COMPOUND IDENTIFICATION BY GAS CHROMATOGRAPHY A COMPARISON TO THE PAPER CHROMATOGRAPHY METHOD OF SCHAUER AND BULIRSCH

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INTRODUCTION

Structural analysis by paper chromatography, first described by SCHAUER AND BULIRSCH[1] and discussed by MELOAN AND KISER[2], is potentially a very powerful technique for compound identification. The basic concept is that each individual group within a molecule contributes to the R_F value and that when these individual groups are combined into a molecule there is a further contribution to the R_F which is called a group constant. This group constant and the contributions per functional group are determined by solving mathematical equations involving R_F values. By using two different solvents to elute the components of two separate paper chromatograms it is possible to determine the number of each of two different functional groups within a compound such as the CH_2 and COOH of an acid. In order to determine three groups, three different solvents are necessary, for four groups, four solvents, etc.

The problem here was to see if the retention parameters of gas chromatography could be incorporated into the equations developed by SCHAUER AND BULIRSCH. Although qualitative gas chromatographic structural analysis has been tried by many others, MERRIT AND WALSH[3] for example, there seems to have been no attempt to correlate it to the above mentioned work.

EXPERIMENTAL

Instrumentation

The instruments used were an F and M 609 equipped with a hydrogen flame ionization detector and the second instrument was constructed in this laboratory[4], and employed 2000 Ω thermistor detectors.

Chemicals

Methylamine, propylamine, ethylenediamine, 1,4-butanediamine dihydrochloride and 1,6-hexanediamine were obtained from Eastman; 1,5-pentanediamine from K and K Laboratories, *n*-butylamine from Union Carbide and Carbon Co., and *n*-hexylamine from the Matheson Company.

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Those amines obtained as water solutions were dried over potassium hydroxide pellets. In the case of methylamine and ethylamine, the vials were covered with septum caps obtained from Fisher Scientific Company and a Yale syringe was used for sampling and injecting the gases. Since 1,6-hexanediamine solidified when the water was removed, the vial was warmed until the amine melted and a warmed syringe was used to inject the sample. The 1,4-butanediamine was liberated from its hydrochloride salt by mixing it with some potassium hydroxide pellets and adding a few drops of water.

Column materials and preparation

The columns were 6 ft. long and made of 1/4 in. O.D. aluminum tubing. Gas-Chrom Z was used as the solid phase in all of the columns. The liquid phases studied were Apiezon M Grease, Dow-Corning Silicone Oil 550, and Silicone Gum Rubber.

Column conditions

The retention times of the amines, Table I, were obtained at a column temperature of 95°, an injection port and detector block temperature of 110°, an inlet pressure of 7.5 p.s.i.g. and the exit at atmospheric pressure.

RESULTS AND DISCUSSION

Calculations

The "R_F" values were calculated in a manner similar to that for paper chromatography. The solvent front was taken to be the air peak and thus the movement of the solvent front is equal to the column length. The movement of the component in the column when the air peak emerges is given by:

$$\text{Movement of solute} = t_{air}/t_R \times \text{length of column.}$$

Using these definitions the "R_F" values for gas chromatography were obtained from the relation:

$$\text{"}R_F\text{"} = \frac{\text{movement of solute}}{\text{movement of solvent front}} = \frac{t_{air}/t_R \times \text{length of column}}{\text{length of column}} = t_{air}'/t_R.$$

Then according to SCHAUER AND BULIRSCH:

$$R_M = -\log (1/R_F - 1) = \log R_F/(1 - R_F).$$

And for gas chromatography using:

$$\text{"}R_M\text{"} = -\log (1/\text{"}R_F\text{"} - 1).$$

Plotting "R_M" *versus* the number of CH_2 groups for each column is shown in Figs. 1–3.

Next the matrix calculations were done for the three possible pairings of the three columns. In each case the knowns were taken to be *n*-propylamine, *n*-hexylamine, and 1,4-butanediamine. The *n*-pentylamine was used as the unknown. The calculations for the Apiezon M–Silicone Gum Rubber combination follow.

TABLE I

VALUES OF "R_F" AND "R_M" FOR AMINES ON DIFFERENT COLUMN LIQUID PHASES

No.	*Compound*	*20 % Apiezon M*			*20 % Silicone Gum Rubber*			*20 % Silicone Oil 550*		
		t_R	"R_F"	"R_M"	t_R	"R_F"	"R_M"	t_R	"R_F"	"R_M"
	Air	0.68			0.68			0.70		
1	Methylamine	0.96	0.708	+0.387	0.88	0.722	+0.530	0.83	0.844	+0.733
2	Ethylamine	1.25	0.544	+0.076	0.93	0.730	+0.432	0.90	0.777	+0.541
3	*n*-Propylamine	1.43	0.475	−0.046	1.18	0.575	+0.131	0.98	0.715	+0.398
4	*n*-Butylamine	2.18	0.312	−0.344	1.63	0.417	−0.146	1.22	0.573	+0.128
5	*n*-Pentylamine	3.35	0.203	−0.594	2.43	0.280	−0.410	1.58	0.443	−0.100
6	*n*-Hexylamine	6.08	0.112	−0.900	4.10	0.166	−0.702	2.32	0.302	−0.365
7	Ethylenediamine	1.98	0.343	−0.283	1.90	0.353	−0.253	1.75	0.400	−0.176
8	1,4-Butanediamine	6.38	0.107	−0.992	4.82	0.141	−0.785	3.84	0.182	−0.654
9	1,5-Pentanediamine	13.15	0.0517	−1.264	9.30	0.073	−1.104	6.65	0.105	−0.931
10	1,6-Hexanediamine	26.80	0.0254	−1.584	16.60	0.041	−1.370	11.95	0.0585	−1.207

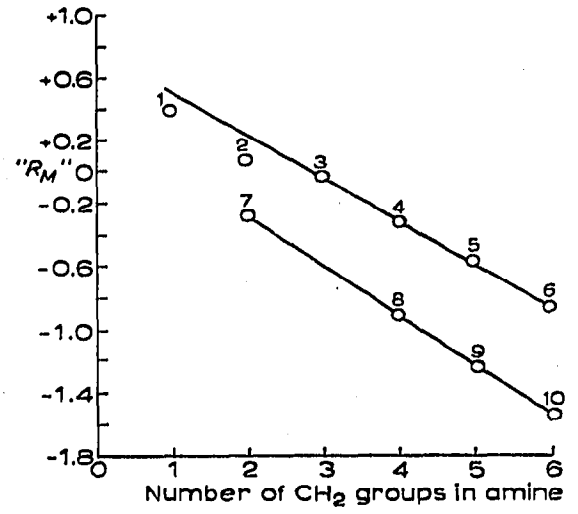

Fig. 1. Linear relation between "R_F" and the number of CH_2 groups in a molecule after transformation into "R_M" = — log (1/"R_F" — 1). The column was 6 ft. long and contained Apiezon M Grease on Gas-Chrom Z. The points represent the amines having the corresponding numbers in Table I, and the "R_M" values are those given in the table for the above column.

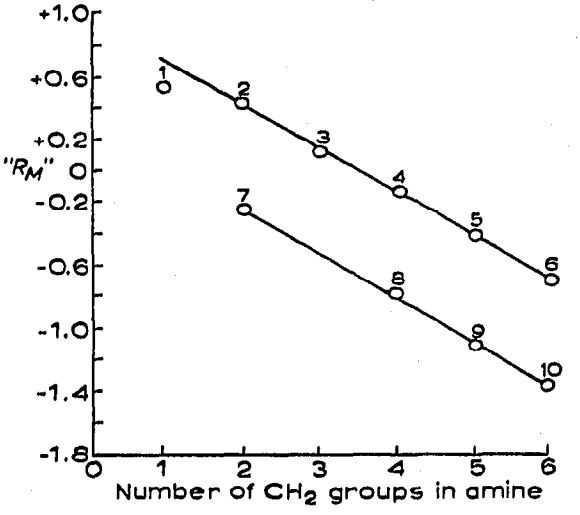

Fig. 2. Linear relation between "R_F" and the number of CH_2 groups in a molecule after transformation into "R_M" = — log (1/"R_F" — 1). The column was 6 ft. long and contained Silicone Gum Rubber on Gas-Chrom Z. The points represent the amines having the corresponding numbers in Table I, and the "R_M" values are those given in the table for the above column.

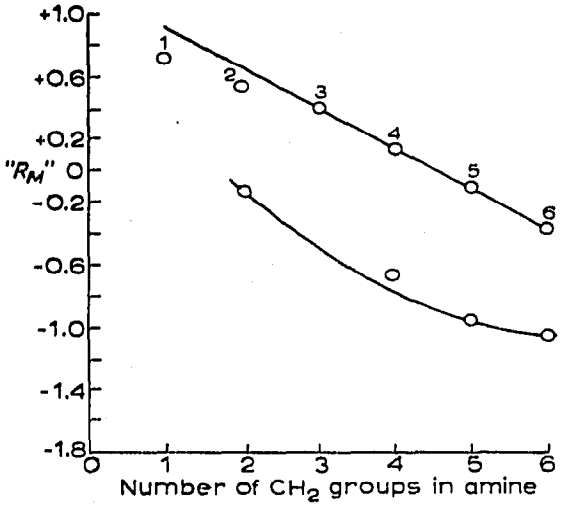

Fig. 3. Linear relation between "R_F" and the number of CH_2 groups in a molecule after transformation into "R_M" = — log (1/"R_F" — 1). The column was 6 ft. long and contained Dow-Corning Silicone Oil 550 on Gas-Chrom Z. The points represent the amines having the corresponding numbers in Table I, and the "R_M" values are those given in the table for the above column.

Test substance	*Apiezon M* $''R_M{}^1''$	*Silicone Rubber* $''R_M{}^2''$	*No. of groups*	
			CH_2	NH_2
Propylamine	—0.046	+0.131	3	1
Hexylamine	—0.900	—0.702	6	1
1,4-Butanediamine	—0.922	—0.785	4	2
Unknown	—0.594	—0.410	5	1

The determinant for this is:

$$\begin{pmatrix} Y_{CH_2} \\ Y_{NH} \end{pmatrix} = \begin{vmatrix} 1 \\ -0.046 + 0.131\ 1 \\ -0.900 - 0.702\ 1 \\ -0.922 - 0.785\ 1 \end{vmatrix} \times \begin{pmatrix} 3 \\ 1 \end{pmatrix} \begin{vmatrix} ''R_M{}^1'' & ''R_M{}^2'' & 1 \\ -0.900 & -0.702 & 1 \\ -0.922 & -0.785 & 1 \end{vmatrix}$$

$$+ \begin{pmatrix} 6 \\ 1 \end{pmatrix} \begin{vmatrix} ''R_M{}^1'' & ''R_M{}^2'' & 1 \\ -0.922 & -0.785 & 1 \\ -0.046 & +0.131 & 1 \end{vmatrix} + \begin{pmatrix} 4 \\ 2 \end{pmatrix} \begin{vmatrix} ''R_M{}^1'' & ''R_M{}^2'' & 1 \\ -0.046 & +0.131 & 1 \\ -0.900 & -0.702 & 1 \end{vmatrix}.$$

The solutions for each terms are as follows, using the standard sign convention for matrices, +, —, +:

The denominator:

$$-0.046 \begin{vmatrix} -0.702 & 1 \\ -0.785 & 1 \end{vmatrix} + 0.900 \begin{vmatrix} +0.131 & 1 \\ -0.785 & 1 \end{vmatrix} - 0.922 \begin{vmatrix} +0.131 & 1 \\ -0.702 & 1 \end{vmatrix}$$

$$= -0.046\ (+0.083) + 0.900\ (+0.916) - 0\ 922\ (+0.833)$$

$$= -0.004 + 0.825 - 0.768 = +0.053.$$

The first term:

$$''R_M{}^1'' \begin{vmatrix} -0.702 & 1 \\ -0.785 & 1 \end{vmatrix} + 0.900 \begin{vmatrix} ''R_M{}^2'' & 1 \\ -0.785 & 1 \end{vmatrix} - 0.922 \begin{vmatrix} ''R_M{}^2'' & 1 \\ -0.702 & 1 \end{vmatrix}$$

$$= +0.083\ ''R_M{}^1'' - 0.022\ ''R_M{}^2'' + 0.061.$$

The second term:

$$''R_M{}^1'' \begin{vmatrix} -0.785 & 1 \\ +0.131 & 1 \end{vmatrix} + 0.922 \begin{vmatrix} ''R_M{}^2'' & 1 \\ +0.131 & 1 \end{vmatrix} - 0.046 \begin{vmatrix} ''R_M{}^2'' & 1 \\ -0.785 & 1 \end{vmatrix}$$

$$= -0.916\ ''R_M{}^1'' + 0.876\ ''R_M{}^2'' - 0.157.$$

The third term:

$$''R_M{}^1'' \begin{vmatrix} +0.131 & 1 \\ -0.702 & 1 \end{vmatrix} + 0.046 \begin{vmatrix} ''R_M{}^2'' & 1 \\ -0.702 & 1 \end{vmatrix} - 0.900 \begin{vmatrix} ''R_M{}^2'' & 1 \\ +0.131 & 1 \end{vmatrix}$$

$$= +0.833\ ''R_M{}^1'' - 0.845\ ''R_M{}^2'' + 0.150.$$

In order to solve for the number of CH_2 groups present the first term was multiplied by 3, the second term by 6 and the third term by 4. Adding the results together gave:

$$-1.915\ ''R_M{}^1'' + 1.774\ ''R_M{}^2'' - 0.159.$$

Dividing this by the denominator value of +0.053 gave:

$$-36.1\ "R_M{}^1"\ +33.5\ "R_M{}^2"\ -3.00.$$

Substituting the values of "$R_M{}^1$" and "$R_M{}^2$" of the unknown into this gave 4.7 for the number of CH_2 groups. This is nearest to 5, and thus the number of CH_2 groups in the unknown is calculated to be 5. To solve for the number of NH_2 groups the first term was multiplied by 1, the second term by 1 and the third term by 2. Adding the results together gave:

$$+0.833\ "R_M{}^1"\ -0.854\ "R_M{}^2"\ +0.204.$$

Dividing this by the denominator value of +0.053 gave:

$$+15.71\ "R_M{}^1"\ -16.10\ "R_M{}^2"\ +3.85.$$

Substituting the values of "$R_M{}^1$" and "$R_M{}^2$" of the unknown into this gave 1.1 for the number of NH_2 groups. This is nearest to 1, and thus the number of NH_2 groups in the unknown is calculated to be 1.

Thus, for this combination of columns the compound is correctly identified as pentylamine, $C_5H_{11}NH_2$. The results for the three column combinations are given in Table II. Notice that the results are not valid when a column is used which has a non-linear plot of "R_M" *versus* number of groups. This is the case with column 3 and neither set of results are correct when this column was used. It was found that if a least squares treatment was made to obtain a straight line that all of the values involved were changed too much to give accurate results.

TABLE II

RESULTS OF THE MATRIX CALCULATIONS OF THE NUMBER OF CH_2 AND NH_2 GROUPS IN THE UNKNOWN, PENTYLAMINE

*Column No. combinations**	*Calculated*		*Actual*	
	Y_{CH_2}	Y_{NH_2}	Y_{CH_2}	Y_{NH_2}
1 and 2	+4.7	+1.1	5	1
1 and 3	+4.8	−1.3	5	1
2 and 3	−0.9	−0.9	5	1

* For column No. 1 the liquid phase is Apiezon M, for No. 2: Silicone Gum Rubber, and for No. 3: D-C Silicone Oil 550.

With each sample a small amount of air was intentionally injected so that the reference air peak could be used to locate the "solvent front". Since the amines used covered such a wide range of boiling points and molecular weights, not all of the peaks were of satisfactory shape for quantitative analysis purposes, however, satisfactory retention time data was readily obtained. The variation of the points for methylamine and ethylamine from a straight line in Figs. 1–3 is common for the lower members of a homologous series in gas chromatography[5].

In general, the plots of "R_M" *versus* the number of CH_2 groups (Figs. 1–3) give straight lines similar to paper chromatographic results. The slope of the lines are of

opposite sign to those obtained by SCHAUER AND BULIRSCH, due to the organic liquid being a part of the stationary phase in gas chromatography whereas it is the mobile phase in paper chromatography.

It can be seen that an analogy between paper chromatography and gas chromatography does exist for this "structure determination", however, the calculations are rather tedious for the obtaining of the final equation into which the "R_M" values from two columns for the unknown are substituted. Nevertheless, once a satisfactory combination of columns is selected, and the final equation calculated, the substitutions and subsequent calculations can be done readily.

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SUMMARY

It is shown that the method of "structural analysis" developed for paper chromatography by SCHAUER AND BULIRSCH gives analogous results using gas chromatography when the equations are corrected for gas chromatography parameters and the proper liquid phases are used for partitioning agents. Aliphatic amines were used to show the analogy.

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