THERMAL CONDUCTIVITY CELL RESPONSE AND ITS RELATIONSHIP TO QUANTITATIVE GAS CHROMATOGRAPHY

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(Received September 30th, 1959)

INTRODUCTION

Since the appearance of the technique of gas–liquid chromatography many papers have appeared in the literature dealing with the quantitative aspects of the resulting chromatograms[1-10]. There also have been publications dealing with the effects of temperature, pressure and flow rate[11-13] upon gas–liquid chromatographic analyses. In 1958 there was a very elaborate article dealing with the selectivity of liquid substrates for use in gas–liquid chromatography[14]. More recently we have witnessed publications on data presentation[15,16], column efficiency[17], effect of sample size on height of a theoretical plate (HETP) and retention volume[18], and evaluation of detectors for quantitative work[19]. This paper concerns itself with the relationship between thermal conductivity cell response and quantitative gas–liquid chromatography.

For our study we chose a series of alcohols up through hexanol. This project was prompted by the results published previously on hydrocarbons[8].

THEORETICAL DISCUSSION

Most effort in this field (from the quantitative aspects) has been conducted with an empirical choice of substrates, apparatus and general operating conditions necessary for the separation of specific systems. The main objective we seek is an explanation of why there is a difference in the response of different compounds and in particular, how properties of the various compounds are related to this difference.

It is a known fact that when a thermal conductivity cell is employed as a detector the carrier gas should have a thermal conductivity vastly different from any of the compounds to be determined. Thus, the carrier gas should have a molecular weight extremely large or extremely small (thermal conductivity is inversely related to the square root of the molecular weight of a compound) in order to obtain a significant response from the detector. The low molecular weight of helium and its safety make it ideal for the carrier gas.

If one further assumes that the difference between the thermal conductivity of

helium and the compounds under study is large, then one could say the area under the peak is a measure of molar concentration. In so doing the experimenter would introduce sizable errors into his calculations. Most experimenters have found that the peak area is more closely related to weight per cent of a particular component than to the mole per cent. Even so we still may have a sizable error if we correlate peak area to weight per cent. Thus, one must improve his accuracy by calibration.

The big advantage of using peak area (*i.e.* per cent peak area relative to concentration) is that the sample size put onto the column need not be known. Another advantage is that any change in the flow rate during a run will not affect the area of the peak significantly. A change in flow, however, will drastically affect peak height. Therefore, previous calibration by peak height would require extreme care for each sample run. A third advantage is that over fluctuations in the current going through the thermal conductivity cell. This current may change from day to day and cause a change in the sensitivity of the detector. Thus, by using per cent peak area instead of absolute area or peak height calibration you decrease your chances of error.

This use of peak area is the approach we used in this work. All our calculations were made relative to the peak area for a known amount of an alcohol. This is then converted to area per mole.

APPARATUS AND MATERIALS

Fractometer: Perkin-Elmer Vapor Fractometer, Model 154C, manufactured by the Perkin-Elmer Corporation, Norwalk, Conn.

Recorder: Leeds and Northrup Speedomax Type G Recorder, 10 mV.

Balance: Christian Becker Chainomatic Magnetically Damped Balance, Model AB-2.

Column: ¼ inch O.D. copper tubing, 10 ft. in length.

Column support: Fisher Columnpak, 30–60 mesh, purchased from the Fisher Scientific Company, Pittsburgh, Pa.

Liquid substrate: Eastman technical tritolyl phosphate purchased from Eastman Kodak Company, Rochester, New York.

Carrier gas: Helium.

Alcohols: High purity alcohols purchased from Eastman Kodak Company, Rochester, New York or Fisher Scientific Company, Pittsburgh, Pa.

METHOD

Each alcohol investigated was blended with a known weight of internal standard. The internal standard used for this investigation was normal propyl alcohol. Each blend was run ten times and the operation repeated on a second similar blend. 0.05 ml samples were used for all the runs.

After separation through the 10 ft. column of tritolyl phosphate the area for each alcohol was determined by two methods. First by integral calculation, *i.e.* multiplying

the peak height by one-half the band width in centimeters; second by cutting out the peak and weighing it on an analytical balance.

For the second method the uniformity of the paper was determined by cutting out and weighing known areas from different portions of the chart roll. Error due to non-uniformity of the paper and the cutting and weighing processes was found to be less than 1 %.

The area of the peak was then determined on the basis if 1 mole of the alcohol was passed through the column. This area per mole value was in turn used to calculate the relative response per mole setting the internal standard to a value of unity.

EXPERIMENTAL RESULTS

To measure the detector response of a particular alcohol on either a mole or weight basis and compare this response value to other alcohols, it is necessary to introduce on to the partition column a precisely known amount of each alcohol. Also the sensitivity of the detector, the flow rate and the temperature must be the same for each determination. Maintaining these conditions the same from run to run and day to day is not easy, thus each alcohol is blended with an internal standard. In this manner the only requirement is that the operating conditions remain constant for the duration of a run. Thus the ratio of the area of the internal standard to that of a particular alcohol in question is independent of sample size and the volume and weight of sample need not be known.

Table I shows the alcohols investigated and the average value of the response per mole (R.P.M.) for each one. The response per mole was calculated on both a weight

TABLE I

RELATIVE RESPONSE VALUES PER MOLE OF ALCOHOL

Alcohol	*R.P.M.* by weight*	*R.P.M.* by integral*
Methanol	0.45	0.45
Ethanol	0.74	0.74
n-Propanol	1.00	1.00
Isopropanol	1.04	1.04
n-Butanol	1.27	1.27
tert.-Butanol	1.27	1.27
Isobutanol	1.86	1.86
sec.-Butanol	1.20	1.20
n-Pentanol	1.46	1.46
Isopentanol	1.56	1.56
tert.-Pentanol	1.54	1.54
3-Pentanol	1.38	1.38
2-Methyl-1-butanol	1.32	1.32
3-Methyl-2-butanol	1.65	1.65
2-Hexanol	1.59	1.59
2-Methyl-2-pentanol	1.59	1.59

* Response per mole (all values calculated relative to *n*-propanol; *n*-propanol = 1.00). Conditions: 130°, 25 psi helium; 10 ft. column of tritolyl phosphate on Columnpak 40:60.

basis (cutting out and weighing the peaks on an analytical balance) and an integral basis (product of peak height and one-half the band width). The same value for response per mole was obtained by both methods. From this we concluded that it makes little difference which method was used for determining the area under the peak.

Fig. 1 shows a plot of these response values, for the normal alcohols, versus the square root of the molecular weight. A linear relationship was found. The values for the isomeric forms of the alcohols could not be plotted on a similar graph because:

1. Their values did not follow any linear relationship.
2. We did not have enough isomers to justify such a plot.

We then plotted our response values against certain properties of the alcohols to see if any correlation could be found other than square root of the molecular weight. Fig. 2 shows a plot of these response values versus molecular volume. Here too a linear relationship was found. This linear relationship could be expected since molecular volume is related to molecular weight and density of a compound. Looking at the response values for the normal alcohols we find that as we add a carbon atom to the chain from methanol to butanol the increase in R.P.M. is fairly constant. But when we increase to five carbons (*n*-pentanol) our increment is decreased. If we carry this further to six carbons (2-hexanol) we again find a decrease in the increment. Table II

TABLE II

CHANGE IN R.P.M. VALUES PER CARBON ATOM

Alcohol	*R.P.M.*	*Change in R.P.M.*
Methanol	0.45	
		0.29
Ethanol	0.74	
		0.26
Propanol	1.00	
		0.27
Butanol	1.27	
		0.19
Pentanol	1.46	
		0.13
2-Hexanol	1.59	

shows the change in R.P.M. from methanol through 2-hexanol. From this we could postulate that as we increase the number of carbons on the chain we would eventually reach a point where very little change would occur in our R.P.M. values. If this were true then with higher molecular weights the area under the peak for all alcohols would essentially be the same and we could obtain accurate analyses by assuming peak area was directly related to weight per cent. Our inability to obtain high purity alcohols in this molecular weight range prevented any further investigation in this area.

Fig. 3 shows that we also obtain a reasonable relationship between boiling point and response per mole (again only a plot of the normal alcohols is shown because they alone follow a pattern).

Figs. 4 and 5 show a similar correlation for vapor pressure at 20° and 130°, respectively.

Once having obtained these values for the response per mole of our alcohols we then proceeded to test them under actual experimental conditions. Blends made up

of four and five alcohols were investigated. These blends were run under the same conditions as our initial two-component blends, *i.e.*, 130° temperature, 25 psi pressure of helium and 0.05 ml sample size. Table III shows the results of these runs. Each blend was run six times and the average values used.

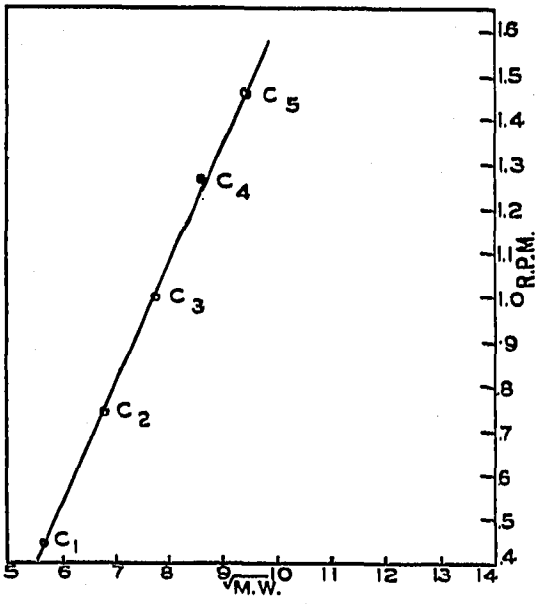

Fig. 1.

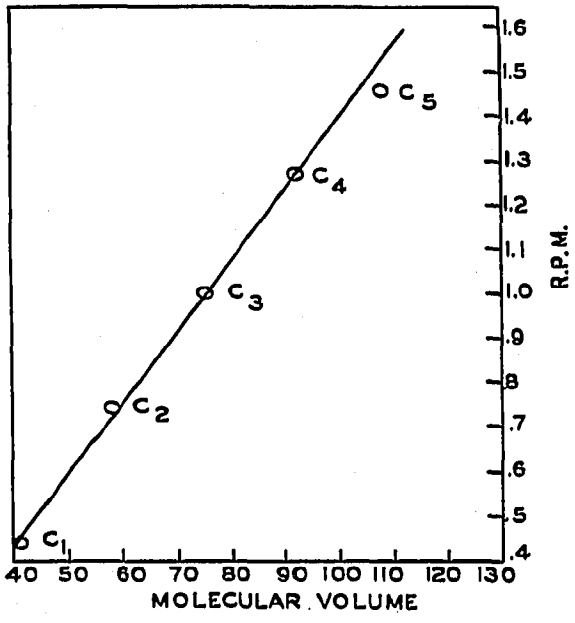

Fig. 2.

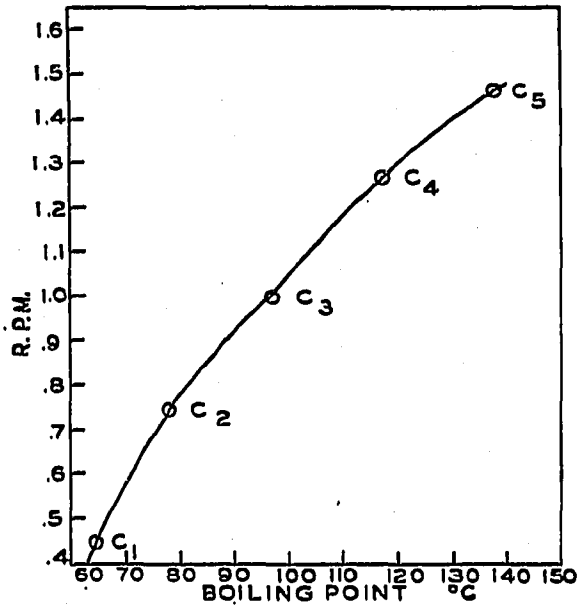

Fig. 3.

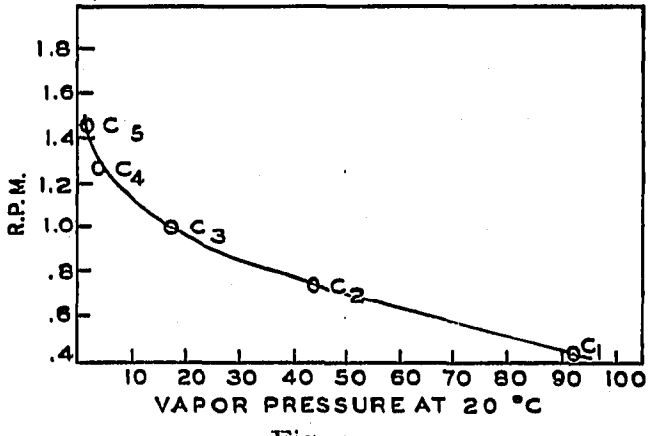

Fig. 4.

If one assumed that area was equal to mole per cent, errors as high as 26.3 % were encountered; when area assumed equal to weight per cent, errors as high as 10.7 % were encountered. If the areas were corrected by the response values the error was less than 1.0 %.

TABLE III

ANALYSIS OF SYNTHETIC BLENDS

Blend alcohols	*True wt. %*	*True mole %*	*Observed area %*		*Calculated* %*	
			by weight	*by integral*	*by weight*	*by integral*
101-D						
n-PrOH	16.71	17.30	14.21	14.02	16.86	16.67
n-BuOH	24.11	20.19	25.79	25.62	24.18	24.03
iso-AmOH	20.39	14.42	27.00	27.34	20.48	20.31
n-AmOH	21.77	15.38	26.64	26.66	21.63	21.69
MeOH	17.02	32.69	6.36	6.36	16.95	16.98
102-D						
n-PrOH	19.47	21.90	16.07	16.10	19.54	19.41
n-BuOH	18.97	17.14	19.82	19.85	19.06	18.92
iso-AmOH	20.53	15.23	26.46	26.47	20.57	20.42
n-AmOH	21.07	16.19	25.40	25.38	21.16	20.97
EtOH	19.95	29.52	12.24	12.20	20.06	19.84
103-D						
n-PrOH	19.91	25.00	14.12	14.09	20.03	19.86
2-HxOH	19.64	13.88	22.05	22.03	19.74	19.58
iso-BuOH	20.70	21.29	27.30	29.87	20.78	20.63
iso-PrOH	20.93	25.92	15.39	15.42	20.97	20.87
2-Me-2-AmOH	18.80	13.88	21.15	21.16	18.86	18.74
104-D						
n-PrOH	28.09	35.29	22.76	22.78	28.14	28.01
tert.-BuOH	20.58	21.17	21.27	21.25	20.64	20.52
3-AmOH	23.79	20.00	26.62	26.60	23.85	23.70
2-Me-1-BuOH	27.53	23.52	29.34	29.37	27.58	27.47

* Percentages calculated using the R.P.M. values in Table I.

It was previously shown[8] that relative response values were independent of temperature, over a small range. This was later supported and shown to be true[6]. We, therefore, analyzed several of our multi-component blends using different sample volumes to see if we obtained a linear relationship when area is plotted against sample size. The results are shown in Figs. 6 and 7. As these plots show, a linear relationship is held over the range of 5 μl through 50 μl whether we calculated the area by weight or by integral calculation. The areas depicted in these plots are the total areas under all the peaks of a single blend. For the composition of these blends see Table III.

In some of our runs it was necessary to switch from one sensitivity setting (attenuation) to another to have all the peaks distinct. Thus, it was necessary to check to see whether or not any appreciable error was introduced by this change in sensitivity. Fig. 8 shows that we obtained a fairly good relationship between sensitivity and total area under the peaks. The maximum relative error due to change in attenuation, in any one run was less than 1 %.

Our last point to investigate was whether a linear relationship was held when the weight per cent of an alcohol was varied in a blend. This was done by means of blends made up on a weight ratio basis. A series of eleven blends were made using methanol

and *n*-propanol. The blends were made up by adding drops of each alcohol to a vial. The weight of each alcohol was found by means of an analytical balance. The total number of drops of solution was the same in each blend, just the ratio of methanol to propanol was varied. The first blend contained 10 drops of *n*-propanol and 0 drops of methanol. The drops of methanol were increased while the drops of propanol were decreased, keeping the total always 10 drops, until the eleventh blend which contained 10 drops of methanol and 0 drops of *n*-propanol.

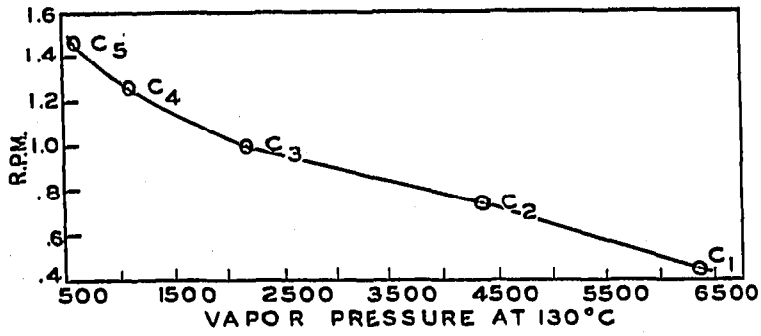

Fig. 5.

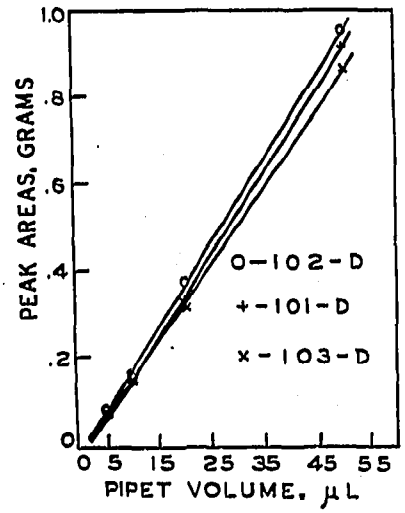

Fig. 6.

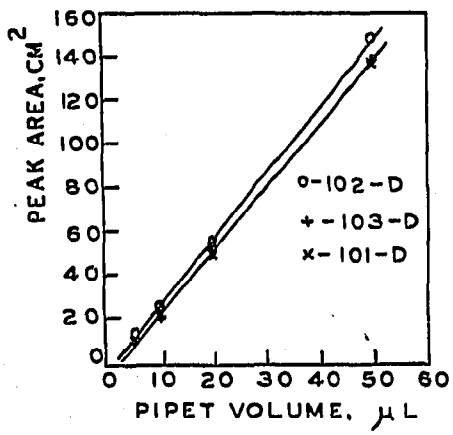

Fig. 7.

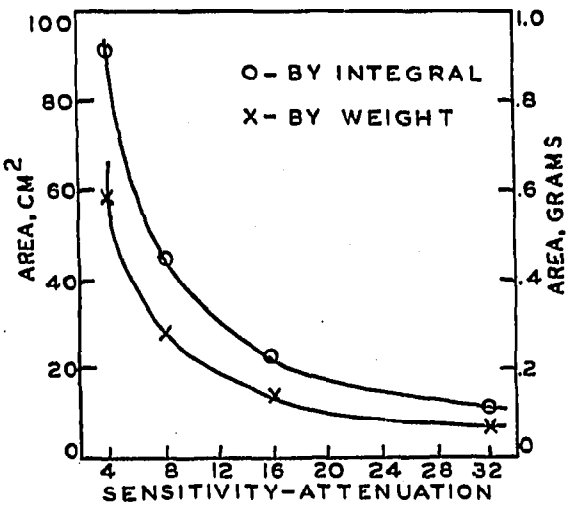

Fig. 8.

Table IV shows the weight of each alcohol, the peak height, peak area, mole per cent and weight per cent of each alcohol for the eleven blends.

All blends were run at a sensitivity of 32 and a 0.05 ml sample size employed for each run. From the results one sees that the response values hold over a wide concentration range.

TABLE IV

EFFECT OF CONCENTRATION ON PEAK AREA

Blend	*Weight in blend* g	*Weight per cent*	*Mole per cent*	*Peak height* cm	*Area by weight* g	*Area by integral* cm^2
1E						
n-PrOH	0.1705	100.0	100.0	7.59	0.0858	13.05
2E						
MeOH	0.0145	8.6	14.95	1.34	0.0075	1.11
n-PrOH	0.1541	91.40	85.05	6.93	0.0800	10.79
3E						
MeOH	0.0285	16.99	27.59	2.94	0.0151	2.22
n-PrOH	0.1392	83.01	72.41	6.33	0.0744	10.85
4E						
MeOH	0.0433	29.68	44.26	5.23	0.0274	3.97
n-PrOH	0.1026	70.32	55.74	5.44	0.0651	9.40
5E						
MeOH	0.0563	36.49	51.78	6.39	0.0345	4.94
n-PrOH	0.0980	63.51	48.22	4.96	0.0602	8.60
6E						
MeOH	0.0672	46.60	62.02	7.98	0.0448	6.41
n-PrOH	0.0770	53.40	37.98	4.18	0.0511	7.35
7E						
MeOH	0.0952	58.73	72.79	9.62	0.0583	8.35
n-PrOH	0.0669	41.27	27.21	3.37	0.0412	5.87
8E						
MeOH	0.1108	69.86	81.37	11.22	0.0724	10.33
n-PrOH	0.0478	30.14	18.63	2.41	0.0313	4.45
9E						
MeOH	0.1425	81.48	89.34	12.50	0.0856	12.35
n-PrOH	0.0324	18.52	10.66	1.45	0.0194	2.81
10E						
MeOH	0.1652	92.24	95.72	13.73	0.0973	14.24
n-PrOH	0.0139	7.76	4.28	0.55	0.0080	1.20
11E						
MeOH	0.1778	100.0	100.0	14.78	0.1047	15.90

ACKNOWLEDGEMENTS

This research was supported in part by a grant from the Petroleum Research Fund administered by the American Society. Grateful acknowledgement is hereby made to the donors of said fund.

The authors would also like to thank the Research Corporation of New York for its financial support, without which most of our equipment could not have been purchased.

SUMMARY

By analyzing two component blends of alcohols (one being an internal standard) we were able to compute response values, on a mole basis, for various alcohols. These computed values were then used to calculate weight per cents of alcohols in multi-component blends. The blends were analyzed by gas chromatography using a thermal conductivity cell as the detector. As a result of this investigation we found that the area under the peak of a chromatogram is a measure of the weight per cent of an individual component rather than the mole per cent. If the per cent area was used directly as a measure of weight per cent errors as high as 10.7% were encountered. The use of our computed response values cut the error to less than 1.0 %

Correlation between concentration and peak area, sensitivity and peak area, peak height and concentration, and peak area and concentration were also investigated. In all cases a low error relationship was found. This indicated that our response values were affected little by sensitivity (attenuation) changes, concentration changes or sample size.

We hope later to be able to correlate all these data with specific properties of various compounds.

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