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## Note

### Ozone as an *in situ* cross-linking agent for silicone gum stationary phases in capillary gas chromatography

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Much effort has been devoted to the preparation of immobilized stationary phases by cross-linking initiated by free radicals. Such curing stabilizes the stationary phase film and leads to increased thermal stability. Furthermore, the film becomes non-extractable.

Several techniques for the cross-linking of stationary phases are available. Initiation may be achieved by: peroxides<sup>1-3</sup>, azo compounds<sup>4</sup>, radiation from a <sup>60</sup>Co source<sup>5-7</sup>, and by accelerated electrons from a Van der Graaf generator<sup>8,9</sup>.

One disadvantage of using peroxides or azo compounds is that they give rise to residues, which may be harmful to the stationary phase<sup>4</sup>. The use of radiation or a Van der Graaf generator has the advantage that no foreign materials are introduced into the stationary phase. These curing methods are considered to give phases with physical properties slightly better than those derived using the peroxide technique<sup>8</sup>. A disadvantage of the <sup>60</sup>Co source and the Van der Graaf generator is that most laboratories do not have access to the necessary facilities.

Ozone can act as a cross-linking agent for silicones<sup>8</sup>. This reaction is of limited industrial importance, because only relatively thin sheets can be vulcanized due to the low rate of diffusion of ozone into the silicones. The method is, however, very suitable for curing thin silicone stationary phase films, and furthermore is generally available.

An additional advantage of ozone-promoted cross-linking is that the column can be pretested, thus providing the opportunity to select only the best columns for curing and thereby diminishing column waste<sup>10</sup>. This is also true for the method published by Blomberg and Wännman<sup>11</sup>, where tetrachlorosilane was used as a cross-linking agent.

This paper describes an *in situ* cross-linking technique for some silicone gum stationary phases using ozone as the curing agent.

## EXPERIMENTAL

### Preparation and testing of the columns

Fused-silica capillaries (Hewlett-Packard, Avondale, PA, U.S.A.), 15 m × 0.25 mm I.D. were deactivated with octamethylcyclotetrasiloxane, D<sub>4</sub> (Petrarch Sys-

tems, Bristol, PA, U.S.A.) without pretreatment. This was achieved by heating the sealed D<sub>4</sub>-coated column at 5°C min<sup>-1</sup> to 440°C, maintaining this temperature for 2 h, and then cooling slowly<sup>13</sup>. During heating, the columns were protected in an atmosphere of nitrogen.

The columns were rinsed with 3 ml of methylene chloride, and then statically coated with a solution of 0.4% w/v stationary phase in methylene chloride; the film thickness was *ca.* 0.25 μm. Following the coating procedure and flushing with dry nitrogen for 3 h, the columns were conditioned by heating at 2°C min<sup>-1</sup> to 200°C, then isothermally for 5 h prior to various tests.

After preliminary tests, the columns were filled with ozone (3% ozone in O<sub>2</sub>) by suction of the ozone-oxygen mixture through the column for 15 min. The ozone was produced by an ozonizator, Neontransformer, type 4045 (SEM, Sweden), with an inlet flow-rate of oxygen of 100 ml/min. For SE-33 and SE-54 phases, the columns were immediately after ozonization flushed with dry nitrogen for at least 3 h. Immediately after ozonization columns coated with SE-30 and SE-52 were sealed and quickly placed in a hot oven at 150°C, and after 15 min flushed at room temperature with dry nitrogen for 3 h. In order to check whether any change had occurred, the columns were tested before rinsing with 5 ml of methylene chloride. After rinsing, the columns were conditioned by heating at 2°C min<sup>-1</sup> to 300°C, then isothermally overnight. Some columns were rinsed two or three times with methylene chloride; no further decrease in capacity ratio was observed.

The columns were tested in a Hewlett-Packard, Model 5790, gas chromatograph with a flame ionization detector and hydrogen as carrier gas. Test results were computed on a Hewlett-Packard integrator, Model 3391 A. The test mixtures were (a) Grob's test mixture and (b) a polarity mixture, containing dodecane, *n*-octanol and naphthalene. Each peak in the chromatograms corresponds to *ca.* 1 ng of substance.

## RESULTS AND DISCUSSION

The thermal stability of poly-organosiloxanes is influenced by the structure of the polymer chains. Rupture of one silicon-oxygen bond is sufficient for the cleavage of linear macromolecules, but for polymers with a three-dimensional structure, cleavage requires the rupture of siloxane bonds at two or even three points<sup>12</sup>. Oxygen does not act directly on the silicone bond, but is responsible for the formation of active groups which accelerate depolymerization<sup>12</sup>.

Andrianov and Sokolov<sup>14</sup> consider that oxygen attacks a carbon atom attached to silicon in a polymer molecule; a hydroperoxide is first formed which rapidly decomposes to formaldehyde and an HO· radical, which adds to the silicon atom. Condensation of the polymer molecules then takes place via the hydroxysilyl groups. Thermal decomposition of formaldehyde yields carbon monoxide and hydrogen, but on oxidation, carbon dioxide and formic acid are produced.

Ozone cleaves to give oxygen and an O· radical which has a *t*<sub>1/2</sub> of *ca.* 20 min. It is well known in organic chemistry that ozone readily attacks vinyl groups, forming carbonyl groups. It is not known if this is true for silicone stationary phases, *e.g.* SE-33 and SE-54, in which 1% of vinyl groups are incorporated. These stationary phases are easily converted into insoluble compounds by the action of ozone; it may

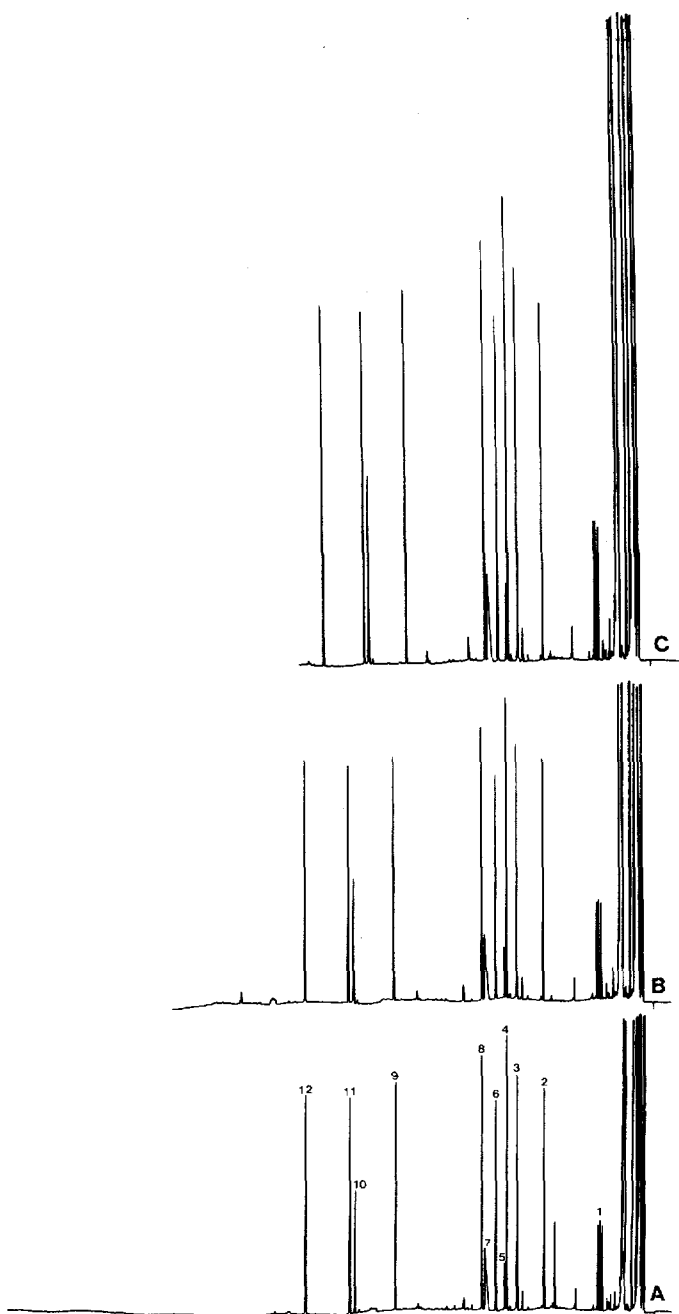


Fig. 1. Gas chromatograms of Grob's test mixture on a fused-silica column, 15 m  $\times$  0.25 mm I.D., coated with SE-33,  $d_f = 0.25 \mu\text{m}$ . (A) Before ozone treatment; (B) after ozone treatment and (C) after ozone treatment and rinsing with 5 ml of methylene chloride (rinsing overnight). Injection at 50°C, programmed at 5°C min<sup>-1</sup>. Peaks: 1 = 2,3-butanediol; 2 = decane; 3 = *n*-octanol; 4 = 2,6-dimethylphenol; 5 = *n*-nonanal; 6 = undecane; 7 = 2-ethylhexanoic acid; 8 = 2,6-dimethylaniline; 9, 11, 12 = C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub> acid methyl esters, respectively; 10 = dicyclohexylamine.

be assumed that polymerization follows initial cleavage. After the ozonization and short conditioning to 150°C of the columns coated with stationary phases incorporating vinyl groups, no increase of acidity could be observed.

It was found that, after the ozonization, it was necessary before conditioning to flush the columns with dry nitrogen for at least 3 h at room temperature, or else the columns showed a high adsorptive activity to *n*-octanol and amines; severe tailing could thus be observed. Even after rinsing with methylene chloride, the activity of such columns was still too high.

The cross-linking procedure with ozone could be performed only with silicone gums of high molecular weight, *e.g.* SE-30, SE-33, OV-1, SE-52, SE-54, etc. With OV-101 it was not possible to obtain a non-extractable film of stationary phase on the column wall.

If a small number of vinyl groups is present in the silicone phase, *e.g.* SE-33, SE-54, ozone acts as a cross-linking agent at room temperature. On the other hand, polydimethylsiloxanes such as SE-30, OV-1 and SE-52 are relatively inert to ozone at room temperature, but if they are heated to 150°C for 15 min in the presence of ozone, cross-linking occurs.

Fig. 1 shows typical chromatograms obtained from a Grob's mixture on a column: (A) before ozone treatment, (B) after ozone treatment and (C) after rinsing with 5 ml of methylene chloride. The computed Kovats indices for *n*-octanol and naphthalene, height equivalent to a theoretical plate (HETP) and capacity ratios before and after ozone treatment are shown in Table I. Only small changes were

TABLE I  
CHARACTERISTICS OF SOME FUSED-SILICA CAPILLARY COLUMNS COATED WITH DIFFERENT SILICONE STATIONARY PHASES

Column dimensions, 15 m × 0.25 mm I.D.;  $d_f = 0.25 \mu\text{m}$ . (a) Before ozone treatment, (b) after ozone treatment and (c) after rinsing with 5 ml of methylene chloride. HETP and capacity ratio for dodecane measured at 90°C.

Column no.	Stationary phase	UTE* (%)	HETP (mm)	Capacity ratio	Kovats retention index at 90°C	
					Octanol	Naphthalene
1 a	SE-30	83.5	0.26	7.8	1054	1156
b		83.5	0.26	7.8	1055	1150
c		83.3	0.26	7.5	1054	1150
2 a	SE-33	88.4	0.25	8.5	1053	1149
b		88.4	0.25	8.5	1051	1151
c		87.9	0.25	7.8	1052	1150
3 a	SE-52	88.3	0.27	7.1	1070	1183
b		88.3	0.27	7.1	1069	1184
c		87.2	0.28	6.5	1069	1183
4 a	SE-54	85.7	0.26	10.8	1072	1183
b		85.1	0.26	10.9	1071	1182
c		84.9	0.26	10.8	1071	1182

\* Utilization of the theoretical best efficiency.

TABLE II

## STATISTICAL EVALUATION OF FUSED-SILICA COLUMNS COATED WITH DIFFERENT SILICONE STATIONARY PHASES

Kovats retention index, mean  $\pm$  S.D. ( $n = 5$ ). No statistical significance between the different treatments was observed ( $P > 0.05$ ).

Stationary phase	Kovats retention indices at 90°C						
	Before ozone		After ozone		After rinsing		
	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	S.D.	
SE-30	1054.7	0.49	1055.0	0.11	1054.8	0.29	:ol*
	1152.9	1.78	1151.8	0.77	1151.7	0.69	:naph*
SE-33	1052.6	0.46	1052.0	0.26	1052.2	0.27	:ol
	1150.1	0.53	1150.3	0.42	1150.0	0.44	:naph
SE-52	1070.0	0.30	1069.9	0.41	1070.0	0.30	:ol
	1183.1	0.38	1183.5	0.38	1183.4	0.48	:naph
SE-54	1071.9	0.36	1071.6	0.19	1071.6	0.33	:ol
	1183.0	0.36	1182.8	0.31	1183.0	0.22	:naph

\* ol = *n*-octanol; naph = naphthalene.

observed in the Kovats indices for *n*-octanol and naphthalene, before and after ozone treatment, and after rinsing the columns with methylene chloride ( $n = 5$ ). The differences were not statistically significant ( $P > 0.05$ ). The mean differences of the Kovats retention index for *n*-octanol and naphthalene from untreated columns were tested according to the Student's *t*-test for dependent means (paired observations). The overall relative standard deviation for the retention index was about the same for *n*-octanol and naphthalene on all four columns, *i.e.* coated with SE-30, SE-33, SE-52 and SE-54, which was less than  $\pm 0.15\%$  of the mean retention index (Table II). The relative standard deviation for HETP of these columns was  $\pm 1.5\%$  of the mean HETP.

## CONCLUSION

Ozone curing produces efficient, well-deactivated and thermostable capillary columns, which can be tested before curing. Problems encountered with peroxide or azo compound decomposition products are avoided. The method is simple and only ordinary laboratory equipment is needed.

Ozone curing of medium-polar silicones will be described in a future article.

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