QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF TERNARY MIXTURES OF BENZYL CHLORIDE, BENZAL CHLORIDE AND BENZOTRICHLORIDE

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INTRODUCTION

Gas–liquid chromatography (GLC) is a very sensitive and selective technique, which enables us (1) to separate components of a mixture and (2) to obtain qualitative or even quantitative data about the relative amounts of the components present in the sample studied.

Since the gas chromatographic literature reveals that no general relationship exists between amount of component injected and peak height or peak area produced, for accurate quantitative analysis by GLC, the instrument used has to be calibrated with predetermined amounts of the compounds to be analysed or with mixtures of known composition. In certain cases though, a simple relationship may be found. For example, in a study of the liquid-phase photochlorination of toluene it has been found that, when using a Perkin Elmer Vapor Fractometer 116 with a thermistor detector and equipped with type C column (silicone oil), peak area ratios of the side-chain chlorinated compounds proved to be numerically equal to mole ratios[1]. However, when platinum wire thermal conductivity cells are used instead of thermistors, the peak area ratios distinctly differ from those of the mole ratios given in the synthetic mixtures.

In this case, for the purpose of routine analysis, calibration curves have been determined, for the conversion of peak area ratios into mole ratios, or weight percentages, of the components in binary mixtures. For the analysis of ternary mixtures, a nomographic method is described using two binary calibration curves.

APPARATUS AND PROCEDURE

The gas chromatographic instrument used was a Perkin-Elmer Fractometer 116, equipped with platinum wire thermal conductivity cells and a column, type "C" (silicone oil). Hydrogen was the carrier gas, flow rate 70 ml/min at a pressure of 0.4 atm., column temperature 160°.

Fig. 1 shows an example of a chromatogram thus obtained. The relative retention times are 1.00 for benzyl chloride, 1.85 for benzal chloride, and 2.72 for benzotrichloride.
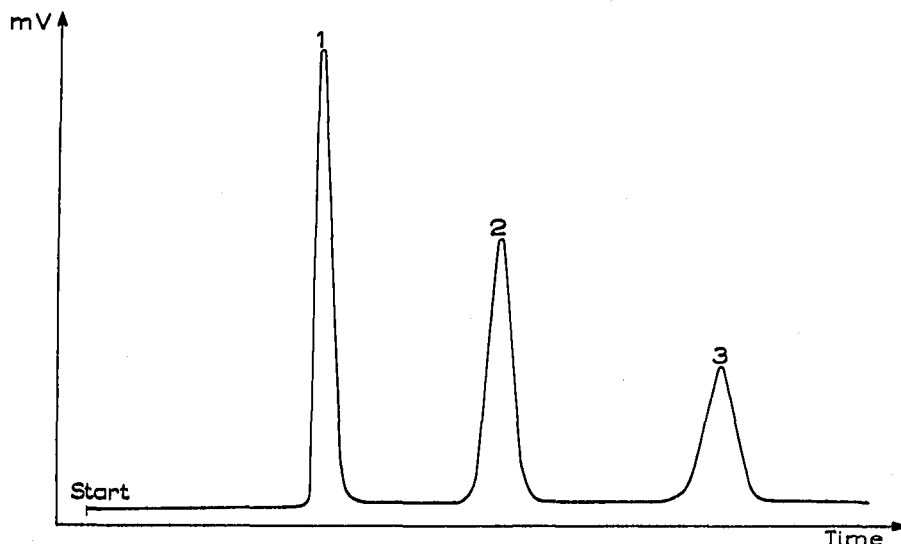
Fig. 1. Gas chromatogram of a mixture of benzyl chloride (1), benzal chloride (2) and benzotrichloride (3).

INSTRUMENT CALIBRATION

The gas chromatograph was calibrated by analysing a series of synthetic mixtures, composed of accurately weighed amounts of the pure components, benzyl chloride, benzal chloride and benzotrichloride.

A series of binary mixtures of benzyl chloride and benzal chloride was first analysed, then a series of mixtures of benzal chloride and benzotrichloride, and finally a series of ternary mixtures obtained by adding known amounts of benzyl chloride to the benzal chloride–benzotrichloride mixtures.

The data obtained with the binary mixtures were used for construction of calibration curves, the results with the ternary mixtures served as an experimental check of the nomographic method for converting peak area percentages into weight percentages (see below).

For checking the reproducibility of the results each sample was analysed immediately after composing it, as well as after a few days, samples having been kept cool and stored in closed bottles.

Peak area determination

Several methods for determination of the peak area (see *e.g.* ref. 2) are known. In our case, the most accurate and least subjective method proved to be the calculation of the peak height times the peak width at half height. A method consisting of dividing the peak area into a number of triangles, the areas of which were subsequently summed, proved to be particularly tedious and subjective (differences of 8 % between various analysts occurring).

RESULTS AND DISCUSSION

Calibration curves for binary mixtures

Table I summarizes the data obtained from the two series of binary mixtures used for calibration, where it can be seen that the peak area percentages found are approxi-

TABLE I

ANALYSIS OF BINARY MIXTURES

Benzyl chloride/Benzal chloride			Benzal chloride/Benzotrichloride		
Wt. % intake	Mole % calcd.	Peak area % found	Wt. % intake	Mole % calcd.	Peak area % found
0.0*	0.0	0.0	0.0**	0.0	0.0
0.88	1.14	0.9	8.0	9.6	8.4
1.96	2.50	1.8	20.1	23.6	21.7
4.71	6.0	4.6	35.0	39.6	38.0
9.10	11.4	9.8	50.2	55.4	53.3
12.1	15.1	11.2	69.9	73.9	73.6
30.0	35.6	33.2	90.1	91.7	92.7
50.4	56.6	55.8	92.5	93.7	94.5
53.2	59.4	59.4	95.0	95.9	96.7
70.6	75.5	75.1	97.5	97.9	98.5
89.6	91.7	92.5			
89.9	92.0	91.7			
95.1	96.0	97.4			
98.0	98.4	98.9			
98.1	98.5	98.9			

* 100 % Benzal chloride.
** 100% Benzotrichloride.

mately equal to the calculated mole percentages, the largest deviation being 4 %! More accurate results can be obtained, however, by using *calibration curves* as shown in Figs. 2 and 3. These curves were constructed by plotting percentages of total peak area against weight percentages given, for benzyl chloride in mixtures with benzal chloride (Fig. 2) and for benzal chloride in mixtures with benzotrichloride (Fig. 3).

Peak area percentages found when analysing binary mixtures of unknown composition can thus be readily converted into weight percentages.

Reproducibility of the data

Table II shows the data obtained when analysing samples in duplicate, with a time interval of a few days. The reproducibility of the peak area percentages proves to be very good: a mean deviation of only 0.4–0.5 % is shown to occur.

The total peak area is less reproducible, however; the standard deviation amounts to about 2.5 %. This means that an accurate quantitative analysis cannot be based on the determination of a single peak area in comparison with the peak area of the pure component in a calibration chromatogram.

Analysis of ternary mixtures

In the case of ternary mixtures, the relationship between peak area percentage and corresponding weight percentage cannot be obtained from a simple two-dimensional calibration graph, but must be represented by a three-dimensional diagram. This diagram will consist of a right triangular prism with ternary composition diagrams as base and top surfaces, and binary plots of peak area percentages *versus* weight percentages as side surfaces.

This space model would not, however, be suitable for analytical purposes, but it can be "unfolded" into a simplified nomograph shown in Fig. 4.

Fig. 2. Calibration graph for converting percentages of total peak area into weight percentages of the components of binary mixtures. Benzyl chloride with benzal chloride.
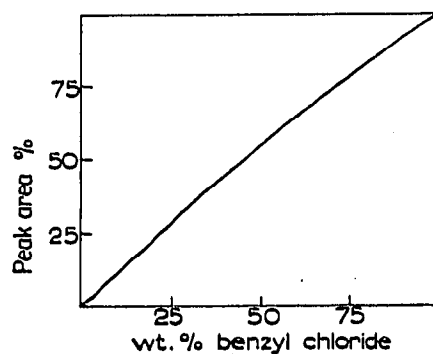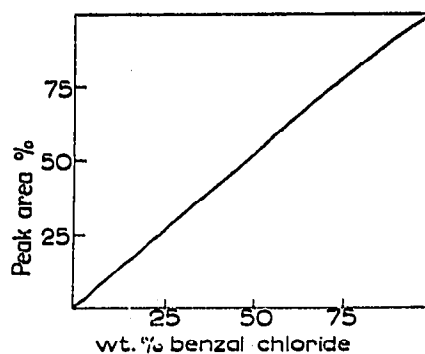

Fig. 3. Calibration graph for converting percentages of total peak area into weight percentages of the components of binary mixtures. Benzal chloride with benzotrichloride.
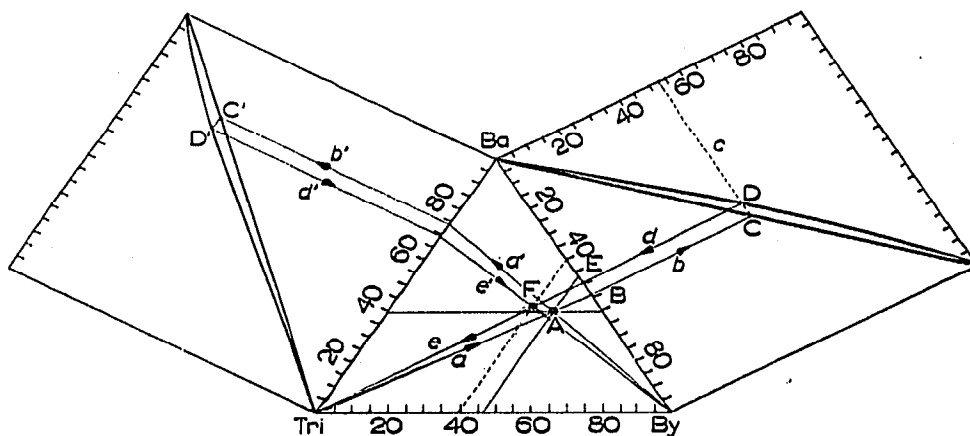

Fig. 4. Nomograph for converting percentages of total peak area into weight percentages of the components of ternary mixtures.

TABLE II

COMPARISON OF DUPLICATE ANALYSES

Benzyl chloride/Benzal chloride			Benzal chloride/Benzotrichloride		
Wt. % intake	% Peak area	Total peak area	Wt. % intake	% Peak area	Total peak area
			8.0	7.9	671
0.88	0.92	783		8.9	683
	0.85	761	20.1	21.2	669
4.71	4.6	799		22.2	668
	4.6	772	35.0	37.2	657
9.1	9.6	792		38.5	658
	10.0	771	50.2	54.8	678
30.0	33.2	763		54.8	671
	33.2	771	69.9	73.8	688
50.4	56.4	768		73.4	696
	55.4	751	90.1	92.8	674
70.6	75.9	389*		92.7	704
	74.3	379	92.5	94.4	686
89.9	91.5	393		94.6	689
	91.9	368	95.0	96.9	757
95.1	97.5	380		96.4	698
	97.4	372	97.5	98.5	725
				98.5	708
Mean-deviation	0.4	2.1 %		0.5	2.5 %

* At reduced sensitivity.

The nomograph consists of a triangular composition diagram and two binary calibration graphs, by which means the ternary system can be split up into two binary systems. A graphical artifice is furthermore introduced by drawing the diagonal in the binary calibration graphs, which enables one to use the triangular diagram for plotting both peak area percentages and weight percentages on the same axis.

As an example, a peak area percentage of 53.5 on the ordinate of the right-hand calibration graph of Fig. 4 may—via line c, point C and line b—now be represented by a point B = 53.5 % on the absciss of the graph. The weight percentage corresponding to the 53.5 % of total peak area mentioned, represented by point D according to the calibration graph, then can be read—via line d— from the same absciss, in point E = 48.2 wt %.

Using the nomograph

An example of how to convert the peak area percentages into weight percentages of the components of the ternary mixture analysed is given below; one proceeds as follows:

1. Let the peak area percentages be: 46.1 % for benzyl chloride (By), 40.0 % for benzal chloride (Ba) and 13.9 % for benzotrichloride (Tri). This "composition" will then be represented by point A in the triangular diagram of Fig. 4.

2. Now draw a line a from angular point Tri through A till it intersects side By–Ba in B. Line a represents the locus of all "compositions" having the same By/Ba peak area ratio, irrespective of the percentage of Tri; point of intersection B gives a

measure for this ratio, *viz.* 53.5 % By to 46.5 % Ba. This result may be checked arithmetically as follows:

$$\frac{46.1}{46.1 + 40.0} \cdot 100\% = 53.5\% \quad \text{and} \quad \frac{40.0}{46.1 + 40.0} \cdot 100\% = 46.5\%.$$

3. When normal graph paper has been used for the square diagrams the next step is to follow the millimeter division 53.5, line *b*, till it intersects the diagonal in point C.

4. Draw a line *c* from point C, parallel to the absciss By–Ba; line *c* intersects the calibration curve in D.

5. Then follow line *d*, parallel to *b*, till it intersects the absciss By–Ba in point E = 48.2. Point of intersection E now presents a measure for the weight percentage ratio of By and Ba, irrespective of the percentage of Tri; this ratio is found here to be 48.2 wt % By to 51.8 wt % Ba.

6. Finally draw line *e* from point E to angular point Tri; line *e* will be the locus of all ternary compositions having the By/Ba ratio mentioned. Somewhere on this locus *e* the composition required will be situated.

7. In order to find the unknown point on line *e*, a *second locus e'* may now be constructed by repeating the above procedure using the binary calibration graph Ba–Tri; locus *e'* will represent weight percentage compositions having a Ba/Tri ratio corresponding to the initially given ternary "peak area composition" A.

The construction is presented in Fig. 4 by lines *a'*, *b'*, *c'*, *d'*, and *e'*:

Locus *a'* represents peak area compositions having a Ba/Tri ratio of:

$$\frac{40.0}{40.0 + 13.9} \cdot 100\% = 74.2\% \text{ Ba to } \frac{13.9}{40.0 + 13.9} \cdot 100\% = 25.8\% \text{ Tri.}$$

After conversion into weight percentages locus *e'* represents sample compositions given by point E', corresponding to a Ba/Tri ratio of 70.0 wt % Ba to 30.0 wt % Tri.

8. The point of intersection of the loci *e* and *e'*, point F, finally represents the ternary composition of the sample analysed, *viz.* 39.4 % By, 42.3 % Ba and 18.3 % Tri.

This result may be arithmetically checked as follows: From the calibration graphs have been derived locus *e*:

By:Ba = 48.2:51.8, and locus *e'*:

Ba:Tri = 70.0:30.0.

Hence: By:Ba:Tri = 48.2:51.8:(30.0·51.8/70.0) = 48.2:51.8:22.2.

By reducing these values, the sum of which is 122.2, to a total of 100 % (*i.e.* dividing each by 1.222) the weight percentage composition of the mixture analysed is found: By:Ba:Tri = 39.4 %:42.3 %:18.3 %.

Experimental check of the method

Table III presents the data for a series of synthetic ternary mixtures of benzyl chloride (By), benzal chloride (Ba) and benzotrichloride (Tri). These mixtures have been analysed by GLC using the above mentioned technique for converting percentages of total peak area into weight percentages.

TABLE III

ANALYSIS OF A NUMBER OF TERNARY MIXTURES OF PREDETERMINED COMPOSITION, FOR CHECKING THE METHOD

No.	Wt. % by intake			% of total peak area			Wt. % found		
	By	Ba	Tri	By	Ba	Tri	By	Ba	Tri
1	17.9	80.0	2.1	20.0	78.3	1.7	18.7	79.6	1.7
2	16.6	79.2	4.2	17.2	80.3	2.5	16.9	79.3	3.8
3	16.6	77.1	6.3	19.0	76.5	4.5	17.5	76.4	6.1
4	16.6	75.2	8.2	19.3	74.2	6.5	17.8	73.3	8.9
5	16.6	6.7	76.7	21.3	5.9	72.8	17.0	5.8	77.2
6	16.7	58.2	25.1	19.4	61.0	19.6	16.8	59.5	23.7
7	16.7	41.6	41.7	19.8	44.5	35.7	17.0	43.0	40.0
8	16.7	29.1	54.2	20.6	36.1	48.3	16.6	30.8	52.6
9	16.7	16.8	66.5	20.5	17.1	62.4	16.7	16.7	66.6
10	41.0	57.5	1.5	44.6	54.9	0.5	40.1	58.9	1.0
11	40.0	57.0	3.0	43.8	54.8	1.4	39.7	57.2	3.1
12	40.0	55.5	4.5	43.5	54.1	2.4	38.5	56.9	4.6
13	40.0	54.1	5.9	45.2	51.0	3.8	40.1	54.5	5.4
14	40.1	4.8	55.1	46.5	4.5	49.0	40.0	4.8	55.2
15	40.2	41.8	18.0	44.6	41.0	14.4	39.0	42.5	18.5
16	40.1	30.0	29.9	45.8	29.5	24.7	39.4	31.0	29.6
17	40.0	21.0	39.0	48.2	20.4	31.4	40.2	21.2	38.6
18	40.0	12.1	47.9	47.4	11.0	41.6	41.3	12.3	46.4
	Mean deviation in %						0.6	0.8	0.6
	Maximum deviation in %						1.5	1.9	1.7

The mixtures have all been analysed in duplicate, which showed a very good reproducibility: the mean difference between duplicate analyses proved to be less than 1 %. For the sake of simplicity in Table III values are mentioned for one series only.

A comparison of the weight percentages taken with the weight percentages found by analysis shows that the mean deviation is less than 1 %, with a maximum deviation of less than 2 %. This shows the nomographic method to be distinctly more accurate than the original approximation method which puts peak area percentages equal to mole percentages.

Note. The nomographic method described above is particularly suitable for routine analysis of large numbers of samples. In the case of a very limited number of analyses it may be advantageous to use only the arithmetical check method in combination with the two binary calibration graphs.

SUMMARY

A nomographic method is described for the quantitative gas chromatographic analysis of ternary mixtures of benzyl chloride, benzal chloride and benzotrichloride. The nomograph converts percentages of total peak area on the gas chromatogram into

weight percentages of the components of the sample. The nomograph is constructed by combining a triangular composition diagram with two binary calibration graphs. The latter graphs have been experimentally determined by gas chromatographic analysis of two series of synthetic binary mixtures. An experimental check shows the method to be accurate to within 1–2 wt. %.

REFERENCES

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[2] J. F. K. HUBER, *Chem. Weekblad*, 59 (1963) 445.