

GAS CHROMATOGRAPHY: A QUALITATIVE  
METHOD OF ANALYSIS FOR HIGH SCHOOL

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METHOD OF ANALYSIS FOR HIGH SCHOOL

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## TABLE OF CONTENTS

CHAPTER	PAGE
I. Purpose of this Report . . . . .	1
II. A Look at the History of Chromatography . . . . .	3
III. Directions for the Operation of this Column . . . . .	7
IV. The Elution Development Method . . . . .	10
Selected Bibliography . . . . .	18

### List of Figures and Charts

Figure 1, Gas Chromatography Column . . . . .	9
Graphs I and II . . . . .	13
Graphs IIIa and IIIb . . . . .	14

## CHAPTER I

### PURPOSE OF THIS REPORT

This project describes a tool of analysis that may be constructed and used by any high school that has a laboratory equipped with gas and electricity. The electricity may be omitted if other methods of heating the column are available. It will enable the students of the high school to practice chromatographic separation and identification of compounds. Chromatographic techniques may be introduced when and where needed, eliminating much of the time spent in old methods of analysis. Their use will permit the complete separation of many compounds in a laboratory period.

Gas chromatography, as described in this report, represents only a beginning in this field. It is limited to low boiling organic compounds, mostly the combustible type of compound. Separation of ethers, alcohols, hydrocarbons and aldehydes with low boiling points have been accomplished, as has also the separation of carbon disulfide from other substances. The apparatus can be used as a class lecture-demonstration and as a laboratory tool that could be built by the student. This would minimize the cost to the school. The writer feels that this project can eliminate the routine in laboratory work and due to its colorfulness and rapid completion can serve equally well as a very good lecture-demonstration tool. It will minimize purchasing problems for the

instructor as well as save much of his laboratory preparation time.

Ten high school text books, and some college chemistry texts were examined very thoroughly, but no mention of chromatography was made. Many of the latest developments mentioned in most high school textbooks are from five to ten years old. From these and other observations, it is evident that students will not receive the latest information from books, but must rely on the teacher, science journals, and magazines. Many of our teachers, as well as ninety nine per cent (99 %) of our students, have never heard of chromatography. This project would give them a chance to use it and to learn of the many principles involved in the simple application of it.

Many reports on the progress of gas-solid chromatography have been written in books, articles in journals, and other sources. Of all those examined, none were adaptable to the high school curriculum or written so that the high school could make use of it. Most, or all, of those examined were too technical for the average high school science teacher to understand. The equipment used was expensive and not attainable at the high school level. It was too large for classroom or laboratory adoption.

For the reasons stated above, the writer feels justified in making a study of this problem and presenting it for adoption as an aid to those who would like to improve their curriculum.

## CHAPTER II

### A LOOK AT THE HISTORY OF CHROMATOGRAPHY

Chromatography may be defined as a physical method of separation, in which the components to be separated are distributed between two phases, one of which constitutes a stationary bed of large surface area, the other being a fluid or gas (vapor) that percolates through or along the stationary bed.<sup>1</sup>

Use of the word "percolates" makes this definition very unique in that the definition of "percolation" means that the separation is carried out in a column and is intrinsically a batch process and not continuous.

Gas-solid chromatography was used in 1941 by Hesse and his co-workers. More recent works have been published by Cremer of Austria, Janak in Czechoslovakia, Turkeltaub in Russia, Ray in England, and Patton, Lewis and Kaye in the United States.

There are many types of chromatography and though they seem to vary a great deal, they are in some ways quite similar. To illustrate, all chromatographic separations involve the transport of a sample of a mixture through a column, or the physical equivalent

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<sup>1</sup>A. I. M. Keulemans, Gas Chromatography (New York, 1959) p. 2.

of a column. The mixture may be a liquid or vapor (gas). The column contains a stationary phase which may be either a solid or a liquid. The mixture is transported through the column by a gas or liquid -- the moving phase or effluent. The mixture moves through the column at different effective rates due to the selective retardation of the different components by the stationary phase. Thus, the components separate into zones and these zones are detected at the end of the column by various methods. In the work reported here, color changes of the flame, time of travel through column, and height of flame are used as a means of detection and characterization.

Gas-solid chromatography (G.S.C.) or (elution analysis) has many advantages over the gas-Liquid (G.L.C.) method. The G.L.C. method has no way to separate low temperature gases or liquids. The low boiling hydro-carbons and other low boiling liquids can be separated by G.S.C. only. The G.S.C. method may be used as a qualitative method of analysis as well as a quantitative method as was evidenced by Janak's work.

Chromatographic techniques were used long before 1941. It is not known just when they were first used, but long before Scheele, the Swedish chemist, noted it in 1773, men used cloth in natural dyes to change their color. Pliny described a method for the detection of iron, applying a drop of solution to papyrus impregnated with extract of oak-gall. This could have been the beginning.

The first serious work in this phenomena of separation was in the early part of the nineteenth century. The German dye-chemist,



F. F. Runge, investigated in detail the chromatographic possibilities in inorganic analysis. His results were published in 1855 in a rare book, Der Rildungstrieb der Stoffe, in which he hand-pasted his chromatograms.

Runge was followed by Goppelsraeder who gave us our present  $R_F$  factor. He was followed by others like Liesegang, Martin, Matteucci, Way, Engler and Boehm, Day, Albrecht, Tsweet and many more.

Tsweet was a Russian botanist and from his work, many of our present ideas had their beginning. Despite the extensive work of Tsweet, Kuitka, Day, and others, the use of chromatographic columns lapsed until about 1931. Kuhn made its use known in his studies of carotenoids.

From 1931 until the writing of this paper, means of separation of mixtures have been devised through chromatographic methods. G.S.C., G.L.C., or paper chromatography used in one way or another, has revolutionized the laboratory of the chemist in organic and inorganic research. His time has been shortened in analytical work, purification methods hastened, and identification made fast and sure. The time thus saved he could therefore devote to other aspects of the problem. The separation of compounds from mixtures of isomers, and many other fetes that would have consumed weeks of time and very careful work can now be done in hours through the use of techniques devised in connection with chromatography.

G.S.C. was slow or late in getting a start, but at the present, it is used extensively in analysis, separation, and purification of

of substances. It is believed that its use in every high school as a means of analysis will eventually come. Surely it will be used in the colleges in one form or another as a tool in all types of analytical work as well as in research.

CHAPTER III  
GENERAL DIRECTIONS FOR THE USE OF THIS COLUMN

Refer to diagram on page 9 when necessary.

1. Be sure that the connections at A, B, C, and E are tight and there is no chance of gas leaks.
2. Have manometer filled with mercury to the desired height.
3. Connect heating tape or other heating unit\* used to 110 V. a. c. outlet and let it heat from two to five minutes before using column.
4. Turn on gas at B and light at D. Then adjust flame height by adding more gas through E until a blue flame without any red coloration is produced.
5. Using mixture or a pure compound in a hypodermic syringe, inject from 0.01 to 0.1 ml into the column at A.

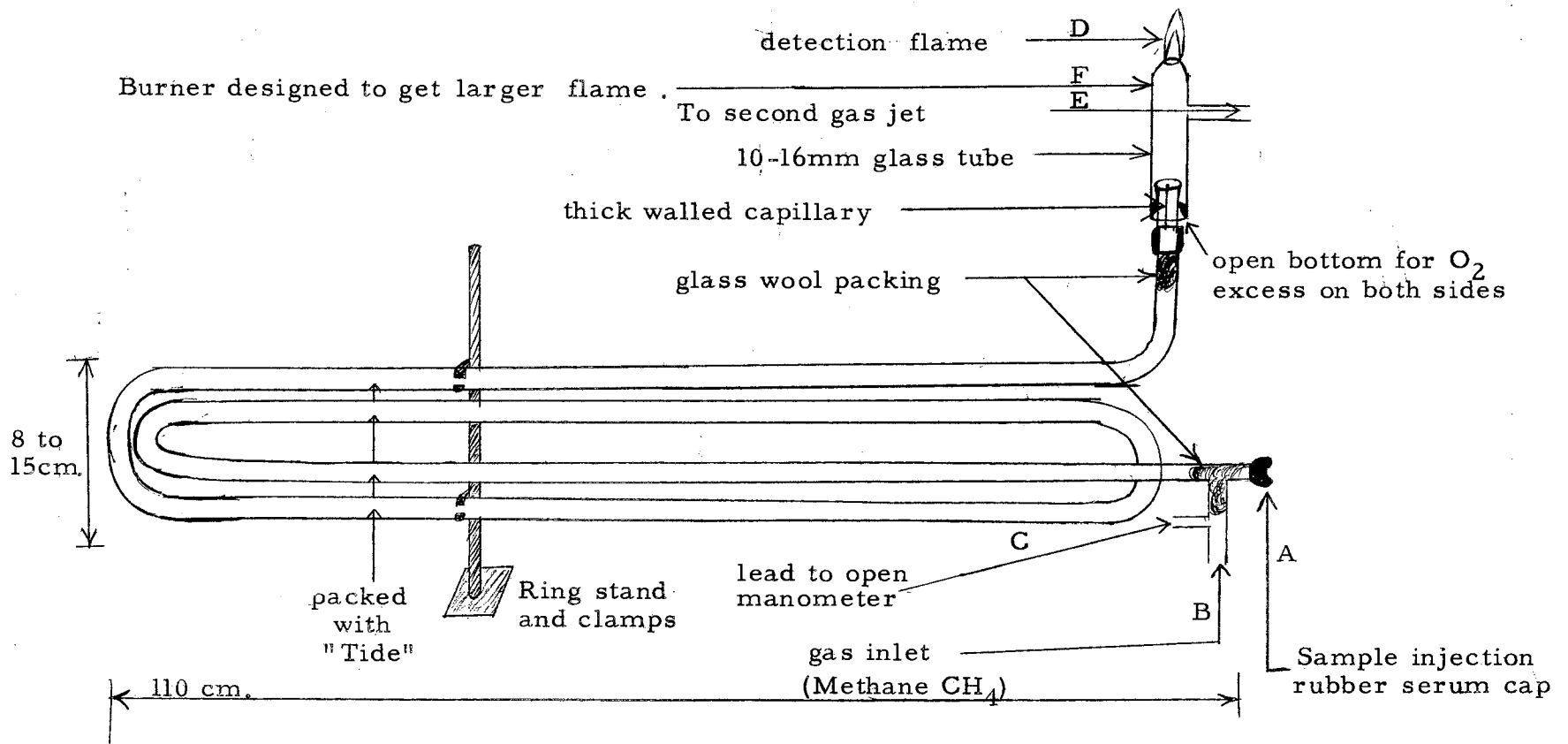
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\* Nicrome wire may be used to wrap the column if it is connected to a rheostat so that the temperature can be controlled and held stationary at a given point. This is an advantage over the heating tape because the tape gives only one temperature -- one that is pretty low for most of the compounds that one would use.

6. Start stopwatch at this time and watch for color change and flame height to change, at which time one stops the watch and records the time and color change.

This may be repeated as often as necessary or at the beginning of each series of runs on the column. The apparatus may be closed off in the reverse order from number 4 through number 3 of instructions.

Figure 1. Gas Chromatographic Column



## CHAPTER IV

### THE ELUTION DEVELOPMENT METHOD

This method of analysis was used in this investigation. The adsorbent used was the washing powder "Tide." The carrier gas or eluent used was methane gas,  $\text{CH}_4$ , (natural gas as it is piped to your laboratory). The column is fitted or wrapped with an electrical tape to keep it at a constant temperature of about  $68^\circ\text{C}$ . The thermal unit serves as a vaporizer for the liquids injected as samples and to increase the flow of the samples through the column. It also desorbs different compounds from the adsorbent at different rates. This allows those substances or compounds that are least adsorbed to come off at the detection end of the apparatus at one time with a lapse of time before the next one comes off. This process is repeated until the last one comes off, each in its own time and with each producing its own characteristic color change in the flame at the end.

There are unfavorable characteristics of this process. One is referred to as the "tailing of peaks", or "tailing effects." When a sample comes through, the flame changes height and color immediately. That is, it reaches a peak almost instantly, but it does not go back to normal as readily. This is the tailing effect of the peak.

Compounds that come off close to each other will have overlapping peaks or a peak will begin a decrease and suddenly increase again.

This can be overcome in two ways, maybe more. The column may be made longer to eliminate the overlapping of the peaks or one may use chemicals that are called "tailing reducers." These reducers are selective in their activity; therefore one must choose carefully the reducer to be used. Some of such chemicals are "Pelletex,"\* Squalane, Silica gel, and carbon. These compounds affect the separation in three ways:

1. The bands become sharper and move symmetrically.
2. The adsorptivity of the solid (Tide) is reduced, as evidenced by the lower temperature required for comparable times of emergence.
3. The paraffin/naphthene selectivity is somewhat reduced, as may be seen from the ratio of the times of emergence.<sup>2</sup>

The apparatus used in this investigation is shown in plate I. The column was wrapped with a heating tape capable of holding a constant temperature, about 68° C. The compounds to be analyzed were injected at "A", in the amount of 0.01 cc. The sample would vaporize immediately and flow, along with the eluent gas, methane, through the column. The rate of flow was approximately 60 ml/min. Each of the compounds tested had a different rate of flow through the column, this rate being established by several runs timed by a stop watch. This is

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\* Pelletex is marketed by the Godfrey Cabot Co., Boston, Mass.

<sup>2</sup> Time of emergence, or critical time, is the time from the beginning to the end of a peak

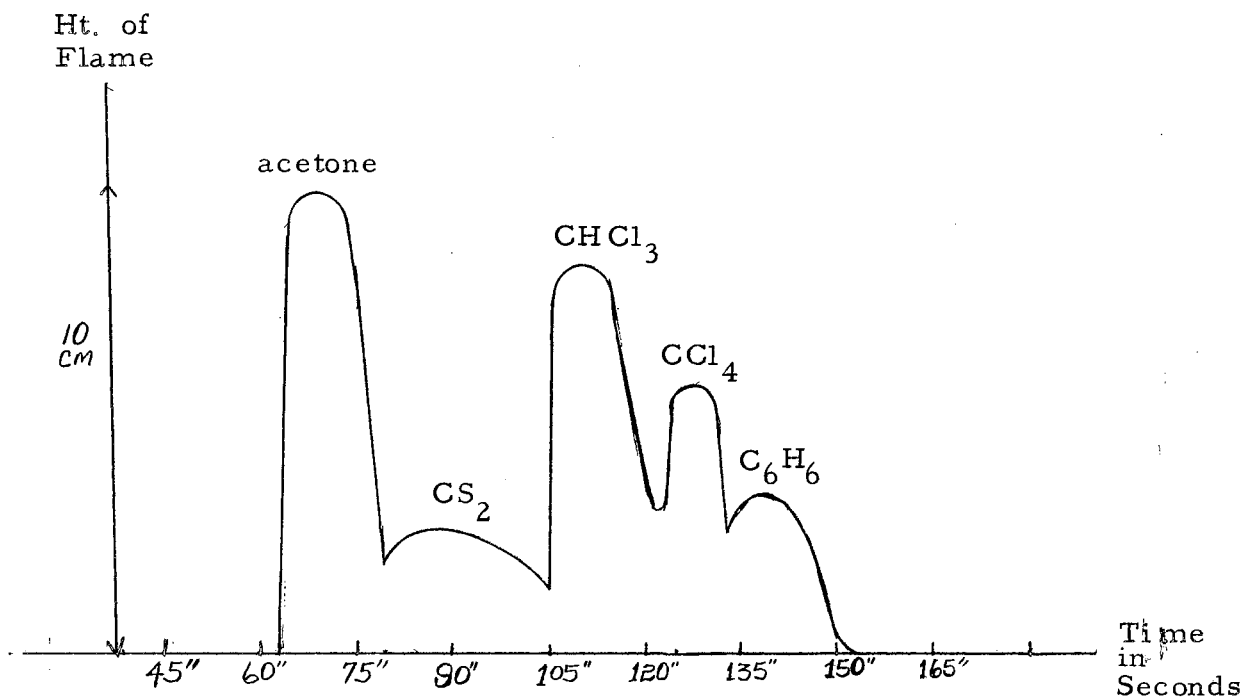
called "standardizing the column." When a compound came through, there were two noticeable changes. The flame color would change and the flame would increase in height, the latter being called a "peak." Table I shows the time, flame change, and color change for the compounds named.

TABLE I

COMPOUND	TIME MIN.-SEC.	FLAME COLOR	FLAME HT.
Carbon tetrachloride	2:05	Blue green base, orange tip	5mm
Acetone	1:05	Blue base, orange red tip	10mm
Carbon disulfide	1:18	Purple white	2cm (No Change)
Benzene	2:12	Blue - with red tip	3mm
Chloroform	1:45	Green - with red tip	7mm

It is apparent from the table above that there would be an overlap of some of these peaks if the sample's critical or emergence time is longer than 7 to 15 seconds. This is one disadvantage in the analysis of an unknown mixture although for a high school teacher and student this problem could be overcome by the selection of the compounds to be tested. This would immediately become advantageous because upon standardization of the column, one could place the compounds whose peaks would overlap in different classes. This would classify groups so that suitable mixtures could be made without overlapping peaks.

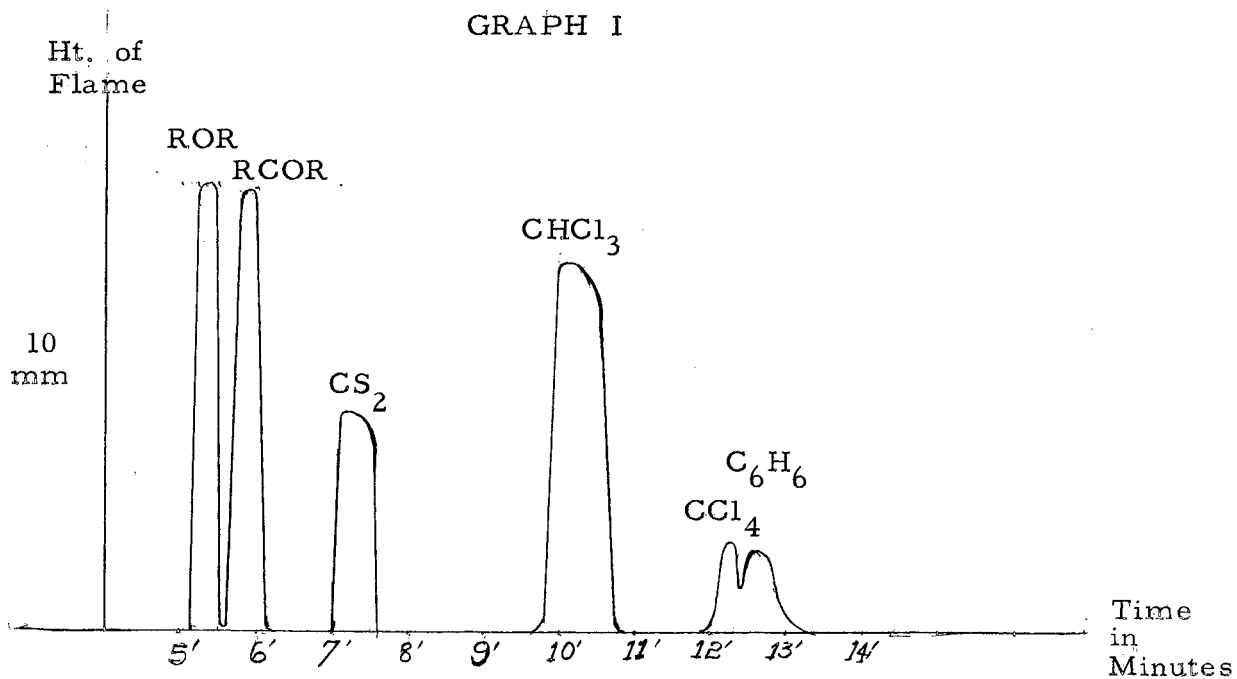




200 cm. Column

A color change at 80" seconds that is detectable makes the overlap quite harmless

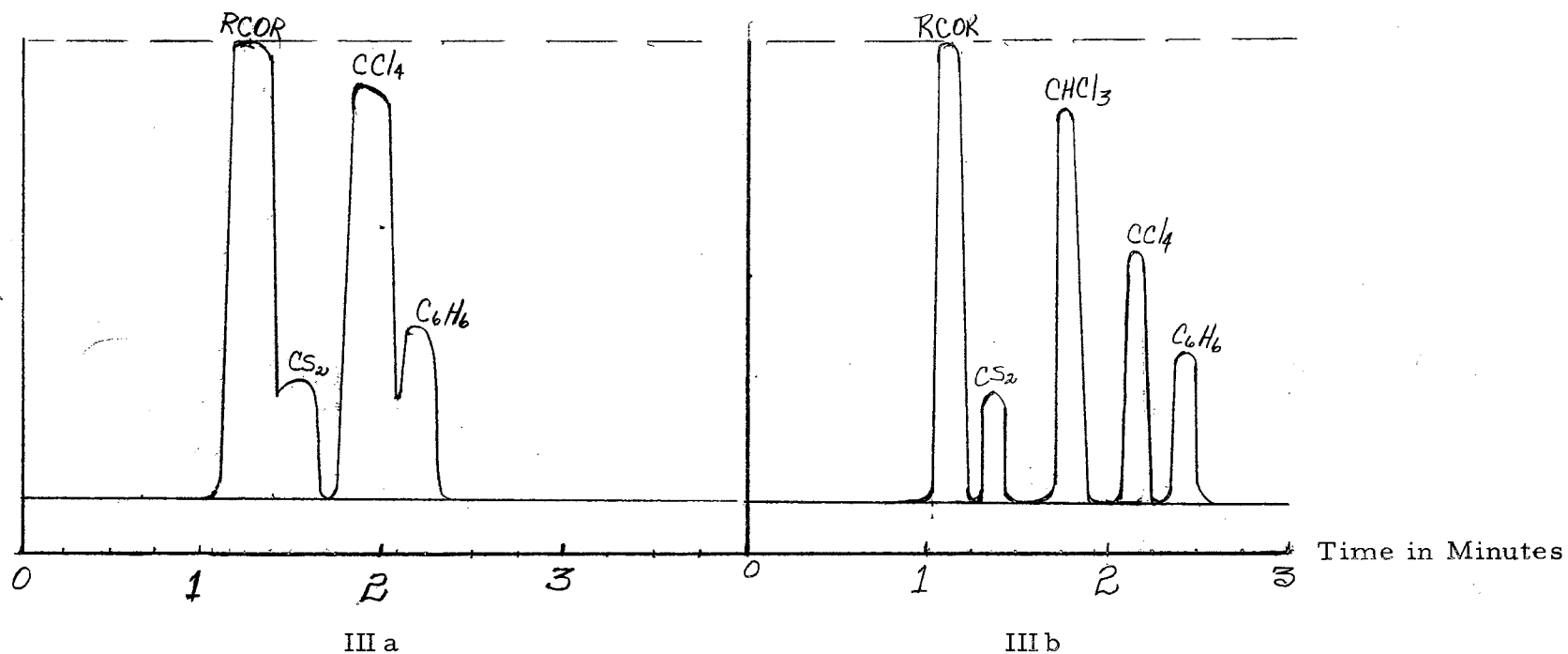
GRAPH I



400 cm. Column

Flow rate 60 ml/sec. Overlap at only one point.

GRAPH II



GRAPH III

- (a) A 100 cm. column packed with tide was used. Note the overlaps in the flame peaks. Only four peaks were recognized indicating  $\text{CCl}_4$  and  $\text{CHCl}_3$  came off so close that they were inseparable in this column.
- (b)<sup>1</sup> This is a chart of the flame peaks using pelletex and squalane as tailing reducers. Note five compounds were separated, as indicated by the peaks, and there is no overlap in the peaks.

<sup>1</sup> This graph was redrawn from the literature.  
A.I.M. Keulemans, Gas Chromatography (New York, 1959) p. 187.

A graphical representation of Table I is shown in graph I. Graph II shows the results obtained when the length of the column is extended from 200 to 400 cm. The results may be read from the graph.

With the longer column, the tailing effect is still observed but does not interfere with the separation of these compounds; however, one may have other compounds that will come off of the column between these peaks or in one of the critical time periods, causing an overlapping. From the literature, this is the best time for the use of Pelletex and other tailing agents. They will eliminate the tail and produce a very smooth symmetrical peak as illustrated in Graph III.

It is suggested that anyone using this technique of analysis raise the heat on the unit to approximately  $100^{\circ}$  C.; at this temperature, many more compounds can be used in the column. After standardizing the column, the compounds may be classified and separated according to the time of their departure from the column. This will enable the instructor to prepare many mixtures for analysis without the danger of overlapping peaks and the tailing effect will not interfere with a true analysis as long as there is a 45 second to 70 second interval between the time that any two compounds come off. For a selective number of compounds this makes a very fast and definite analysis.

Although gas chromatography can be used for both quantitative and qualitative analyses, the apparatus described here is intended for qualitative purposes only.

A thirty foot piece of rubber hose was used as a column to see if it would divide the mixture and bring each compound off at a different

time. The tube was heated in hot water and no packing was used. Some separation was observed, but the overlap of peaks was so great that there were no distinct peaks and troughs. Here again selectivity is encountered because rubber inhibits the flow of some gases more than others.

Another column was packed with Tide coated with Norit-A (carbon, powdered). This method gave no results as the fine carbon prevented the steady flow of the carrier gas (methane) and at the pressure used it was ineffective. The column, therefore, was unpacked and all of the mixture from it was sieved leaving only those particles of Tide larger than 100 mesh coated with carbon. The column then was repacked with this Tide, the treatment removing the fine particles of Norit-A and leaving the black Tide. This column was very effective in the separations, the tailing of the peaks being reduced about 20%. However, particles of the carbon would come through causing the flame to change color, rise and recede momentarily. This would appear to indicate a compound coming through unless one knew the cause. However, after a few hours of running, these sparks were eliminated and the peaks obtained were well defined. The carbon-coated Tide inhibited the flow of eluent and samples by approximately three minutes, but the peaks were symmetrical with less tailing.

It was observed that the time for a single compound to pass through the column was about one minute and twenty seconds, shorter than the time for that same compound when it was introduced as a mixture. The reason for the time differences is believed to be in the vaporization of

the liquid sample injected.\* The temperature at which this work was done is below the boiling point of most of them and when they are placed in a mixture the boiling point is raised which causes the liquid mixture to evaporate more slowly. Therefore, the length of time for a mixture to come through is a little longer than the time for the compound when injected alone.

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\* A hypothetical compound X comes through the column in 10 minutes, but when in a mixture, A, B, X, Y, Z, it comes through from 10 min., 50 sec. to 11 min., 20 sec.

## A SELECTED BIBLIOGRAPHY

- Brimley, R. C., and F. C. Barrett: Practical Chromatography, New York, Rheinhold Publishing Corporation, 1953.
- Desty, D. H.: Gas Chromatography, New York, Academic Press Inc., 1958.
- Keukmans, A. I. M.: Gas Chromatography, New York, Reinhold Publishing Corporation, 1959.
- Lederer, Edgar and Michael: Chromatography, New York, Elsevier Publishing Company, 1953.
- Phillips, Courtenay: Gas Chromatography, London, Butterworths Scientific Publications, 1956.
- Smith, Orsino C.: Inorganic Chromatography, New York, D. Van Nostrand Co., Inc., 1953.
- Strain, H. H.: Chromatographic Adsorption Analysis, New York. Interscience Publishers, 1942.
- Surak, John G.: "Chromatography As A Class Unit In Qualitative Analysis," Journal of Chemical Education (Sept., 1953), pp. 457-459.
- Zechmeister, L.: Progress In Chromatography, 1938-1947, London, Chapman and Hall Ltd., 1950.

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