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## EVALUATION OF PRIMARY, SECONDARY AND TERTIARY AMINO-SILANES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

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### SUMMARY

The performance of support-bonded aminoalkylsilanes as stationary phases is described following reports that on-column chemical reaction occurs with carbonyl compounds and polyalkylimines and silanes containing both primary and secondary amino groups. To determine the relative reactivity of primary, secondary and tertiary amino groups a series of silanes of similar molecular weight has been considered containing individually each type of amino group. The phases have a particular polar character and the tendency to form hydrogen bonds is shown by the separation of isomeric alcohols.

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### INTRODUCTION

Studies in these laboratories<sup>1-5</sup> have been reported concerning the effect of the molecular structure of various oxygenated compounds on retention on a series of stationary phases of increasing polar character. Polysiloxane solvents possessing a common backbone structure where the effective character is due largely to the substituent groups have been considered as these may be suitable for further theoretical studies.

The phases may be conveniently characterised in terms of the Rohrschneider concept, based in theory on an additivity of various types of intermolecular forces. Within the scheme, a polysiloxane considered to exhibit high proton acceptance was not available and silanes rich in amino groups and with reactive alkoxy functions bonding to the support were examined.

Polysiloxanes with an ethylenediamine moiety with both primary and secondary amino groups in their structure when examined were shown to effectively abstract aldehydes, lactones and most ketones<sup>6</sup>. Supina<sup>7</sup> noted that the various polyalkylimines which have been reported as conventional stationary phases could be used to selectively abstract aldehydes and ketones. Examination of these compounds<sup>8</sup> showed that polyethyleneimine was rich in primary amino groups and was more reactive than the propylene homologue, which contained a significant concentration of tertiary amino groups. With careful control of the reaction conditions, aldehydes and ketones may be preferentially abstracted by the propylene and ethylene derivatives, respectively.

To determine the relative reactivity of primary, secondary and tertiary amino

TABLE I  
PHYSICAL CONSTANTS OF AMINOSILANES

Trade designation	Manufacturer*	Chemical composition	Formula	Viscosity at 25° (cS)	Specific gravity at 25°	Boiling point (°C)	Refractive index at 25°
Z6020	1	N-β-Aminoethyl-γ-aminopropyltrimethoxysilane	$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	10.0	1.01	146 (15 mm)	1.4418
A1120	2			6.5	1.038	259	1.448
KBM-603	3			6.0	1.03	259	1.445
A1100	1	γ-Aminopropyltriethoxysilane	$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{O}_2\text{CH}_3)_3$	1.6	0.942	217	1.420
X12-563	3	N-Allyl-γ-aminopropyltrimethoxysilane	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ $\text{CH}_2-\text{CH}_2$	3.0	0.975	107 (7.5 mm)	1.434
X12-570	3	γ-Morphinylpropyltrimethoxysilane		4.1	1.05	122 (5 mm)	1.444
S4150/41	4	N,N-Dimethyl-γ-aminoethoxymethylpolysiloxane		106.0	—	—	1.462

\* 1 = Dow Corning Corp., Midlands, Mich., U.S.A.; 2 = Union Carbide Corp., New York, N.Y., U.S.A.; 3 = Shin-Etsu Chemical Industries, Tokyo, Japan; 4 = Imperial Chemical Industries, Organics Division, Stevenston, Ayrshire, Great Britain.

TABLE II  
McREYNOLDS CONSTANTS OF AMINOSILANES

<i>Compound</i>	<i>X'</i>	<i>Y'</i>	<i>Z'</i>	<i>U'</i>	<i>S'</i>	<i>General polarity</i>
Z6020	247	700	393	454	433	2227
A1100	145	426	226	313	297	1407
X12-563	323	653	441	593	555	2665
X12-570	72	539	129	511	469	1720
S4150/41	-8	143	76	69	82	362

groups in stationary phases for gas chromatography a series of silanes of similar molecular weight have been considered containing individually each type of amino group. Similarly, the tendency to form hydrogen bonds with isomeric alcohols has been studied following the observation of retardation of the normal primary alcohols with polysiloxanes containing primary and secondary amino groups.

## EXPERIMENTAL

### *Gas chromatography*

The data were obtained on a Hewlett-Packard Model 5750 B research chromatograph fitted with column splitters. Multiple columns were used in parallel with flame ionisation detection and the signals were recorded on a multi-channel recorder. Aluminium columns (12 ft.  $\times$   $\frac{1}{4}$  in. O.D.) were packed with 10% of the phases on 72-85 mesh acid-washed Celatom. The injection temperature was 190° and the column temperature 120°.

### *Stationary phases*

The chemical composition of the compounds used as stationary phases together

TABLE III  
REACTION OF KETONES AND AMINOSILANES

<i>Compound</i>	<i>Z6020</i>	<i>A1100</i>	<i>X12-563</i>	<i>X12-570</i> <i>S4150/41</i>
2-Propanone	100	100	0	0
2-Butanone	100	86	8	0
2-Pentanone	100	86	28	0
2-Hexanone	100	95	50	0
2-Heptanone	100	99	65	0
3,3-Dimethyl-2-butanone	46	50	40	0
3-Pentanone	86	33	0	0
3-Heptanone	92	46	21	0
4-Heptanone	76	79	24	0
2,4-Dimethyl-3-pentanone	58	5	50	0
Cyclohexanone	100	100	100	0
2,3-Butanedione	100	100	100	0
2,4-Pentanedione	99	100	100	0
Methyl pyruvate	100	100	100	0

with their physical constants as available are shown in Table I, while the McReynolds constants are shown in Table II. All of the compounds are aminosilanes, with the exception of S4150/41, which is a low-molecular-weight polysiloxane with an  $M/D$  ratio of approximately 0.04 and end-capped with trimethylsilyl groups.

## RESULTS

The behaviour of a variety of representative ketones was examined using the aminoalkylsiloxane materials at 120° with primary and secondary amino groups with results as shown in Table III. The data of Z6020 are as previously reported<sup>6</sup> and with the straight-chain methyl ketones (2-alkanones) essentially complete abstraction occurs. The performance of the primary amino compound (A1100) is very slightly inferior, with abstraction of 86–100%.

The 3-alkanones were only partially abstracted with both species and with A1100 the variable performance previously observed was apparent. Branched-chain ketones again were only partially removed, the reaction being lower with the primary aminosilane.

The relationship between molecular structure and reaction is shown in Table IV together with the results of earlier studies<sup>6,8</sup>. The branched chains partially shield the carbonyl group from the reactive amino groups. 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

TABLE IV

PERCENTAGE ABSTRACTIONS OF BRANCHED-CHAIN KETONES ON AMINOSILANE COLUMNS

Flow-rate: 30 ml/min.

No.	Compound	Structure	Z6020	A1100	X12-563
1	3,3-Dimethyl-2-butanone	$\begin{array}{c} \text{O} \quad \text{C} \\    \quad   \\ \text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	46	50	40
2	4-Methyl-2-pentanone	$\begin{array}{c} \text{C} \quad \quad \text{O} \\   \quad \quad    \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	67	38	45
3	5-Methyl-2-hexanone	$\begin{array}{c} \text{C} \quad \quad \quad \text{O} \\   \quad \quad \quad    \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	100	86	74
4	2,4-Dimethyl-3-pentanone	$\begin{array}{c} \text{C} \quad \text{O} \quad \text{C} \\   \quad    \quad   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	58	5	50
5	2,6-Dimethyl-4-heptanone	$\begin{array}{c} \text{C} \quad \quad \text{O} \quad \quad \text{C} \\   \quad \quad    \quad \quad   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\   \\ \text{C} \end{array}$	43	28	20

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 Ackman<sup>9</sup> 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.

The performance of X12-563 with secondary amino groups showed very significantly reduced reaction with ketones. With the 2-alkanones as the most reactive series abstraction tended to increase with the carbon number and with 2-hexanone a maximum of 20% reaction was observed. With the other species abstraction was minimal while retardation of elution was observed with significant peak broadening. The increased retention might be expected as the general polarity<sup>10,11</sup> is somewhat higher than that of the other two phases considered (Table II).

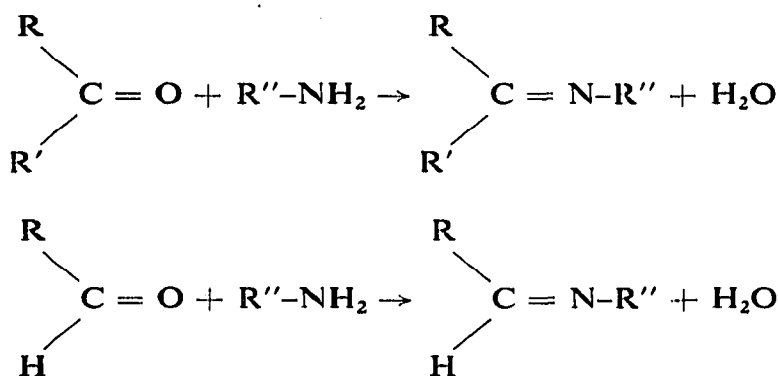
The compounds bearing tertiary amino groups were unreactive with the ketones although the two compounds showed marked differences in McReynolds constant and general polarity.

The homologous straight-chain aldehydes, the aromatic aldehyde benzaldehyde and also citral (Table V) were more reactive than the ketones and were virtually completely removed by reaction with secondary amino groups although there was no reaction with the phases containing tertiary amino groups.

TABLE V  
REACTION OF ALDEHYDES AND AMINOSILANES

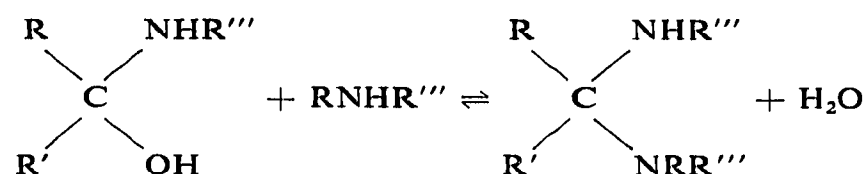
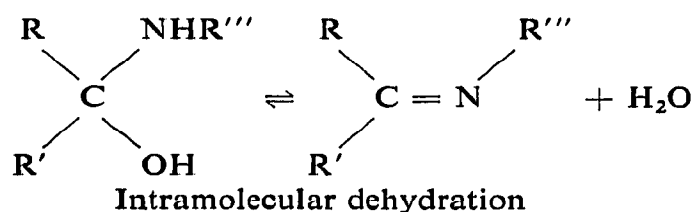
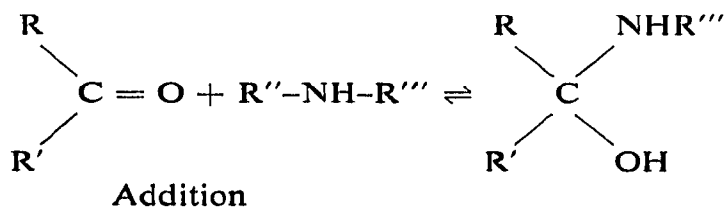
Compound	Z6020	A1100	X12-563	X12-570 S4150/41
Methanal	100	100	100	0
Ethanal	100	100	100	0
Propanal	100	100	100	0
Butanal	100	100	100	0
Pentanal	100	100	100	0
Hexanal	100	100	100	0
Citral	100	100	100	0

The mechanism of the abstraction reaction with aminoalkylsilanes 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 the carbonyl compound injected was observed,



while the presence of unsaturated reaction products has been reported with reactive silanes<sup>12</sup>.

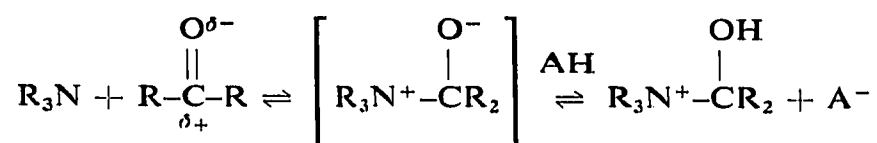
The reactivity of the aldehydes with secondary amino groups is thus not explained but the reactions of carbonyl compounds with both primary and secondary amines have been reported<sup>13</sup> to generally involve one or two of the following processes demonstrated with a secondary amine



The addition is considered to be the fundamental step of all amine-carbonyl reactions although the  $\alpha$ -amino alcohol is generally too unstable to be isolated.

Weak bases including secondary amines have been shown to produce alkylidenediamines or *gem*-diamines by intermolecular dehydration of the  $\alpha$ -amino alcohol and the base<sup>14-16</sup>.

The unshared electron pair of amines (primary, secondary or tertiary) gives them both nucleophilic and basic properties, as is evident with the alkylation with alkyl halides<sup>6</sup>. The same nucleophilic characteristics of amines enable them to attack the carbonyl atoms of aldehydes and ketones, relatively positive sites<sup>17</sup>. The initial product of bond formation between carbon and nitrogen is suggested to be a zwitterion<sup>18</sup> as the negative charge is borne on an alcoholic oxygen. The species would be expected to be of high energy and to dissociate readily into its components, as shown below, if no other reactions occur.



A proton may be acquired from materials present as solvent or the reaction medium although the resulting compounds remain amenable to dissociation.

With primary and secondary amines the charge separation can be easily dissipated by proton transfer, giving rise to carbonolamines, which are usually not of sufficient stability to allow isolation but react readily with aldehydes and reluctantly with aromatic ketones.

The reaction experienced in this work again appears to occur with the liberation of water and this might be accepted as some evidence for the type of reaction shown. The reactivity of the aldehydes and not the ketones might be attributed to the absence of an additional group on the carbonyl carbon and the consequent greater accessibility to chemical reaction. The effects of molecular shape and reactivity have been demonstrated previously.

From Table II it is apparent that the  $Y'$  values indicative of hydrogen bonding, *i.e.* hydrogen donor, as shown with *n*-butanol, are high. This effect, due to hydrogen bonding of the type (OH  $\cdots$  NH-), has been reported with Z6020 (ref. 6), which

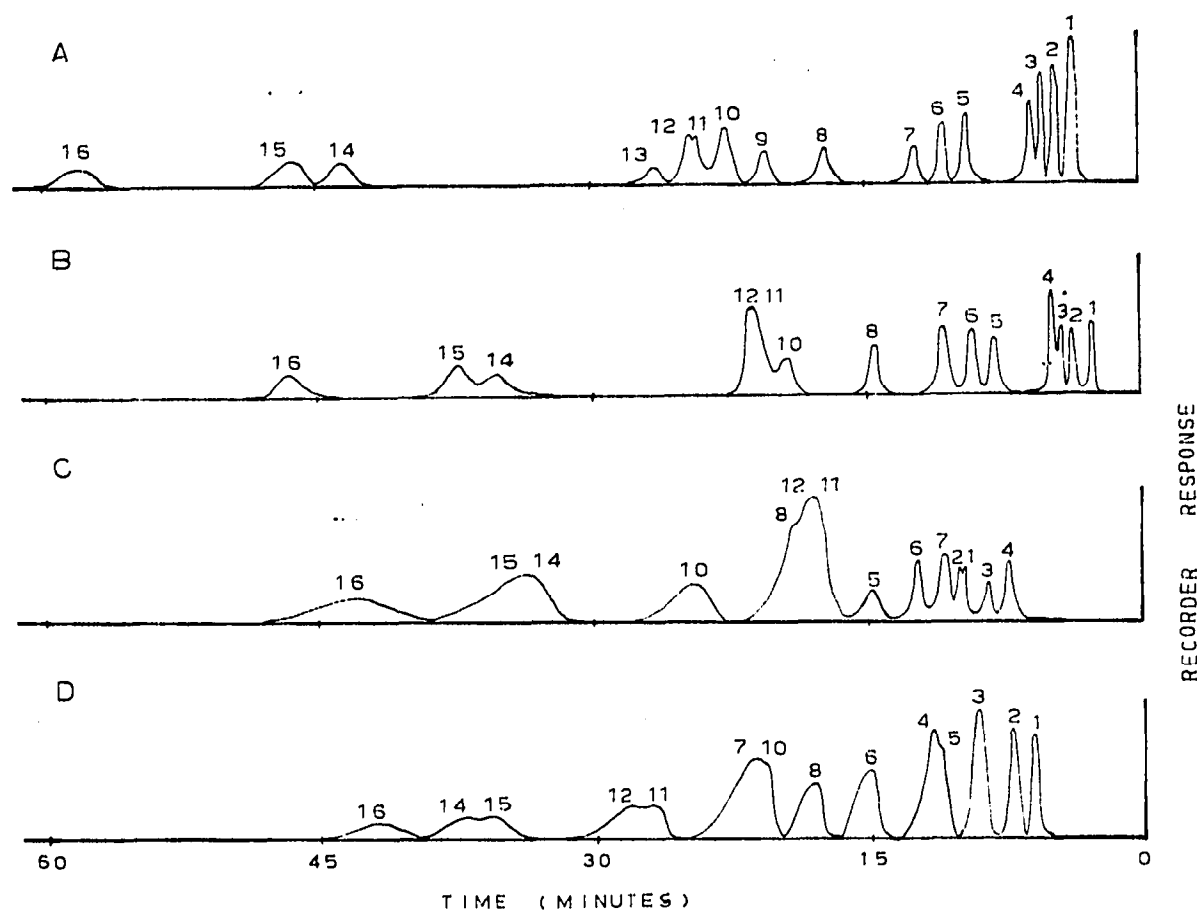


Fig. 1. Chromatograms showing separation of isomeric alcohols using: (A) a 30-m capillary column coated with Armeen SD at 65°; (B) a 20 ft.  $\times$   $\frac{1}{8}$  in. O.D. column packed with 10% Armeen SD at 75°; (C) a 24 ft.  $\times$   $\frac{1}{8}$  in. O.D. column packed with 10% Z6020 at 100°; and (D) a 24 ft.  $\times$   $\frac{1}{8}$  in. O.D. column packed with 10% S4150/41 at 100°. 1 = Methanol; 2 = ethanol; 3 = 2-propanol; 4 = *tert.*-butanol; 5 = 1-propanol; 6 = 2-butanol; 7 = 2-methyl-2-butanol; 8 = isobutanol; 9 = 2-methyl-3-butanol; 10 = 1-butanol; 11 = 3-pentanol; 12 = 2-pentanol; 13 = 2,2-dimethyl-1-propanol; 14 = 3-methyl-1-butanol; 15 = 2-methyl-1-butanol; 16 = 1-pentanol.

contains both primary and secondary amino groups, and the effect is examined with silanes containing each type of amino group.

The work of Zlatkis<sup>19</sup>, showing the separation of isomeric alcohols using Armeen SD, is shown in Fig. 1A with a chromatogram from a 30-m capillary column. Armeen SD is a mixture of normal primary amines with the approximate composition 20% hexadecyl-, 17% octadecyl-, 26% octadecenyl- and 37% octadecadienylamines and suitable for use at low column temperatures due to excessive column bleed.

Fig. 1B shows separations achieved with a 20 ft.  $\times$   $\frac{1}{8}$  in. O.D. stainless-steel column containing 10% Armeen SD. The efficiency of the packed column is reduced and the partial resolution of the 2- and 3-pentanol (Fig. 1A) is not apparent. The elution order of the isomeric alcohols on Armeen SD is the same as that on SE-30 and essentially follows boiling point, this being in agreement with data from McReynolds' compilation<sup>20</sup>.

The elution of branched-chain species is enhanced with Z6020, *tert.*-butanol, *i.e.* 2-methyl-2-propanol, and 2-propanol both being eluted before methanol and ethanol, which in admixture are not resolved. 2-Methyl-2-butanol and 2-butanol are eluted before isobutanol. Similar behaviour has been reported<sup>6</sup> with the highly polar phase DEGS except that isobutanol is eluted before the composite peak of 2- and 3-pentanol.

The silane bearing primary amino groups shows some increased retardation of the straight-chain alcohols, as is apparent from Table VI with the advancement of *n*-propanol and *n*-butanol. With X12-563 (secondary amino groups) behaviour generally similar to Z6020 is observed although ethanol is eluted before 2-propanol and isobutanol before 2- and 3-pentanol. While this would indicate some reduction in the polarity of X12-563, the McReynolds constants are additively higher than those of X6020 but with *Y'* slightly lower.

TABLE VI  
ELUTION SEQUENCE OF ISOMERIC ALCOHOLS  
The alcohols are identified in the legend to Fig. 1.

Armeen SD	Z6020	A1100	X12-563	X12-570	S4150/41
1	4	4	4	4	1
2	3	3	1	3	2
3	1	7	3	1	3
4	2	1	7	2	5
5	7	6	2	7	4
6	6	11	6	6	6
7	5	2	5	5	8
8	11	12	8	8	7
9	12	5	11	11	10
10	8	15	12	12	11
11	10	14	10	10	12
12	14	8	14	15	14
13	15	10	15	14	15
14	15	10	15	14	15
15	16	16	16	16	16



The silane bearing tertiary amino groups (X12-570) shows an elution order similar to Z6020. The high general polarity of this material must be attributed largely to the effect of the morphinyl group. This group has not been considered in materials used as stationary phases and the simpler polysiloxane containing tertiary amino groups (S4150/41) prepared by Imperial Chemical Industries Ltd. was considered. The siloxane, as might reasonably be expected, showed McReynolds constants lower than those shown by the other materials listed in Table II. The elution order tends to follow the boiling point sequence, as shown with SE-30 and Armeen SD, with the exception that 1-propanol (b.p. 97°) was eluted before *tert.*-butanol (b.p. 82.8°) and 2-methyl-2-propanol (b.p. 108°) before 2-methyl-2-butanol (b.p. 101.8°).

A most unusual feature of S4150/41 is the extremely rapid elution of benzene with a lower retention index than with squalane such that a negative value is obtained for the  $X'$  constant. This constant has been shown qualitatively to be a measure of aromatic selectivity<sup>21,22</sup> and rapid elution of aromatic compounds might be expected. Benzene is, however, eluted after 1-propanol and only marginally before cyclohexane, while toluene has a slightly greater retention time than 1-butanol.

## CONCLUSION

On-column chemical reaction of ketones and aldehydes is demonstrated with both primary and secondary amino groups in aminoalkylsilanes of approximately equivalent molecular weight. The reactivity is shown with ketones, which are generally less reactive than aldehydes, to be dependent on molecular shape. With branched-chain compounds shielding of the carbonyl group occurs.

The primary amino groups are shown to be more reactive than the secondary amino groups but the compound containing both species is most reactive due simply to the increased concentration of amino groups. While reaction with tertiary amines might be expected on theoretical grounds, this does not occur, although two substrates of significantly different polar character were considered.

Retardation of alcohols due to the formation of hydrogen bonds is exhibited with each of the types of aminoalkylsilane.

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## REFERENCES

- 1 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 60 (1971) 33; 62 (1971) 39.
- 2 J. K. Haken and V. Khemangkorn, *J. Chromatogr. Sci.*, 10 (1972) 556.
- 3 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103.
- 4 J. K. Haken, D. K. M. Ho and C. E. Vaughan, *J. Chromatogr.*, 106 (1975) 317.
- 5 J. K. Haken, D. K. M. Ho and M. Wainwright, *J. Chromatogr.*, 106 (1975) 327.
- 6 J. R. Ashes and J. K. Haken, *Anal. Chem.*, 45 (1973) 1133.
- 7 W. R. Supina, private communication to J. K. Haken (November 1972) and J. R. Ashes (April 1973).

- 8 J. Appleyard and J. K. Haken, *J. Chromatogr.*, 99 (1974) 319.
- 9 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 506.
- 10 J. J. Leary, J. B. Justice, S. R. Lowry and T. L. Isenhour, *J. Chromatogr. Sci.*, 11 (1973) 201.
- 11 J. K. Haken, *J. Chromatogr.*, 99 (1974) 329.
- 12 *Silanes*, Union Carbide Corp., New York, N.Y., 1968.
- 13 Y. Ogata and A. Kawasaki, in J. Zabicky (Editor), *The Chemistry of the Carbonyl Group*, Vol. 2, Interscience, New York, 1970, 42 pp.
- 14 J. F. Walker, *Formaldehyde*, Reinhold, New York, 2nd ed., 1953, pp. 281-325.
- 15 M. Imoto, H. Kakiuchi and K. Ko, *Formaldehyde*, Asakura, Tokyo, 1965, pp. 173-232.
- 16 N. J. Leonard and J. V. Pautskelis, *J. Org. Chem.*, 28 (1963) 3021.
- 17 M. M. Sprung, *Chem. Rev.*, 26 (1940) 297.
- 18 P. A. S. Smith, *Open-Chain Nitrogen Compounds*, Benjamin, New York, 1965, pp. 23-27.
- 19 A. Zlatkis, in E. Bayer (Editor), *Gas Chromatography*, Elsevier, Amsterdam, 1961, 117 pp.
- 20 W. O. McReynolds, *Gas Chromatographic Data*, Preston Technical Abstracts, Evanston, Ill., 1966.
- 21 W. R. Supina, *The Packed Column in Gas Chromatography*, Supelco Inc., Bellefonte, Pa., 1974.
- 22 S. J. Hawkes, *J. Chromatogr. Sci.*, 13 (1975) 115.