

## GLC Determination of the Resin Acid Composition in Rosins and Oleoresins: State of the Art

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### ABSTRACT

Gas chromatographic methods using packed or capillary columns are reviewed for the analysis of resin acids in rosins and oleoresins. In general, polyesters are the preferable liquid phases (EGSS-X for packed columns and BDS for capillary columns) for the common resin acids found in rosin. However, oxygenated resin acids often require a second gas chromatographic determination using a nonpolar methyl silicone stationary phase. The implications of sampling, ester preparation, columns and instrument parameters on the analysis of resin acids are discussed.

### Introduction

Prior to the advent of gas chromatography, the determination of resin acid composition in rosins, oleoresins, or extractives was difficult and usually approached through the use of inaccurate spectroscopic or time consuming liquid chromatographic methods. The first application of gas chromatography to resin acid analysis was reported in 1959 by J. A. Hudy, who used a packed column containing the polyester, butanediol succinate. Subsequently, a number of publications described the GLC characteristics of resin acids for packed columns with a variety of liquid phases: these publications have been summarized.<sup>1</sup> More recently, the previously unattained resolution of levopimarate/palustrate has been achieved with cyanosilicone stationary phases.<sup>2</sup>

An ASTM method (D3008)<sup>3</sup> for resin acid analysis was adopted in 1972, based on the diethylene glycol succinate (DEGS) packing described by Nestler and Zinkel.<sup>4,5</sup> In the course of our efforts in reevaluating this method as part of the routine ASTM reappraisal process, we considered a wide

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variety of changes in the method including the replacement of packed columns by capillary columns. Because many quality control laboratories still have equipment suitable only for use with packed columns, the official method will continue to be based on packed columns. However, determination of resin acid composition using capillary col-

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**TABLE I. Loss of Resin Acids on Air Oxidation**

Storage time (days)	GLC throughput (%)	Loss (%)
0	89.7	0
1	84.5	5.8
4	74.1	17.4
6	69.9	22.1

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**TABLE II. Rates of Methylation of Dehydroabiatic Acid by Diazomethane in Various Solvents**

Solvents	Reaction time *		
	5 min	3 min	1 min
Benzene	97%	91%	--
Toluene	95%	96%	--
Ether	95%	34%	11%
<u>Ether/MeOH (9/1)</u>	<u>100%</u>	<u>100%</u>	<u>100%</u>

\*Add 5 to 15 sec. for evaporation of diazomethane.

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umns has become the primary method in research laboratories.

This paper reviews the status of the technology for both packed and capillary columns as applied to the determination of resin acid composition. The packed column aspects will focus on the ASTM method and revisions to that method. The discussion of capillary column technology will be based on a publication from this laboratory<sup>6</sup> and subsequent observations and developments.

## General Chromatographic Parameters

### Sampling and Sample Preparation

(1) Sampling As in any analysis, sampling is a universal consideration with numerous facets. The primary concerns are sample homogeneity and proper handling of the samples to avoid any changes.

Although oleoresins are almost always nonhomogeneous because of crystallization, homogeneity can be achieved simply through redissolving the crystals by gentle heating, either with or without added solvent (the problem of representative sampling of the original source is another question). To obtain a representative sample of a rosin, it is prudent to take several small portions from various points in the rosin to be analyzed, analogous to the approach of ASTM D 509.<sup>7</sup> The small portions can either be dissolved in solvent for appropriate further sampling, or the portions can be ground together and an appropriate amount sampled immediately for further analytical processing.

The potential for oxidative changes is the main problem in maintaining the integrity of samples containing resin acids. Keeping samples (solids or solutions) under an inert gas will minimize problems of sample degradation. The rapidity of air oxidation of ground rosin is seen in the data of Table I. The throughput data include only the resin acids (nonoxidized) eluting in the pimarate through neoabietate region.

(2) Separation of Resin Acids from Neutrals: Oleoresins and rosins consist of resin acids and a small portion of neutrals many of which elute on gas chromatography in the region of the resin acids. Thus, removal of the neutrals from the sample will permit a more accurate picture of the resin acid composition. A quantitative method to effect such a separation has been developed using DEAE-Sephadex.<sup>8,9</sup> In this method the acids exchange onto the DEAE-Sephadex, and the neutrals pass through the column; quantitative recovery of acids is subsequently achieved by elution with CO<sub>2</sub>-saturated Et<sub>2</sub>O:MeOH:H<sub>2</sub>O (89:10:1) eluent. The method as described<sup>8,9</sup> provides data on the content of neutrals and acids but is rather time consuming allowing an analyst to process only 4 to 8 samples per day. However, when such neutrals content data are not needed and only data on resin acid composition are required, the DEAE-Sephadex procedure can be reduced in size. This is accomplished by scaling-down the original column<sup>8</sup> to one having a column portion 3 mm x 55 mm and reservoir of 2.0 x 5.2 cm. The separation is effected similar to that described<sup>9</sup> except for the following

important modifications: a) use of 79:20:1 diethyl ether:methanol:water in place of the 89:10:1 ratio and b) use of a slight CO<sub>2</sub> rather than nitrogen pressure to the column during elution of the acids. Although both modifications are necessary for the elution of the acids from the DEAE-Sephadex, the 79:20:1 solvents ratio is used during the entire procedure. The separation procedure using this semi-micro scale adaptation can be accomplished in 15 minutes; an analyst can process about 40 samples per day doing 4-5 separations simultaneously.

In general, the procedure for this semi-micro system is the same as described for the macro columns.<sup>9</sup> The sample, dissolved in the 79:20:1 solvent, to be applied to the DEAE-Sephadex semi-micro column should contain about 10 mg of resin acids. The neutrals are eluted with 10 ml of solvent with application of slight nitrogen pressure as appropriate. The elution of the resin acids is accomplished with 15 ml CO<sub>2</sub>-saturated solvent under a slight CO<sub>2</sub> pressure generated from dry ice in an attached, pressure controlled reservoir (we used a 150-ml Dannley pressure filter funnel, Ace Glass #7188).

(3) Esterification: The current ASTM<sup>3</sup> method gives a choice of two procedures for methylation of the resin acids.

One procedure involves preparation of the resin acid tetramethylammonium (TMAH) salts and pyrolysis of the salts in the injection port of the gas chromatograph to yield methyl esters. It is recommended that the resin acids be titrated with TMAH/methanol to a pH of 12.0-12.5 with a pH meter rather than to a pink endpoint using phenolphthalein.<sup>10</sup>

The second procedure consists of the facile and clean methylation with diazomethane. The use of benzene as solvent in this methylation, as was called for in the ASTM procedure would not be expected to give quantitative yield of methyl esters in light of the work by Schlenk and Gellerman<sup>11</sup> with fatty acids. The data in Table II confirm that expectation.

In this experiment, dehydroabietic acid and methyl heptadecanoate (internal standard) were dissolved in various solvents and ethereal diazomethane added drop by drop into the sample until the sample just retained a faint yellow color. After the indicated time, the reaction was stopped by evaporating the diazomethane under an impinging stream of nitrogen. It is clear from the results that the methylation reaction in single solvents is not completed in a short time period, but the inclusion of methanol with diethyl ether results in instantaneous reaction. This is consistent with the work of Schlenk and Gellerman<sup>11</sup> who showed that the reaction is not complete after 1 hour in either diethyl ether or methanol alone. However, when the two are combined at a 9:1, ether:methanol ratio, the reaction is instantaneous.

Resin acid methyl esters can be prepared with the analogous trimethylsilyldiazomethane<sup>12</sup> but the specifics for quantitative conversion have not been defined. Trimethylsilyldiazomethane is reported to be a safe, stable, conveniently handled liquid, and is commercially available as a 10% solution in heptane. The cost of the reagent is considerably higher than diazomethane.



Other esters of resin acids (prepared by diazoalkylation or by reaction with dimethylformamide dialkylacetals) have been evaluated for potential improvements in the GLC separation characteristics of the resin acids in rosins.<sup>2</sup> With the possible exception of the *t*-butyl ester for special purposes, most of the other alkyl esters did not provide any advantages. However, ethyl esters have been useful for differentiating between co-occurring pinifolic acid (a diacarboxylic labdane acid) and its monomethyl ester in *Pinus nigra* foliage.<sup>13</sup> Interestingly, the esterification with diazoethane did not require the presence of methanol for instantaneous reaction. Ethyl esters prepared by reaction with triethyloxonium tetrafluoroborate have been used in the analysis of resin and fatty acids in pulp mill effluents.<sup>14</sup>

(4) Stability of Methylated Samples: Proper precautions must be observed in handling methylated samples to prevent oxidative changes. Usually dissolving the sample in a polar solvent (we prefer methyl *t*-butyl ether because peroxides do not form) and flushing the vial with nitrogen before closing is adequate for very short term storage before GLC analysis. Storage in a nonpolar solvent can lead to the concerted oxidation-dehydration of levopimarate and palustrate to form dehydroabietate, but this can be ameliorated by addition of a small amount of methanol to the solution. It is preferable to analyze samples as soon as possible after methylation.

Another concern in sample handling is the potential contamination by the closures of the sample vials. In general, only teflon lined caps or teflon faced septa should be used. Once a lined septum is punctured to remove an aliquot for GLC, extracts from the silicone rubber of the septum can contaminate the sample resulting in a large number of artifact peaks throughout the gas chromatograms. The use of teflon liners for standard laboratory screwcap vials prevents contamination of samples by the organic solvent-soluble coating in the caps.

### Injection System

The injection system for packed column systems is splitless in that the entire aliquot of sample and solvent are flashed to the column. With capillary column systems, however, a variety of split, splitless and on-column injection procedures are available. Of these, only split techniques have been used in the capillary GLC of resin acid methyl esters. We do not have any evidence in our work that discrimination among the resin acids of rosin occurs during split injection. However, in other resin acid samples containing a wide-boiling range of compounds, including *e.g.*, C-10 fatty acids, resin acids and oxygenated resin acids, on-column or splitless techniques may be needed to avoid split discrimination.

It has been our experience that a *ca.* 3-microliter volume from a 10-microliter syringe is necessary for quantitative reproducibility. This volume holds for both the splitless injection with packed columns or the split injection with capillary columns, and for automatic or manual injection.

### Detector

The early research on GLC of resin acids used the thermal conductivity detector because of its greater reliability *vis-à-vis* the flame ionization detector (FID) at that time. Now, the FID is nearly universally used for both packed and capillary columns and is prescribed in the ASTM method. Attention to detector maintenance and the optimization of gas flow rates is essential for quantitative results.

### Integration of Peak Areas

A number of methods are available to measure peak areas on chromatograms, but the most prevalent method is electronic integration. Although most state-of-the-art instruments use post-run integrators, earlier instruments are equipped with the real-time integrators which must recognize a peak at its onset and establish a corrected baseline immediately at the end of the peak. In contrast, the post-run integrators store raw area data, then analyze it after the chromatography is completed. Although the real-time integrator provides satisfactory results with packed column data, the integrator is the limiting factor in quantitation when using capillary columns. Special attention must be paid to slope sensitivity settings. In addition, we have experienced sporadic situations with our Hewlett Packard model 5880 instrument in the capillary GLC of resin acids in which some peaks of significant size were not recognized and integrated. The problem as traced to a peak width parameter in the peak recognition program (residing in ROM). However, this problem was a "go" or "no-go" situation in that peaks were either recognized or not recognized: all recognized peaks were properly integrated. Although the program was modified by the instrument manufacturer, the occasions of malfunction were rare and solvable by re-chromatography with slight modification of conditions.

### Quantitation

In the ASTM method, the composition of resin acids is calculated by normalizing total peak areas to 100%. Although this approach is adequate for many purposes, it is not fully quantitative in that detector responses for individual resin acids can vary by nearly 10%. Other factors such as linearity of response and detection limits will affect final data.

#### (1) Response/Correction Factor

We have determined the differences in detector response among the major resin acids for both packed and capillary systems (Table III). These relative response data (*i.e.*, factor, RF) are related to an area correction factor (CF) as a simple reciprocal:

$$CF = 1/RF$$

To use the correction factor CF, the area of a peak or the normalized percent composition is multiplied by the correction factor and the recalculated values recomputed for percent composition. Many instruments can perform this operation automatically. The correction factors as determined



with the polar and nonpolar capillary columns are essentially the same. For the most part, the correction factors for the EGSS-X packed column agree with the capillary data with the exception of levopimarate and abietate. In this work we have taken extraordinary precautions in working with these two esters but have not been able to improve, i.e., obtain values consistent with the capillary data. We have no explanation for these apparent anomalies.

In our experience and with our instrumentation, the minimum amount of an individual component into the column for quantitative work is 2 micrograms for packed columns and >20 nanograms for capillary columns.<sup>6</sup>

### (2) Recovery or Throughput of Resin Acids.

Rosin generally contains 5 to 20% of nonvolatile or polymeric materials which do not elute from the polyester columns. Although the relative composition of the individual resin acids can be calculated by normalization of peak areas, information on the total amount of volatile acid components and the composition of resin acids on a total sample basis is often needed. An internal standard that is well resolved from any component of the sample is needed to accomplish this. Choice of an internal standard has been a concern since some of the early research on the GLC of resin acids. For example, Nestler and Zinkel<sup>7</sup> found that the long chain *n*-alkanes and acids (as methyl esters) gave anomalous responses with a katharometer as detector and were not usable. A hydrocarbon would be expected to be the preferable internal standard because it should be completely inert to the chromatographic process. Hydrocarbons compatible in the retention region of resin acid methyl esters on polyesters contain from 24 to 28 carbons. With FID and a packed (EGSS-X) column however, we have found that the hydrocarbons particularly above C-24 give correction factors with much greater (a factor of *ca.* 4) relative standard deviation than do fatty acid methyl esters. Because of this problem, we generally use methyl eicosanoate (20:0) as the internal

standard for the analysis of oleoresins and gum and wood rosins; methyl heptadecanoate (17:0) is used with tall oil rosins to avoid possible interference from 20:0 present in tall oil rosins. A comparison of detector response data (for both EGSS-X packed column and BDS capillary systems) for methyl pimarate, isopimarate and dehydroabietate with that of 20:0 show that the response on a weight basis is greater for the resin acids. Therefore, an additional correction factor for the internal standard [i.e., 0.96 x resin acid methyl ester area x C<sub>r</sub> (related to pimarate, Table III)] is needed in calculating quantitative data.

We and others have attempted to develop recovery or throughput data for a variety of rosins but have found that the throughput of components eluting in the diterpene resin acid ester region have ranged from 80-100%. The lowest values have generally been for gum rosins and the highest values for tall oil rosins. Although we have gained some insight into the throughput problem by evaluating the potential effects of the presence of resin acid anhydrides, dimers, and neutrals (obtained by both steam distillation or DEAE-Sephadex separation), further research is necessary to obtain a complete material balance and understanding of rosin composition.

### Packed Column Chromatography

Polar liquid phases are more effective than nonpolar liquid phases in the gas chromatographic separation of diterpene resin acids of rosins. This is due to selectivity in the interactions between the polar sites of the liquid phase and the unsaturation (double bonds) in the resin acids. ASTM D 3008<sup>8</sup> calls for diethylene glycol succinate (DEGS) as the liquid phase for the official method. Although we used DEGS in the early years of our research, we now use the ethylene glycol-silicone copolymer EGSS-X because it is somewhat more stable yet has almost identical resin acid retention characteristics as DEGS (Table IV). "Stabilized"

**TABLE III. Relative Correction Factors for Resin Acid Methyl Esters**

	Capillary		Packed
	BDS	SE-30	EGSS-X
Pimarate	1.00	1.00	1.00
Levopimarate	1.04	1.03	1.07
Palustrate	1.04	1.06	1.04
Isopimarate	1.00	1.00	1.00
Abietata	1.00	1.00	1.08
Dehydroabietate	1.00	1.00	1.01
Neoabietate	1.02	1.02	1.04

**TABLE IV. Relative Retention Characteristics of Resin Acid Methyl Esters on DEGS and EGSS-X Packed Columns,**

Resin Acid Methyl Ester	DEGS	EGSS-X
Pimarate	1.00	1.00
Sandaracopimarate	1.13	1.12
communate	1.28	1.27
Lavopimarate	1.33	1.34
Palustrate	1.35	1.36
Isopimarate	1.49	1.46
Abiatate	2.14	2.10
Dehydroabietate	2.33	2.32
Neoabietate	2.47	2.46



DEGS packings have been offered commercially from time to time. However, these packings are not generally satisfactory in that quality is inconsistent, with the result that many preparations of the packings are chemically reactive and cause on-column isomerization of the abietadienoic esters, particularly levopimarate and palustrate. The cyanosilicones have polarity characteristics similar to the polyesters and could offer better liquid phases because of their greater stability. Indeed, the resolution of levopimarate and palustrate, previously not attained with polyester packings, was achieved with a cyanosilicone but with loss in resolution of the important dehydroabietate/neoabietate pair. However, the major drawback of the cyanosilicones is the difficulty, which both we and others (including commercially prepared packings) have experienced, in preparation and maintenance of satisfactory columns.

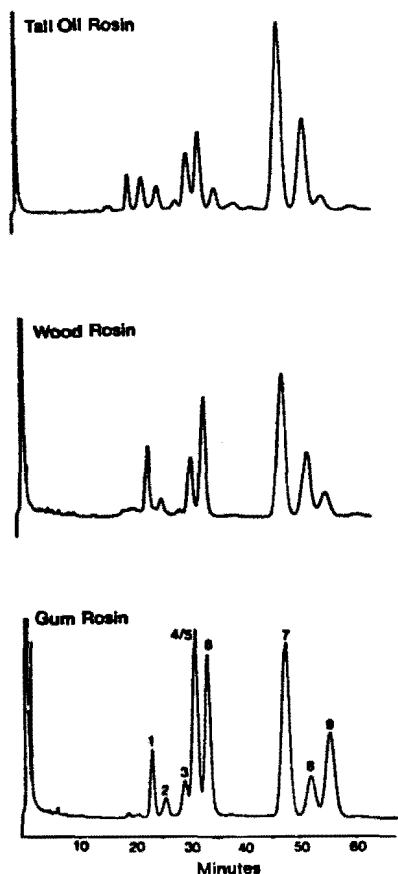
During our early research with packed columns, we found that a well washed, silylated diatomaceous earth support was necessary to minimize support activity. Anakrom ABS, an acid-washed, base-washed, and HMDS-treated support,

was selected. However, several years later, we found it increasingly difficult to prepare efficient packings with polyesters using the ABS support. Discussions with the manufacturer revealed that the silylating procedure had been "improved," yielding a more inert support, particularly for use with sterol samples. It became apparent that the increased silanization and hydrophobic character of the support surface resulted in poor wetting of the surface of the polyester liquid phase leading to inefficient packings. Fortunately, however, improvements had been made in the commercial preparation of acid-washed supports. Methyl levopimarate can thus be chromatographed with only minimal isomerization using EGSS-X on the acid-washed, nonsilylated support, Chromosorb W-AW. The optimum support particle size is 80/100 mesh.

Although glass may well be the best column material with respect to activity, the main drawback with coiled glass columns is the difficulty in packing columns of good efficiency. Thus, the usual 1/8 in. od stainless steel columns provide the best compromise in inertness and efficiency.

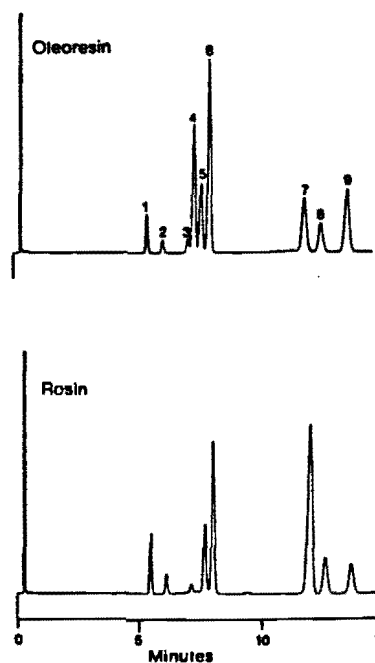
**FIGURE 1. Typical Tall Oil, Wood and Gum Rosin (New 10% EGSS-X Column: 8 ft. x 1/8 in., 200 C)**

- |                     |                               |
|---------------------|-------------------------------|
| 1 = pimarate        | 2 = sandaracopimarate         |
| 3 = communate       | 4/5 = levopimarate/palustrate |
| 6 = isopimarate     | 7 = abietate                  |
| 8 = dehydroabietate | 9 = neoabietate               |



**FIGURE 2. Gas Chromatograms of Resin Acid Methyl Esters from Slash Pine Oleoresin and Rosin Using a 7-meter BDS Fused Silica Column at 180 C.**

- |                 |                       |
|-----------------|-----------------------|
| 1 = pimarate    | 2 = sandaracopimarate |
| 3 = communate   | 4 = levopimarate      |
| 5 = palustrate  | 6 = isopimarate       |
| 7 = abietate    | 8 = dehydroabietate   |
| 9 = neoabietate |                       |





Nickel columns have been advertised as being superior to stainless steel. In our experience, nickel provides as good a column as stainless steel but we have no evidence that it is better.

The gas chromatography of resin acids using packed columns is best accomplished as described in the upcoming revision (1986) of ASTM D 3008. Basically, this involves the use of a 1/8 in. x 8 ft. stainless steel column packed with 10% EGSS-X on 80/100 Chromosorb W-AW as the best compromise of analysis time and component resolution. Although the polyesters have been the best liquid phases of resin acid gas chromatography, the stability of the polyesters is less than desirable at the temperatures necessary for practical chromatography. With a new column, it is necessary to operate the column oven at an isothermal temperature of 200 C. As the column ages from liquid phase bleeding, the column oven temperature is decreased to 195 C and then to 190 C to extend column life. The efficiency of a new EGSS-X column should be about 500 theoretical plates/foot. Chromatograms of typical rosins (methylated with diazomethane) on an EGSS-X column are shown in Figure 1.

### Capillary Column Chromatography

Although the capillary gas chromatography of resin acid methyl esters has been noted in several publications, the first extensive investigation on the subject was carried out by Foster and Zinkel<sup>6</sup> using a range of 6 nonpolar to polar liquid phases in glass capillary columns for over 70 resin acids. Butanediol succinate (BDS) was found to be the most useful liquid phase for the common resin acids, resolving all of them including the levopimarate/palustrate pair.

The convenience of fused silica for polyester columns has not been generally available as stock commercial columns because of difficulties in coating the polyesters on fused silica surfaces. Recently, however, we obtained a quality custom-coated 0.25 mm id BDS-fused silica column (Supelco Inc., Bellefonte, PA) having a 0.25 micron film thickness. From extensive data on the correlation of column temperature with separation factors and resolution we determined that the optimal column temperature for BDS is 180 C.<sup>15</sup> A column length of 7 meters provides sufficient plates for resolution, along with a short analysis time: column efficiency is about 2300 plates/meter with methyl neoabietate eluting under 15 minutes. Figure 2 shows chromatograms using a 7-meter BDS fused silica column at 180 C of the methylated resin acids (resin acids obtained by the DEAE-Sephadex method) from slash pine oleoresin and rosin.

As with the polyester packed columns, BDS capillary columns provide good resolution of the common resin acids, but the analysis time may extend to 1-2 hours when oxygenated derivatives are present, such as the acetylisocupressate, acetyltrimricatololate and the corresponding deacetylated derivatives found in slash pine oleoresin and rosin.<sup>16</sup> When oxygenated resin acids are encountered, the use of a nonpolar stationary phase reduces analysis time to within reasonable limits. For example, a methyl silicone such as the familiar SE-30 will resolve all the common resin acids if the column temperature is about 170 C. However, prob-

lems can occur in quantitative analysis in that the minimum amount of resin acids necessary for reliable quantitative data often results in overloading the column with consequent loss in the resolution of the components. The best solution is to combine the data from analysis on two columns, BDS and methyl silicone. In the last few years we have used the bonded methyl silicone, DB-1 (J & W Scientific, Rancho Cordova, Calif.) as a fused silica column rather than a glass SE-30 column. Although the common resin acids have nearly identical retention characteristics for both columns, retention values relative to methyl pimarate for oxygenated derivatives are slightly smaller for the DB-1 column. Cyanosilicone-coated capillary columns are being used in several laboratories for resin acid analysis. Such columns have the advantage of being temperature programmable to higher temperatures than BDS columns with significantly less column bleed but the cyanosilicone columns show the same tendency for overloading as do the methyl silicones.

The 0.53 mm diameter columns have been promoted as bringing the benefits of fused silica capillary column technology to packed column users in that the inertness of fused silica is combined with a capacity through the use of thick films of liquid phases. This could be particularly useful with instruments that cannot be readily converted to capillary GLC. However, our limited trials with such columns have not been encouraging. For example, a IO-meter methyl silicone column having a 5.0 micron film thickness at a nonoptimal temperature of 210 C (He at 4 ml/min) resulted in a 22 minute retention for methyl pimarate with unacceptable resolution of several peaks. Results with a cyanosilicone column having a 0.5 micron film thickness (one-tenth that of the methyl silicone column) were of no greater promise.

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