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## PRELIMINARY INVESTIGATION OF THE EFFECTS OF GAMMA-RADIATION ON THE SURFACE OF RAW FUSED-SILICA TUBING

J. A. HUBBALL\* and P. R. DIMAURO

*The Foxboro Company, 80 Republic Drive, North Haven, CT 06473 (U.S.A.)*

S. R. SMITH

*Departments of Chemistry and Materials Science, University of Connecticut, Storrs, CT 06268 (U.S.A.)*  
and

E. F. BARRY

*Department of Chemistry, University of Lowell, Lowell, MA 01854 (U.S.A.)*

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### SUMMARY

This paper is a preliminary report concerning the effects of gamma-radiation on the surface of raw fused-silica capillary tubing. Included in this report is a discussion of how these effects pertain to the preparation of columns coated with polar liquid phases. Improved deactivation and wettability by polar phases are observed when raw fused-silica tubing is subjected to various dosages of gamma-radiation. It was also found that capillary columns exhibiting optimum chromatographic performance require a specific pretreatment dosage which increases with the polarity of the liquid phase.

It is proposed that this correlation may be related to surface dehydration (surface deactivation) combined with an increase in surface irregularities at the molecular level (improved wettability). The role of gamma-radiation in altering the surface of fused-silica columns is discussed in terms of the surface phenomena described and the subsequent chromatographic performance of coated columns.

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### INTRODUCTION

The reproducible preparation of well-deactivated, highly efficient and thermally stable fused-silica capillary columns requires consideration of the silica surface and the interaction of the surface with an appropriate liquid phase.

Capillary column activity can be attributed to both Lewis acid sites and surface silanol groups. Considering the inherent low levels of metal ions in synthetic fused silica, silanol groups can be expected to be the dominant factor contributing to fused-silica column activity. Free silanol groups are extremely active and are strongly adsorptive towards many compounds. In addition, it has been shown that a fully hydroxylated surface is quite acidic<sup>1</sup>. As noted by Wright *et al.*<sup>2</sup>, these groups can also contribute to stationary phase deterioration, leading to reduced column efficiency and reduced thermal stability. Several values for surface hydroxyl groups on

silica have been published<sup>2-5</sup>. Wright *et al.*<sup>2</sup> determined the surface hydroxyl concentration of fused-silica tubing by tritium labeling and found that there were 0.2 hydroxyl groups per square nanometer. They attributed this low value to the elevated drawing temperature in the manufacture of the material. These workers also postulated that this relative paucity of surface silanol groups contributed to the difficulties encountered in coating polar liquid phases on fused silica.

A variety of treatments has been developed to neutralize surface hydroxyls of fused silica, including high-temperature silylation, prepolymer deposition, thermal degradation of various liquid phases, and thermal reaction of cyclic siloxanes. Methods such as thermal degradation of organic polymers and high-temperature silylation result in chemical modification of the surface and serve a two-fold purpose. Besides masking the activity of surface silanols, they also enhance wettability by providing a chemically compatible layer over which a corresponding liquid phase can be coated. Several workers<sup>6-9</sup> have developed techniques for both glass and fused-silica capillaries which utilize silylation reagents. More recently, modification of glass and fused-silica capillary columns has been accomplished through the use of cyclic siloxanes. Stark *et al.*<sup>10</sup> used octamethylcyclotetrasiloxane (D<sub>4</sub>) to deactivate the surface of fused silica and to enhance the wettability of non-polar liquid phases. Subsequent work by Blomberg's group<sup>11-14</sup> has resulted in a series of cyclic siloxane modifiers which include functional groups representative of a wide range of polarity. Cyclic siloxane compounds apparently undergo a ring opening reaction to produce a non-extractable, chemically unique deactivation layer. This mechanism is probably not unlike the methods developed by Schomburg *et al.*<sup>15</sup> and Lee and Wright<sup>16</sup>, who proposed the thermal degradation of linear polysiloxanes to produce a deactivated and chemically compatible apolar surface.

Several workers<sup>17-19</sup> have described the use of gamma-radiation to cross-link various liquid phases. However, the use of gamma-radiation to alter the surface of raw fused silica has not been investigated. If gamma-radiation does alter the surface, it is of interest to know what effect this alteration has on deactivation and wettability. One method of determining the effects of gamma-radiation on the wettability of raw fused silica is to use capillary rise measurements. Plotting the cosine of the contact angle ( $\theta$ ), calculated from these measurements, *versus* the surface tension ( $Y_1$ ) for a series of liquids results in a straight line or narrow rectilinear band (Zisman plot). Bartle and Novotny<sup>20</sup> were the first to use such plots to characterize the surface of glass capillary columns. More recent work by Bartle *et al.*<sup>21</sup> compared the wettability of both fused-silica and glass capillaries subjected to various surface treatments. In addition to providing information concerning the overall wettability of capillary columns, data obtained from capillary rise measurements can be used to determine the relative roughening of surfaces subjected to various treatments. The  $\cos \theta$  value for a non-treated and a treated capillary can be used to calculate the Wenzel coefficient ( $r$ )<sup>22</sup> or measure of surface roughening, defined as the ratio of cosines of the contact angles ( $\cos \theta' / \cos \theta$ ) or specific surface areas after and before surface treatment. Nečasová and Tesařík<sup>23</sup> proposed the use of a "wettability factor", which they considered analogous to the Wenzel coefficient or roughening factor.

As discussed above, the surface hydroxyl population plays an important role in the activity of a fused-silica capillary surface. A convenient method for measuring the hydroxyl content of a surface is to measure the atomic oxygen content by selective

wavelength-dispersive spectrometry (WDS). A comparison of the ratio of oxygen to silicon atoms for untreated and treated surfaces provides a qualitative value of a particular treatment with regard to the population of surface hydroxyl groups.

Since the surface hydroxyl content and the surface texture are interrelated when one considers the overall deactivation and wettability of a surface, a discussion of the effects of gamma-radiation as they pertain to these two factors is presented and related to the chromatographic performance of columns coated with polar liquid phases.

## EXPERIMENTAL

All fused-silica tubing used in this study was purchased from Maxlight Fiber Optics Division of Raychem, Phoenix, AZ, U.S.A. (recently changed to Polymicrotechnologies). All cobalt-60 radiations were performed in the radiation facility at the University of Lowell, Lowell, MA, U.S.A. This facility has been described previously<sup>24</sup>.

### *Capillary rise measurements*

Duplicate fused-silica samples of *ca.* 20 m each, obtained from two different tubing lots were coiled and subjected to gamma-radiation. The final dosage for each set of four samples was 2, 7, and 15 Mrad. In addition, two control columns were obtained from each lot. The capillary rise measurements were performed on 20-cm sections from coils later used for column preparation. The sections were held in place by a PTFE ferrule and Swagelok fitting, connected to a 0.25-in. O.D. glass tube. A 40-ml thin-walled test tube served as the reservoir. Both the reservoir and glass tube/sample were secured to a standard ringstand by extension clamps. Calibration liquids for these measurements were analytical grade hexane, acetone, and benzene. Calibrations were carried out as described by Bartle *et al.*<sup>21</sup>. In a second series of experiments, distilled/deionized water and methanol were used. Because of the opaque nature of the polyimide outer coating, the samples were illuminated via a high-intensity lamp to facilitate the location of the meniscus. The height of the meniscus in each capillary was measured with a cathetometer.

### *Scanning electron microscopy (SEM)*

Sections of *ca.* 5 cm were cut from a length of flame-sealed capillary and embedded in epoxy cement, which was spread over a standard SEM mount. After an appropriate curing time, the embedded samples were carefully polished with fine silicon carbide abrasive paper, ultrasonically cleaned in redistilled dichloromethane and coated with *ca.* 300 Å of carbon with a carbon evaporation unit. An Amray 1000 A scanning electron microscope equipped with a Microspec 2A wavelength-dispersive spectrometer was used to obtain all SEM photos.

### *Wavelength-dispersive spectrometry (WDS)*

All samples were prepared as above and all comparative measurements were made with the SEM instrument described above. Measurements were taken on duplicate samples at four different locations along a line *ca.* 1 mm in length. The accelerating voltage was 5 kV, resulting in a depth of measurement of *ca.* 3000 Å (0.3 μm). The incident current was  $2.0 \cdot 10^{-8}$  A.

### Gas chromatography

Gas chromatography was performed on a Perkin-Elmer Sigma 2B unit with split injection, flame ionization detection, and helium as carrier gas. Chromatograms were displayed on a Hewlett-Packard Model 7131A 1-mV recorder or a Model 4270 Spectra-Physics Integrator. Neat samples of octanol were injected to determine  $k'$  data on the raw fused silica. Comprehensive Grob test mix evaluations were performed according to published guidelines. Columns (15 m) of raw fused silica subjected to various dosages of gamma-radiation were used to generate  $k'$  data for octanol. Coated columns were prepared from material that had been pretreated with gamma-radiation and used in the capillary rise experiments. The columns were rinsed at room temperature with dichloromethane and acetone and coated with a pretreatment dosage-compatible liquid phase (see Table III) via the static method. After coating, the columns were purged with dry nitrogen, flame-sealed, and irradiated at an appropriate dosage and dosage rate<sup>19,25</sup>. Details of the modification and immobilization of polar liquid phases via gamma-radiation will appear in a future article.

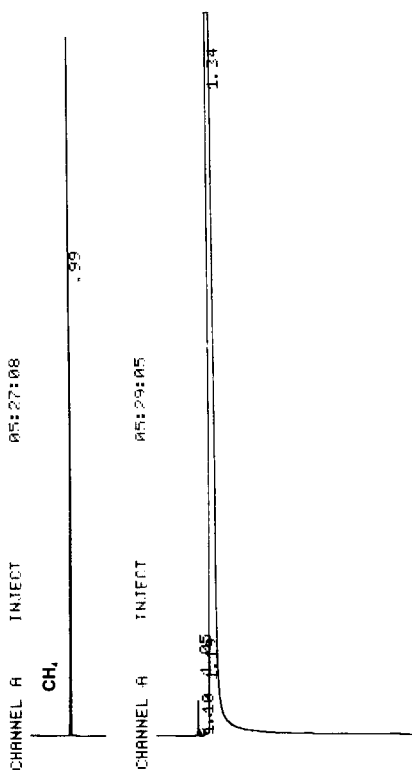


Fig. 1. Neat injection of octanol into a nonirradiated column of raw fused silica (15 m  $\times$  0.25 mm I.D.). Temperature, 110°C isothermal;  $k' = 0.35$ .

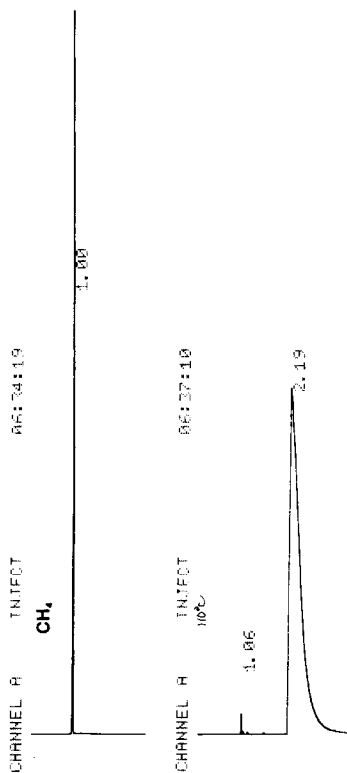


Fig. 2. Neat injection of octanol into an irradiated (10 Mrad) column of raw fused silica (15 m  $\times$  0.25 mm I.D.). Temperature, 110°C isothermal;  $k' = 1.19$ .

## RESULTS AND DISCUSSION

The fact that gamma-radiation does indeed affect the surface of raw fused-silica tubing is illustrated in Figs. 1-3. The increased retention and skewed peak shape of a free hydroxyl-containing compound such as octanol would seem to indicate that, as the dosage of gamma-radiation is increased, so is the population of surface hydroxyl groups. This reasoning correlates with the work of Wright *et al.*<sup>2</sup>, who noted that alcohol adsorption and retention increased when it is chromatographed on an uncoated fused-silica column, treated with water. An increase in surface hydroxyl groups should have an effect on the surface energy. To test this hypothesis, a series of capillary rise measurements were performed. Measurements on non-irradiated and irradiated tubing drawn over a period of several months were taken to determine the reproducibility and uniformity of the fused-silica surface. The results from these measurements proved to be quite scattered and offered no logical correlation between nonirradiated and irradiated tubing. This variability of the raw fused-silica surface has proven to be a significant problem. Factors such as adsorbed moisture, impurities adsorbed from purging gases or solvent rinsings, and condensation of manufacturing by-products (HCl)<sup>26</sup> appear to alter the surface in a non-reproducible manner.

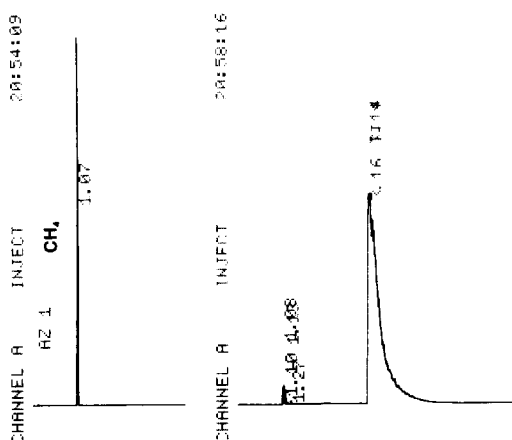


Fig. 3. Neat injection of octanol into an irradiated (20 Mrad) column of raw fused silica (15 m  $\times$  0.25 mm I.D.). Temperature, 110°C isothermal;  $k' = 1.95$ .

Because of the surface variability, it was decided to evaluate the raw material by preparing a series of columns from tubing originating from several lots. The raw tubing which yielded the most efficient, deactivated, and thermally stable columns was used to generate the data in Tables I-III.

The reproducibility of the contact angle measurements over four capillary samples was  $\pm 0.03$  in  $\cos \theta$ . Since water has a higher surface tension value than commonly used chromatographic liquid phases, it was postulated that the capillary rise measurement of this liquid would be more reflective of subtle surface alterations.

Several features relating to the surface energy are evident from the data in Table I. First, as has been previously determined by Bartle *et al.*<sup>21</sup>, raw fused-silica

TABLE I

COMPARISON OF SURFACE WETTABILITY MEASURED AS  $\cos \theta$  FOR RAW FUSED-SILICA TUBING SUBJECTED TO VARIOUS DOSAGES OF GAMMA-RADIATION\*

<i>Dosage (Mrad)</i>	<i>Cos <math>\theta</math>, advancing capillary rise, water</i>	<i>Cos <math>\theta</math>, retreating capillary rise, water</i>	<i>Cos <math>\theta</math>, advancing capillary rise, methyl alcohol</i>	<i>Cos <math>\theta</math>, retreating capillary rise, methyl alcohol</i>
0	0.836	0.997	0.990	0.992
2	0.801	0.992	0.994	0.994
7	0.767	0.997	0.982	0.982
15	0.784	0.996	0.982	0.981

\* See text for details.

TABLE II

COMPARISON OF THE RATIO OF OXYGEN TO SILICON AS MEASURED BY WDS\* FOR RAW FUSED-SILICA TUBING SUBJECTED TO VARIOUS DOSAGES OF GAMMA-RADIATION\*\*

<i>Dosage (Mrad)</i>	<i>Ave. counts/sec oxygen</i>	<i>Ave. counts/sec silicon</i>	<i>Ratio O/Si</i>
Control**	45.0	242	0.186
0	61.1	234	0.261
15	54.7	240	0.228

\* Wavelength-dispersive spectrometry.

\*\* See text for details.

capillary tubing possesses a high energy surface. Second, little or no change in the surface energy occurs when the tubing is subjected to gamma-radiation. As indicated by the lower values of  $\cos \theta$ , there may actually be a slight decrease in surface energy as the radiation dosage is increased. Third, a comparison of the  $\cos \theta$  values obtained from non-wetted and wetted irradiated tubes indicates that any surface alteration which does occur is not permanent and can be negated by hydration of the surface. This would indicate that the primary effect of irradiation is not an increase in the surface silanol population, but rather dehydration of the surface.

Because of this finding and the important role that silanol groups play in both deactivation and wettability, we felt that it was necessary to characterize further the surface silanol population. Surface compositions have been characterized by using energy-dispersive X-ray analysis (EDAX) and an electron-beam microprobe (EMP). However, these methods of analysis penetrate the surface to a depth of *ca.* 10  $\mu\text{m}$  and do not reveal a true surface composition. Alternatively, by using a wavelength-dispersive X-ray spectrometer (WDS) method at an accelerating voltage of 5 kV, surface penetration is reduced to 0.3  $\mu\text{m}$  and a more accurate surface composition can be deduced. A comparison of the control *versus* the surface values indicates that the composition of the non-irradiated surface differs significantly from the composition of the bulk material. This is not unexpected, since most manufacturers of fused silica pretreat the surface of the raw material before drawing<sup>27</sup>.

TABLE III

McREYNOLD'S CONSTANTS AND RAW TUBING DOSAGE OF SEVERAL LIQUID PHASES

Liquid phase	McReynold's constants total	Raw tubing dosage (Mrad)
OV-1	222	0.5
SE-52	334	0.5
OV-17 (vinyl)*	884	1.0
XE-60*	1785	3.0
XF-1150*	2495	10.0
Silar 10 C	3678	—

\* Modified.

The data presented in Table II corroborate the finding inferred from the capillary rise measurements that there is surface dehydration and/or a reduction in the population of surface hydroxyl groups of irradiated tubing. There is a 12.6% decrease in the oxygen/silicon ratio between the nonirradiated and the 15 Mrad irradiated tubing. Although this is not a large value, it may be significant when one considers the relatively low levels of surface hydroxyl groups present<sup>2</sup>.

The fact that octanol is retained on raw fused silica as a function of the radiation dosage indicates that some alteration of the surface occurs. It is well known that surface roughening increases the wettability of a surface by reducing the interfacial forces of the liquid. Roughening of fused silica capillaries has been accomplished by leaching with both acidic and alkaline reagents<sup>11,21</sup>. To determine the degree of surface roughening caused by gamma-radiation, an experiment patterned after the work of Necásová and Tesáfik<sup>23</sup> was performed. As evidenced by the data in Table I, there appears to be no obvious roughening of the surface as indicated by the near identical  $\cos \theta$  values obtained with methyl alcohol.

In an attempt to verify the fact that no obvious surface roughening occurs, the surfaces were analyzed by SEM. No discernible surface roughening could be seen when the nonirradiated and the 15-Mrad irradiated tubing were compared at several magnifications up to  $5000 \times$ . Both the SEM photos and the calculated surface roughening factors indicate that no distinguishable surface roughening occurs. It is possible, however, that subjecting the fused-silica tubing to gamma-radiation renders it irregular on the molecular level.

It was noted by Lee *et al.*<sup>28</sup> that, in theory, fused-silica capillary tubing should be readily wetted by a wide range of liquid phases, including the highly polar cyanoalkylpolysiloxanes. From practical experience, however, it is well known that deactivation and/or wettability treatments are necessary in order to prepare columns displaying optimum chromatographic performance. Richter *et al.*<sup>29</sup> have published work describing the synthesis of a highly polar gum phase. Fused-silica columns were coated directly with this phase and, although applications chromatograms are presented, there is no illustration of surface deactivation or neutrality. Recently, Lipsky<sup>30</sup> presented results on the direct coating of fused-silica with silanol-terminated gum phases. However, the effectiveness of this procedure with regard to the more polar liquid phases has not been demonstrated.

The effects of a gamma-radiation pretreatment on surface deactivation and

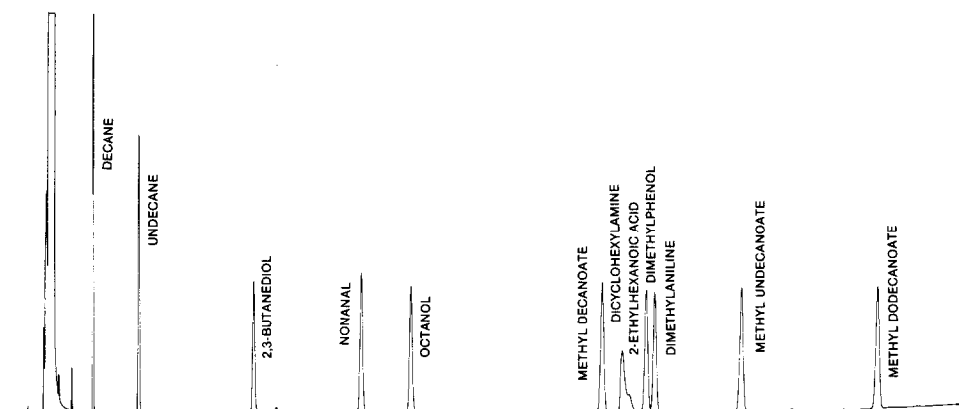


Fig. 4. Comprehensive Grob test mix on an XE-60 fused-silica column (15 m). Column temperature, from 40°C to 140°C at 1.7°C/min; carrier gas, helium; flow-rate, 30 cm/sec; flame ionization detector,  $2 \cdot 10^{-11}$  ( $1 \times 4$ ); chart speed, 1.25 cm/min.

enhanced wettability by polar liquid phases are demonstrated in Figs. 4–7. Figs. 4 and 5 depict the deactivation and neutrality of the fused-silica surface when the proper pretreatment dosage (Table III) is followed by coating with a moderately polar (XE-60) and an increasingly polar (XF-1150) liquid phase. The efficiency of the more polar column is demonstrated in Fig. 6 by the separation of *trans/cis*  $C_{16:1}$ ,  $C_{18:1}$  FAME isomers. Fig. 7 illustrates the effectiveness of a gamma-radiation pretreatment for a highly polar liquid phase, containing 88% cyanopropyl and 10% tolyl groupings (this phase was kindly supplied by Dr. Milton Lee, Brigham Young University, Provo, UT, U.S.A.). The required pretreatment dosage for fused silica used in this study was 15 Mrad.

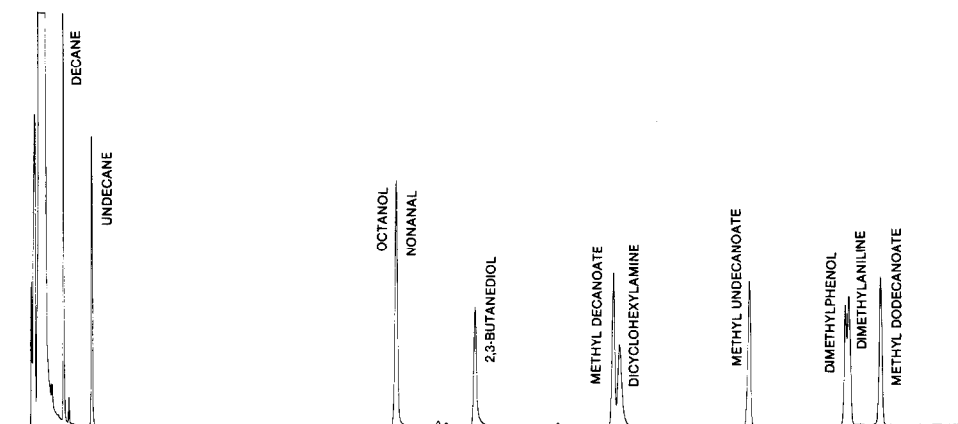


Fig. 5. Comprehensive Grob test mix on an XF-1150 fused-silica column (15 m). Details as in Fig. 4.



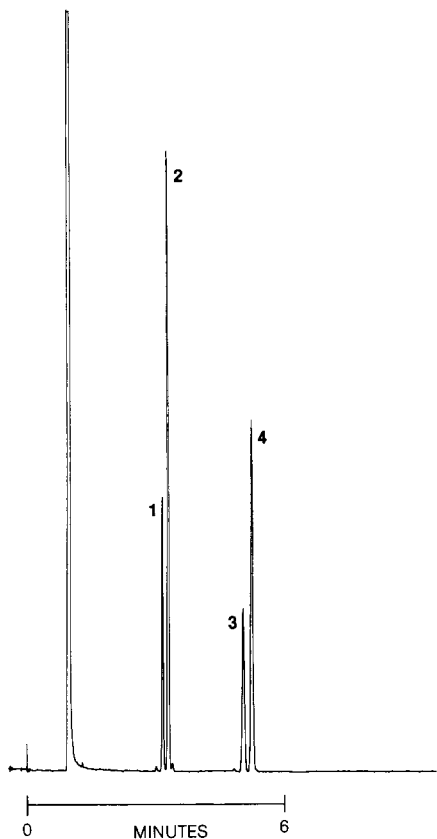


Fig. 6. Separation of *trans/cis* FAME isomers on an XF-1150, column (15 m). Column temperature, 175°C; flame ionization detector,  $4 \cdot 10^{-11}$  ( $1 \times 8$ ); chart speed, 1.25 cm/min. Peaks: 1 = *trans*-methyl palmitelaidate; 2 = *cis*-methyl palmitoleate; 3 = *trans*-methylelaidate; 4 = *cis*-methyl oleate.

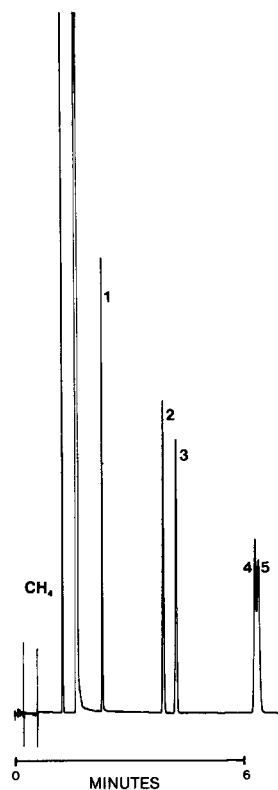


Fig. 7. Test mix chromatogram of a 88% cyanopropyl, 10% tolyl-substituted phase, coated directly on fused silica (15 m  $\times$  0.25 mm I.D.). Column temperature, 100°C isothermal; carrier gas, helium; flow-rate, 24 cm/sec; flame ionization detector,  $4 \cdot 10^{-11}$  ( $1 \times 8$ ); chart speed, 1.25 cm/min. Peaks: 1 = octanol; 2 = methyl dodecanoate; 3 = naphthalene; 4 = dimethylphenol; 5 = dimethylaniline.

## CONCLUSION

It is evident from this preliminary study that gamma-radiation does indeed alter the surface of raw fused silica and render it more suitable for the preparation of polar phase capillary columns. The results presented here are of a preliminary nature and further studies are going on with particular emphasis on the problem of raw material variability. It is hoped that this work will lead to the production of fused-silica tubing having a more chemically uniform and reproducible surface.

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