

## Note

### Immobilization of silicone stationary phases for capillary chromatography through the action of azoisobutyronitrile

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There are a variety of reasons for the continuing development of immobilized stationary phases for capillary gas chromatography (GC). The thermal stability of immobilized layers is often enhanced as compared to mechanically deposited films. Phase displacement at the column inlet due to large solvent injections is eliminated because of the low solubility of the stationary phase. Proper synthesis of the polymer can impart mechanical stability to the coating allowing either thick films or highly polar phases to be evenly coated without droplet formation. An additional impetus for such developments in this laboratory is the use of capillary columns in supercritical fluid chromatography (SFC) as described in previous communications<sup>1,2</sup>.

The phase immobilization methods reported in the literature for use in capillary GC involve either prepolymerized fluids attached to the glass surface via the reactive surface silanol groups<sup>3,4</sup> or *in situ* cross-linking of conventional, mechanically coated stationary phases, as reported by Grob *et al.*<sup>5</sup> and others<sup>6-9</sup>. The latter approach, using techniques widely employed in rubber vulcanization processes, appears to have the distinct advantage of simplicity. Because cross-linking occurs in the polymer rather than to the substrate, this immobilization technique is applicable to both glass and fused-silica column technology.

Several cross-linking agents have been described for phase immobilization efforts. *In situ* generation of free radicals from various organic peroxides, such as benzoyl peroxide<sup>5-9</sup>, dicumyl peroxide<sup>8,9</sup>, *tert.*-butyl peroxide<sup>9</sup> has been investigated. Lee *et al.*<sup>7</sup> also recommended the use of azo-compounds to meet similar goals. In addition, gamma rays were found effective<sup>10</sup> in inducing free-radical polymerization of coated polysiloxanes.

The above procedures for polymer immobilization vary in degree of difficulty. The generation of free radicals during the phase treatment inside the column and along the entire column length should be both homogeneous and controllable. Introduction of some volatile peroxides in the vapor phase during the column treatment is inconvenient due to the hazard<sup>11</sup> as well as possible non-uniform decomposition along the column length. Solid initiators are considerably more convenient to use as additives to the stationary phase solution so long as they do not influence the wettability of the column wall or deposit undesirable reaction products upon decomposition. While the former problem was observed by Lipsky and McMurray<sup>9</sup> with benzoyl peroxide, the same agent is blamed for the generation of products<sup>12</sup> harmful

to the column. Lee *et al.*<sup>7</sup> have chosen azo-compounds as cross-linking agents to avoid similar difficulties as only volatile decomposition products were formed.

This communication reports the successful use of azoisobutyronitrile (AIBN) as a convenient initiator of cross-polymerization of conventional silicone stationary phases. While this solid substance has been known<sup>13</sup> for its easy generation of free radicals, its major decomposition products do not adversely affect column performance and can be easily removed at elevated temperatures. Simultaneously, its use as a phase additive during the coating process does not seem to alter wettability of the surfaces of glass or fused-silica capillaries. Its low decomposition temperature ( $t_{1,2} = 1.3$  h at 80°C) makes AIBN superior to other commonly used free-radical initiators.

In our numerous experiments, AIBN was employed to effectively immobilize commercially available silicone stationary phases (SE-30, SE-52 and SE-54) to the inner wall of either glass or fused-silica capillary columns. The glass capillaries (15–20 m  $\times$  0.25 mm I.D.) were first dynamically leached<sup>14</sup> and silylated at 400°C<sup>15</sup>, while the fused-silica columns were used as received. Coating solutions for the static coating procedure contained 0.5% (w/v) of the silicone gums in *n*-pentane and 0.5

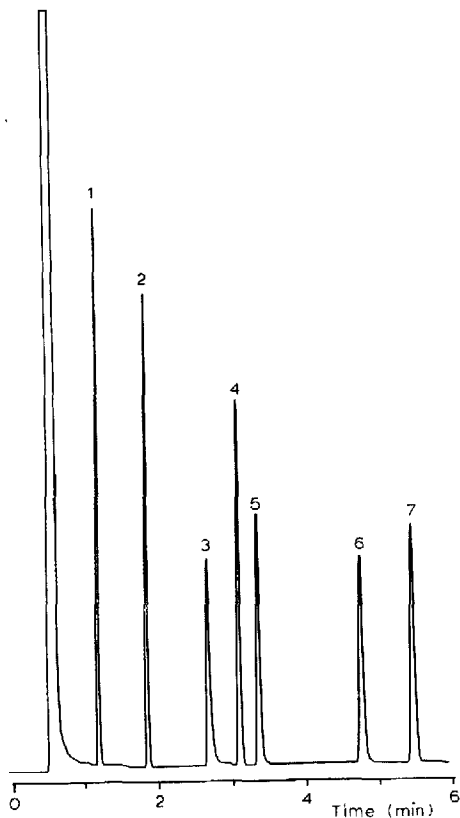


Fig. 1. Capillary gas chromatogram of a polarity mixture after extensive methylene chloride washing. Sample: 0.4 ng per component on column after split of 1 to 150. Column: 14 m  $\times$  0.25 mm, *i.e.*, 0.3- $\mu$ m film thickness of SE-54, cross-linked with 10% (w/w) AIBN. Column temperature: 100°C. For peak labeling see Table I.

TABLE I

COMPARISON OF RETENTION INDICES BEFORE AND AFTER A METHYLENE CHLORIDE WASH OF AN SE-54 COLUMN CROSS-LINKED WITH AIBN

Compound	<i>I</i> (before wash)	<i>I</i> (after wash)
1 Nonane	900.0	900.0
2 Decane	1000.0	1000.0
3 1-Octanol	1073.9	1073.9
4 Undecane	1100.0	1100.0
5 2,6-Dimethylphenol	1118.8	1119.2
6 2,6-Dimethylaniline	1178.3	1178.9
7 Dodecane	1200.0	1200.0

mg/cm<sup>3</sup> of AIBN. Following the coating step, the columns were sealed under vacuum and cured at 80°C for 3 h. The capillary columns were then conditioned in a conventional manner. Their performance and capacity ratios were measured before and after a wash with 25 ml methylene chloride. The usual "polarity mixture" was used to compare characteristics of the immobilized phases with those conventionally prepared.

A typical loss of retention after the extensive wash with methylene chloride was found to be only 4% (an average of five columns). A relatively high percentage of AIBN was found to be essential; lesser amounts produced inferior results. This fact might explain the difference between our results and those of Lee and co-workers<sup>16</sup> who recently reported less positive results with the same agent.

Column efficiencies were typically between 2500 and 3000 effective plates per

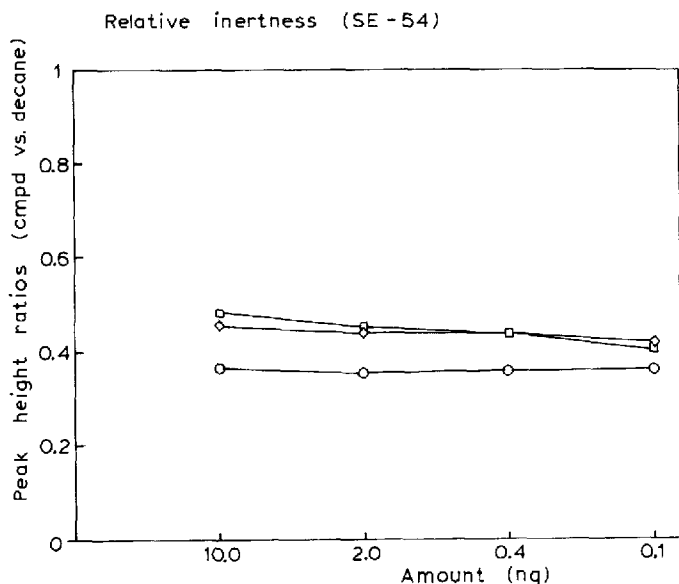


Fig. 2. Plots showing the relationship between peak height ratio of an active compound to decane vs. the amount injected. Active compound: octanol (□); 2,6-dimethylphenol (◇) and 2,6-dimethylaniline (○).

meter (which corresponds to efficiencies of 75–80%). A typical chromatogram of the polarity mixture at a subnanogram level, obtained with an immobilized and excessively extracted film of SE-54 elastomer, is shown in Fig. 1, while Table I lists the average values of retention indices for the solutes chromatographed prior to and after methylene chloride extraction. Comparisons with retention values obtained with conventionally coated columns (without AIBN addition) indicated that neither the substance nor any of its degradation products measurably affect chromatographic retention. In addition, AIBN does not appear to adversely affect the column wettability with the stationary phases under study.

To determine adequately the degree of irreversible column adsorption, a polarity test mixture should be applied, starting with concentrations close to the minimum detectable amount and, eventually, spanning the concentration range of analytical interest. This procedure, described by Purcell<sup>17</sup>, is not always sufficiently appreciated in the literature. When the peak heights of more polar (and, relatively more sensitive) mixture components are ratioed to a near alkane peak, for different amounts, the slopes of corresponding curves should provide an adequate description of column inertness. This method assumes that adsorption of alkanes is negligible. As shown in Fig. 2, adsorptive properties of the glass columns prepared through the action of AIBN are minimal. Very similar behavior was exhibited by fused-silica columns.

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