

CHROM. 7573

AN EVALUATION OF POLYALKYLIMINES AS SPECIFIC CARBONYL ABSTRACTORS IN GAS CHROMATOGRAPHY

J. APPELYARD* and J. K. HAKEN**

Department of Polymer Science, The University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

SUMMARY

An evaluation of polyethyleneimine and polypropyleneimine as specific carbonyl abstractors for ketones and aldehydes, respectively, shows that with careful control of the reaction conditions aliphatic ketones and aldehydes may be preferentially abstracted. Alicyclic and diketones display anomalous behaviour and are abstracted with aldehydes while some reaction occurs with epoxides, lactones, oxygenated compounds and alkyl halides.

INTRODUCTION

Although the ease of application of reaction gas chromatography and of subtractive procedures provides a potentially powerful aid in tentative identification, acceptance of these techniques has been retarded. The early works were often of limited scope¹⁻³ and the results on further examination were not found to be generally applicable. Several recent works⁴⁻⁶ have shown the effect of column temperature and gas flow-rate on the abstraction of carbonyl compounds, the variability of abstraction within a homologous series and of anomalous reactions with other functional classes.

Acceptable abstraction of both ketones and aldehydes using sodium metabisulphite⁵ and aminoalkylpolysiloxanes⁶ has been reported and the evaluation of polyalkylimines has recently been suggested by Supina⁷, whose preliminary work indicated that ketones and aldehydes could be preferentially abstracted with polyethyleneimine and polypropyleneimine, respectively. Although the reason for the varying selectivity was not investigated, it was assumed⁸ that the additional methylene group was responsible and accounted for the very much lower McReynolds constants of the polypropyleneimine.

Both polymers have previously been reported as simple stationary phases. Grob⁹ used both materials as coatings for capillary columns for the separation of bases in cigarette smoke while Lindsay Smith and Waddington coated polyethyleneimine onto porous beads to reduce tailing in the separation of aliphatic amines¹⁰ and di-

* Present address: Dulux Aust. Ltd., Cabarita, N.S.W. 2137, Australia.

** To whom requests for reprints should be addressed.

amines²⁰. Polyethyleneimine²¹ and polypropyleneimine¹¹ with polyethylene glycols have been used for the separation of aliphatic amines.

The selective abstraction of these chemical classes has been reported by Bierl and co-workers¹². A 6-in. precolumn containing 5% *o*-dianisidine abstracted most aldehydes but not ketones when operated between 50 and 175°. A more reactive amine, benzidine, formed Schiff's bases with both aldehydes and ketones when a similar column containing 20% of the amine was used as 50–175°. The performance of *o*-dianisidine has been reproduced but independent examination of benzidine^{5,13} has shown the removal of ketones to be much less successful than suggested in the initial report. The bleed rate of both columns is high with short operating lives.

The present work describes the examination of the two polyalkylimines where it is apparent that on-column chemical reaction occurs with carbonyl compounds. The results suggested by Supina of specific abstraction are generally supported, but there are definite optimum areas of operation for the columns where the selectivity and efficiency of abstraction are highest.

It is shown that the shape of the molecule to be abstracted is of prime importance. With branched-chain ketones the carbonyl group is partially shielded from the reactive amino groups and the extent of the abstracting reaction is reduced, this being in agreement with studies using polyalkylaminosiloxanes.

Study of the polymers shows that both are of substantially branched structure, the polyethyleneimine containing a high proportion of primary amine groups apparently on the ends of polymer branches while the polypropyleneimine is high in tertiary nitrogen atoms.

EXPERIMENTAL

Gas chromatography

The data were obtained on a Hewlett-Packard 5750B research chromatograph using flame ionization detection. Aluminium columns (6 ft. × ¼ in. O.D.) were packed with 20% of the commercial stationary phases on 72–85 mesh acid-washed and silanized Celatom. The injection temperature was 190° and column temperatures of 100° and 120° were used each at flow-rates of 30 and 45 ml/min.

Stationary phases

The polyethyleneimine Cat. No. 02-1195 and polypropyleneimine Cat. No. 02-1198 (Supelco, Bellefonte, Pa., U.S.A.) were used as supplied. Two columns for each phase were prepared, one of each was used as a reference column after exhaustion of the reactive groups by repeated injections of 2-octanone.

Analysis

The relative amounts of primary, secondary and tertiary amino groups were determined by non-aqueous titration using the procedure of Wagner and co-workers¹⁴. Total amine, combined secondary and tertiary amine and tertiary amine contents were determined for both polymers, together with the elemental analyses and non-volatile matter. The total amine content of the polymer solution in ethylene glycol-isopropanol was determined by potentiometric titration with acid while the combined secondary and tertiary amine content was determined similarly with a sample

TABLE I
 PERCENTAGE REMOVAL OF KETONES, ALDEHYDES AND MISCELLANEOUS COM-
 POUNDS ON POLYETHYLENEIMINE AT 100° AND 120°

Compound	Flow-rate (ml/min)			
	30	45	30	45
	100°		120°	
<i>Aliphatic ketones</i>				
2-Propanone	100	43	95	0
2-Pentanone	100	53	79	45
2-Heptanone	100	0	83	69
2-Octanone	100	0	93	71
4-Methyl-2-pentanone	100	12	67	65
3,3-Dimethyl-2-butanone	58	0	54	53
5-Methyl-2-hexanone	100	9	75	30
3-Pentanone	100	8	76	60
3-Heptanone	100	33	71	55
3-Octanone	94	0	51	42
4-Heptanone	97	31	55	46
2,4-Dimethyl-3-pentanone	36	33	62	49
4-Octanone	100	21	65	28
2,6-Dimethyl-4-heptanone	61	4	56	20
1,1-Dimethoxy-3-butanone	60	29	50	0
4-Methyl-4-methoxy-2-pentanone	100	27	63	59
<i>Unsaturated aliphatic ketones</i>				
1-Butene-3-one	59	46	66	
<i>Alicyclic ketones</i>				
Cyclopentanone	100	69	97	0
Cyclohexanone	100	23	99	51
Cycloheptanone	100		99	39
4-Methylcyclohexanone	100	54	100	0
2-Methylcyclohexanone	100		89	5
<i>Turpenic ketones</i>				
Pulegone			78	
<i>Diketones</i>				
2,4-Pentanedione	100	16	87	0
2,4-Hexanedione	100	40	86	61
Trifluoroacetylacetone	86	0	83	0
<i>Miscellaneous compounds</i>				
Methyl pyruvate	92	26	95	0
<i>Aliphatic aldehydes</i>				
<i>n</i> -C ₃	100	0	6	0
<i>n</i> -C ₄	100	0	0	0
<i>n</i> -C ₅	95	0	0	0
<i>n</i> -C ₆	91	0	0	0
<i>n</i> -C ₇	96	0	16	0
Benzaldehyde	100	0	0	0
Salicylaldehyde	100	0	0	0
Furfural	100	0	0	0

(Continued on p. 322)

TABLE I (continued)

Compound	Flow-rate (ml/min)			
	30	45	30	45
	100°		120°	
<i>Epoxides</i>				
1,2-Epoxypropane	78	28	86	27
1-Chloro-2,3-epoxypropane	87	61		0
<i>Oxygenated compounds</i>				
Tetrahydrofuran	72	52	88	55
Dioxane	69	26	77	37
<i>Alkyl halides</i>				
Perchloroethylene	26	0	72	0
Ethylene dichloride	64	0	78	22
Ethyl bromide	10	0	50	0
Ethyl iodide	20	0	56	0
<i>Lactones</i>				
1,3-Propiolactone	74	0	84	24

where the primary amine groups had been converted to a Schiff's base by the addition of salicylaldehyde.

The tertiary amine content was determined by titration of a sample where the primary and secondary amines had been previously reacted with acetic anhydride.

RESULTS AND DISCUSSION

The behaviour of a variety of representative ketones, aldehydes and several miscellaneous compounds that had been reported as anomalies in earlier studies^{5,6} was examined using the polyethyleneimine column at 100 and 120° with flow-rates of 30 and 45 ml/min at each temperature with results as shown in Table I. The majority of 2-alkanones was completely abstracted at 100° and 30 ml/min flow-rate. The ethyl homologues, *i.e.* the 3-alkanones, showed a slightly variable performance as was observed with the earlier studies using aminoalkyl polysiloxanes as reactive stationary phases. Branched-chain ketones were only partially abstracted, the relationship between structure and reaction is shown in Table II with the results of earlier studies using *N*- β -aminoethyl- γ -aminopropyl trimethoxy silane (Z6020; Dow Corning, Midland, Mich., U.S.A.).

Partial shielding of the carbonyl groups is evident due to the proximity of the branched structure. With the structures shown as 1, 2 and 3 increased reaction occurs as the branched chain becomes more remote from the carbonyl group compounds, 1 and 4 are not completely comparable and 2 and 5 show reduced activity with replacement of a hydrogen atom with a methyl group. Compounds 4 and 5, where the two methyl groups are simply separated by a methylene group, show increased reactivity due to less steric hindrance. While the variability of reaction is obviously due to the molecular shape, it has been observed by Ackman¹⁵ with methyl branched ketones that the peak width is considerably greater than for a straight-chain ketone of the same carbon number when eluted on the same column.

TABLE II
PERCENTAGE ABSTRACTION OF BRANCHED-CHAIN KETONES ON POLYETHYLENE-
IMINE AND Z6020 COLUMNS

Flow-rate, 30 ml/min.

No.	Compound	Structure	Polyethylene- imine		Z6020	
			100°	130°	100°	130°
1	3,3-Dimethyl-2-butanone	$\begin{array}{c} \text{O} \quad \text{C} \\ \parallel \quad \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	58	54	46	22
2	4-Methyl-2-pentanone	$\begin{array}{c} \text{C} \quad \text{O} \\ \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	100	67	67	59
3	5-Methyl-2-hexanone	$\begin{array}{c} \text{C} \quad \text{O} \\ \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	100	75	100	98
4	2,4-Dimethyl-3-pentanone	$\begin{array}{c} \text{C} \quad \text{O} \quad \text{C} \\ \quad \parallel \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \quad \quad \\ \text{C} \quad \quad \quad \text{C} \end{array}$	36	62	58	0
5	2,6-Dimethyl-4-heptanone	$\begin{array}{c} \text{C} \quad \text{O} \quad \text{C} \\ \quad \parallel \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \quad \quad \\ \text{C} \quad \quad \quad \text{C} \end{array}$	60	50	43	0

Partial abstraction of 1-butene-3-one occurred as previously observed with bisulphite abstraction. With the same conditions normal and aromatic aldehydes were almost completely abstracted while the epoxides and oxygenated compounds were all appreciably abstracted.

The performance of the column at 100° when the flow-rate was increased to 45 ml/min was found to be quite unpredictable. The percentage abstraction of the *n*-alkyl ketones ranged from 0 to 50% while the reaction with all of the other ketones, the two epoxides, tetrahydrofuran and dioxane, was reduced and the reaction with aldehydes was minimal. The overall effect of the shorter residence time generally being to reduce the abstraction reaction.

Increasing the column temperature to 120° with the lower flow-rate results in aliphatic ketone abstraction between 50 and 95%, virtually complete removal of the alicyclic ketones and minimal reaction with aldehydes. An increase in flow-rate at this temperature reduced the removal of ketones and the other substances.

Polypropyleneimine at 100° and 30 ml/min showed moderate reaction with aliphatic ketones while with a flow-rate of 45 ml/min abstraction did not occur with most compounds. The alicyclic ketones, pulegone, 1-butene-3-one and the diketones were appreciably abstracted at both flow-rates. Aldehydes were completely reacted at both flow-rates while limited abstraction of the other compounds examined occurred. The data for abstraction with polypropyleneimine are shown in Table III.

At 120° aliphatic ketones were only moderately abstracted at 30 ml/min and generally not affected at the higher flow-rate while alicyclic ketones were essentially completely removed at both flow-rates. Aldehydes were completely abstracted at 30

TABLE III
 PERCENTAGE REMOVAL OF KETONES, ALDEHYDES AND MISCELLANEOUS COM-
 POUNDS ON POLYPROPYLENEIMINE AT 100° AND 120°

Compound	Flow-rate (ml/min)			
	30	45	30	45
	100°		120°	
<i>Aliphatic ketones</i>				
2-Propanone	0	0	28	0
2-Pentanone	0	5	76	0
2-Heptanone	0	35		18
2-Octanone	46	73	100	46
4-Methyl-2-pentanone	0	0	38	0
3,3-Dimethyl-2-butanone	17	0	23	0
5-Methyl-2-hexanone	29	30	100	0
3-Pentanone	14	0	0	0
3-Heptanone	27	0	35	0
3-Octanone	30	0	33	0
4-Heptanone	38	0	26	0
2,4-Dimethyl-3-pentanone	35	0	21	0
4-Octanone	50	0	58	0
2,6-Dimethyl-4-heptanone	55	0	23	0
1,1-Dimethyloxy-3-butanone	0	0	27	0
4-Methyl-4-methoxy-2-pentanone	38	0	54	0
<i>Unsaturated aliphatic ketones</i>				
1-Butene-3-one	90	75	81	10
<i>Alicyclic ketones</i>				
Cyclopentanone	25	95	100	71
Cyclohexanone	100	100	100	100
Cycloheptanone	100	100	100	100
4-Methylcyclohexanone	100	100	100	100
2-Methylcyclohexanone	57	100	100	100
<i>Turpenic ketones</i>				
Pulegone		100		
<i>Diketones</i>				
2,4-Pentanedione	100	100	100	100
2,4-Hexanedione	100	100	100	100
Trifluoroacetylactone	88	15	80	58
<i>Miscellaneous compounds</i>				
Methyl pyruvate	51	47	69	22
<i>Aliphatic aldehydes</i>				
<i>n</i> -C ₂	100	100	100	100
<i>n</i> -C ₄	100	100	100	100
<i>n</i> -C ₅	100	100	100	100
<i>n</i> -C ₆	100	100	100	100
<i>n</i> -C ₇	100	100	100	84
<i>Epoxides</i>				
1,2-Epoxypropane	0	0	78	15
1-Chloro-2,3-epoxypropane	30	32	56	

TABLE III (continued)

Compound	Flow-rate (ml/min)			
	30	45	30	45
	100°		120°	
<i>Oxygenated compounds</i>				
Tetrahydrofuran	14	0	42	0
Dioxane	6	0	0	0
<i>Alkyl halides</i>				
Perchloroethylene	0	17	12	0
Ethylene dichloride	28	7	0	0
Ethyl bromide	0	5	0	24
Ethyl iodide	0	33	0	27
<i>Lactones</i>				
1,3-Propiolactone	0	0	0	0

ml/min and at 45 ml/min a slight decrease in reaction was observed with the higher-boiling aldehydes, which might have been expected to be less affected by the reduced residence time than the lower homologues.

From the studies it is apparent that a definite optimum area of operation for the columns exists where the selectivity and efficiency of abstraction are highest. Polyethyleneimine was more reactive than the propylene homologue and the consequence was that polyethyleneimine reacted with and abstracted aldehydes as well as ketones, especially at the lower temperature. As a ketone abstractor the material should be used at 120° and 45 ml/min where its selectivity towards ketones is highest and abstraction of aldehydes and other compounds is lowest.

Polypropyleneimine is generally less reactive towards ketones than polyethyleneimine. The best conditions for the use of polypropyleneimine as an aldehyde abstractor are 120° and 45 ml/min where the abstraction of aliphatic ketones, epoxides, oxygenated compounds, alkyl halides and propiolactone is virtually zero while the abstraction of the aldehyde is almost 100%. The alicyclic and diketones display anomalous behaviour as abstraction occurs under these conditions.

Examination of the polyalkylimines showed that the phases as supplied contained a substantial amount of material volatile at 100°. The materials were extremely

TABLE IV

McREYNOLDS CONSTANTS OF POLYETHYLENE- AND POLYPROPYLENEIMINE

	<i>X'</i>	<i>Y'</i>	<i>Z'</i>	<i>U'</i>	<i>S'</i>
<i>Polyethyleneimine</i>					
New column	352	605	475	606	596
Depleted column	308	462	352	374	346
Supplier's data ¹⁸	322	800	—	573	524
<i>Polypropyleneimine</i>					
New column	209	291	219	266	239
Depleted column	176	258	190	234	247
Supplier's data ¹⁸	122	425	168	263	224

TABLE V
RETENTION DATA OF NORMAL ALKANES ON POLYALKYLIMINE COLUMNS

<i>n</i> -Alkane	Polyethyleneimine				Polypropyleneimine			
	Newly prepared		Exhausted		Newly prepared		Exhausted	
	V_g	V_R	V_g	V_R	V_g	V_R	V_g	V_R
Heptane	—	—	—	—	0.36	0.279	—	—
Octane	0.05	0.551	0.04	0.570	0.70	0.543	—	—
Nonane	0.09	1.000	0.07	1.000	1.20	1.000	0.08	1.000
Decane	0.16	1.782	0.11	1.573	2.46	1.908	0.15	1.875
Undecane	0.26	2.890	0.18	2.570	4.68	3.630	0.31	3.880
Dodecane	0.46	5.120	0.29	4.141	8.78	6.820	0.70	8.750
Tridecane	0.89	9.763	0.48	6.860	—	—	1.30	16.400

hygroscopic and as elemental analyses showed the carbon-to-nitrogen ratio to be unaffected by drying the suspected presence of water was established by examination of a sample of the volatile material extracted by semi-micro vacuum fractionation¹⁶.

McReynolds constants of the polyalkylimines from the supplier's literature are shown in Table IV together with values obtained in the laboratory. While the increased polar character of the ethylene derivative is clearly evident from both sets of data, poor agreement between the determinations is evident. It is suggested that the phases examined are somewhat different in structure to the materials originally considered as previous determinations of McReynolds constants from this laboratory¹⁷ have been in good agreement with data from the same source¹⁸. The McReynolds constants of the depleted columns are also shown and the alteration of the chemical nature of the columns with use is apparent.

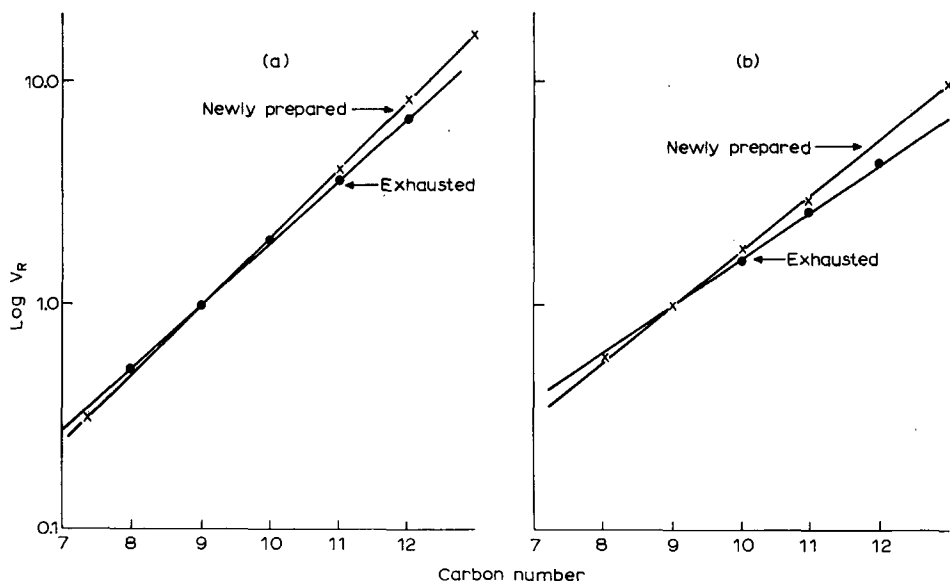


Fig. 1. Retention plot of normal alkanes on newly prepared and exhausted (a) polyethyleneimine and (b) polypropyleneimine columns.

The variation in general polarity of the columns is shown by the retention data of normal alkanes at 100° tabulated in Table V and as plotted in Fig. 1. The slope of the plots for the saturated columns are greater than for the plots of the columns as prepared, this being in agreement with studies of alkane behaviour on a series of columns with established acceptor and donor properties¹⁹.

The nitrogen-to-carbon ratios of the polymers were determined as 1.70 and 2.59 for polyethylene- and polypropyleneimine, these values being in agreement with values of 1.71 and 2.59 calculated for the structures $-(CH_2-CH_2-NH)_n-$ and $-(CH_2-CH_2-CH_2-NH)_n-$, respectively. The results of the non-aqueous titrations are shown in Table VI.

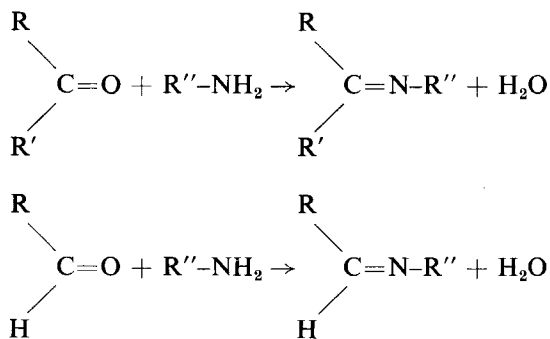
TABLE VI
ANALYTICAL DATA FOR POLYETHYLENE- AND POLYPROPYLENEIMINE

	<i>Polyethyleneimine</i>	<i>Polypropyleneimine</i>
Non-volatile matter, %	52.3	46.9
Total amine concn., ml/g	0.0667	0.0457
Secondary and tertiary amine concn., ml/g	0.0223	*
Tertiary amine concn., ml/g	0.0167	0.0304
Primary amine, %	67.0	32.0
Secondary amine, %	8.0	
Tertiary amine, %	25.0	68.0

* Titration not successful as obvious inflection not observed.

Analysis of the samples shows that the structure of the two polymers is quite different although both are highly branched, the more reactive polyethyleneimine possessing a high proportion of primary amino groups while the polypropyleneimine is high in tertiary amino groups. The unsatisfactory titration of secondary and tertiary groups is indicative of a low concentration of secondary groups and thus the concentration of primary amino groups may be close to 32%.

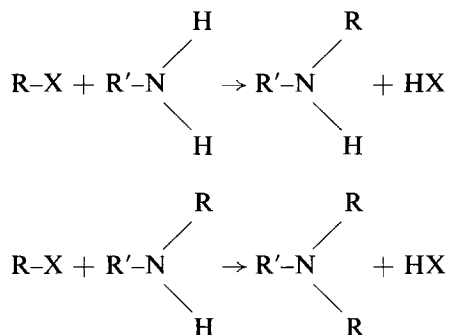
The mechanism of the abstraction reaction with polyethylimines is not completely understood although the reaction of primary amino groups with carbonyl compounds is well known and the presence of a water peak proportional to the size of carbonyl compound injected was observed.



Although this reaction was observed with the polyaminoalkyl silanes⁶ that contained both primary and secondary amino groups, it is not known whether both

groups are reactive and studies are currently being carried out using silanes containing a single primary, secondary or tertiary amino group.

The reaction of alkyl halides occurs as both primary and secondary amino groups form secondary and tertiary amino groups, respectively



ACKNOWLEDGEMENT

The authors are indebted to Dr. W. S. Supina of Supelco, Bellefonte, Pa., U.S.A. for suggesting this investigation as an extension to an earlier report and for providing the polyalkylimines used.

REFERENCES

- 1 J. A. Kerr and A. F. Trotman-Dickenson, *Nature (London)*, 182 (1958) 466.
- 2 R. R. Allen, *Anal. Chem.*, 38 (1966) 1287.
- 3 F. E. Regnier and J. C. Hung, *J. Chromatogr. Sci.*, 8 (1970) 267.
- 4 M. K. Withers, *J. Chromatogr.*, 66 (1972) 249.
- 5 J. K. Haken, D. K. M. Ho and M. K. Withers, *J. Chromatogr. Sci.*, 10 (1972) 566.
- 6 J. R. Ashes and J. K. Haken, *Anal. Chem.*, 45 (1973) 1131.
- 7 W. R. Supina, personal communication to J. K. Haken, Nov. 1972.
- 8 W. R. Supina, personal communication to J. R. Ashes, April 1973.
- 9 K. Grob, *J. Chromatogr. Sci.*, 2 (1964) 80.
- 10 J. R. Lindsay Smith and D. J. Waddington, *Anal. Chem.*, 40 (1968) 522.
- 11 Anonymous, *Chromatogr. Lipids*, 6, No. 7 (1974) 1.
- 12 B. A. Bierl, M. Beroza and W. F. Ashton, *Mikrochim. Acta*, (1969) 637.
- 13 D. A. Cronin, *J. Chromatogr.*, 64 (1972) 25.
- 14 C. D. Wagner, R. H. Brown and E. D. Peters, *J. Amer. Chem. Soc.*, 69 (1947) 2609.
- 15 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 506.
- 16 J. Haslam, A. R. Jeffs and H. A. Willis, *J. Oil Colour Chem. Ass.*, 45 (1962) 325.
- 17 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 60 (1972) 33.
- 18 *Supelco Inc. Chromatography Catalogue 1974*, Supelco, Bellefonte, Pa.
- 19 J. R. Ashes and J. K. Haken, unpublished data.
- 20 J. R. Lindsay Smith and D. J. Waddington, *J. Chromatogr.*, 42 (1969) 195.
- 21 J. R. Lindsay Smith and D. J. Waddington, *J. Chromatogr.*, 42 (1969) 183.