

16% nitrogen from the value of 9.6% found on a Kjeldahl determination on the hydrolyzate. These final values are given in Table II with those determined in the same manner by adding valine rather than leucine. Table II includes the values reported by Greenberg (6) for the composition of gelatin; they are in good agreement with the duplicates reported here.

Gas phase chromatography of the *N*-acetylated butyl esters of amino acids can be used for the quantitative determination of these six amino acids. How far the method can be extended to include additional ones remains to be seen. A number of peaks were obtained beyond proline for the gelatin hydrolyzate and work is continuing to identify these and to see if quantitative data can be obtained. It is likely that there will be difficulty with acids such as cystine, tyrosine, arginine, histidine, and lysine.

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Table I. Analysis of Known Mixtures of Amino Acids

Amino Acid	Actual, %	Run			Actual, %	Caled., %
		1	2 Caled., %	3		
Glycine	20.0	20.2	20.4	20.5	20.0	31.4
Alanine	..	20.4	20.0	20.4	10.0	9.8
Valine	..	19.6	20.6	19.3	5.0	5.5
Leucine	20.0	39.8	38.8	39.8	20.0	39.7
Isoleucine	20.0				20.0	
Proline					15.0	13.8

Table II. Analysis of Gelatin Hydrolyzate

	Amino Acid on Basis of 16% Nitrogen, %				Reported by Greenberg (6)
	Detd. by Addition of Valine		Detd. by Addition of Leucine		
Glycine	22.6	23.0	22.2	21.7	22.6
Alanine	8.7	8.7	7.7	8.1	8.2
Valine	2.2	2.2	2.2	2.2	2.4
Leucine + isoleucine	4.5	4.0	3.8	3.8	4.6
Proline	12.5	12.8	11.9	12.0	12.6

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Gas Chromatographic Analysis of Hydrocarbon Streams from Butane Dehydrogenation

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► Gas-solid and gas-liquid chromatography have been investigated in order to provide a faster, more specific analytical technique for multi-component stream analysis as typically found in butadiene-producing facilities. Procedures are described for the separation and analysis of all hydrocarbon gases from hydrogen through C_4 using columns at room temperature. Separations are sufficiently complete that peak height, half band width calculations can be made on all components without resorting to chromatographic calibration factors. Variations in column parameters are evaluated. The analytical scheme presented fills a void that has existed in gas chromatography for laboratories engaged in the analysis of light hydrocarbons. The methods eliminate the need for ice baths and attendant equipment, and are rapid, definitive, and capable of accurate determinations with a minimum of instrumentation.

THE synthesis of butadiene from butane requires a thorough knowledge of plant streams composed of gases from hydrogen to C_4 hydrocarbons. To carry out complete analyses of gas streams of this nature, a combination of gas-solid and gas-liquid chromatography must be employed. A program of column evaluation was completed to determine the most favorable set of operating conditions and still obtain the required separations with a minimum of analysis time.

APPARATUS

The instrument used in this work was a Perkin-Elmer Model 154-B Vapor Fractometer. Helium was the only carrier gas used. Carrier gas flow rates were measured with a soap-film bubble tube attached to the column exit line. Peak widths were measured with a Bausch & Lomb measuring magnifier.

SAMPLING TECHNIQUE

Originally, liquefied petroleum gases were charged directly to the instrument sampling injector from the hydrocarbon liquid phase. However, fractionation of the sample occurred at room temperature and pressure. This method was abandoned and is not recommended for accurate quantitative work.

A more accurate method developed in this laboratory consists of vaporizing the sample from the liquid phase into a liquid displacement system of at least 250-ml. capacity and then charging this vaporized sample to the column by displacing it with confining liquid. Any liquid in which the gases will not dissolve serves as a suitable confining medium. A comparison of the procedures is illustrated in Table I.

EXPERIMENTAL

Several solid-absorbent materials were tested to achieve the required separation.

rations of the permanent gases in the gas streams to be analyzed. Columns of high-activity charcoal, low-activity charcoal, silica gel, Molecular Sieves, activated alumina, and chrome-alumina catalyst were constructed and coiled from copper tubing 6 feet long and 1/4 inch in outside diameter. Both low activity charcoal and Molecular Sieves produced the required separations, when charged with mixed samples of permanent gases and higher hydrocarbons. However, undesirable hydrocarbon elution effects were experienced with the Molecular Sieves column after a short period of use. Therefore, low-activity charcoal was selected for prolonged operations. Gases determined on this column were hydrogen, oxygen, nitrogen, carbon monoxide, and methane. Retention times may decrease as the column becomes saturated with hydrocarbons heavier than methane, but this does not affect the results. These hydrocarbons can be eluted by removing the column and heating it to 105° C. for a short time. It is then ready for use again.

Table I. Comparison of Sampling Methods

Component	B.P., ° C.	Direct ^a	Confining Liquid ^a
Isobutane	-11.7	2.33	3.23
Isobutene	-6.9	9.50	10.72
1-Butene	-6.3	7.88	8.40
1,3-Butadiene	-4.4	9.51	10.79
n-Butane	-0.5	52.07	50.45
trans-2-Butene	0.9	10.31	9.23
cis-2-Butene	3.7	8.38	7.04

^a Average of 20 analyses expressed as weight %.

The following variables have been evaluated in the construction of all gas-liquid partition columns utilized in this analysis. Applications of the results were used to provide a system of analysis with a minimum of instrument changes such as extra valving, ice baths, and exterior columns.

Liquid Substrates. Of approximately 25 substrates selected for testing, those producing the best results, when used to effect a separation of Phillips hydrocarbon mixture No. 37, were the sulfone compounds, β - β' -oxydipropionitrile, and 2,5-hexanedione. Further development work was concentrated on constructing a column of 2,4-dimethylsulfolane (Matheson, Coleman, and Bell Division, Matheson Co., East Rutherford, N. J.), because of the low vapor pressure, excellent separating power, and long column life of the substrate.

Solid Supports. Three types were investigated: C-22 firebrick (30-50 mesh), C-3 firebrick (30-50 mesh), and Chromosorb regular (30-60 mesh), all manufactured by Johns-Manville. C-3 and C-22 firebricks were relatively soft and subject to a high fines content, thus making an irregular packing pattern and a high resistance to carrier gas flow.

Chromosorb can be packed in a column of copper tubing 0.25 inch in outside diameter. Moderate tapping is used to obtain a density of from 2.15 to 2.35 grams per foot with consistent reproduction. The amount of Chromosorb that can be packed into a column without crushing apparently depends only on the average particle size of the particular lot of material and, within

normal limits, is independent of the amount of substrate used. Chromosorb produced the best column performance with respect to pressure drop and sample resolution.

Column Length. No well-defined program of column length with respect to resolution was carried out. However, columns 4, 6, 8, 12, 17, 20, 25, 30, 40, and 48 feet in length were constructed in the course of this work. Understandably, the longer columns resulted in a better resolution of components, and a point of diminishing returns with respect to resolution vs. length was not noticed with the 48-foot columns when compared to the 40-foot columns. This work was completed on 48-foot columns, as a matter of convenience.

Column Diameter. One each 48-foot column was made using copper tubing 1/8, 3/16, 1/4, and 5/16 inch in outside diameter and filled with a 30% dimethylsulfolane-70% Chromosorb packing of 30 to 60 mesh. An attempt was made to establish an optimum flow rate and sample size in each of the columns with all other operating conditions being the same, in order to compare analysis time and the degree of separation between 1-butene and isobutene. The results obtained on Phillips 36 mixture are listed in Table II. A plot of the per cent resolution of the 1-butene and isobutene double peak against column inside diameter, produces a nearly straight line, with the 100% intercept occurring at a column inside diameter of 0.24 inch, thus indicating complete separation with a column 5/16 inch in outside diameter. However, this efficiency was not achieved.

Ratio of Liquid Substrate to Solid Support. Four 48-foot columns 1/4 inch in outside diameter were prepared using dimethyl sulfolane on 30 to 60 mesh Chromosorb regular. The amount of substrate was varied to produce columns containing 20, 25, 30, and 40% liquid, by weight, of the finished coated packing material. The columns were filled under as nearly identical conditions as possible to produce comparable results. Phillips Hydrocarbon Mixtures 32, 35, 36, 37, and 40 were analyzed on each under the same operating conditions.

The data indicated an optimum dimethyl sulfolane concentration of 30 to 40%, therefore, a 34% dimethyl sulfolane column was constructed and tested. Table III lists the results obtained. The 34% column was found to be most stable to changes in flow rate.

Flow Rate. The effect of different flow rates was studied on the 34% column by analyzing Phillips hydrocarbon mixture No. 36 at various carrier gas rates. The changes in per cent resolution of double peaks and the height equivalent to a theoretical plate values are shown in Table IV. The optimum flow rate for the system was determined to be 36 ml. per minute, measured at the column outlet at atmospheric pressure and room tem-

Table II. Effect of Column Diameter

Column Diameter Outside, Inch	Sample Size, Ml.	Peak Resolution, %		Uncorr. Retention Time to 2-Butene (cis), Min.	HETP, 2-Butene, cis
		1-Butene	Isobutene		
1/8	1/8	70.5	57.5	29.1	0.401
3/16	1/4	84.3	77.8	37.0	0.315
1/4	1	90.2	85.6	52.6	0.287
5/16	1	63.4	47.4	82.7	0.549

Table III. Comparison of DMS Concentration

(Phillips mixture No. 36)

DMS, Wt. %	Partition Coefficients		Peak Resolution, %		HETP, 2-Butene, cis
	1-Butene	Isobutene	1-Butene	Isobutene	
20	7.9	8.5	53	33	0.572
25	11.6	12.4	74	62	0.385
30	12.1	13.0	86	80	0.287
34	12.0	12.9	86	79	0.313
40	10.1	10.9	81	74	0.361

Table IV. Effect of Flow Rate

(25° C. Phillips No. 36, 34% DMS column, 1-ml. sample at room temperature)

Flow rate, ml./min.	25.2	31.3	36.9	40.75	46.45
% Resolution					
1-Butene	84.80	85.41	85.56	84.79	82.92
Isobutene	78.05	79.00	79.20	78.10	75.56
HETP					
2-Butene, cis	0.307	0.304	0.313	0.308	0.316

perature. The peak heights are sensitive to flow rate in this instrument. An earlier report (1) states that the peak height is insensitive to changes in flow rate. The results from the earlier report were obtained from an instrument employing a different detector cell design and using filaments rather than thermistors. The present work indicates the peak height to decrease approximately 0.75% per ml. per minute increase in flow rate over the range studied. This change is evidently a function of cell design only and is independent of the column construction.

Column Temperature. A partitioning column was sought that would separate, within a short analysis time, all the hydrocarbons from methane through C₄, including the two isomers 1-butene and isobutene, at room temperature, or above. The percent resolution of 1-butene in Phillips mixture 36 changed from 86.3% at 25° C. to 79.4% at 35° C. when the 30% dimethylsulfolane column was used. An increase in temperature reduces the column efficiency in the system of analysis under study. A previous report (2) pointed out that even greater efficiencies can be obtained at ice bath temperatures, but with an analysis time of approximately 3 hours. By adjusting operating conditions and column parameters, the authors have found that an analysis can be made at 25° C. with good resolution of all components through C₄, in approximately 1 hour.

CALCULATION OF ANALYSIS

The composition of a sample requiring both gas-solid and gas-liquid chromatography was determined as weight per cent using peak heights, calibrations from pure compounds, and molecular weights. The calibrations were expressed in partial pressures as:

$$\text{Factor} = \frac{\text{peak height}}{\text{sample pressure}}$$

and were made on both the solid absorbent and liquid partitioning columns. Each column was check calibrated just prior to an analysis, using one pure compound (methane) common to both, and all other component factors were proportioned by any change found in this calibration. The calculation of concentration was made by proportioning the individual component partial pressures to the total pressure and correcting for molecular weight. Carbon dioxide and hydrogen sulfide were determined by Orsat and iodine reactions, respectively, and then added into the calculations. A sample calculation is:

$$\begin{aligned} \text{Mole fraction CO}_2 \text{ (or H}_2\text{S)} \times \\ \text{mol. wt.} \times \text{sample pressure} = \\ Ki \text{ (independent analysis)} \end{aligned}$$

$$\begin{aligned} \text{Peak height} \times \text{factor} \times \text{mol. wt.} = \\ Ka \text{ (absorption column components)} \end{aligned}$$

$$\begin{aligned} \text{Peak height} \times \text{factor} \times \text{mol. wt.} = \\ Kp \text{ (partition column components)} \end{aligned}$$

$$\text{Component wt. \%} = \frac{\text{component } K \times 100}{\text{sum of } Ka's + \text{sum of } Kp's + \text{sum of } Ki's}$$

The accuracy of this method appears adequate for control purposes, but the linearity of the calibrations should be investigated before attempting more critical analyses.

The calculations of samples requiring only gas-liquid chromatography has been made by using the peak height^{-1/2} band width method and correcting for molecular weight. The results are expressed as weight per cent. The accuracy has been tested on Phillips mixtures and found to be satisfactory for routine use.

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Analysis of Phosphate Mixtures by Paper Chromatography

Recent Improvements in Technique

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► To increase the precision and accuracy of the analysis of phosphate mixtures and glasses, for the critical appraisal of distribution theories, an ascending solvent technique at 4° C. has been developed. Phosphorus is estimated by a colorimetric method which saves considerable time and labor. Results are quoted to show over-all accuracy.

CHROMATOGRAPHY has been applied to the separation of phosphate anions in various fields—e.g., biology and agriculture, food and soap indus-

tries, and inorganic research. A comprehensive review of separation techniques for inorganic phosphate has appeared recently (5). The rapid physical method for the estimation of the phosphorus bands in the paper developed by Bernhart and Chess (1) is interesting for routine phosphate analysis.

Greater precision and accuracy were necessary for the critical appraisal of theories concerning the distribution of phosphorus between the molecules of various chain lengths present in a glass (9). They were achieved by recent developments in procedure, reported

in detail. The most significant changes from the technique described earlier (3) are substitution of an ascending-solvent method for the downward-flow apparatus, reduction of the hydrolysis effects of acid solvents by running the chromatograms at 4° C., and use of a single reagent (8) for the colorimetric determination of phosphorus; the latter saves considerable time and labor. Precision and over-all accuracy are improved.

APPARATUS AND REAGENTS

Schleicher and Schüll filter paper No. 589, green ribbon.