of the $m/z$ 185 from glycerol at a resolution of 25 000 showed no peak shift when the glycerol was observed from either target face.

Table III lists some accurate mass determinations using the rotatable probe.

The results using the rotatable probe are almost as good as those using internal standards. We believe that the somewhat greater error is due to the longer interval between presentation of standard and unknown peaks which arises from the present need to manually rotate the probe.

Although this split probe geometry was necessary to obtain good mass measurements on our 731 mass spectrometer, we do not know if it is necessary for mass spectrometers having other ion optical geometries. Generally we have found the rotatable probe to be preferable for accurate mass measurements because of the wide choice of mass standards it allows and the steady nature of the ion currents which it provides.

## ACKNOWLEDGMENT

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**Registry No.** Zonyl FSB, 57534-42-6.

## LITERATURE CITED

(1) Barber, M.; Bordoli, R. S.; Sedgewick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, *7*, 325–327.
(2) Surman, D. J.; Vickerman, J. C. *J. Chem. Soc., Chem. Commun.* **1981**, *7*, 324–325.
(3) Torgerson, D. F.; Skowronski, R. P.; Macfarlane, R. D. *Biochem. Biophys. Res. Commun.* **1974**, *60*, 616.
(4) Heller, D.; Hansen, G.; Yergey, J.; Cotter, R. J.; Fenselau, C. "Abstracts"; 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI; American Society for Mass Spectrometry: 1982; pp 560–561.
(5) Rinehart, K. L., Jr.; et al. *J. Am. Chem. Soc.* **1981**, *103*, 6517–6520.
(6) Van Langenkove, A.; Costello, C. E.; Chen, H. F.; Biller, J. E.; Biemann, K. "Abstracts"; 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI; American Society for Mass Spectrometry: 1982; pp 558–559.
(7) Rinehart, K. L., Jr. *Science* **1982**, *218*, 254–260.
(8) Morgan, R. P.; Reed, M. L., *Org. Mass Spectrom.* **1982**, *17*, 537.
(9) Olson, K. L.; Rinehart, K. L., Jr.; Cook, J. C., Jr. *Biomed. Mass Spectrom.* **1977**, *4*, 284–290.

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# Determination of Reactive Components in Silicone Foams

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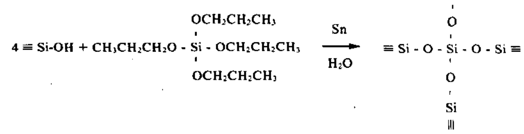
**Analytical methods have been developed for the determination of reactive components used in the formulation of room temperature vulcanized (RTV) silicone foams. The reactive components include total silanol (SiOH), silane hydrogen (SiH), tetrapropoxysilane (TPS), and diphenylmethylsilanol (DPMS). Total SiOH and SiH are determined by Fourier transform infrared (FTIR) spectrometry. the SiOH peak at 3687 cm$^{-1}$ and the SiH peak at 2168 cm$^{-1}$ were used for quantitation. The TPS content was determined by gas chromatography (GC), using a solid capillary open tubular (SCOT) column and linear programmed temperature control. The DPMS content was determined by gel permeation chromatography (GPC) using THF solvent.**

Recently, much interest has been shown in silicone polymers. Their use in industry is well documented (*1–5*). Studies on theories of rubber elasticity have used end-linked poly(dimethylsiloxanes) as models (*6–8*). Another class of silicones includes foams that are cured at room temperature by mixing an organotin catalyst with a silicone prepolymer (*9*). They have thus been called room-temperature-vulcanized (RTV) silicone foams. Their use as encapsulants for integrated circuits has been described (*10, 11*).

It would be expected that the concentration of reactive end groups and cross-linking agents would greatly affect the properties of the silicone polymer produced. A review of analytical methods for silicones described general methods without giving experimental details (*12*). However, specific methods for determining the reactive end groups SiH and SiOH have been developed. Hexafluoroacetone has been used to determine total –OH content (*13*), but hexafluoroacetone is hazardous and not commercially available. Titration with the Karl Fischer reagent can determine SiOH content (*14, 15*) but is subject to interferences from water and SiH. The IR bands caused by SiOH and SiH have been characterized for some time (*16*) but are subject to interferences from water, solvent, and siloxane bands. The advent of Fourier transform infared (FTIR) spectrometry and computer software has made possible the technique of subtractive FTIR to remove these interferences. For the determination of cross-linking agents, chromatographic methods are preferred. Two possible cross-linking agents are tetrapropoxysilane (TPS) and diphenylmethylsilanol (DPMS). Gas chromatography of TPS, as well as a number of other silicon-containing compounds, has been described (*17*); however, no analytical methods for the determination of DPMS are available.

In the Bendix laboratory, a RTV silicone consisting of TPS, DPMS, silanol terminated poly(dimethylsiloxane), and poly(methylhydrosiloxane) was prepared. The following polymerization reactions involving TPS, SiOH, and SiH have been described (*18*).

$$\equiv\text{Si-OH} + \equiv\text{Si-H} \xrightarrow[H_2O]{Sn} \equiv\text{Si-O-Si}\equiv + H_2 \quad (1)$$



$$4 \equiv\text{Si-OH} + CH_3CH_2CH_2O\text{-}\underset{OCH_2CH_2CH_3}{\overset{OCH_2CH_2CH_3}{Si}}\text{-}OCH_2CH_2CH_3 \xrightarrow[H_2O]{Sn} \equiv\text{Si-O-}\underset{\underset{\underset{\equiv}{Si}}{O}}{\overset{O}{Si}}\text{-O-Si}\equiv \quad (2)$$

$$\equiv\text{Si-OH} + \equiv\text{Si-OH} \xrightarrow{Sn} \equiv\text{Si-O-Si}\equiv \quad (3)$$

Because of their importance in cross-linking, Bendix has developed methods for the determination of SiOH, SiH, DPMS, and TPS. These methods involve FTIR, gas chro-

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matography (GC), and gel permeation chromatography (GPC).

## EXPERIMENTAL SECTION

**GC.** GC was performed on a Perkin-Elmer Model 3920B gas chromatograph using a flame ionization detector. Samples were dissolved in carbon disulfide. Injection volume was 5 $\mu$L. A 15.24-m stainless steel solid capillary open tubular (SCOT) column with a Carbowax 20M liquid phase was used with a split injection ratio of 15 to 1. The injection port temperature was 250 °C. The column temperature was held at 70 °C for 4 min and then programmed at 4 °C/min to 170 °C. This temperature was held for 16 min. The flow rate of helium carrier gas through the SCOT column was 5 mL/min. The makeup gas to the flame ionization detector was 25 mL/min. Peak areas were determined with a Perkin-Elmer PEP-2 data system.

**GPC.** GPC was performed on a Waters Model 200 GPC using a cross-linked polystyrene low-porosity column set. This column set consisted of four tandemly linked columns with porosities of 250, 100, 60, and 60 Å. Tetrahydrofuran (THF) was used both as the sample solvent and as the GPC mobile phase at a flow rate of 1 mL/min.

A 1.5% (w/v) solution of the silicone polymer formulation containing DPMS was made in THF. This sample solution contains about 0.075% (w/v) DPMS. After complete dissolution of the sample, it was injected on the GPC by use of a 2-mL sample loop.

Peaks were detected with a differential refractometer.

**FTIR.** FTIR spectra were obtained with a Nicolet Model 7199, with a TGS detector. All spectra were obtained by using 2 $cm^{-1}$ resolution and 300 scans. Samples were dissolved in $CCl_4$ and were put into a 10 mm path length liquid cell. Tetramethyldisiloxane-1,3-diol standards in $CCl_4$ were used to obtain a calibration curve for SiOH determination. Triphenylsilane standards in $CCl_4$ were used to obtain the calibration curve for SiH determination.

The method used for silanol determination is as follows. The spectra of the moist $CCl_4$, a 5 g/L solution of W-97 gum in $CCl_4$, tetramethyldisiloxane-1,3-diol standards (0.03 to 0.20 g/L in $CCl_4$) and RTV-silicone gum in $CCl_4$ were recorded. The W-97 gum is a polysiloxane, containing vinyl, phenyl, and dimethyl functionality, but no silanol. The vinyl and phenyl functionalities are of no consequence in these analyses.

After these spectra are recorded, the moist $CCl_4$ was substracted from the W-97 spectrum until the moisture peak at 3617 $cm^{-1}$ (in the W-97 spectrum) disappeared. The resulting spectrum was labeled "dry W-97". The moist $CCl_4$ spectrum was likewise substracted from each of the tetramethyldisiloxanediol standards to obtain "dry" spectra. A silanol calibration curve was then obtained by plotting the absorbance at 3687 $cm^{-1}$ vs. the concentration of OH in the standard.

The moist $CCl_4$ spectrum was then substracted from the RTV-silicone sample to obtain the "dry" spectrum. The "dry W-97" spectrum was then subtracted from the RTV-silicone until the peak at 3763 $cm^{-1}$ disappeared. The absorbance at 3687 $cm^{-1}$ was then recorded and the OH content was obtained from the silanol calibration curve previously described.

The method used for determination of silane hydrogen is as follows. First, standards of triphenylsilane in $CCl_4$ (0.1 g to 1.0 g/L) were prepared. Their spectra were recorded, and the moist $CCl_4$ spectrum was subtracted until the peak at 2300 $cm^{-1}$ disappeared. The absorbance at 2168 $cm^{-1}$ was then recorded and plotted against percent H in the standards. Spectra of 1.0 g/L RTV-silicone were obtained, and the $CCl_4$ spectrum was substracted until the peak at 2300 $cm^{-1}$ disappeared. The percent H in the RTV-silicone was calculated from the absorbance at 2168 $cm^{-1}$ and the calibration data.

**Nuclear Magnetic Resonance (NMR).** NMR spectra were recovered with a Varian FT80A Fourier transform NMR. The $^{1}H$, $^{13}C$, and $^{29}Si$ NMR spectra were measured at 79.542, 20.000, and 15.801 MHz, respectively. In every case, deuterated solvents were used for field lock. Chemical shifts are reported with tetramethylsilane at 0 ppm being used as the reference.

**Tetrapropoxysilane (TPS).** To 480 g (8 mol) of 1-propanol in 400 mL of methylene chloride was added dropwise 340 g (2 mol) of tetrachlorosilane. The temperature was maintained at 30 °C during this addition of tetrachlorosilane. The mixture then sat 1 h more at 30 °C. After this time, the methylene chloride, unreacted 1-propanol, and HCl product were removed by fractional distillation from 35 to 97 °C. The TPS product was then recovered by vacuum distillation at 70–75 °C and 3 torr. The TPS was 93.3% pure by GC analysis. Positive structural identification was achieved by using $^{1}H$, $^{13}C$, and $^{29}Si$ NMR. The chemical shifts were as follows: $^{1}H$, 3.39 ppm (triplet), 1.26 ppm (sextet), 0.62 (triplet); $^{29}Si$, −79.1 ppm; and $^{13}C$, 65.20 ppm, 26.02 ppm, 10.30 ppm.

**Diphenylmethylsilanol (DPMS).** Six-hundred milliliters of methylene chloride and 116 g (0.5 mol) of diphenylmethylchlorosilane were placed in a 1000-mL reaction kettle. The reaction mixture was cooled to 0 °C, and 55 mL of 10 N NaOH was added slowly with rapid stirring. The temperature was kept below 40 °C during the addition of NaOH. After 20 min, 200 mL of deionized water was added. The mixture was then placed in a separatory funnel and the lower, organic layer separated. The aqueous layer was washed with 100 mL of methylene chloride and the organic layer was washed with 300-mL portions of deionized water until the pH of the water was 7. The combined methylene chloride (i.e., organic) layers were then subjected to fractional distillation. The methylene chloride was removed at ambient pressure and the DPMS removed at 1 torr and 134–138 °C. The DPMS was stored at −40 °C until used. Positive structural identification was achieved by NMR. The observed chemical shifts were as follows: $^{1}H$, 0.76 ppm (singlet), 5.7 ppm (broad singlet), 7.4–7.5 ppm (multiplet), 7.7–7.9 ppm (multiplet); $^{29}Si$, −3.21 ppm; and $^{13}C$, 139.37 ppm, 134.94 ppm, 130.45 ppm, 128.74 ppm, −0.28 ppm.

**Polymers.** The silicone polymer used as a source of silane hydrogen (SiH) was the poly(methylhydrosiloxane) PS-120 from Petrarch Systems, Inc. (Levittown, PA). The silane hydrogen content of PS-120 was found to be 1.39% by FTIR. The silicone polymers used as sources of silanol (SiOH) were the silanol terminated poly(dimethylsiloxanes) PS-198 (Petrarch Systems, Inc.) and Y-7005 (from Union Carbide). The OH contents of PS-198 (0.090%) and of Y-7005 (2.15%) were also determined by FTIR. The other source of silanol was diphenylmethylsilanol (DPMS), which had 7.80% OH. The silicone polymer used to subtract interfering siloxane IR bands was W-97 from Union Carbide. The W-97 contained no OH. (Any DC-200 fluid may be substituted for W-97.) Tetrachlorosilane and diphenylmethylchlorosilane reagents were from Petrarch Systems, Inc.

## RESULTS AND DISCUSSION

**GC of TPS.** TPS has been shown to react both with water and with SiOH (*18*). In either reaction, 1-propanol is a product of the reaction. Thus, it was desirable to develop a GC method that would simultaneously determine TPS and 1-propanol. Carbon disulfide was chosen as the best solvent for the prepolymer, because it interfered the least (of all solvents tested) with the 1-propanol peak. As seen in Figure 1, the 1-propanol (bp = 97 °C) and TPS (bp = 225 °C) peaks were well resolved in both the standard and the sample. It was found that the injection port temperature had to be carefully controlled. When an injection port termperature of 275 °C was used, the TPS peak area decreased slightly and the 1-propanol area increased slightly (compared to 250 °C injection port). This indicated that the TPS was partly hydrolyzed to 1-propanol. With the proper injection port temperature (250 °C), linear calibration curves for both 1-propanol and TPS were obtained (correlation coefficient was 0.9999 by linear regression analysis).

The results of an analysis of RTV-silicone formulations are shown in Table I. No 1-propanol was added to any sample; yet it was found in every sample. Thus, some of the TPS was at least partly hydrolyzed or reacted with SiOH. This is not unexpected because the samples were stored at room temperature before analysis. Moreover, aliquots of these same formulations were rerun 3 months later and in every sample the percent TPS decreased while the percent 1-propanol increased indicating that the RTV-silicone prepolymers should be stored at lower temperatures. It should be added that

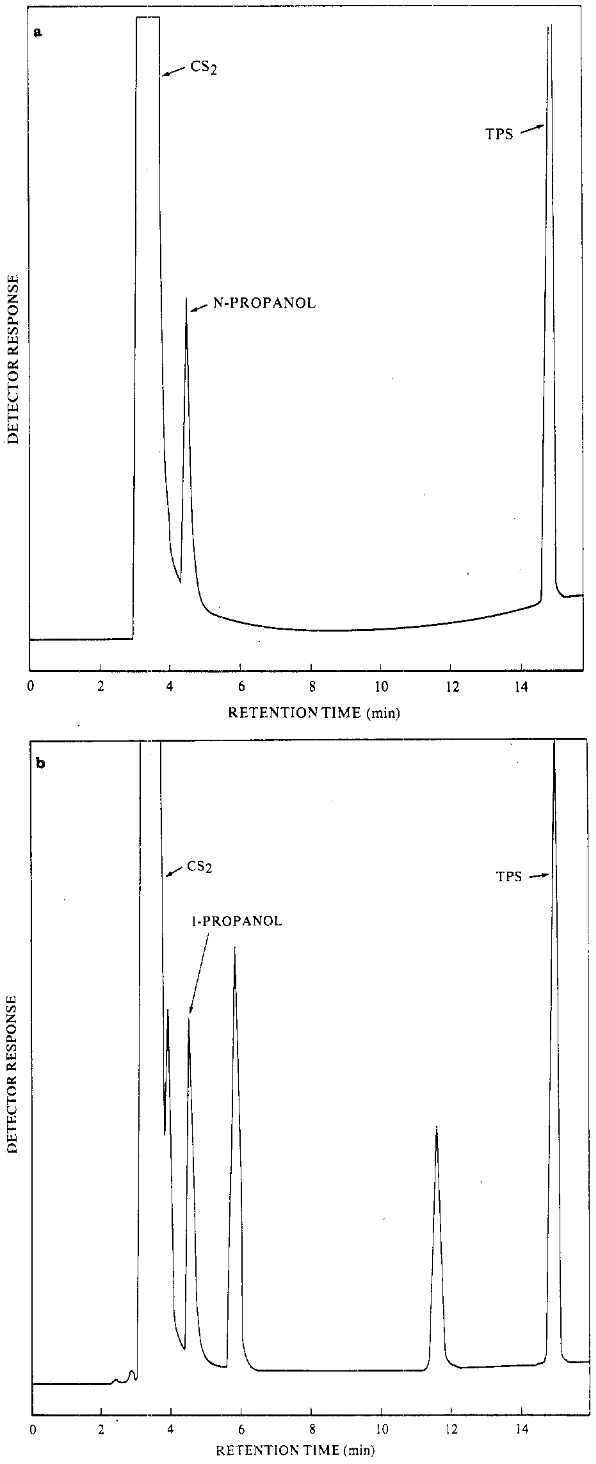


**Figure 1.** Gas chromatography of: (a) standard containing 0.320 mg of 1-propanol and 1.459 mg of TPS in 10 mL of $CS_2$5 solvent; (b) sample containing 0.2165 g of prepolymer in 10 mL of $CS_2$. Not shown are additional peaks eluting after 16 min.

**Table I. GC Tetrapropoxysilane (TPS) and 1-Propanol in Known RTV-Silicone Formulations**

| | wt % TPS | | wt % 1-propanol | |
|---|---|---|---|---|
| formulation | added | found | added | found |
| 1 | 1.87 | 1.50 | 0 | 0.27 |
| 2 | 2.80 | 2.20 | 0 | 0.41 |
| 3 | 0.93 | 0.87 | 0 | 0.043 |
| 4 | 0.93 | 1.03 | 0 | 0.059 |
| 5 | 2.80 | 2.18 | 0 | 0.48 |
| 6 | 1.87 | 1.68 | 0 | 0.12 |
| 7 | 1.87 | 1.60 | 0 | 0.20 |
| 8 | 1.87 | 1.61 | 0 | 0.15 |
| 9 | 1.87 | 1.64 | 0 | 0.21 |
| 10 | 1.87 | 1.64 | 0 | 0.22 |
| 11 | 3.36 | 2.62 | 0 | 0.63 |
| 12 | 0.37 | 0.49 | 0 | 0.039 |

**Table II. Rate of Conversion of Diphenylmethylsilanol to Tetraphenyldimethyldisiloxane at Three Temperatures**

| time exposed, | % tetraphenyldimethyldisiloxane | | |
|---|---|---|---|
| days | 25 °C | 0 °C | −40 °C |
| 0 | 1.7 | 1.7 | 1.7 |
| 5 | 32.8 | 11.7 | *a* |
| 20 | 36.8 | 17.6 | *a* |
| 56 | 45.8 | 17.8 | 2.4 |

[a] Sample not analyzed.

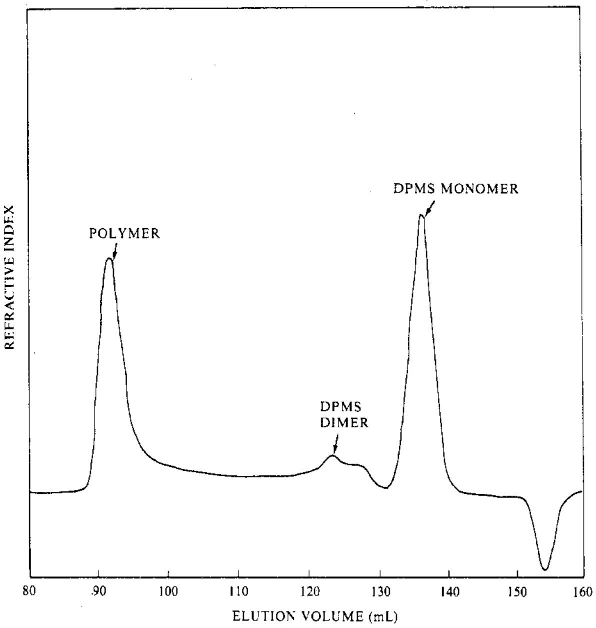
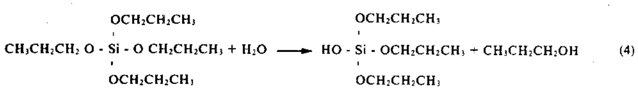
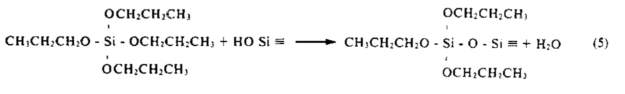


**Figure 2.** Gel permeation chromatography of prepolymer. Void volume of the column is about 92 mL. The DPMS elutes at about 135 mL.

presently this GC method only determines free TPS, not partially reacted TPS. In other words, one could consider the partially reacted TPS:


$$CH_3CH_2CH_2O-\underset{OCH_2CH_2CH_3}{\overset{OCH_2CH_2CH_3}{Si}}-OCH_2CH_2CH_3 + H_2O \longrightarrow HO-\underset{OCH_2CH_2CH_3}{\overset{OCH_2CH_2CH_3}{Si}}-OCH_2CH_2CH_3 + CH_3CH_2CH_2OH \quad (4)$$


$$CH_3CH_2CH_2O-\underset{OCH_2CH_2CH_3}{\overset{OCH_2CH_2CH_3}{Si}}-OCH_2CH_2CH_3 + HOSi\equiv \longrightarrow CH_3CH_2CH_2O-\underset{OCH_2CH_2CH_3}{\overset{OCH_2CH_2CH_3}{Si}}-O-Si\equiv + H_2O \quad (5)$$

The products of eq 4 and 5 would not be expected to have the same retention times as TPS. The chromatogram of RTV-silicone samples had several peaks eluting after the TPS peak. For ease of comparing standards to sample GC data, Figure 1b does not show these later-eluting peaks.

**GPC of DPMS.** GPC was used to quantitate the diphenylmethylsilanol (DPMS). The other components in the prepolymer (i.e., poly(dimethylsiloxanes), TPS, 1-propanol, and poly(methylhydrogensiloxane)) all have refractive indexes very close to that of the tetrahydrofuran (THF) solvent. However, the refractive index of the DPMS is significantly different from the THF. This makes the differential refractometer a very selective detector for the DPMS in this system. As seen in Figure 2, DPMS (which elutes at about 135 mL) is well separated from the other peaks present. A plot of the detector response vs. concentration of DPMS produced a straight line (correlation coefficient of 0.9997).

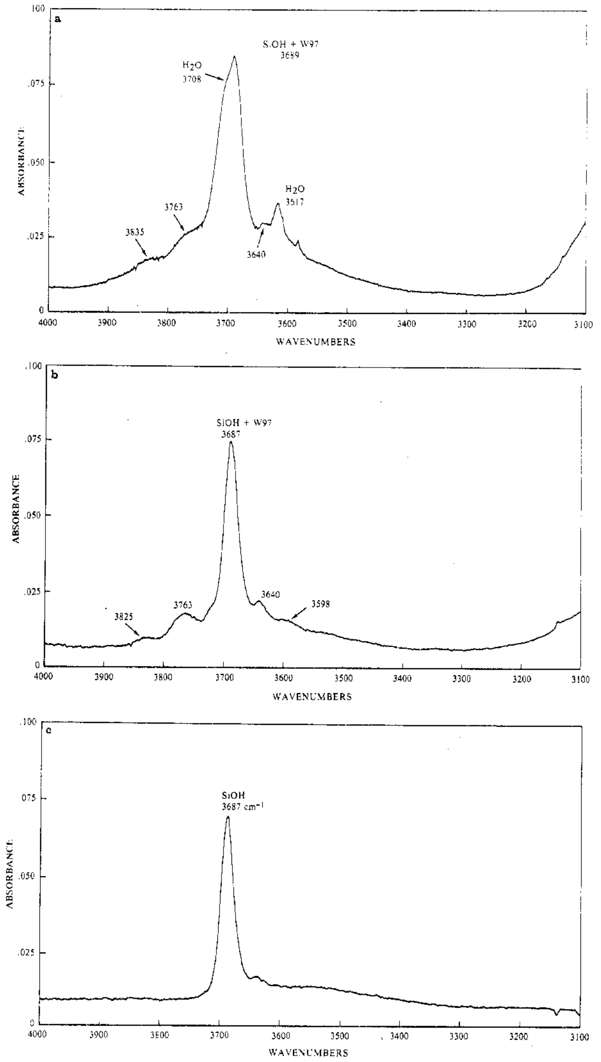


**Figure 3.** FTIR in SiOH region: (a) solution of 2 g/L prepolymer in $CCl_4$; (b) after subtracting the moist $CCl_4$ spectrum; (c) after subtracting the dry W-97 spectrum.

DPMS was found to be very reactive, easily dimerizing at room temperature. As seen in Table II, the rate of dimerization can be decreased significantly by storing the DPMS at low temperatures. Therefore, the DPMS used for standard calibration data was stored at −40 °C. However, RTV-silicone formulations were prepared at room temperature and kept at room temperature for a short time before GPC analysis. As a result, not all the DPMS added was detected as seen in Table III. These samples were analyzed again after 3 months of aging at room temperature and the DPMS content had decreased further. In other words, the DPMS peak at 135 mL decreased and the DPMS dimer peak at 123 mL increased (see Figure 2 for peak identification).

**FTIR of SiOH and SiH.** FTIR was used to quantitate total silanol (SiOH) and silane hydrogen (SiH). For silanol determination, care must be taken to avoid conditions leading to hydrogen bond formation. The hydrogen bonded SiOH IR band is not suited for quantitation because it is broad and its frequency depends greatly on the structure of the other components present in the silicone rubber. As a result, the nonpolar solvent $CCl_4$ and low sample concentrations are required.

The free silanol (i.e., nonhydrogen bonded) IR band occurs at 3687 $cm^{-1}$. Interfering bands from moisture in the $CCl_4$ solvent and from siloxane must be eliminated. The moisture bands in $CCl_4$ occur at 3617 $cm^{-1}$ and 3708 $cm^{-1}$. The siloxane bands occur at 3763 $cm^{-1}$, 3700 $cm^{-1}$, and 3640 $cm^{-1}$.

Table III. GPC Determination of Diphenylmethylsilanol (DPMS)

| formulation | wt % DPMS added | wt % DPMS found |
|---|---|---|
| 1 | 4.9 | 4.21 |
| 2 | 4.9 | 4.04 |
| 3 | 4.9 | 4.09 |
| 4 | 4.9 | 4.62 |
| 5 | 4.9 | 4.30 |
| 6 | 4.9 | 4.21 |
| 7 | 4.9 | 4.26 |
| 8 | 4.9 | 3.50 |
| 9 | 4.9 | 3.58 |
| 10 | 4.9 | 4.53 |
| 11 | 4.9 | 4.03 |
| 12 | 4.9 | 4.44 |

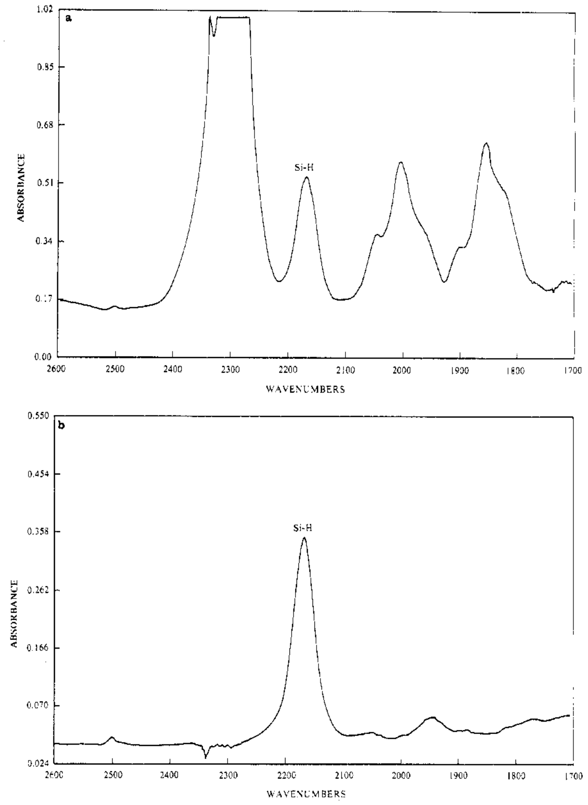


**Figure 4.** FTIR in SiH region: (a) solution of 1 g/L prepolymer in $CCl_4$; (b) after subtracting the moist $CCl_4$ spectrum.

The spectrum of a 2 g/L solution of an RTV-silicone in $CCl_4$ in the OH region is shown in Figure 3a. The largest peak, at 3689 $cm^{-1}$, is caused not only by SiOH but also by moisture and siloxane bands. The spectrum, after subtracting the moist $CCl_4$ spectrum, is shown in Figure 3b and, after subtracting "dry W-97", is shown in Figure 3c. The sharp, single peak is caused by SiOH and has its maximum absorbance at 3687 $cm^{-1}$. The absorbance at 3687 $cm^{-1}$ of tetramethyldisiloxane-1,3-diol standards is plotted against the OH content, having a correlation coefficient of 0.9996.

The determination of silane hydrogen requires only one subtraction. As seen in Figure 4a, the spectrum of 1 g/L of an RTV-silicone in $CCl_4$ contains several bands in the SiH region. The bands at 1855 $cm^{-1}$, 2005 $cm^{-1}$, and 2300 $cm^{-1}$ are removed by subtracting the $CCl_4$ spectrum. The spectrum of the RTV-silicone after this subtraction is shown in Figure 4b. One peak, with maximum absorbance at 2168 $cm^{-1}$ is observed. A plot of the absorbance at 2168 $cm^{-1}$ vs. the percent H in triphenylsilane standards gives a straight line with a correlation coefficient of 0.9999.

Table IV. FTIR Determination of SiOH and SiH in Known RTV-Silicone Formulations

| formulation | wt % OH added | wt % OH found | wt % H added | wt % H found |
|---|---|---|---|---|
| 1 | 0.69 | 0.70 | 0.083 | 0.089 |
| 2 | 0.56 | 0.62 | 0.050 | 0.053 |
| 3 | 0.60 | 0.63 | 0.117 | 0.124 |
| 4 | 0.80 | 0.81 | 0.050 | 0.053 |
| 5 | 0.80 | 0.82 | 0.117 | 0.089 |
| 6 | 0.87 | 0.89 | 0.083 | 0.089 |
| 7 | 0.70 | 0.73 | 0.083 | 0.089 |
| 8 | 0.52 | 0.54 | 0.083 | 0.088 |
| 9 | 0.70 | 0.68 | 0.139 | 0.146 |
| 10 | 0.70 | 0.72 | 0.028 | 0.029 |
| 11 | 0.70 | 0.72 | 0.083 | 0.089 |
| 12 | 0.70 | 0.72 | 0.083 | 0.089 |

Total SiOH and SiH were determined in the RTV-silicone formulations immediately after their preparation. The results in Table IV show excellent agreement between the amount added and the amount found. However, when these same formulations were analyzed after aging at room temperature, the total SiOH content decreased. This lends further support to the idea that the low results seen for percent DPMS and TPS were because they were not analyzed immediately.

**Registry No.** TPS, 682-01-9; DPMS, 778-25-6; tetraphenyldimethyldisiloxane, 807-28-3.

## LITERATURE CITED

(1) Noll, W. "Chemistry and Technology of Silicones"; Academic Press: New York, 1968.
(2) Warrick, E. L.; Pierce, O. R.; Polmanteer, K. C.; Saam, J. C. *Rubber Chem. Techol.* **1979**, *52*, 437.
(3) Horn, G. *Plaste Kautsch.* **1979**, *11*, 634–637.
(4) Owen, J. J. *CHEMTECH* **1981**, *11*, 288.
(5) Caprino, J. C. *Rubber World* **1982**, *185*, 33–34, 39.
(6) Mark, J. E.; Andrady, A. L. *Rubber Chem. Technol.* **1981**, *54*, 366–373.
(7) Andrady, A. L.; Llorento, M. A.; Sharaf, M. A.; Rahalkar, R. R.; Mark, J. E. *J. Appl. Polym. Sci.* **1981**, *26*, 1829–1836.
(8) Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039–1046.
(9) Jones, K; Biddle, K. D.; Das, A. K.; Emblem, H. G. *Silic. Ind.* **1981**, *46*, 107–111.
(10) White, M. L.; Serpiello, J. W.; Striny, K. M.; Rosenzweig, W. *IEEE Proc. Int. Rel.-Phys.* **1981**, 430–47.
(11) Wong, C. P. *ACS Symp. Ser.* **1982**, 171–183.
(12) Rotzsche, H.; Clauss, H.; Hahnewald, H. *Plaste Kautsch.* **1979**, *11*, 630–632.
(13) Kohler, R. R. *Anal. Chem.* **1974**, *46*, 1302.
(14) Gilman, H.; Miller, L. S. *J. Am. Chem. Soc.* **1951**, *73*, 2367.
(15) Kellum, G. E.; Smith, R. C. *Anal. Chem.* **1967**, *39*, 1877.
(16) Smith, A. L. "Analysis of Silicones"; Wiley: New York, 1974; pp 248–285.
(17) Wurst, M.; Churaceck, J. *Collect. Czech. Chem. Commun.* **1971**, *3*, 3497–3506.
(18) Dallimore, G. R.; Milligan, R. J. *SAMPE J.* **1982**, *18*, 8–13.

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# Pulsed Laser Induced Thermal Diffraction for Absorption Measurements in Small Volumes

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**Absorption of radiation from an interference pattern, formed at the intersection of two laser beams, can be used to generate a thermal diffraction grating in a sample. This grating can be probed with another laser beam, producing a sensitive, small volume absorption measurement. In this work, a pulsed laser forms the grating, thus making more effective use of the laser energy than continuous wave excitation. In addition, time resolution of the diffraction signal allows discrimination against fluorescence and Raman scattering from the sample. The effective volume of the thermal grating and the diffraction efficiency vs. beam spot size are studied, and the results are discussed relative to small volume absorption measurements. Practical matters affecting the analytical application of the technique, such as alignment constraints and sources of background, are also considered.**

The introduction of lasers into analytical spectroscopic instrumentation has produced, in many cases, significant advances in detection compared to the use of conventional light sources. These improvements arise not simply from the increased optical power of the laser but more often from the unique coherence properties of the beam. For example, the spatial coherence of laser radiation allows the beam to be focused to a diffraction limited spot suitable, for example, for exciting fluorescence in extremely small volume samples (*1–4*). The small rate of divergence of laser radiation, another manifestation of the spatial coherence, is responsible for the production and detection of a thermal lens within a sample, which can be used to measure the absorbance of trace-level, nonfluorescent species (*5*). The temporal coherence of laser radiation, related to the monochromaticity, allows one to detect small optical path differences interferometrically, which has been applied to both thermooptical absorption measurements and refractometry (*6*).

Another thermooptical absorption method, thermal diffraction or real-time holography, has been made possible because of the unique properties of laser radiation. By splitting a laser beam and recombining the two beams within a sample, we can utilize both the spatial and temporal coherence of the beams to generate a regular interference pattern which produces excited states only at the planes of constructive interference. Following nonradiative relaxation of the excited molecules, the resulting periodic temperature distribution can be probed as a transmission grating by diffraction of a another laser beam into a detector. While the generation and detection of thermal gratings or real-time homograms have been studied for many years (*7–9*), the use of this thermooptical element for calorimetric absorbance measurements has only recently been considered (*10*). In this first analytical study of laser-induced thermal diffraction, a

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