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Note

Damage to gas chromatographic columns caused by peroxides in liquid chromatographic eluents for coupled liquid chromatography–gas chromatography

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We wish to report a technical problem encountered when working with coupled liquid chromatography–gas chromatography that considerably hindered us. Using diethyl ether as an LC eluent, we repeatedly observed that apolar, polysiloxane-coated GC capillary columns were ruined after a single or a few transfers of 500 μl volumes of eluent. The general column test[1] showed broadening and tailing of all peaks, as shown in Fig. 1. Removal of the column inlet did not result in any improvement, ruling out that the problem was caused by contamination of the inlet with high boiling or involatile by-products. One of these columns was broken into two, both of

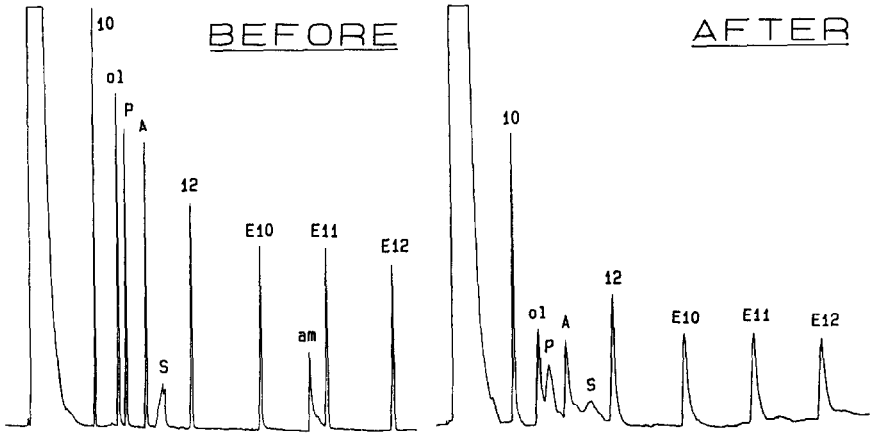

Fig. 1. Test chromatograms of a 5 m × 0.32 mm I.D. glass capillary column coated with PS-255 (a methylsilicone) of film thickness 0.23 μm. Left: column test before passage of ether. Right: column test after introduction of a 500-μl volume of ether containing 200 ppm of peroxides. Peaks: 10 = *n*-decane; ol = 1-octanol; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; S = 2-ethylhexanoic acid; 12 = *n*-dodecane; E10–E12 = methyl esters of the acids C_{10}–C_{12}; am = dicyclohexylamine.

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which were retested. These tests indicated that the exit half of the column was severely damaged, too, although somewhat less than the first half. We first assumed that the damage was due to contamination of the column with packing material from the LC column. However, experiments described below showed that the damage of the GC column was caused by peroxides present in the ether.

Diethyl ether is an important eluent for LC–GC with concurrent eluent evaporation[2,3] because of its low boiling point, allowing transfer at relatively low temperature. Further, its use is convenient as all mixtures with *n*-pentane have practically the same boiling point[4].

EXPERIMENTAL

Volumes of solvent (500 μl) were introduced into apolar GC columns by concurrent solvent evaporation[5] using an experimental set-up that resembles a loop-type LC–GC interface. The inlet of the test capillary column was drawn out of the GC oven and mounted into a six-port switching valve. This valve was equipped with a 500-μl loop and the two fill ports. The last port was occupied by the carrier gas supply line.

The sample loop was filled with the solvent to be tested by suction through metal capillary tubes into a 10-ml plastic syringe. Diethyl ether was transferred to the GC column at an inlet pressure of 1.5 bar and an oven temperature of 85°C. Columns were tested before and after such treatment, using the standard procedure and test II[6]. Sections (5 m) of long 0.32 mm I.D. GC glass capillary columns were used as test columns. They were coated with PS-255 and SE-54 of film thickness 0.2–0.3 μm.

RESULTS

Peroxides as the source of the problem

Without having passed through an LC column, "HPLC-grade" diethyl ether and ether distilled about 1 year ago (stored in a bottle packed into aluminium foil) produced the same damage to the test columns as described above after a single introduction of a 500-μl volume into the GC column. Peroxide concentrations, determined by the "Perex-Test" (Merck, Darmstadt, F.G.R.), were between 100 and 200 ppm. Ethers stabilized with 2,6-di-*tert.*-butyl-*p*-cresol did not damage the column after ten transfers of 500-μl volumes. These ethers contained up to 2 ppm of peroxides.

The LC column involved in the LC–GC experiments (packed with Nucleosil CN) did not contribute to the problem. This was established from the fact that ether containing 1 ppm of peroxides did not damage the GC test columns after passage through the LC column (10 transfers of 500-μl volumes).

We do not know how peroxides damage methylpolysiloxane stationary phases. However, the damage produced phenomera resembling those observed when using old stationary phase solutions for coating the column[7]. Hydroxy groups might be introduced either by oxidation of methyl groups or by opening of siloxanes. In fact, resilylation of the columns with hexamethyldisilazane (HMDS) improved the column performance, but did not fully restore it. On the other hand, even non-adsorptive compounds such as alkanes were more or less strongly affected (strongly in Fig. 1.).

Excessive cross-linking within the stationary phase ("lacquering"), occurring through the same mechanisms as used for immobilizing the stationary phase, is unlikely to be the cause of the column deterioration as this usually reduces the retention power of the column. However, the elution temperature of the last peak of the test mixture (E12) did not decrease by a single degree.

Removal of peroxides

Ethers stored in an atmosphere of nitrogen and stabilized with copper metal might appear to solve our problem as they are free of organic additives disturbing GC. However, a sample taken from a bottle opened a few months ago rapidly ruined a GC column. In fact, it contained 100 ppm of peroxides (another ether sample from the same source, taken from a new bottle, contained 2 ppm of peroxides and did not damage GC columns). Hence, periodic tests for peroxides are a prerequisite when using such ethers. Organic antioxidants seem to be safer in keeping ether free of peroxides, but must be removed before use because the amounts involved severely disturb GC.

Antioxidants as well as peroxides can be removed from ether using basic aluminium oxide: with 7 g aluminium oxide 90 active, basic (70–230 mesh) (Merck, Darmstadt, F.R.G.) and ether containing some 500 ppm peroxides, a 90-ml volume of ether was freed from peroxides to less than 1 ppm, while the following 10 ml of ether contained 200 ppm of peroxides.

DISCUSSION

Use of ether for coupled LC–GC necessitates previous removal of organic stabilizers as well as of peroxides. In practice, there are various ways of solving this problem. Often ether must be distilled before use because of interfering impurities. This also removes antioxidants, and, if some iron(II) sulphate is added, the peroxides. However, the resulting ether is unprotected, and the peroxide concentration tends to increase rapidly upon storage. Brown bottles or bottles shielded with aliminium foil must be used as solvent reservoirs, and periodic checks on peroxides are important. If the ether is of sufficient purity and distillation is not required, stabilizers and peroxides are most conveniently removed using basic aluminium oxide (see above). This can be done at short intervals, ensuring that the peroxide concentration remains low.

Stabilizers and peroxides can be removed from the eluent by an aluminium oxide column installed between the LC pump and the LC injector. The required size of this column and the frequency of exchanging its content strongly depends on the eluent flow-rate and the eluent composition. Using pure ether, about 8 ml of ether can be cleaned per gram aluminium oxide. The capacity of the aliminium oxide column rapidly increases when using pentane–ether mixtures, as chromatographic retention volumes of stabilizers and peroxides are increased. Such on-line cleaning rules out peroxide formation in the cleaned ether during storage, but care is required to avoid contamination of the LC system after exchanging the aluminium oxide.

Finally, problems concerning peroxides can be avoided by replacing diethyl ether by *tert.*-butyl methyl ether. The latter does not form any peroxides, but its boiling point is 55°C, about 20° above that of diethyl ether.

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