass spectrometer controls are used manually in the normal operating manner.

Any portion of the mass spectrum may be viewed at will, the adjustments involved are extremely simple to perform, and the results of adjustment may be continuously viewed on the oscilloscope screen.

The adjacent mass resolution of the time-of-flight instrument is sufficient for any conceivable gas-chromatographic applications. Figure 12 shows the appearance of the spectrum of mercury. The resolution between adjacent masses is, for all practical purposes, complete. Beyond mass 200, adjacent mass resolution gradually is lost, until in the mass range of 600 to 700 no adjacent mass resolution is obtained (Figure 13). Figure 13 is a portion of the mass spectrum of a perfluorinated kerosine showing the ion peaks from this compound at masses 617, 631, and 643. No trace of resolution between these and the corresponding carbon-13-containing fragments at 618, 632, and 644 is observed.

A very finely controllable needle valve placed in the line between the gas-liquid partition chromatography apparatus and the mass spectrometer acts as the mass spectrometer leak and allows the amount of sample being drawn into the mass spectrometer to be varied at will. During normal operation the pressure in the gas-liquid partition chromatography apparatus is 760 mm. of mercury and the pressure in the mass spectrometer ion source is adjusted to about 1×10^{-4} mm. of mercury by means of the needle valve. Under these conditions, the mass spectrometer is consuming the effluent vapor from the chromatographic column at a rate of about 0.003 cc. per second—before this vapor reaches the conductivity cell.

With a flow rate of 60 cc. per second this loss is equivalent to 0.3% of the stream, which is not considered serious enough to affect the chromatogram to a point where quantitative determinations

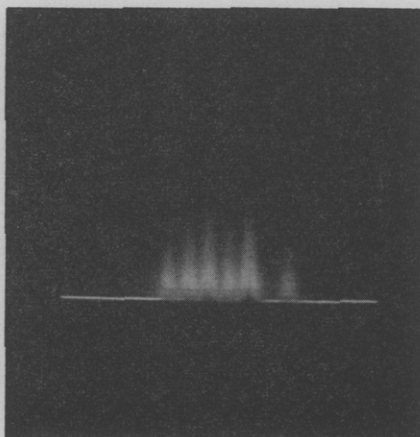


Figure 12. Mass spectrum of mercury

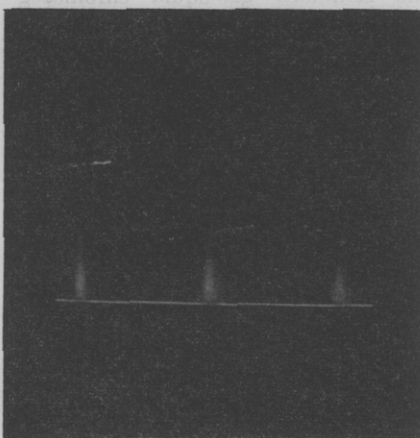
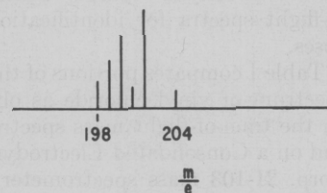
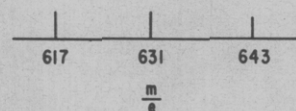


Figure 13. Portion of mass spectrum of a perfluorinated kerosine, illustrating appearance of ion peaks in the m/e 600 region



of the components present based on the area of the chromatogram peak become inaccurate.

Any quantitative determination of the components is therefore performed in the usual manner—integration of the peak area and adjustment of this area by predetermined constants to relate the area per cent directly to mole or weight per cent.

SUMMARY

The technique of combined mass spectrometry and gas-liquid partition chromatography has been used in this laboratory for the characterization of samples whose great complexity makes normal analytical procedures prohibitive from the standpoint of time and analytical cost, and has resulted in an analytical tool of near ultimate power when applied to chemical mixtures boiling below 350°C . to 760 mm.

ACKNOWLEDGMENT

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Identification of Pigments in Paint Products by Infrared Spectroscopy

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► Infrared spectroscopy is a useful tool for the qualitative identification of pigments in paint products of unknown or questionable formulation. Positive identification can be made of most of the inorganic pigments in common use, as well as of organic pigments. A generalized procedure for isolation of the pigment from the vehicle is given. The pigment can usually be classified as inorganic and/or organic by the number and shape of the absorption bands observed in its infrared spectrum. More positive identification is then made by consulting a compilation of reference spectra obtained on known materials. The reference spectra of 21 inorganic pigments and five typical organic pigments are presented.

A TYPICAL PAINT PRODUCT is formulated by dissolving one or more synthetic and/or natural resins, along with other minor ingredients, in an organic solvent mixture and dispersing therein one or more pigments. Modern paint formulators have at their disposal a great variety of pigments, including both inorganic and organic materials. Several different pigments are often used in a formulation to achieve the desired color effects and other properties. Because of the inherent complexity of these formulations, the analytical identification of all components present by wet chemical procedures can be a time-consuming and difficult undertaking.

The literature contains no extensive description of the application of infrared spectroscopy to the analysis of such pigment systems. Kendall (5)

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has published partial spectra of several polymorphic forms of crystals of para red, copper phthalocyanine, and titanium dioxide. Tyler and Ehrhardt (8) presented the spectra of benzidine yellow and copper phthalocyanine in connection with the spectra of evaporated films.

Only a few authors have treated the infrared spectra of inorganic materials extensively. Miller and Wilkins (6) presented a useful compilation of spectra of 159 inorganic compounds found in a chemical laboratory. Other work has dealt with the spectra of minerals, rocks, clays, and related inorganic compounds (2, 4). More recently, Tai and Underwood (7) described a quan-

titative infrared method for the determination of inorganic sulfates.

Chemical methods of pigment analysis, including methods of separating pigment from vehicle, have been recently outlined by Hanson (1).

EXPERIMENTAL

Generalized Procedure. To prepare the sample, the pigment is first separated from the paint product by high speed centrifugation. This is best accomplished with a supercentrifuge capable of at least 40,000 r.p.m. The separated pigment is isolated and washed with a suitable solvent to remove any traces of adhering resin and any other vehicle components.

Figure 1. Titanium dioxide, TiO₂

Figure 2. Calcium sulfate (hydrous), CaSO₄·xH₂O

Figure 3. Diatomaceous earth (amorphous silica) SiO₂

