Open Tubular Columns for Gas Liquid Chromatography: Cleaning and Recoating Procedures

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ABSTRACT

Procedures have been developed that permit the routine reuse of open tubular columns for the analysis of fatty acid methyl esters. Cleaning techniques are given that permit essentially endless recycling of the expensive capillary tubing with nearly 100% success in obtaining excellent columns upon recoating when using polyester liquid phases. Cost, including preparation of column, is equal to or less than the usual conventional packed column. These procedures make it both practical and economical to take advantage of the improved resolution and the reduced time for an analysis obtained with the open tubular column.

INTRODUCTION

Open tubular columns (OTC) (or wall coated open tubular columns, as some prefer) for gas chromatography offer, not only improved resolution, but also permit faster analysis of routine samples. In our laboratory, OTC have been found to be superior on both counts to packed columns for the analysis of fatty acid methyl esters (FAME). These columns have not, however, found extensive use in analytical laboratories because of difficulties in cleaning and coating, coupled with the initial cost of the tubing. This article will describe techniques that have been applied in the successful use and reuse of OTC in routine FAME analysis. Improvements in cleaning techniques will be emphasized, particularly the removal of used liquid phases.

MATERIALS AND METHODS

The special stainless steel tubing (200 ft x 0.03 in. inside diameter) for chromatography was obtained from Handy and Harman Tube Co., Norristown, Pa. One in. lengths of one-eighth inch outside diameter stainless steel tubing were brazed close to the ends to permit direct coupling to the fittings on the gas chromatograph. This small amount of braze did not present any problems when exposed to the cleaning solutions. The 300 ml cylinder used for cleaning was a Whitey HDF4-300-304, Oakland, Calif., as suggested by R. Teranishi, et al. (1). It was found to be convenient and time-saving to make the modifications shown in Figure 1. The Swagelok fitting mounted on the side permits new solvent changes to be added quickly without having to disconnect the gas inlet line. The fine mesh screen in the bottom is particularly useful in preventing plugging of columns with lint and other particles that accumulate from various sources, such as filter paper surfaces, etc. The same cylinder also is used for coating purposes, there being no obvious reason to use separate cylinders for each operation.

With columns of this diameter and length, a pressure of 100 psi was quite sufficient for all cleaning operations. All solvents used were either reagent grade materials obtained in glass containers or commercial grade solvents that were redistilled in all glass systems.

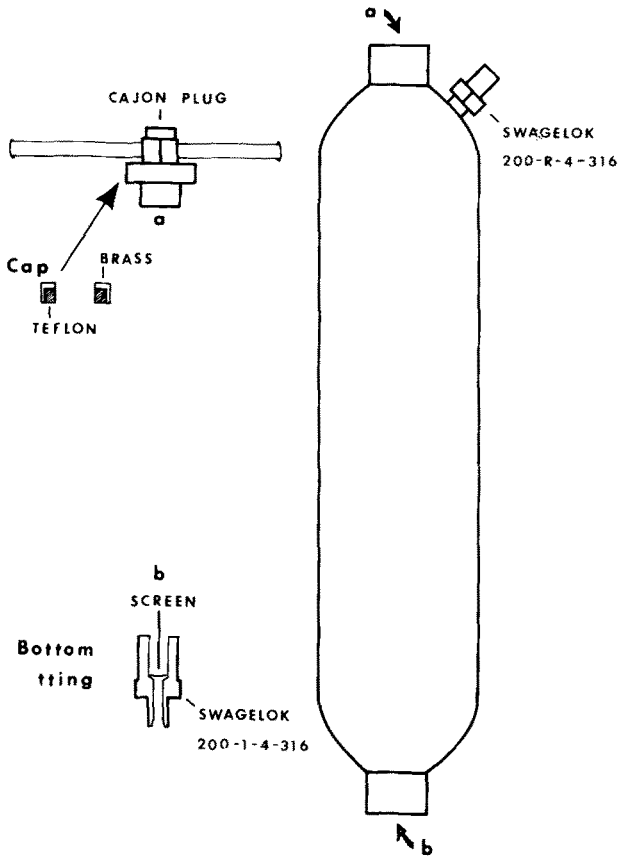

FIG. 1. Modifications to the cleaning and coating cylinder. Detailing shows the brass cap that was brazed to the Cajon plug supplied with the cylinder. The top of the plug is equipped with a sliding fit rod used to tighten the cap to the cylinder. Also shown is the position of the 200 mesh screen in the bottom fitting which then is threaded into the cylinder using Teflon tape. The side fitting is brazed into a one-fourth in. hole in the cylinder wall.

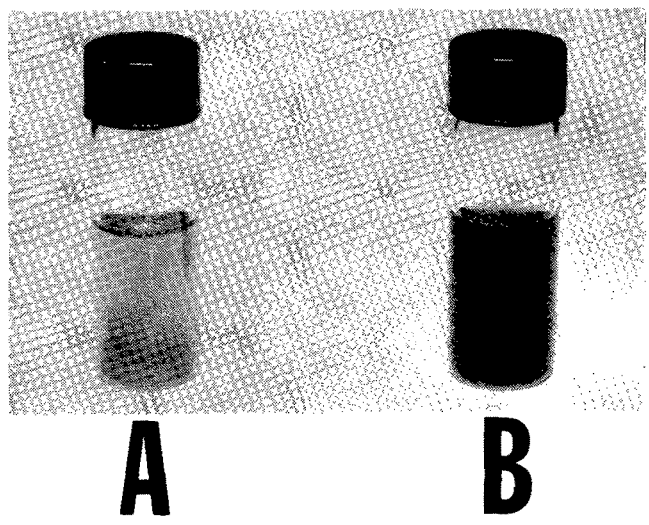

FIG. 2. Comparison of 23 C (A) and 100 C (B) temperatures for stripping efficiency. Conditions: vials represent the first 10 ml out of a total 50 ml chloroform used at each temperature for cleaning the same column in sequence. Liquid phase: Silar 10 C, lot 1. Courtesy R.R. Claeys, National Council of the Paper Industry for Air and Stream Improvement, Inc., Oregon State University, Corvallis, Oregon.

TABLE I

Solvents for Cleaning, in Order of Use and the Amount

New tubing		Old columns[a]	
Chloroform	300 ml	Chloroform	300 ml
Acetone	300	Acetone	200
Water	100	NH_4OH:MeOH[b]	300
Nitric acid (conc)	100	Methanol	200
Water	100	Chloroform	200
NH_4OH:MeOH[b]	300		
Water	200		
Acetone	300		
Chloroform	300		

[a]All cleaning of old columns was carried out at 100 C.

[b]NH_4OH:MeOH, concentrated ammonium hydroxide 20%: methanol 80% (v/v). This must be made up immediately before use, as the mixture is supersaturated with gaseous ammonia.

RESULTS AND DISCUSSION

The solvents listed by Teranishi (1) or by Mon (2) failed to remove the polymeric residues from an ethylene glycol succinate (EGS) liquid phase. However, with two modifications, the complete removal of the EGS polymer was accomplished allowing successful recoating of the column. First, it was reasoned that having the polymer in the liquid state and using the solvents at elevated temperatures should enhance the solution process and the efficiency of the stripping procedure. The column was, therefore, immersed in a boiling water bath and the cleaning was improved considerably. Figure 2 gives an indication of the effect of temperature upon cleaning efficiencies.

The recommended alkaline cleaning step (2) was still unsatisfactory, since almost every attempt to use it resulted in plugging of the column even when the 10% KOH in methanol was filtered directly into the cylinder and used at either 20 or 100 C. In addition, little of the polymeric residue was removed. Thus, the second modification involved replacement of KOH with a 20% ammonium hydroxide (concentrated reagent) -80% methanol solution. This removed the polymeric material quite effectively, and we found it entirely unnecessary to use the nitric acid, except in the initial cleaning of new tubing. It would appear that nitric acid treatment can be detrimental to cleaning efforts with old columns containing a liquid phase. With these procedures, OTCs have been cleaned successfully, recoated, and reused now for more than seven successive cycles, and it seems reasonable to expect continued service for the physical life of the tubing. Our current cleaning procedure has been summarized in Table 1.

Occasionally, in cleaning an old column, particularly if considerable unpolymerized liquid phase is present, the hot chloroform will cause the column to plug. If this occurs, the column can be heated in an oven at a temperature in excess of the normal operating temperature with gas pressure applied. This melts the liquid phase and apparently allows it to resume the conformation of a thin coating on the walls in place of a solid plug. Then chloroform should be flushed through, first at room temperature and then at 100 C, to prevent formation of a new plug.

The liquid phase was applied as a 5% solution in 100 ml $CHCl_3$ with 15 psi nitrogen pressure and was coated in the inverse direction from normal gas flow through the column. The cleaning proedure also was carried out using this flow direction. Since the thickness of the film deposited is directly related to the rate of travel and the amount of the solution, optimum film coatings may require pressures lower or higher than that suggested.

Using this procedure, it is possible for a technician to clean and recoat a used column in less than a day, using ca. 5 min out of each hr to accomplish the solvent changes, etc. This compares quite favorably with the time required to prepare the packed columns used previously. Additionally, the OTC last three times longer than their packed column counterpart.

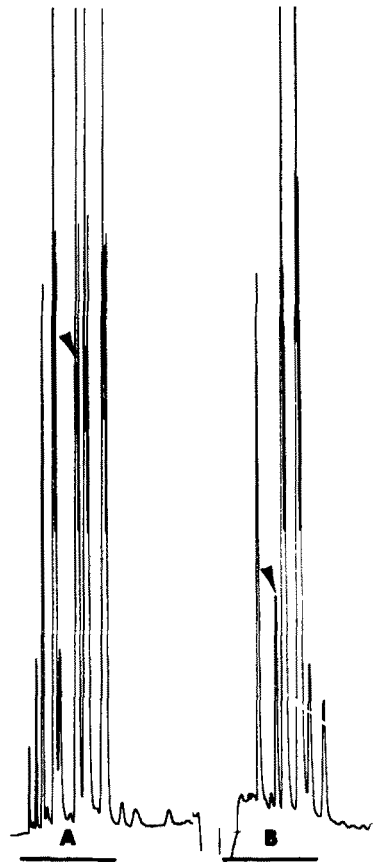

FIG. 3. Comparison of chromatograms after cleaning-recoating cycles. A. New tubing; B. After seven cycles. Arrows point to stearate peaks; solid bars at the bottom are each 5 min long and begin at the approximate location of the air peak. Instrument: Hewlett-Packard model 700, hydrogen flame detector, Oven 170 C, 18 cc/min. helium carrier gas, "solventless" injection, no splitter used. Ethylene glycol succinate was the liquid phase in both cases. Sample size ca. 10 ng for full-scale peak.

The two chromatograms in Figure 3 were made 42 months apart and after 7 cycles of cleaning and recoating, showing that the tubing can be successfully recycled. The samples unfortunately are not the same but do show that the stearate-oleate-linoleate separations are essentially identical. The peaks following linoleate are different fatty acids in the two chromatograms. Both injections were made by the use of a modification of a previously described injector system (3) that permits application of the sample to the column in a nearly solvent-free condition.

It must be stressed that procedures for stripping off old liquid phases may need to be tailored to liquid phase involved, no single set of solvents can be expected to work for all liquid phases. The described cleaning procedure should be successful with all organic polymers of the polyester type and with hydrocarbon greases. Attempts by coworkers to remove silicone or silicone-organic polymers with the outlined procedure have not always been successful.

REFERENCES

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