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THE IDENTIFICATION OF PEAKS IN GAS CHROMATOGRAPHY BY THE USE OF SUBTRACTOR COLUMNS

II. THE ACTION OF FREE FATTY ACID PHASE ON ALDEHYDES

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SUMMARY

The use of FFAP as an aldehyde subtractor has been re-examined. The material is an unsatisfactory aldehyde subtractor as it has low capacity, deteriorates on keeping, and often causes a large increase in the retention time of non-aldehydic compounds. The subtraction is also time- and temperature-sensitive. It is suggested that the subtraction involves an acid-catalyzed aldol condensation.

INTRODUCTION

A number of workers have reported the use of the stationary phase FFAP to selectively remove aldehydes from mixtures during gas chromatography (GC). As part of a continuing study on the use of subtractor columns in GC the behaviour of FFAP was re-investigated.

FFAP is stated to be "an esterification product of a polyethylene glycol (Carbowax 20M) and the dibasic acid, 2-nitroterephthalic acid"[1]. The activity of FFAP towards aldehydes was first reported by ALLEN[2] in 1966 and further investigated in 1967 by workers at Varian Aerograph[1]. More recently BIERL *et al.*[3] have used the material in their studies but apparently did not find it very satisfactory. ALLEN, in his original paper, reported the removal of five aliphatic aldehydes from a synthetic mixture using a column 12 in. in length. A 3-ft. column was necessary to remove the aromatic aldehydes benzaldehyde, anisaldehyde, veratraldehyde and vanillin.

The present work was done to define the range of application of FFAP and to determine its specificity.

EXPERIMENTAL

A Perkin-Elmer Model 800 gas chromatograph was used. All columns were made from 3/16 in. O.D. (0.123 in. bore) aluminium tubing packed with 20% FFAP

on 85–100 mesh (BSS) "Celite" (Johns Manville Corp.). Three column lengths were used, *viz.*, a 1-ft. FFAP column in conjunction with a 12-ft. 10% SE-30 column and 6- and 12-ft. FFAP columns without any additional column. In each case the FFAP column was compared with a column of the same length filled with 20% Carbowax 20M on the same support. Carrier gas was nitrogen at 30 ml/min. Air and hydrogen flow rates were optimized for maximum response. Samples were injected as 1% solutions in *n*-pentane, acetone or methanol. A careful check was kept on the total amount injected.

The amount of aldehyde removed was estimated from either peak area or peak height. These estimates are only approximate but this is of small importance as the desirable situation is one where removal is quantitative. When the percentage removal was low results were generally variable. In these cases the values given are the mean of a number of determinations.

RESULTS AND DISCUSSION

The results of experiments using a 1-ft. column of FFAP are given in Table I.

The short-chain aldehydes are not removed at 100° but hexyl aldehyde is completely removed. This is clearly the effect of reaction time. The hexyl aldehyde apparently has a sufficiently long residence time for complete reaction to take place.

TABLE I

REMOVAL OF ALDEHYDES BY A 1-ft. 20% FFAP COLUMN

Compound	*Temperature of subtractor column (°C)*	*% Removal*
Normal aliphatic aldehydes		
C_4	100	0
C_5	100	0
C_6	100	100
C_7	110	98
C_9	130	100
C_{10}	160	100
C_{11}	190	100
C_{12}	220	100
Furfural	120	
	130	
	140	0
	160	
	190	
Citral	180	85
	190	*ca.* 10
Benzaldehyde	95	
	110	
	120	0
	140	
o-Nitrobenzaldehyde	190	50
Dimethylaminobenzaldehyde	195	93
	200	90
	210	90
	230	0
Cinnamic aldehyde	150	
	180	0
	195	

Higher aldehydes are all completely removed. The behaviour of aromatic aldehydes is rather variable and mostly reflects the known order of reactivity of the compounds examined.

The case of dimethylaminobenzaldehyde is especially interesting and clearly illustrates the effect of reaction time. A small reduction in retention time competing with a relatively large 5° increase in temperature actually results in a fall in the amount removed from 93% to 90%. A similar situation is observed with citral.

To test the relative effects of reaction temperature and residence time a 6-ft. column was constructed. The results obtained with this column are listed in Table II.

The apparently anomalous results with *n*-hexanal and *n*-heptanal occur because the residence time is actually shorter with the 6-ft. column. The 1-ft. column was used in conjunction with a 12-ft. SE-30 fore-column.

TABLE II

REMOVAL OF ALDEHYDES BY A 6-ft. 20% FFAP COLUMN

Compound	*Temperature of subtractor column (°C)*	*% Removal*
Normal aliphatic aldehydes		
C_4	110	0
C_5	110	0
C_6	110	0
C_7	110	*ca.* 5[a]
C_9	130	95
C_{10}	130	100
C_{11}	130	100
C_{12}	130	100
Furfural	130	0
Citral	200	95
	210	90
	220	5[a]
Benzaldehyde	130	100
o-Nitrobenzaldehyde	180	100
	200	100
Dimethylaminobenzaldehyde	200	100
Cinnamic aldehyde	150	95
Anisaldehyde	210	30
	220	50
Salicylaldehyde	180	75
	185	5[a]
	200	0
Vanillin	235	0
	240	0
Acetovanillin	235	0
	240	0[a]

[a] Peak considerably retarded.

Furfural is not removed. Benzaldehyde, which was not removed by a 1-ft. column, is quantitatively subtracted as are a number of other aromatic aldehydes. Anisaldehyde is incompletely removed and salicylaldehyde shows a fall in the amount removed with increasing temperature.

Once again this fall seems to be related to the decrease in residence time in the subtraction column.

Results obtained with a 12-ft. FFAP column are shown in Table III. It can be seen that all the compounds tested were subtracted. Even vanillin and acetovanillin, which were not removed by the shorter columns, were completely subtracted. The use of a 12-ft. column is indispensible for complete removal of certain compounds. This effect can be clearly seen from the results which are grouped together in Table IV for three selected compounds. In the case of furfural the 12-ft. column is only just adequate.

TABLE III

REMOVAL OF ALDEHYDES BY A 12-ft. 20% FFAP COLUMN

Compound	*Temperature of subtractor column (°C)*	*% Removal*
Dodecanal	140	100
Furfural	140	99
Citral	200	100
Cinnamic aldehyde	150	100
Anisaldehyde	200	100
Salicylaldehyde	180	98
Vanillin	245	100
Acetovanillin	245	100

TABLE IV

PERCENTAGE REMOVAL OF ALDEHYDES WITH COLUMNS OF DIFFERENT LENGTHS

Temperatures of subtraction may be obtained by referring to Tables I–III.

Compound	*Column length (ft.)*		
	1	*6*	*12*
Citral	10%	95%	100%
Furfural	0%	0%	99%
Cinnamic aldehyde	0%	95%	100%

During use of these columns it was observed that their capacity to subtract aldehydes was rapidly exhausted. The first 1-ft. column constructed was exhausted in a few days without being recognized. After this, the complete removal of *n*-dodecanal was used to monitor the activity of whichever column was in use. As soon as the column passed some dodecanal its use as a subtractor was stopped. This procedure worked equally well with the 6- and 12-ft. columns.

The capacity of the 6-ft. column was carefully measured by this procedure and found to be 0.52 mg of various aldehydes spread over a total operating time of 18 h on six separate days. When this column was exhausted a duplicate column was placed in the gas chromatograph and it was found to be inactive as a subtractor column. The duplicate column had been packed at the same time, from the same batch of packing and had been stored for seven days with ends open to the air. The same behaviour was found at a later date for a duplicate 12-ft. column which had been packed with a separate batch of packing.

Another 12-ft. column which had been stored for four days with the ends firmly sealed was found to have retained its activity. Further experiments showed that a sample of column packing which had been sealed in a 50-ml glass ampoule soon after preparation retained its activity as an aldehyde subtractor. This packing had been kept for thirty-four days before it was opened and used to pack a 12-ft. column. The column was used for one week, during which time it was always under nitrogen. Apart from this it was used under a variety of conditions with various samples. At the end of this period it retained its activity as an aldehyde subtractor. It seems that exposure to air causes a loss of activity towards aldehydes. Why this should be so is not apparent.

In addition to the limited life and poor capacity of FFAP subtractors there is the fact that retention times are increased by as much as five-fold for some compounds. This makes assignment of peaks by retention time very difficult.

No mechanism for the subtraction reaction has been suggested by the previous authors[1-3]. ALLEN[2] observed that water is generated by the reaction and CHRISTAKOS[4] reported that if the acidity is carefully neutralized then FFAP becomes inactive as an aldehyde subtractor. It seems reasonable to postulate an acid-catalyzed aldol condensation as the primary reaction leading to subtraction. This may be followed by further condensations or by esterification with the 2-nitroterephthalic acid.

CONCLUSION

FFAP cannot be said to be a satisfactory aldehyde subtractor. Its disadvantages are too great. These are:

(1) Reaction with aldehydes is slow.

(2) Subtraction is time- and temperature-dependent to a marked degree.

(3) Long columns are required for reliable removal of aldehydes. In the present work 12-ft. columns were necessary and it is possible that even longer columns would be required for other compounds not tested in the present work.

(4) FFAP is oxygen-sensitive and its activity towards aldehydes declines on storage when exposed to air.

(5) The material has a low capacity for aldehydes and columns in regular use must be constantly checked and frequently replaced.

Until a material is found which is both selective towards aldehydes and more reliable than FFAP the subtraction of aldehydes is not likely to attain a high degree of popularity.

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REFERENCES

1 K. HAMMERSTRAND AND D. R. GERE, *Varian Aerograph, Previews and Reviews*, 10 (1967) 6.
2 R. R. ALLEN, *Anal. Chem.*, 38 (1966) 1287.
3 B. A. BIERL, M. BEROZA AND W. T. ASHTON, *Mikrochim. Acta*, (1969) 637.
4 E. CHRISTAKOS, private communication, reported in ref. 1.