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Note

Reduction of tailing due to aluminium tubing used for gas chromatographic columns

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The metal tubing used to make gas chromatographic (GC) columns is usually stainless steel or aluminium. An overwhelming preference exists for stainless steel, but unfortunately, it is about ten times more expensive than aluminium. For this reason it has been the practice for many years to use aluminium for most of the columns made in this laboratory.

It has been observed that some batches of tubing cause considerable peak distortion. This is often no worse than excessive tailing with polar compounds but severe adsorption can occur which shows up as very long tailing peaks, double peaks due to dehydration of alcohols and loss of sensitivity due to apparently irreversible absorption. Tailing was more commonly observed with old pieces of tubing which had been stored for some time and it was thought that it could be associated with a coating of oxide on the inner wall. A method was sought of reducing or eliminating these undesirable properties of aluminium tubing.

EXPERIMENTAL

The instrument used was a Perkin-Elmer Model 800. Carrier gas flow-rate was 30 ml/min nitrogen for the 3/16 in. O.D. aluminium columns and 20 ml/min for the 1/8 in. glass columns. Air and hydrogen flow-rates were adjusted to give optimum response.

Columns were packed with 80–100 mesh Porapak Q and operated at 150°, except for a few experiments, where the packing was 10% SE-30 on 80–100 mesh Celite 560 AW-DMCS. Peak shapes were measured in terms of the asymmetry, which is defined as the ratio of the intercept between the vertical and the tangent to the rear of the peak to that of the intercept between the vertical and the tangent to the front of the peak, both intercepts being measured at the baseline. The peak shape of *n*-butanol, run on Porapak Q, which was packed in a glass column, was arbitrarily taken as representing "zero" absorption.

Initially, attempts were made to coat the inner walls of the tubing with polar tailing reducers. Gas-Quat L (ref. 1), Antarox CO 880 (a polyoxyethylene alkyl phenol)[2], sodium laurate[3] and FFAP were all used. These showed a small improvement if the original tailing was not serious but were quite ineffective in the case of serious absorption. Stripping the oxide coating from the tubing with methanolic

potassium hydroxide or with methanolic hydrochloric acid was also quite useless. In the case of the hydrochloric acid treatment the tailing was much worse after treatment than it was before.

Averill[4] has shown that treatment of stainless-steel tubing used on a GC–MS system with 2,4-pentanedione resulted in greatly improved peak shapes and lower detection limits for steroids. A column was therefore treated with three 3-μl injections of 2,4-pentanedione at 150° and allowed to bleed out for a number of hours. A considerable improvement in peak shape was observed when the column was again tested but a further treatment showed no extra improvement.

Trifluoroacetylacetone is known to form volatile complexes with aluminium and it was therefore thought likely that this would be a superior reagent for the present purpose. Trials quickly showed that this was so; a major improvement in peak shape resulted and in some cases the asymmetry values were almost as low as those obtained with glass columns.

The final procedure adopted was to treat the previously packed column with five 3-μl injections of trifluoroacetyl acetone at 5-min intervals. The flow-rate was reduced to approximately one third of the normal operating flow and the temperature held at 150°. At least 1 h was allowed to elapse after the final injection in order to give time for the aluminium complex to bleed completely from the column. The end of the column could then be reconnected to the detector.

This treatment not only improves peak shape, but as might be expected, increases the sensitivity of detection. Data to illustrate these improvements are given in Table I. Chromatograms are shown in Fig. 1, which demonstrate the improvement that is possible with this treatment. The individual example chosen is one of the more spectacular cases but even where tailing or absorption is not so serious an improvement to a similar level can still be made.

TABLE I

BEHAVIOUR OF n-BUTANOL ON PORAPAK Q COLUMNS

Column	Asymmetry		Sensitivity*	
	Before treatment	After treatment	Before treatment	After treatment
Glass	1.40	—	—	—
1	1.75	1.31	114	300
2	6	1.57	54	156
3	—**	2.5	19.5	75
4	—**	1.58	10	3500

* In arbitrary units.
** Peak shape so poor that asymmetry cannot be measured.

DISCUSSION

The improvement effected by trifluoroacetylacetone treatment appears to be permanent. A number of columns which had been treated were stored with the ends open to the air for six months. At the end of this period they were re-tested with n-butanol and peak shapes were identical with those obtained earlier. The measured
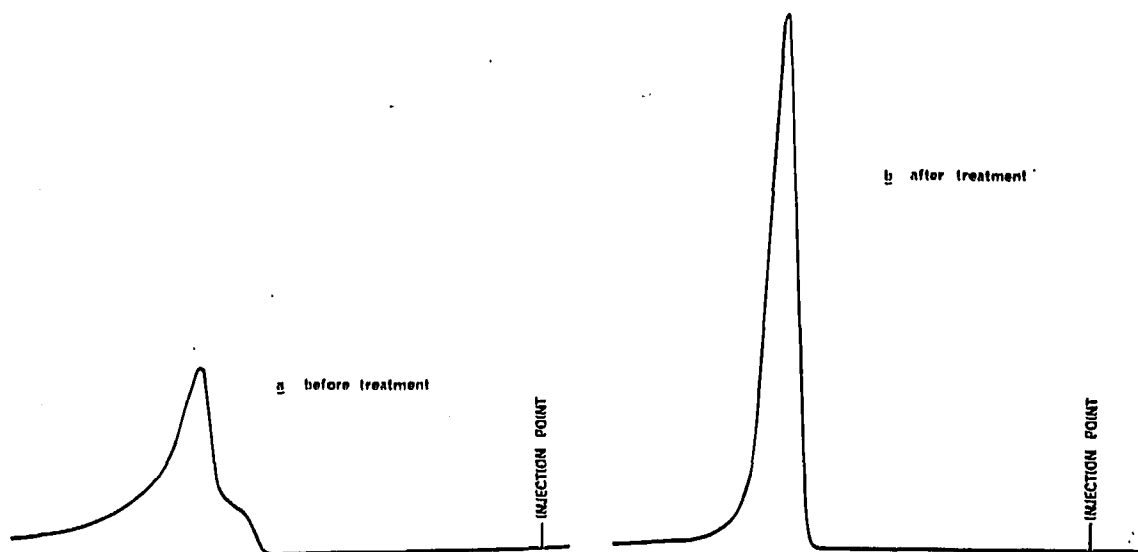
Fig. 1. Behaviour of *n*-butanol in aluminium columns. (a) Before treatment; (b) after treatment.

asymmetry values were almost identical, the small differences (*ca.* 10%) being within the limits of experimental variation.

It should be noted that this treatment makes no improvement if the tubing causes little absorption initially. In the final stages of this work a fresh delivery of tubing from the suppliers was used and this gave good peak shapes when tested with *n*-butanol. No better results were obtained after trifluoroacetylacetone treatment.

When the above work was complete a sample of hexafluoroacetylacetone became available. This was used in the same way as the trifluoroacetylacetone and worked equally as well. However, it offers no advantage over trifluoroacetylacetone and as it is somewhat more expensive the trifluorocompound remains the chemical of choice.

Because it was desired to isolate the effect of the column tubing on peak shape with no contributions from the support or the stationary phase, a packing had to be chosen which was as nearly inert as possible. Porapak Q was used since even the best diatomaceous earth supports show some residual activity. *n*-Butanol is a suitable polar test substance, is available in high purity and was used throughout this work.

Towards the end of this work a few columns were packed with 10% SE-30. Results were substantially the same as with the Porapak columns. Tailing could be almost eliminated with the trifluoroacetylacetone treatment. In this case 2-ethyl-hexanol was used as a test substance since the retention time of butanol was too short to give a useful measure of the tailing.

It is believed that the primary cause of peak distortions with aluminium tubing is the formation of an active layer of oxide on the metal. If this is true then trifluoro-acetylacetone works by stripping this layer off and thus reducing the surface activity.

The treatment proposed is cheap, easy to use and can be applied after the column has been constructed. Its use should enable aluminium to be more extensively employed for metal GC columns.

REFERENCES

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