Glass aerosols have excellent internal pressure strength if properly designed (over 600 lb. per sq. in.) but should always be plastic coated for safety. The plastic coating is very important in restraining the fragments if the container is broken. We also believe that the cold filling method is to be preferred in loading aerosols unless adequate purging is carried out with the pressure filling technique to remove entrapped air. Entrapped air is undesirable as it can increase the internal pressure considerably.

In conclusion I would say that fundamental research in physics and chemistry and progress in engineering and design are contributing new ideas to the glass industry at a greater rate than ever before.

Glass may be one of man's oldest structural materials but it is only now reaching a vigorous youth in research and development.

GAS CHROMATOGRAPHIC ANALYSIS OF AEROSOL PRODUCTS*

By M. J. Root and M. J. Maury

G. Barr & Company, Chicago 9, Ill.

Analyzing the volatile components of an *aerosol* product by conventional analytical means is extremely difficult and time consuming. We may determine the pressure or the specific gravity and arrive at a very crude analysis of the propellents present. A 1 per cent change in the composition of a mixture of equal parts of Freon® 12 (dichlorodifluoromethane) and Freon® 114 (tetrafluorodichloroethane) produces a pressure change of only $^3/_4$ lb. per square inch and a specific gravity change of 0.0015. Measuring these physical properties to within such increments is not readily accomplished. Fluorinated hydrocarbon mixtures have been commonly analyzed by both mass spectrometry and infrared spectrophotometry, but the presence of other volatile components makes even these costly methods of little value.

Determining quantitatively, for example, ethyl alcohol in the presence of trichloromonofluoromethane and dichlorodifluoromethane is extremely difficult. Although ethyl alcohol and trichloromonofluoromethane, which boil at temperatures of 176°F. and 74.7°F., respectively, can be readily separated by fractional distillation, the presence of dichlorodifluoromethane which boils at −21.6°F., introduces a complication. Not only must the distillation flask, column and receiver be kept under a very high pressure

* Presented at the December 13, 1956, Meeting, New York City.

(80 lb./sq. in.) but the receiver, in order to condense the low boiling material, must be kept below −21.6°F. Furthermore, enough sample is required to fill not only the distillation flask but the fractionating column. The fractions must then be weighed and identified either by infrared or mass spectrometry. For one or another of these reasons this technique is not being carried out by many people.

The analysis of not only the liquid phase but also the gaseous phase would be desirable. Also, it would be of great value to be able to determine the amount of air present in both the gaseous and liquid phases. All of these previously difficult operations can now be carried out readily and easily with an instrument which will take a small gaseous or liquid sample, separate it into its components, measure the amount of each, complete the operation in a few minutes with an accuracy of 0.25 per cent, permit the recovery of each component, require no further attention once the sample is introduced and be ready to receive another sample without delay. Now that we have such an instrument, it is being called the greatest analytical advance in the last decade. The instrument that will do this is called a gas chromatograph and the process is called gas chromatography.

Chromatography had its beginning when the Russian botanist, Tswett (1), in 1906 observed that a mixture of colored solutes could be separated by selective adsorption during passage through a tube containing a suitable adsorbent. Since this discovery, many advances have been made, and this principle with modifications successfully applied to many fields requiring the separation and purification of complex organic and inorganic compounds. The prefix, chroma-, soon lost its significance since noncolored solutes were also handled by chromatography. Perhaps a more descriptive name for this technique would be vapor distillation or vapor fractionation.

The earliest application of the techniques of chromatography to the separation of gases and vapors by using stationary solid adsorbents and a moving gas (gas adsorption chromatography) dates from 1942 (2). Gas-liquid partition chromatography with which we are concerned here, was first used in 1951 by James and Martin (3) for the separation and analysis of mixtures of volatile fatty acids in tissues. The popularity of this method is testified to by the publication of more than 100 papers on the subject in the last four years and the appearance of eight commercially available chromatographs in fourteen models.

Gas-liquid partition chromatography is the separation and measurement of the components of a mixture by passing the mixture through a column in a stream of gas. The column, made of copper, glass or stainless steel tubing, is filled with an inert material called the support. The inert support, Celite, Dicalite or firebrick, is coated with a high boiling organic liquid such as hexadecane, di-*n*-butyl maleate or silicone. Because different equilibria exist between the mobile phase (carrier gas and sample) and

the stationary phase (liquid coated support), the components will separate according to their individual equilibrium constants.

More simply, each component in a mixture has its own affinity for a given column material. Therefore, it will cling to that material for a time characteristic to it alone and to no other component. The time during which it clings to the column before it is driven out by the carrier gas is called its retention time. With a given temperature, carrier gas, flow rate, column material and length, a component will always have the same retention time. Since each component has a unique "clingability" or retention coefficient for a given column material, it will stay a longer or shorter time in the column than other components in the mixture. Eventually, all components will be driven out by the carrier gas, one by one. And as each emerges, a sensing device, usually a thermal conductivity cell, measures its concentration. The result is a series of symmetrical peaks on a recorder. The position of the peak along the ordinate or time axis is the qualitative value—the time the component first appeared at the detector and how long it took to come out. The area of the peak, or its height, is a measure of its concentration in the mixture.

The support material should have the following characteristics:

(1) Inert chemically.
(2) Stable at column temperatures and drying temperatures.
(3) High surface area per unit volume.
(4) Low pressure drop.
(5) Hard and not break under compaction.

The resolution and pressure drop increases as the particle size decreases. A compromise, therefore, must be made between these two factors, and it is found that $-42 +60$ mesh material is optimum.

Requirements for the liquid partitioning agent are as follows:

(1) Boiling point at least 200°C., above the column temperature.
(2) Low vapor pressure.
(3) Should give adequate resolution of components.
(4) Low viscosity.

There are three factors that affect the resolving properties of the liquid partitioning material, polarity, hydrogen bonding and specific or chemical interactions. If the sample components have a low polarity, they will be more soluble in a partition liquid which has a low polarity. If the partition liquid has a low polarity and the sample components have a relatively high polarity, they will move through the column somewhat faster than might be expected on the basis of boiling points. Hexadecane gives good resolution for the chloromethanes, fluorochloromethanes and fluorochloroethanes. If the sample components have a low polarity and the partition liquid a high polarity, they will again move through the column faster than might be expected.

GAS-LIQUID PARTITION CHROMATOGRAPHIC INSTRUMENTS

Instrument	Manufacturer	Model No.
Fisher-Gulf Partitioner	Fisher Scientific Co.	...
Kromo-Tog, Fraction	Burrell Corporation	A-1 B-1
Vapor Fractometer	Perkin-Elmer	154B
Gas Chromatograph	Beckman Instruments, Inc.	...
Aerograph	Wilkins Instruments & Research, Inc.	Model A100
Hallikainen-Shell Chromatograph	Hallikainen Instruments	1111A
Reco Distillograph	Research Equipment Corp.	D-2000
Aromacon	Podbielniak	9400 9475

Figure 1.

Marked retardation of sample components can be made to occur when the strong forces of hydrogen bonding can be used. An example of this would be the use of an alcohol column to separate amines, or the use of an amine column to separate alcohols.

The forces of complex formation and interaction because of similarity of groups can also be brought into play.

Many liquid partitioning materials have been used and include such materials as dibutyl phthalate, silicones, tricresyl phosphate and di-*n*-butyl maleate. The ingenuity of chemists will be challenged for many years in the testing and use of new partitioning liquids.

Figure 1 lists the eight chromatographic instruments now available together with the manufacturers' names and model numbers. There are at least two more manufacturers now working on such instruments.

Figure 2 is a front view of the Gas Chromatograph made by the Beckman

Figure 2.

Division of Beckman Instruments, Inc. There are five dial controls on the instrument as follows:

(1) Coarse Current Control.
(2) Fine Current Control, 0–400 ma. With helium as the carrier gas, 250 ma. is normal. For trace analysis, 350 ma. With nitrogen or air as carrier gas, 150 ma. is normal.
(3) Zero Control. The zero control is used to balance the detector cell filament bridge, adjusting the Gas Chromatograph electrical circuit so that the recorder pen is at zero when carrier gas is flowing through the instrument.
(4) Sensitivity Control. This permits selection of a sensitivity value at which the output trace will be sufficiently high for good analysis and interpretation without exceeding the chart range at peak value. Position 1 gives the greatest sensitivity, then in decreasing order 2, 5, 10, 20, 50, 100 and 200. Positions can be changed during the operation of the instrument.
(5) Polarity Switch. This switch turns on the power to the instrument from the 6-volt storage battery and selects the polarity of the output of the recorder. With helium as the carrier gas, all samples except hydrogen will give relatively positive chart indications with the + position of the polarity switch. With nitrogen as the carrier, several gases, e.g., hydrogen and methane, require setting in the − position.
(6) Carrier Gas Flow. This control is a pressure regulating valve and a capillary orifice. The pressure is indicated on the gauge.
(7) Sample Inlet. The sample inlet on the right of the top of the instru-

Figure 3.

ment is capped by a standard, self-sealing rubber serum cap retained in place by a metal cover. The sample is injected by piercing the cap with the needle of a hypodermic syringe inserted through a hole in the cover, and emptying the syringe.

(8) Gas Sampling Valve. The gas sampling valve on the lower right side permits placing a gas filled loop into the valve system. This loop can be above or below atmospheric pressure. The pressure at which the sample is introduced is dependent on the temperature at which the column is operated and the vapor pressure of the least volatile component at that temperature.

The time required for the various components of a sample to pass through the chromatographic column to the detector cell, and the degree of resolution as indicated by the trace on the strip chart, vary with several factors:

(1) Nature of the sample.
(2) Partitioning liquid and the support material in the column.
(3) Length of the column.
(4) Flow rate of carrier gas.
(5) Operating temperature of instrument.

Figure 3 is a photograph with the top open. A 12-foot column coiled up is shown in place over the heater. Temperature inside the instrument is maintained at 40°C.

Figure 4 is a flow diagram of the instrument. All components are shown in their relative positions.

Figure 5 shows how the gas chromatograph works. When in operation, the gas chromatographic column becomes a two-phase system—a static phase and a moving phase. The static phase is either a solid (gas adsorp-

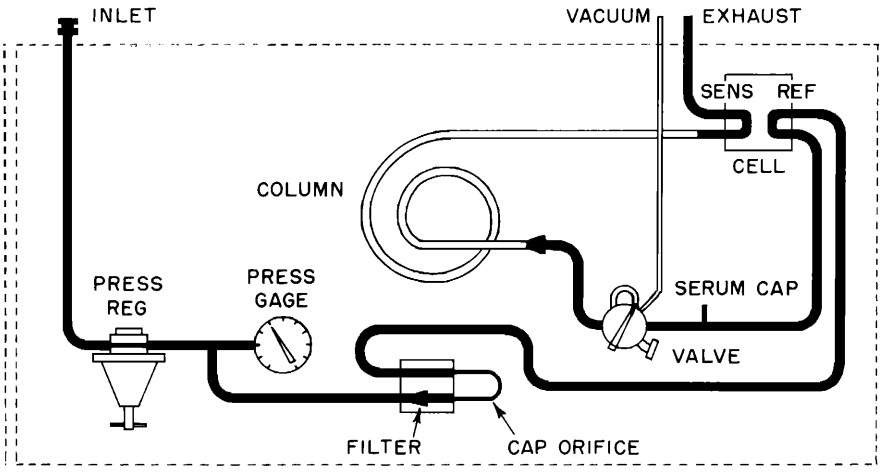

Figure 4.

tion chromatograph) or a solid coated with a high boiling organic liquid (gas-liquid partition chromatography). The moving phase is the carrier gas which is passed through the column continuously. When the sample is swept through the column, the individual components are partitioned between the solid phases and the gas phase. In favorable cases, each component is partitioned at a different ratio between the two phases. Let V_s represent the volume of the components in the solid phase, and V_g represent the volume of the components in the gas phase. Then, if a sample contains components A and B, and the ratios V_gA/V_sA to V_gB/V_sB are different, the components will be separated as they are moved through the column. If V_gA/V_sA is smaller than V_gB/V_sB, component B will be eluted from the column first. This is illustrated in the diagram (Fig. 5). The column has been divided into three sections corresponding to time T_0, T_1 and T_2. Initially, when the sample is injected at time T_0, the components are not separated in the column, but they are partitioned at different ratios between the two phases. The sections of the column corresponding to time T_1 and T_2 then illustrate how the components are separated as they move through the column.

The thermal conductivity cell is the most widely used detector in gas chromatography. This cell consists of a hot wire filament held in the center of a small tube or metal block through which the gas passes. The filament is heated with electric current and the temperature rises to some constant value which depends on the current applied, the resistance of the filament, the temperature of the cell block, the nature of the gas and, to some extent, on the flow rate of the gas. The change in resistance of a heated wire due to the heat lost from the wire through the surrounding atmosphere of the test gas is measured by means of a Wheatstone Bridge. A reference cell with the carrier gas passing through is balanced against a sensing cell containing the carrier gas and sample. The cells are balanced

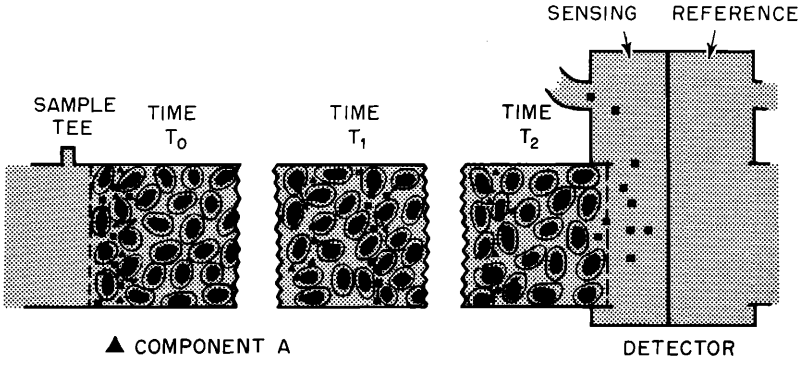

Figure 5.

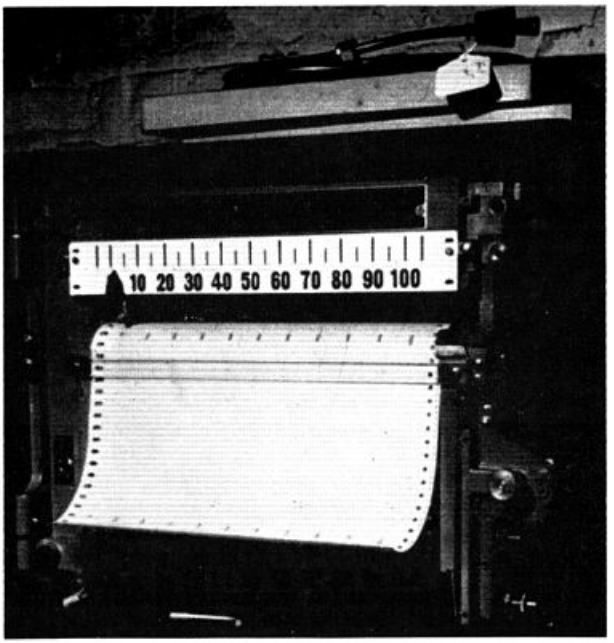

Figure 6.

with only carrier gas passing through both cells, and when the sample is injected an unbalance is caused which is measured by a recorder illustrated in Fig. 6. The unbalance is directly in proportion to the difference in thermal conductivity of the carrier gas and the sample components. Thermal conductivities of commonly used carrier gases are shown in Fig. 7. Although hydrogen has the highest thermal conductivity, because of its explosive quality it is not as commonly used as helium. Nitrogen can also be used but, because of its lower thermal conductivity, would not give as high a sensitivity as helium. Most of the vapors and gases which would be analyzed would have from $^1/_6$ to $^1/_{10}$ the thermal conductivity of the helium.

Quantitative Measurements

The quantity of vapor is directly related to the area under the peak. The area can be measured by means of a planimeter, by cutting out the peak shape on suitable paper and weighing, or for routine analysis, by coupling an automatic integrator to the detector output. Peak areas may

Thermal Conductivities of Carrier Gases at 0°C.

	k*
Hydrogen	15.9
Helium	13.9
Nitrogen	2.28

* k = kilo-erg cm.$^{-2}$ sec.$^{-1}$ (°C. cm.$^{-1}$)$^{-1}$

Figure 7.

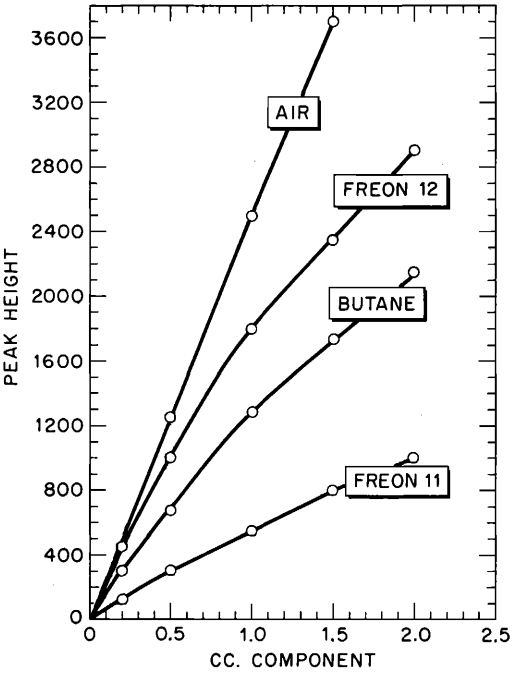

Figure 8.

also be measured by multiplying peak heights by half the base width. The areas of all the peaks present are added to give a total area which is normalized to 100 per cent. The ratios of individual areas to this total give percentage concentrations directly. It is also possible to calibrate a known sample weight against peak heights. Measurement of peak height affords a very simple and rapid method of quantitative analysis.

Because with the liquefied gases it is difficult to introduce an exactly determined liquid sample, internal standardization techniques are most practical. In the internal standard method, suitable volatile substances are made up in known proportions, and unknown peak areas or heights are referred to these peak areas as standard. Figure 8 shows such an internal standardization.

Figure 9 is a chromatogram of 2.0 cc. vaporized liquid sample of Freon® 12, Freon® 114 and Freon® 11. This illustration shows that these Freons® are completely resolved on the 12-foot di-*n*-butyl maleate column. The elution time of Freon® 11 is somewhat prolonged and, if only these three components were present, it might be worth while to shorten the column to reduce the analysis time. The analysis time could be reduced to about fifteen minutes if an 8-foot column were being used. This column should still provide adequate resolution between Freon® 12 and Freon® 114.

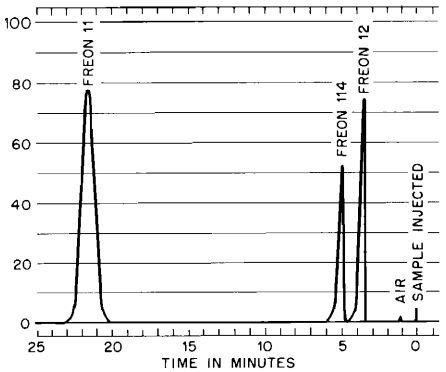

Figure 9.

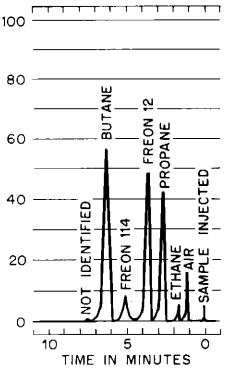

Figure 10.

	Volume Per Cent	Weight Per Cent
Air	0.12	0.025
Freon® 12	39.9	34.50
Freon® 114	26.6	32.60
Freon® 11	33.5	32.90

Figure 10 is a chromatogram of a 2.0 cc. vaporized liquid sample of propane, Freon® 12 solution. It also shows that traces of air, ethane, Freon® 114 and butane were present. The sample had been unintentionally contaminated with ethane, butane and Freon® 114, which were readily detected in the chromatograph by using maximum sensitivity.

	Volume Per Cent	Weight Per Cent
Air	0.33	0.15
Ethane	0.13	0.06
Propane	72.4	50.00
Freon® 12	25.0	47.75
Freon® 114	0.20	0.54
Butane	1.89	1.73
	99.95	100.23

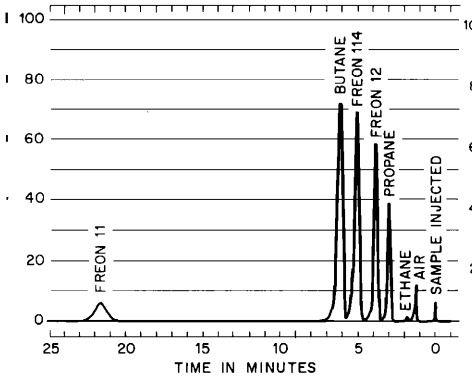

Figure 11.

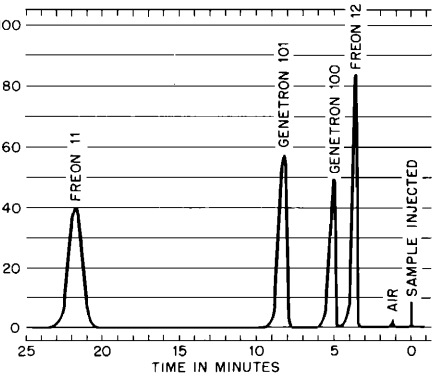

Figure 12.

Figure 11 is a chromatogram of a 2.0 cc. vaporized liquid sample of butane, Freon® 114 solution. Resolution was adequate between Freon® 114 (b.p. 38.4°F.) and butane (b.p. 21.2°F.) and, again, impurities due to contamination of the sample were detected by using maximum sensitivity. Traces of air, ethane, propane, Freon® 12 and Freon® 11 were found in this solution.

	Volume Per Cent	Weight Per Cent
Air	0.25	0.07
Ethane	Trace	Trace
Propane	0.98	0.42
Freon® 12	2.65	3.14
Freon® 114	37.8	63.00
Butane	57.8	32.78
Freon® 11	0.44	0.59

Figure 12 is a chromatogram of a 2.0 cc. vaporized liquid sample of Freon® 12 (dichlorodifluoromethane), Genetron® 100 (difluoroethane), Genetron® 101 (difluoromonochloroethane) and Freon® 11 (trichloromonofluoromethane) solution. These components were completely resolved. However, comparison of the elution time of Genetron® 100 with the elution time of Freon® 114 indicated that these two components would not be resolved with this column if both were present. Checks were made, and it was found that resolution of these two components could be obtained on a 12-foot hexadecane column. As can be seen in the following chart, the percentages found checked the percentages used to make up the mixture very closely.

	Weight Per Cent	Synthetic Mix, Weight Per Cent
Air	0.1	..
Freon® 12	24.5	25.0
Genetron® 100	25.3	25.0
Genetron® 101	25.7	25.0
Freon® 11	24.9	25.0
	100.5	

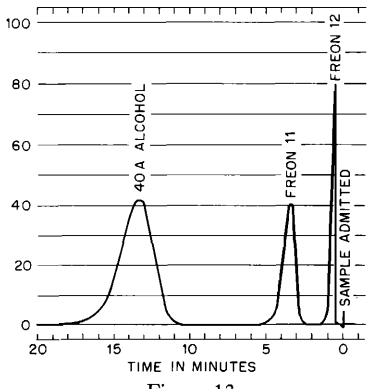

Figure 13.

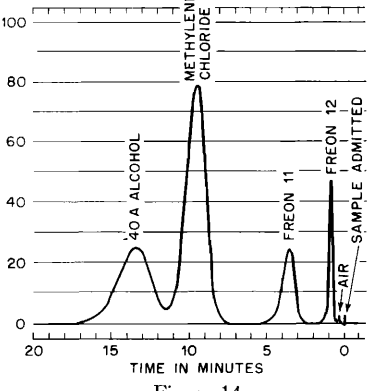

Figure 14.

THERMAL CONDUCTIVITIES OF ETHYL ALCOHOL AND DICHLORODIFLUOROMETHANE (TYPE 11 PROPELLENT) AT 40°C. (104°F.)

k = Btu./hr./sq. ft./°F./ft.

$$\frac{k_{\text{Ethyl Alcohol}}}{k_{\text{Dichlorodifluoromethane}}} = \frac{0.0089}{0.0064} = 1.39$$

Figure 15.

Figure 13 is a chromatogram of a 9.15 cc. sample, at 150 mm. Hg, of the vaporized liquid from a Freon® 11, Freon® 12, ethyl alcohol solution. Alcohol has a rather low vapor pressure at the temperature at which the chromatograph was being operated. In order to reduce the analysis time, the flow rate was increased and the column length shortened to 4 feet. Under these conditions, it was found that the standard columns being used did not permit adequate resolution between ethyl alcohol and methylene chloride. A number of new columns were investigated, and it was found that a 4-foot Span 85 column was best for this mixture. It will be noted that the percentages found by analysis as shown in the following chart did not check the percentage used to make up the synthetic mixture. An explanation of this will be given later in the discussion.

	Weight Per Cent	Synthetic Mix, Weight Per Cent
Air	0.046	..
Freon® 12	45.4	35.0
Freon® 11	38.4	35.0
Ethyl Alcohol	16.2	30.0

Figure 14 is a chromatogram of a 0.15 cc. sample at 150 mm. Hg of the vaporized liquid from a Freon® 11, Freon® 12, methylene chloride and ethyl alcohol solution. The resolution between methylene chloride and ethyl alcohol was not complete, but it was sufficient to permit the accurate analysis of these two components using the peak height method.

Here again it was found that the percentages found as shown on the chart above did not check the amounts put into the synthetic mix. From known samples of alcohol it was found that there was a factor of 1.4 of the amount known to the amount analyzed when peak areas were used. The factor

OPERATING PRESSURES, MM. HG, FOR ETHYL ALCOHOL AT 20°C. AND 40°C.

$$\frac{\text{Vapor Pressure Ethyl Alcohol}}{\text{Mole Fraction Ethyl Alcohol}} = \text{Maximum Total Pressure}$$

% Ethyl Alcohol	Mol Fraction	Maximum Total Pressure, Mm. Hg 20°C.	40°C.
30	0.55	80 mm.	246 mm.
25	0.44	100 mm.	308 mm.

V.P. Ethyl Alcohol, 20°C. . . . 43.9 mm.
V.P. Ethyl Alcohol, 40°C. . . . 135.3 mm.

Figure 16.

	Weight Per Cent	Synthetic Mix, Weight Per Cent
Air	0.2	..
Freon® 12	32.4	25.0
Freon® 11	31.4	25.0
Methylene Chloride	23.5	25.0
Ethyl Alcohol	12.4	25.0
	99.9	

1.4 can be explained on the basis of the thermal conductivities. The fluorinated chlorohydrocarbons have thermal conductivities which are nearly similar, whereas the ratio of the thermal conductivity of alcohol to that of Freon® 11 is shown in Fig. 15 to be 1.39. From this it follows that quantitative results as determined from the area of the curve will be low by a 1.39 factor.

A further reason for error in the analyses obtained from Figs. 13 and 14 was that the alcohol in the samples would condense at the sampling pres-

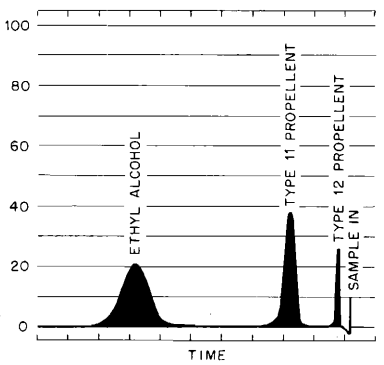

Figure 17.

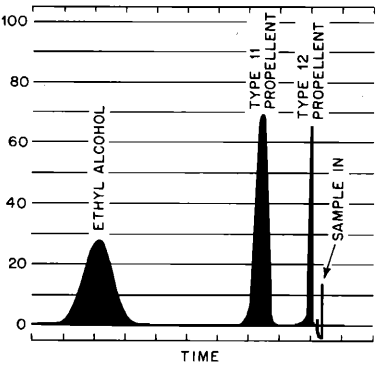

Figure 18.

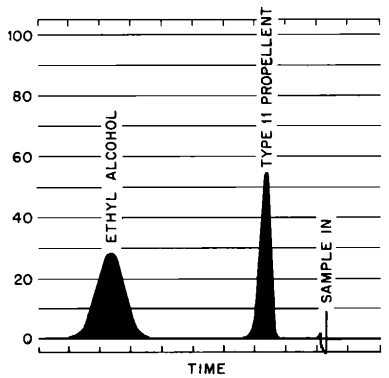

Figure 19.

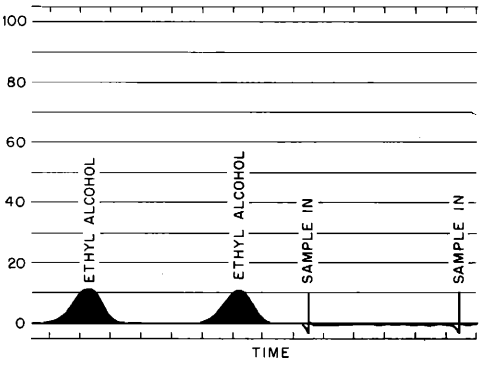

Figure 20.

sure of 150 mm. of Hg at room temperature and, therefore, not be entirely in the vapor state. From Fig. 16 we can see that the maximum pressure that can be used at 20°C. with a sample that contains 30 per cent ethyl alcohol is 80 mm. At a higher temperature (40°C.) or a lower percentage alcohol (25 per cent) the maximum pressure is higher. The use of greater pressure than the maximum shown in this figure results in the condensing of the ethyl alcohol in the gas sampling valve or the column and, hence low results are obtained.

Figure 17 shows a synthetic sample made with equal mole percentages of ethyl alcohol, Freon® 11 and Freon® 12. By using a vapor pressure of 45 mm. Hg and using the factor 1.4, the results indicate a variance between the amount present and the amount analyzed of only a few tenths of a per cent.

Figure 18 shows an analysis of an *aerosol* hair lacquer containing 24.5 per cent by weight of ethyl alcohol and propellents 11 and 12 in a two to one ratio. As can be seen on this figure the analysis checks the amount present very closely.

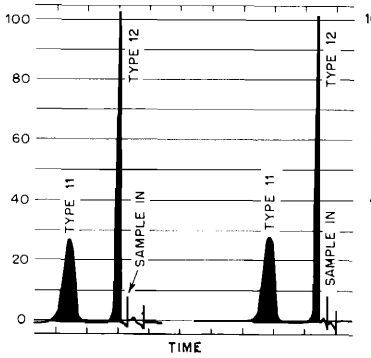

Figure 21.

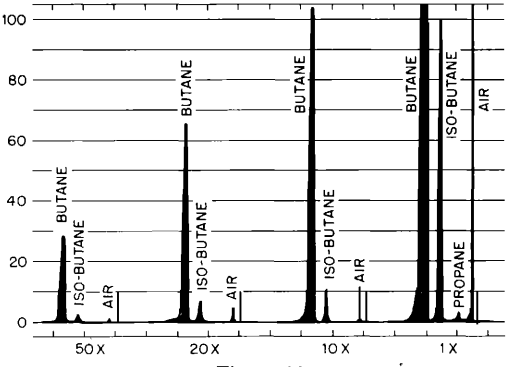

Figure 22.

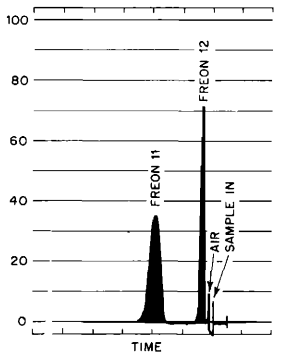

Figure 23.

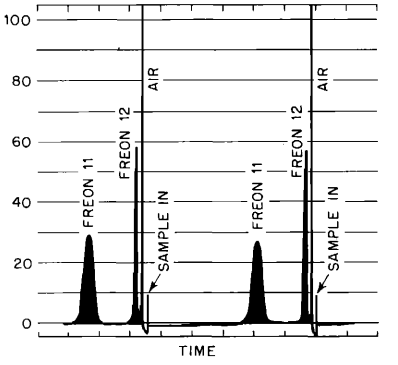

Figure 24.

Figure 19 shows the analysis of a mixture of equal molar parts of ethyl alcohol and Freon® 11. The agreement here again is very good between the analysis and the amount present. With due consideration of the maximum pressure at a given temperature to prevent condensation of the alcohol and the correction for thermal conductivity, very accurate analysis of the ethyl alcohol in propellent mixtures can be obtained.

Figure 20 shows the agreement that can be obtained between two samples of ethyl alcohol (1.55 cc.). This represents only 17 hundred thousandths of a gram, barely enough to be weighed. The pressure used in this case is 4.39 cm. Hg, which is the vapor pressure of the alcohol at 20°C.

Figure 21 shows the reproducibility obtainable with a mixture of 50 per cent propellent type 11 and 50 per cent type 12. Pressure used is 12 mm. Hg. Sample is 1.55 cc. of gas. Reproducibility is ± .3 per cent.

Figure 22 shows an analysis of the vapor phase of a commercial window spray. This analysis was carried out at four different sensitivities to determine at which sensitivity it would be desirable to run each constituent. At the highest sensitivity a trace of propane was detected. Air, butane and iso-butane were quantitatively determined in the vapor phase from this chromatogram.

Aerosol products can be filled by two methods, the cold fill and the pressure fill. With the pressure fill method the propellent is forced into the sealed can; therefore, the air that was in the can when it was sealed remains there. In the cold fill method the propellent is filled cold into the open can which is then sealed. The vaporizing of the propellent before the can is sealed displaces most of the air in the can.

Figure 23 shows a chromatogram of the vapor phase of a cold filled hair lacquer. As can be seen, the air is present to an extent of only 2.5 per cent by volume.

Figure 24 shows a chromatogram of the vapor phase of a pressure-filled hair lacquer. The percentage air in the vapor phase of this pressure filled container is 9.6 per cent by volume. In this manner the difference in air content of the vapor phase of a pressure-filled and a cold-filled *aerosol* product can be shown graphically.

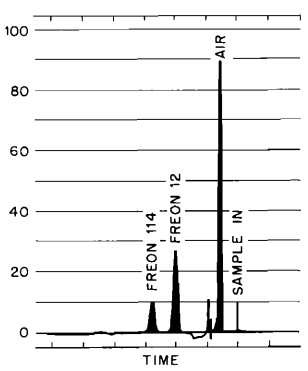

Figure 25.

Trace determination of volatile materials in the air is also possible with the gas chromatograph. Figure 25 gives the analysis of an air sample taken in a filling plant on a day when shaving cream was being pressure filled with a propellent mixture containing 60 per cent Freon® 12 and 40 per cent Freon® 114. The ratio of the gases

found in the air comes very close to the liquid ratio of the gases being used. From this analysis it was determined that the Freon® 12 concentration in the air was 1400 p.p.m. and the Freon® 114 concentration was 800 p.p.m.

From all of these illustrations it can be seen that gas chromatography is a powerful tool for the *aerosol* industry, not only to improve present products but also for the research and development of new products. Gas chromatography is a new analytical tool that could not have been made more useful had it been specifically devised for the *aerosol* industry.

Bibliography

(1) Tswett, M., *Ber. deut. botan. ges.*, **24**, 234, 316, 384 (1906).
(2) Hesse, G., and Tschachotin, B., "Adsorptions-analyse von Gasen und Dampfen (Adsorption Analysis of Gases and Vapors)," *Naturwissenschaften*, **30**, 387–392 (1942).
(3) James, A. T., and Martin, A. S. P., "Gas-Liquid Partition Chromatography: The Separation and Micro-estimation of Volatile Fatty Acids from Formic Acid to Dodecanoic Acid," *Biochem. J.*, **50**, 679–690 (1952).