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THE GAS–LIQUID CHROMATOGRAPHY OF THE CHLOROETHANES AND CHLOROTOLUENES

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SUMMARY

The quantitative chromatography to analyse the reaction products of the photochemical chlorinations of ethylene and toluene (ring and side-chain substitution) is presented as calibrations of component peak height or area ratios *versus* mass ratio.

An empirical procedure is proposed to provide a rapid method of predicting the composition of a mixture of chlorinated components, which are members of the same chromatographic family, by transforming the calibrations obtained using one chromatographic system in order to render them useful for another, different system.

INTRODUCTION

A number of different workers has expressed concern about the difficulty of analysing reaction products from the chlorination of hydrocarbons. In general these products consist of a mixture of many chlorinated hydrocarbons and often include isomers and other compounds whose chemical and physical properties prohibit an accurate yet simple analysis.

Attempts to analyse such mixtures by ordinary physical procedures have been reported and the limitations of these techniques are well documented. For instance, GALITZENSTEIN AND WOOLF[1], who compared the use of rapid density and refractive index determinations, were forced to discard these methods as insufficiently accurate, and to revert to a classical fractionation procedure. Fractionation, however, also has serious disadvantages, since it is a time-consuming method which often cannot be used without suitable precautions. This was recognised by RATCLIFFE[2], who, in searching for an appropriate method to analyse a mixture of temperature-sensitive polychloroethanes, found that while endeavouring to avoid thermal degradation, he was forced to employ continuous fractionation in combination with total reflux with intermittent take-off. The procedure could only produce binary mixtures, which subsequently had to be analysed by refractive index measurements,

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and was complicated further in cases where one or more azeotropes could be formed.

Of the various analytical techniques which have appeared in the literature, gas–liquid chromatography has been shown to be the most satisfactory. The chromatographic method was found[3] faster and more accurate than analysis based on other physical or chemical routes, and its results have proved as precise, accurate and rapid as the more expensive mass spectrometric approach.

Although many authors have studied the chromatography of chlorinated hydrocarbons, very few papers have been published giving calibration curves describing quantitative analysis. Consequently the calibration curves of the reaction products (Table I) of two important industrial reactions, the photochlorination of ethylene and that of toluene, have been developed.

No previous detailed study of the chromatography of the chloroethanes as a group has been reported, though the literature contains information on the separation of mixtures, some of whose components have been chloroethanes. Thus HARRISON[4] tabled retention data for the separation of a large number of chlorinated hydrocarbons including, 1,2-di-, 1,1,2-tri-, 1,1,2,2-tetra- and 1,1,1,2-tetrachloroethane, and listed as being the more suitable of the stationary phases examined, tricresyl phosphate, dinonyl phthalate, silicone fluid MS 710 and paraffin, all on Celite 545 support. WARREN et al.[3] also reported the separation of 1,2-di-, 1,1,2-tri-, and 1,1,2,2-tetrachloroethane using didecyl phthalate, dioctyl phthalate, silicone oil 550 and paraffin, all on Celite 545 support, and claimed that the most satisfactory results were obtained with paraffin. URONE et al.[5] similarly examined the same chloroethanes on six stationary phases — paraffin, Carbowax 4000, Carbowax 20M, triorthocresylphosphate, Apiezon L, and halocarbon stopcock grease — at different temperatures, and although they presented retention data for all three chloroethanes on these columns, only the calibration curves based on peak area and peak height for 1,1,2,2-tetrachloroethane at 97° on the paraffin column were provided.

Few workers, who have specifically been concerned with the chlorination of ethylene and who have analysed their reaction products chromatographically, have carried out their experiments under the conditions required to produce simultaneously the compounds listed in Table I. Thus SHAKHTAKHTINSKII AND SHIK[6] and MAMEDOV et al.[7], who investigated the gas chromatographic analysis of the reaction products of the chlorination and high-temperature chlorination, respectively, of ethylene, featured only 1,2-di- and 1,1,2-trichloroethane among their reaction products. SHAKHTAKHTINSKII AND SHIK[6] carried out their analysis using dinonyl phthalate on a firebrick support and investigated the influence of the chromatograph operating parameters to obtain a convenient analysis time of 18 min. MAMEDOV et al.[7], however, were concerned with the effect of stationary phase polarity on the separation of their reaction products and determined that both polar phases, dioctyl phthalate, dinonyl phthalate, tricresyl phthalate and β,β'-oxydipropionitrile, and a non-polar phase, polymethylphenylsiloxane oil, could be used successfully.

More recently HINSHAW[8] reported the use of SE-30 on firebrick support to analyse the reaction products of the oxychlorination of ethylene, and CAINES et al.[9] analysed the reaction products of the chlorination of 1,2-dichloroethane using a silicone elastomer (E301) stationary phase on Chromosorb support at 120°. Other separations of the chloroethanes have been claimed by FRANKLIN et al.[10], using

tricresyl phosphate on Chromosorb support, and by LODI[11], who separated mixtures of chloroderivatives on polyoxyethylene glycol 400 supported on Celite 22.

While the chloroethanes can be chromatographed with relatively little difficulty, the isomeric ring compounds, *ortho-*, *meta-*, and *para*-chlorotoluenes, cannot easily be differentiated. Thus BECKWITH AND WATERS[12] were unable to separate *ortho-* and *para*-chlorotoluene at 130° under reduced pressure using a 31% dinonyl phthalate on Celite 545 column, and DAVIES[13] could not separate the *meta* and *para* isomers with a 15% dinonyl phthalate on Celite column at 82°. FREEMAN[14], however, after investigating the suitability of various stationary phases determined that, while 7,8-benzoquinoli neon Kromat-FB could effect the separation of the *ortho* and *para* isomers, Ucon 2000, polyethylene glycol 1500, silicone oil 550, didecyl phthalate and bis(2-ethylhexyl)-tetrachlorophthalate could not. LANGER AND PURNELL[15] confirmed this result, noting that all three isomers are separable on either benzyldiphenyl (*ortho* and *para* isomers in the ratio of 6:4), 7,8-benzoquinoline or phenanthrene, at 100° and 110°. They recommended phenanthrene for this separation.

FREEMAN[14] further demonstrated the separation of the side-chain, benzyl and benzal chlorides, in a mixture of chlorotoluenes and chlorobenzyl chlorides using silicone oil 550 at 130°, and reported private communications from both EMERY AND STEWART, and WINSTON AND KOSSOY, who separated these substances on a diisodecyl phthalate column, and silicone oil 200 and silicone grease columns, respectively. The separation of benzyl, benzal and benzochlorides, however, has been achieved on a "Type C" column with silicone oil stationary phase by HARING AND KROON[16], who have presented the calibration curves for the quantitative analysis of each of these compounds using a thermal conductivity detector system.

TABLE I

REACTION PRODUCTS OF THE PHOTOCHLORINATION OF ETHYLENE AND TOLUENE

Reaction products of				
Ethylene	b.p. (°C)	m.p. (°C)	Toluene	b.p. (°C)
1,2-Dichloroethane	83.5		Benzyl chloride	179.4
1,1,2-Trichloroethane	113.6		Benzal chloride	207
1,1,1,2-Tetrachloroethane	129		Benzotrichloride	220.7
1,1,2,2-Tetrachloroethane	146.3		*ortho*-Chlorotoluene	159.5
Pentachloroethane	162		*meta*-Chlorotoluene	161.6
Hexachloroethane		186	*para*-Chlorotoluene	162.2

EXPERIMENTAL

The chromatography of the compounds listed in Table I was investigated in conjunction with four independent kinetic and mass transfer studies of the photochlorinations of ethylene and toluene. In each study quantities of the reaction products were either purchased commercially or prepared and then subsequently purified. Standard mixtures were prepared and analysed chromatographically and calibration charts were constructed from weight fractions and peak heights or areas. In each investigation the chromatographic system employed was selected

on the basis of separations of chloro derivatives reported in the literature. Two studies of the chloroethanes obtained with different chromatographic systems were conducted[17] and are presented with two examinations of the chlorotoluenes corresponding to side-chain[18] and ring substitution, respectively.

Investigation No. 1

The chloroethanes were analysed using a 5-ft. long, 1/8-in. I.D. aluminium column packed with 90–100 mesh Anochrom ADS support coated with 8 % (w/w) dinonyl phthalate liquid phase. The chromatograph was a Carle basic gas chromatograph, Type No. 6500, employing a thermistor type thermal conductivity cell, the response of which was recorded on a Honeywell strip chart recorder. A Hamilton 7101 NCH 1-μl syringe was used to inject the liquid sample.

Although the operating parameters were systematically varied to determine the most favourable operating conditions, it was not possible to obtain the complete resolution of 1,1,2,2-tetra- from pentachloroethane. The following conditions were selected: Helium carrier gas flow-rate, 8 ml/min; column temperature, 142 °; column inlet temperature, 142 °; sample size, 0.5 μl.

Peak heights were used in preference to peak areas in the quantitative analysis, since in the absence of a disc integrator there was no advantage in using a less accurate, but highly time-consuming alternative area measurement technique.

Investigation No. 2

The chloroethanes were analysed on a 10-ft. long, 1/8-in. O.D. stainless-steel column packed with 60–80 mesh AW, HMDS Chromosorb W support and loaded with 20 % (w/w) SE-30 liquid phase. The chromatograph used was an Aerograph Model No. 1520 which employs a hydrogen flame ionisation detector. The detector response was recorded on a Honeywell strip chart recorder with a Ball disc integrator attachment to enable rapid and accurate peak area determinations. A Hamilton 7071 NCH 1-μl syringe was used to inject the liquid sample. In this study pure n-decane was used as an internal standard.

As in the previous investigation the most suitable operating conditions were evaluated: Detector temperature, 250 °; injector temperature, 250 °; nitrogen carrier gas flow-rate, 30 ml/min; column temperature, 122 °; sample size, 0.7 μl.

Investigation No. 3

Mixtures of toluene, benzyl chloride, benzal chloride and benzotrichloride were chromatographed using the system and procedure described in *Investigation No. 1*.

In this investigation, however, a higher helium carrier gas flow-rate of 20 ml/min was employed, while all other conditions used were identical with those in investigation No. 1.

In spite of a systematic search for the most favourable operating conditions, the complete resolution of benzal chloride from benzotrichloride could not be obtained.

Investigation No. 4

The literature clearly suggests the use of phenanthrene, benzyldiphenyl or 7,8-benzoquinoline for the separation of mixtures of the isomeric *ortho-*, *meta-* and *para*-chlorotoluenes. In this investigation, however, considerable difficulty was encountered in attempting to achieve this result.

A number of different columns, 1/8-in. O.D. and 10 ft. in length, were prepared and evaluated using either a Beckman Model GC-2 or Aerograph Model No. 1520 gas chromatograph. The following liquid phases loaded on either Chromosorb W, Gas-Chrom Q, or Anachrom solid supports were examined: dinonyl phthalate and bentone 34 mixture, SE-30, Carbowax 400, Carbowax 20M, Carbowax 600, Porapak Q, diethylene glycol succinate, phenanthrene, and benzyldiphenyl.

These columns were systematically evaluated under various operating conditions, yet in no case could the *meta* and *para* isomers be separated, and, moreover, it was found difficult to resolve the *ortho* isomer from the *meta/para* combination. The SE-30 column was unable to separate the three isomers at all, while the columns using Porapak support gave troublesome adsorption effects. On all the other columns incomplete resolution of the *ortho* peak and the *para/meta* peak was obtained. The most satisfactory results were found using 10 % (w/w) Carbowax 20M liquid phase, which gave nearly complete *ortho* and *para/meta* resolution.

Research into the development of a suitable approach to analyse this mixture is continuing and it is anticipated that the gas chromatographic approach will need to be coupled with infrared (IR) techniques to achieve this result.

RESULTS

The calibration curves and typical chromatograms obtained from investigations Nos. 1–3 are presented in Figs. 1–3 and Figs. 4–6, respectively.

It was found that using these calibration curves, the percentage of each component in their respective mixtures could be estimated to an accuracy of ± 5 % at 95 % confidence level.
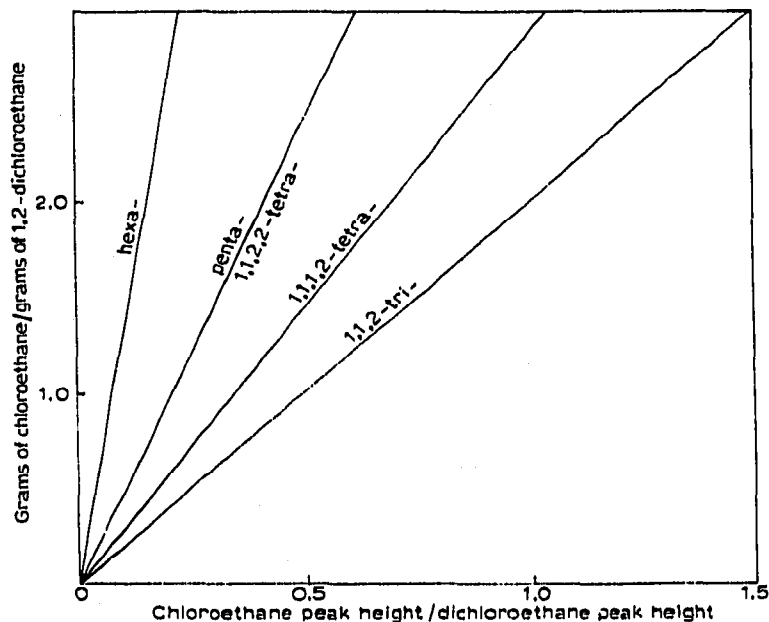

Fig. 1. The calibration curves for the analysis of the reaction products of the photochlorination of ethylene. Investigation No. 1.
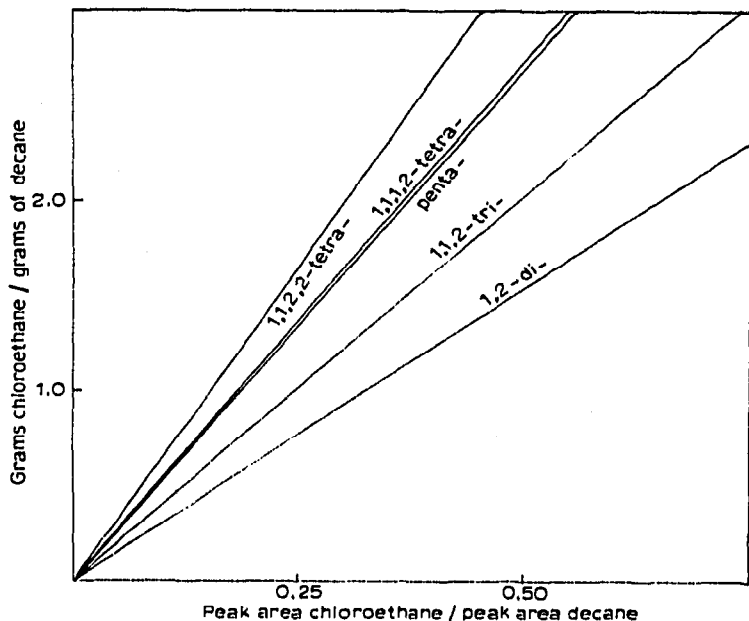
Fig. 2. The calibration curves for the analysis of the reaction products of the photochlorination of ethylene. Investigation No. 2.
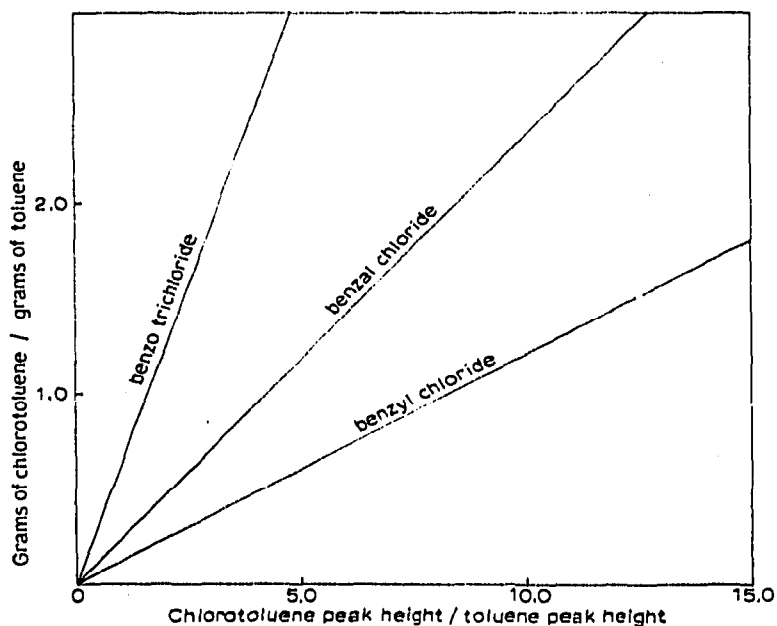

Fig. 3. The calibration curves for the analysis of the reaction products of the photochlorination of toluene. Investigation No. 3.
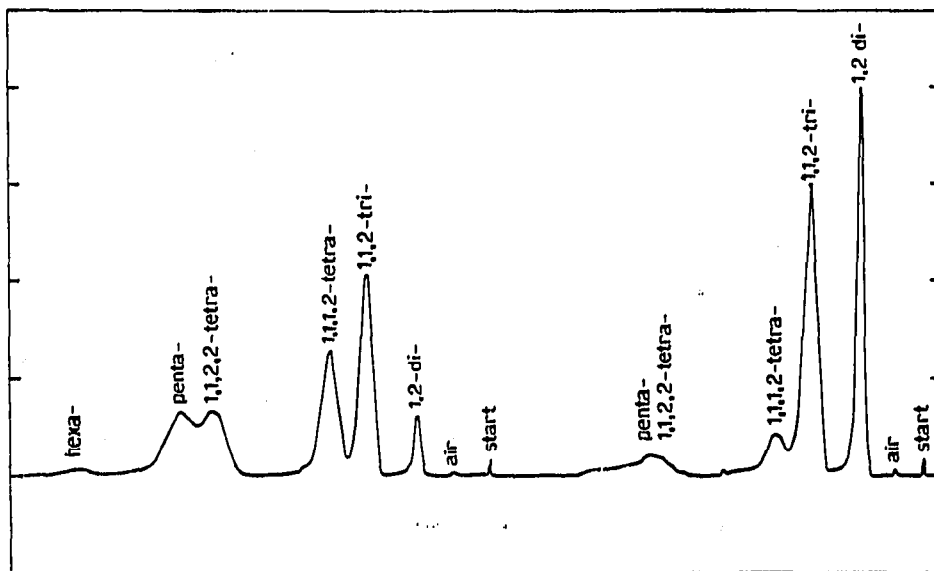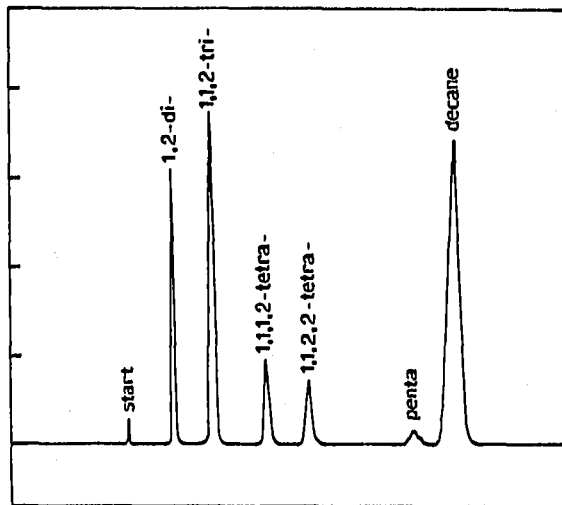
Fig. 4. Typical chromatograms. Investigation No. 1.

Fig. 5. Typical chromatogram. Investigation No. 2.

The relative retention time data obtained from these investigations are listed in Table II.

DISCUSSION

In practical chromatography a number of empirical relationships have been developed to assist qualitative analysis. These relationships, which have been summarised by SCHUPP[10], have been useful for the identification of compounds,
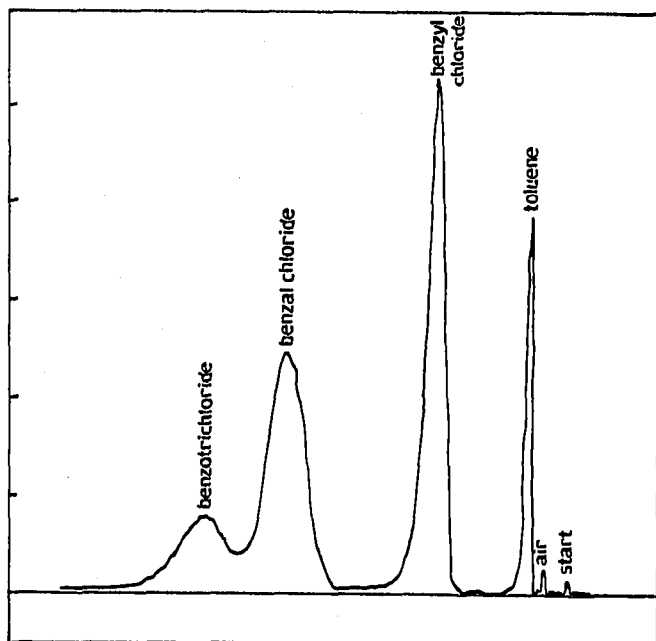
Fig. 6. Typical chromatogram. Investigation No. 3.

TABLE II

RELATIVE RETENTION TIME DATA

Substance	Investigation No. 1	Investigation No. 2	Investigation No. 3
1,2-Dichloroethane	0.112	0.109	
1,1,2-Trichloroethane	0.239	0.241	
1,1,2,2-Tetrachloroethane	0.649	0.549	
1,1,1,2-Tetrachloroethane	0.361	0.416	
Pentachloroethane	0.732	0.867	
Hexachloroethane	1.0		
Decane		1.0	
Toluene			0.238
Benzyl chloride			1.0
Benzal chloride			2.219
Benzotrichloride			3.209

for the characterisation of the chromatographic behaviour of family groups of compounds, and for the determination of stationary phase characteristics. More importantly, perhaps, they have provided the chromatographer with a source of generalised background information indicating behavioural trends which enable him to select intuitively that chromatographic system most suited to his needs.

In contrast the approach that has been taken towards quantitative analysis has avoided empirical and perhaps approximate methods, and has striven continually for increased orders of accuracy. This has occurred despite the fact that it is frequently necessary to predict rapidly, within an acceptable but limited accuracy,

the composition of a mixture of known compounds — a task which currently cannot readily be accomplished when a formal calibration procedure is prohibited owing to restrictions of the time and effort which can be expended. In this situation the only convenient approach is to employ an intuitive prediction technique based on empirical guide lines.

The basis for such an approach has been considered in the literature and has been well summarised by KAISER[20]. It is known for example that the relative response factors obtained from thermal conductivity and flame ionisation detector results for homologous series are linearly related to the molecular weights of the individual series members, and that, consequently, missing response values within a homologous series may be interpolated. Moreover, the linear relationship between the relative molar response for a flame ionisation detector and the molar ionisation value of a substance has also been noted. The approximate estimate, given by ONGKIEHONG[21], for the specific substance correction factor for a flame ionisation detector and applicable to non-halogen containing compounds has also received considerable attention. The problem, however, of obtaining the calibration for the analysis of a chromatographic family of compounds, which either do not form a homologous series or contain halogen groups has not been successfully overcome.

·To satisfy this requirement, the authors have sought to find an empirical method of transforming the calibrations of a family of chloro compounds obtained using one chromatographic system in order to render them useful for another, different system. Initially the results obtained by HARING AND KROON[10] were compared with those of investigation No. 3. In this comparison a given ternary mixture (corresponding to mixture No. 16 of HARING AND KROON) of benzyl, benzal and benzochlorides was hypothetically analysed to obtain the area fractions and peak ratios of each component using the calibrations of HARING AND KROON and investigation No. 3, respectively. The values of these two quantities were then plotted one against the other for each component and a linear relation was obtained (Fig. 7). It should be noted that these compounds form a chromatographic family as demonstrated by the semilog plots of retention time *versus* chlorine number obtained by FREEMAN[14] and confirmed by our own results. Moreover, the chromatographic system used by HARING AND KROON employed a silicone oil column and thermal conductivity cell detector and was operated at entirely different conditions to those of investigation No. 3.

The linearity of the relation in Fig. 7 appears quite significant, since it implies that despite the number of system variables which influence each calibration, it would have been possible to calibrate only two of the three members of this family and by performing this type of comparison with HARINGS AND KROON's calibration as a reference the third component's calibration could have been inferred. Moreover, by extension it might be expected that for a family containing a large number of members this approach would be particularly valuable.

Encouraged by these possibilities a second comparison of the same type was carried out for the chloroethanes using the calibrations obtained in investigations Nos. 1 and 2 and by CAINES *et al.*[9] and WILKINSON[22]. The chromatographic system used in refs. 9 and 22 was very similar to that of investigation No. 2, while the system used in investigation No. 1 was dissimilar in every respect. The results of these comparisons are shown in Figs. 8–10.
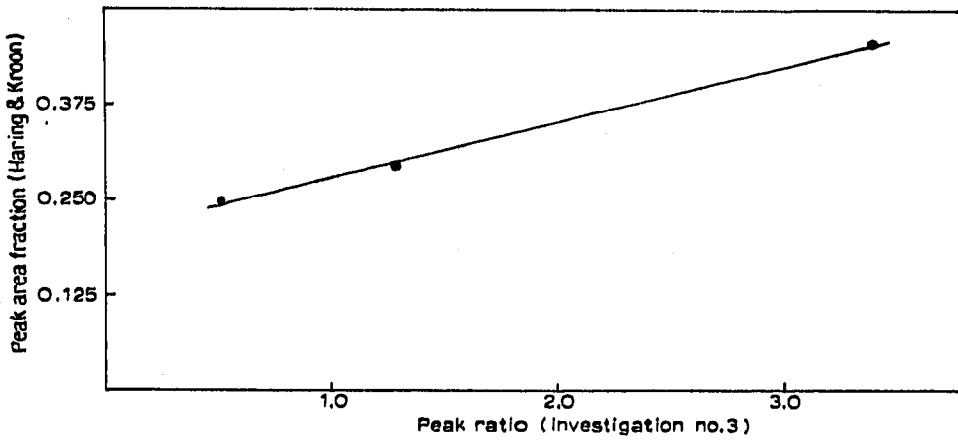
Fig. 7. Comparison of the results from investigation No. 3 with the calibration obtained by HARING AND KROON.
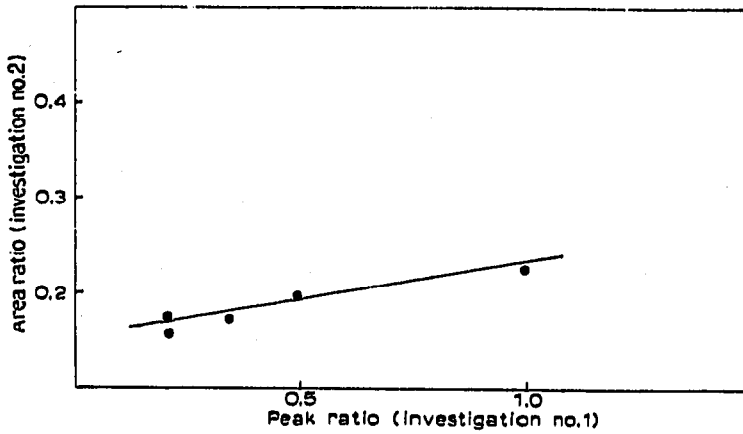

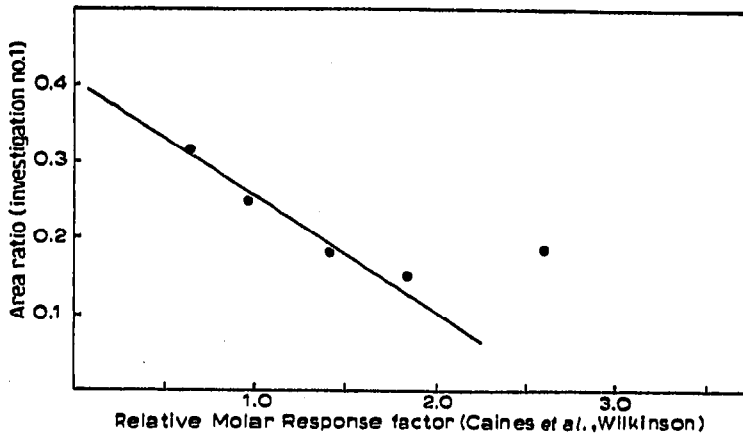Fig. 8. Comparison of the calibrations of investigations Nos. 1 and 2.

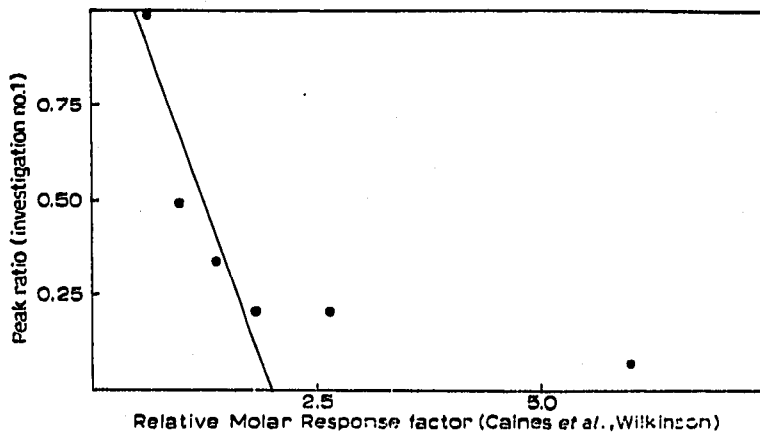Fig. 9. Comparison of the calibrations of investigation No. 2 and the results of CAINES et al.[9] and WILKINSON[22].

Fig. 10. Comparison of the calibrations of investigation No. 1 and the results of CAINES *et al.*[11] and WILKINSON[22].
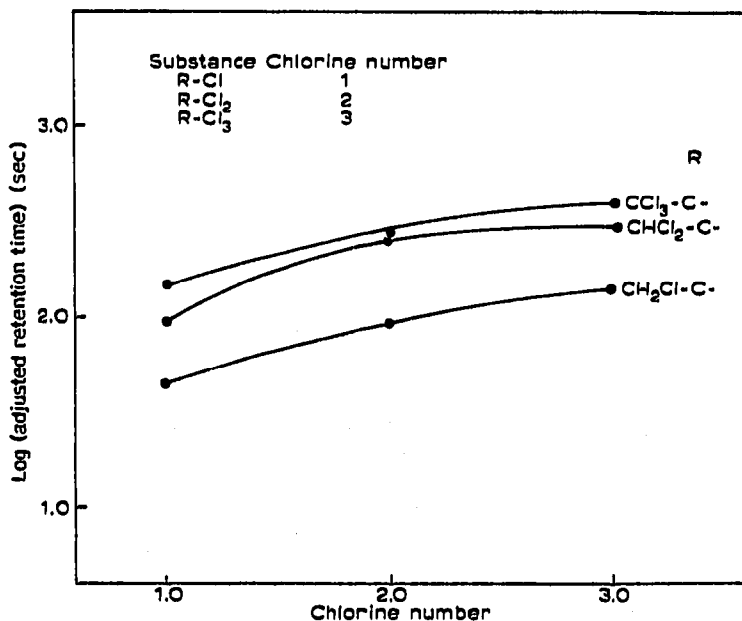

Fig. 11. Chloroethane family plots. Results taken from investigation No. 1.

Unfortunately, these results do not support or disprove this type of comparison as a workable means of initial calibration. If one examines the structural variation of the chloroethanes, three distinct families can be identified based on the chlorine number criterion (Fig. 11), suggesting that this group of compounds should not be treated as a family. Moreover, if a semilog plot of the adjusted retention time *versus* chlorine number of the chloroethanes as a group is drawn (Fig. 12), the loose behaviour of this pseudo-family can be demonstrated. It does not seem unreasonable therefore to expect some degree of scatter when the different calibrations are compared, and under these circumstances the results of Fig. 8 appear quite
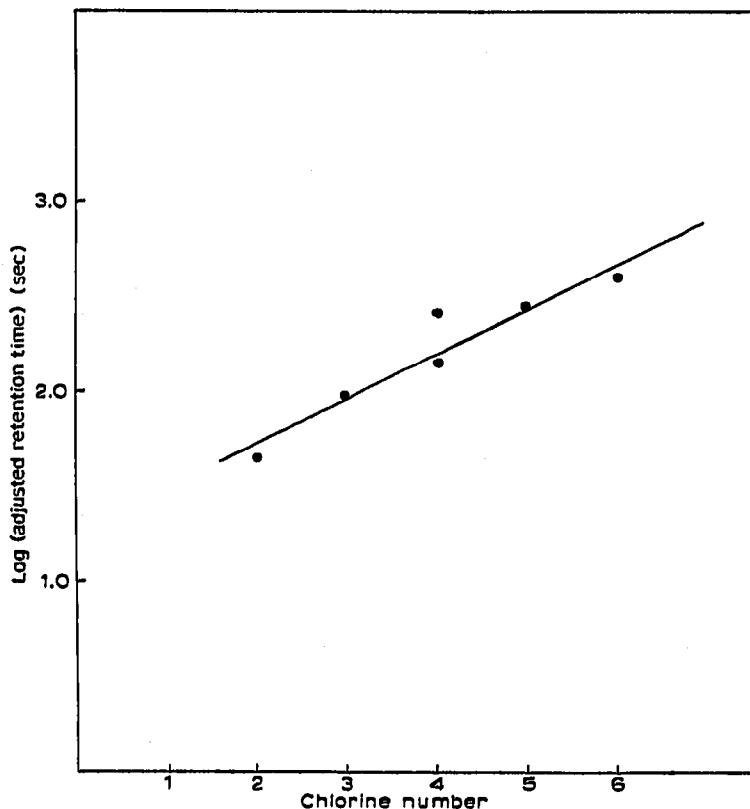
Fig. 12. Logarithm of the adjusted retention time in seconds *versus* the number of chlorine atoms of each chloroethane. Results taken from investigation No. 1.

favourable. The results of refs. 9 and 22, however, cannot be linearly related to those of either investigation No. 1 or No. 2, unless the calibrations for pentachloroethane and hexachloroethane are ignored. It should be pointed out, however, that despite the large response obtained for pentachloroethane which was not experienced in investigation No. 2, there is little justification for this move.

I'aced with these results the authors do not recommend that this proposed method of initial calibration be employed. They do, however, recommend that further attention be directed to this approach to ascertain the criteria under which it may be more generally applicable.

CONCLUSION

Calibrations for the quantitative chromatography to analyse the reaction products of the photochlorination of ethylene and of toluene have been developed. Difficulty, however, was encountered in the analysis of *ortho-*, *meta-* and *para-*chloro-toluene mixtures and work to find a suitable procedure to overcome this is continuing.

The authors recommend the development of empirical techniques to predict rapidly the composition of a mixture of chlorinated compounds and have advanced

one such method with which partial success was obtained. Further investigations along these lines are recommended both to extend the method suggested in this paper and to search for improved alternatives.

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