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GAS CHROMATOGRAPHIC ANALYSIS FOR
TRACE AMOUNTS OF WATER IN
SILICONES

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

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ABSTRACT

Gas chromatography has been utilized to determine very small concentrations (low ppm range) of water in silicone resins and curing agents. Since the silicone or an additive in the silicone reacts with the Karl Fischer reagent and with lithium aluminum hydride (LiAlH_4), gas chromatography is the only reliable method found to date to successfully analyze the moisture content of silicones.

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SUMMARY

Moisture in silicone resins and curing agents was analyzed at the Oak Ridge Y-12 Plant^(a) using a gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector. A 25 percent mix of the curing agent or resin in tetrahydrofuran prepared in a dry box was injected into the chromatograph. The solvent was dried with sodium and its water content determined. By the Karl Fischer method, the water content was found to be 9 - 25 ppm. Tetrahydrofuran dried with anhydrous sodium sulfate was found to contain 130 - 170 ppm water by the Karl Fischer method and served as a standard.

(a) Operated for the US Atomic Energy Commission by Union Carbide Corporation's Nuclear Division.

INTRODUCTION

Considerable interest has been shown in the development of a procedure for the analysis of trace quantities of water in silicones. Several laboratories have experienced difficulty using the Karl Fischer method and lithium aluminum hydride reduction. The Karl Fischer reagent reacts with the silicone or an additive in the silicone giving spurious results. The difficulty in determining the moisture content in silicones with lithium aluminum hydride is that several functional groups (SiCl, SiOSi, SiH, SiOR, and others) may undergo reduction cleavage to form volatile silanes. Since the determination of water depends upon the amount of hydrogen evolved:

other liberated gases would interfere in the reaction.

Gas chromatography has been used infrequently to analyze for trace quantities of moisture in organic systems because water is adsorbed on solid supports, is eluted slowly, and has a low detector sensitivity. However, such problems are overcome by using a column packed with a porous aromatic polymer which elutes water very rapidly to produce a good peak shape. Because of the rapid elution and acceptable peak shape, a thermal-conductivity detector gives ample sensitivity to detect trace quantities of water.

Care should be taken in the choice of a solvent for the analysis since most silicones are too viscous to be injected without dilution. By choosing the proper column, and a solvent which can be dried prior to use and dissolves both the silicone and water, silicones should be amenable to gas chromatographic analysis.

ANALYZING FOR MOISTURE IN SILICONES

ANALYTICAL PROCEDURE

Equipment

The chromatograph used was a Perkin Elmer Vapor Fractometer, Model 154D, equipped with a 1/4-inch-OD by 6-foot-long stainless steel column packed with Porapak Q and conditioned at 225° C for two hours. The carrier gas was helium (30 mls/min at 7 psi) and the oven was maintained at 145° C for the analysis.

Criteria for a Good Solvent

Four important criteria were considered in the choice of a solvent: (1) it must have a retention time greatly different from that of water, (2) it must be dry or capable of being dried, (3) it must dissolve water, and (4) it should dissolve the silicone. Several solvents were tried but none has been as successful as tetrahydrofuran (C₄H₈O).

Drying and Analysis of the Solvent by the Karl Fischer Method

The tetrahydrofuran used (3-kg MCB bottles) contained a maximum of 0.05 percent water prior to drying. To prepare the samples, three bottles of the solvent were placed in a dry box regulated to less than 10-ppm moisture. Sodium metal chips were added to one bottle and anhydrous granular sodium sulfate to the second. The third bottle received no drying agent. After drying for several days, the solvents were analyzed by the Karl Fischer method. The bottle containing the sodium chips was found to contain 9 - 25 ppm moisture, 130 - 170 ppm moisture was found for the sodium sulfate-dried material, and approximately 300 ppm for the undried material. The ranges given are for several different bottles analyzed over a period of six months.

Sample Preparation

The silicones were mixed with the solvent in a dry box. One-half milliliter of the resin or curing agent was added to 1.5 milliliters of solvent in a 3.5-milliliter vial.^(b) The vials, fitted with Teflon-coated rubber septa and screw caps, were shaken to thoroughly mix the components.

(b) Catalog Number 85-0001, ordered from Schwarz BioResearch, Inc, Orangeburg, New York.

Gas Chromatographic Analysis

The sample vials were removed from the dry box for gas chromatographic (GC) analysis. A syringe was injected through the rubber septum and a 10-microliter sample withdrawn and injected into the chromatograph. The syringe should be cleaned with solvent from a separate vial of sodium-dried tetrahydrofuran prior to injection to remove the moisture and air contamination. Samples may be injected every three minutes until the solvent elutes, interrupting the injection time for forty minutes.

RESULTS AND DISCUSSION

Sensitivity

A 10-microliter injection of 10-ppm water gives an average peak height of five percent of the full-scale deflection (FSD) at maximum sensitivity. The sodium-dried solvent was used as a blank, and the water peak resulting from it was used in calculating a correction factor for the sample.

Identification of the Peaks in the Chromatogram

The retention time for water (Peak A shown in Figure 1) was two minutes; that for tetrahydrofuran (Peak C) was twenty minutes. Air (Peak B) had a retention time of less than one minute. Peak D is due to an impurity in the solvent. From Figure 2 it can be seen that the water (Peak A) in the sodium sulfate-dried solvent is roughly ten times larger than Peak A in Figure 1. A chromatogram of a silicone sealant is presented in Figure 3. The silicone samples analyzed to date average less than 100-ppm water. Figure 4 is a chromatogram of water in a silicone curing agent. Peaks E and F are volatile components of the silicone. Infrared absorption indicated that the components contain vinyl and silicon-hydrogen groups. When taking all four chromatograms, the conditions were: a 1/4-inch-OD by 6-foot-long stainless steel Porapak Q-packed column, a helium flow of 30 mls/min, and an oven temperature of 145° C.

Calculations

The water-peak areas of the chromatogram may be measured in a number of ways, namely: (1) the areas may be cut out and weighed; (2) they may be electrically integrated; (3) a planimeter may be used to calculate the area; (4) the method of triangulation can be used whereby the sides of the peak become the sides of a triangle and the base line of the chromatogram becomes the base of the triangle. All four methods should give the same results. When the peaks have a narrow base or the base is constant, a measurement of peak height only is a fair estimate of the magnitude of the peak.

Generally, the triangulation method or peak-height method was used for the calculation. A plot is made of peak height or area as a function of the water content in the solvents obtained by the Karl Fischer method. The silicone number is obtained

Figure 1. GAS CHROMATOGRAM OF WATER IN SODIUM-DRIED TETRAHYDROFURAN.

Figure 2. GAS CHROMATOGRAM OF WATER IN SODIUM SULFATE-DRIED TETRAHYDROFURAN.

by an extrapolation of the area or height of the water in the silicone from the standard curve. The graph in Figure 5 was drawn from the data listed in Table 1. The table is a compilation of numbers obtained when several different aliquots of the sodium-dried tetrahydrofuran (Sample I), sodium sulfate-dried solvent (Sample II), and the undried material (Sample III) were submitted for Karl Fischer analysis with a subsequent gas chromatographic analysis. The average water content for Sample I was 16 ppm; for Sample II it was 150 ppm.

Figure 3. GAS CHROMATOGRAM OF WATER IN THE SILICONE SEALANT. (Part A)

Figure 4. GAS CHROMATOGRAM OF WATER IN THE SILICONE CURING AGENT. (Part B)

Disadvantages of the Method

There are some disadvantages to the method, namely: the long retention time of the solvent and the presence of low-boiling organic compounds that elute at times between those of the solvent and water. Also, when repetitive injections are made, the water peak might be on top of another peak.

Familiarity with the sample aids in surmounting these problems. The septum in the injection port should be changed and the port cleaned frequently since most resins and curing agents when mixed even at room temperature will cure and clog the port.

Figure 5. WATER PEAK AREA OF THE CHROMATOGRAM OF EACH SOLVENT ANALYZED AS A FUNCTION OF THE WATER CONTENT IN THE SOLVENT.

Table 1
COMPILATION OF TYPICAL GAS CHROMATOGRAPHIC
AND KARL FISCHER DATA

Sample Number	Peak Area ⁽¹⁾ (mm ²)	Water Content ⁽²⁾ (ppm)
I a	30	25
b	15	11
c	14	9
d	20	18
		Average 16
II a	225	170
b	192	150
c	164	130
d	196	151
		Average 150
III a	390	310

(1) Derived from GC data.

(2) Derived from Karl Fischer analysis.

CONCLUSIONS

Gas chromatography provides a capability for measuring very small quantities of water in silicones. The reproducibility of the method (usually on the order of $\pm 5\%$ relative) is comparable to that of the Karl Fischer method, and depends upon how well an analyst can use a syringe. The technique could also be adapted to other organic or inorganic systems.