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A Simple Karl Fischer Titration Procedure for Determination of Total Hydroxyl Content in Silanol-Terminated Polysiloxanes

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This paper describes a simple procedure for the determination of total hydroxyl content in simple silanols and silanol-terminated polysiloxanes. The proposed procedure is based on a conventional pyridine-free Karl Fischer titration method. A temperature of 50°C is used to accelerate and complete the reaction between the KF reagent and silanol (SiOH) groups. Validation shows that the procedure is precise and accurate. Typical relative standard deviation of the procedure is 1–2%. When compared to a routine FTIR method, the Karl Fischer titration procedure produced similar quantitative results, but was superior in terms of simplicity in equipment and standardization.

Keywords: Silanol determination, Karl Fischer titration, polysiloxanes, poly(dimethylsiloxane)

INTRODUCTION

Silanols and low molecular weight silanol-terminated polysiloxanes are reactive compounds which polycondensates in the presence of acid or base forming siloxane polymers.^[1,2] Silanol-terminated polysiloxanes can be used in room temperature vulcanizable applications, for example, in making foamed rubber, dip coating and potting applications.^[3] They have also been used as a plasticizer in reducing polymer-filler interaction during the reinforcement of silicone elastomers.^[4]

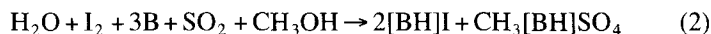
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The amount of silanol groups in siloxane polymers is an important factor due to their high reactivity, which must be known in order to determine the suitability of a polymer for a particular application. The chemical and instrumental methods for the determination of silanol in silicon compounds have been reviewed.^[5,6] Among them, Fourier Transform-infrared spectroscopy (FT-IR) is probably one of the best suited techniques for the quantitative analysis of silanols, even as low a level as 10 ppm.^[7] However, FT-IR requires relatively expensive equipment and potentially toxic solvents such as 1,4-dioxane. Additionally, the technique requires frequent calibration with the same type of material as a sample. The calibration may cause problems because of the lack of commercially available reference standards. Simple silanols (such as commercially available triethylsilanol) are not good reference standards because of possible condensation of the material caused by the high reactivity of the silanol group.

The most common methods for chemical analysis of silanols include manometric, condensation, and titrimetric methods.^[5] The direct titration of silanol group using lithium aluminium di-*n*-butylamide is a fast method applicable to samples from simple silanols to resins.^[8] The disadvantages are that the titrant is air sensitive and the stoichiometry of, for example, silanols and water is different.^[5] Condensation procedures have been used for the determination of silanol in which the produced water has been recovered by azeotropic distillation and measured by, for example, the Karl Fischer titration method.^[5,9] All of these methods, however, require specialized equipment and are difficult to use in routine applications.

The aim of this investigation was to develop a simple and convenient quantitative method for the routine analysis of silanol-terminated low molecular weight polysiloxanes, having the structure of HO(Me₂SiO)_{*n*}H, where *n* = 2–20. The Karl Fischer titration method seemed to best fulfill the requirements and it was thoroughly studied. Moreover, one of the more interesting aspects of Karl Fischer titrations is the ease of calibration. There are several calibration standards available, the simplest being water.

It has long been known that SiOH groups in simple silanols react quantitatively with the Karl Fischer reagent.^[10,11] The reaction can be described as follows:



where B is a suitable base (e.g., imidazole) for the neutralization of the solution. The methoxylation reaction (reaction 1) is driven to the right and hastened by the presence of CH_3HSO_4 from the Karl Fischer reagent.^[11,12] Reaction 2 is the normal Karl Fischer reaction in the presence of water. The stoichiometry of the entire reaction is 1 mole of silanol for 1 mole of produced water.

The alkoxylation reaction of silanol is the rate-limiting step in the Karl Fischer titration method, and it has been found to be incomplete for the quantitative analysis of silanols in siloxane materials. This property has been incorporated in the analysis of water from silanol containing materials using high molecular weight alcohols as a diluent and for cooling the system.^[13,14]

In this paper, we present the results of the Karl Fischer titration method where elevated temperature is used to accelerate and complete the methoxylation reaction in order that the total hydroxyl analysis is fast and precise. The results were compared to FT-IR analysis.

EXPERIMENTAL

Chemicals

The Karl Fischer titrant used was a one-component (5 mg water/mL) pyridine-free reagent for volumetric titration obtained from Fluka Chemica-BioChemika (Buchs, Switzerland) or Riedel-de Haen (Seelze, Germany). The titrant contained 2-methoxyethanol (bp 124°C) or diethylene glycol monoethyl ether (bp 196°C) as the solvent, instead of methanol (bp 64°C). The higher boiling points of solvents prevented the formation of bubbles into the titrant dispensing tube due to the boiling of the solvent during analysis.

Tetramethyldisiloxane-1,3-diol, used as a reference standard for the silanol determination in the FT-IR analysis, was prepared according to a procedure previously described.^[15] The product was white needles with a melting point of 65.8°C. $^1\text{H-NMR}$ (DMSO) results were δ 6.0 (s, OH, 2H) ppm and δ 0.0 (s, CH_3 , 12H) ppm. Gas chromatographic analysis gave an area of 99.8%.

Low molecular weight, siloxanes were obtained from Dow Corning Corp. (Midland, Michigan) and Leiras (Turku, Finland).

Apparatus

A commercial Mettler DL18 volumetric Karl Fischer titrator was used. The endpoint was measured voltametrically using a polarizable two-pin platinum electrode (Mettler DM 142). A 5-mL burette was used and a commercially available thermostated beaker with a capacity of 100 mL was incorporated as a titration cell. The solvent in the titration cell was stirred using a magnetic stirrer with adjustable stirring speed.

A Perkin Elmer System 2000 Fourier Transform infrared (FT-IR) spectrometer was used for the IR analysis. The quantitative measurements were made from 5% solutions in 1,4-dioxane using a sealed liquid cell with a nominal path length of 2 mm. The qualitative measurements were made using KBr plates. Samples for qualitative measurements were extracted with water from the titration cell after the titration procedure had been performed.

Karl Fischer Titration Procedure

About 40 mL of the pyridine-free methanol containing solvent was added into the titration cell, pre-titrated to dryness, and allowed to warm to the desired temperature. The temperature was maintained throughout the standardization or sample titration. After the desired temperature was achieved (10 min), the titrant was standardized as follows: 5 mg of water was introduced into the titration cell with a waiting period of 20 min before the titration was initiated.

The samples of about 0.05 g of low molecular weight siloxanes, which contained 3–4% hydroxyl, were handled in the same manner as the standard.

The standard and sample were introduced into the cell via the titration-head opening using an injection needle. The titration head was opened for a very brief moment. (The titration head and titration cell must be well sealed.) The bottles of titrant, solvent and suction were equipped with drying tubes containing 0.3 nm molecular sieves beads of about 2 mm.

RESULTS AND DISCUSSION

Effect of Temperature and Time on Karl Fischer Titration

The effect of temperature and time on the Karl Fischer titration of silanol was studied owing to the fact that elevated temperature may accelerate the methoxylation reaction, but may also accelerate the loss of water by

volatilization during the reaction time which may cause interference with respect to quantitation.

The effect of temperature on the titration results with regard to the water and sample is shown in Figure 1. The reaction time was fixed at 20 min. At approximately room temperature (25°C), the methoxylation reaction of the sample is slow and incomplete, causing a drifting titration endpoint and low titration result. At higher temperature, the titration is more complete, extending to the maximum value at 50° to 60°C. A temperature higher than 60°C was not studied owing to the vigorous boiling of the solvent (methanol).

Figure 1 shows that the temperature has no dramatic effect on the volatilization of water in this system (solid triangles). An almost straight line is obtained between the temperatures of 25° to 60°C. These values are

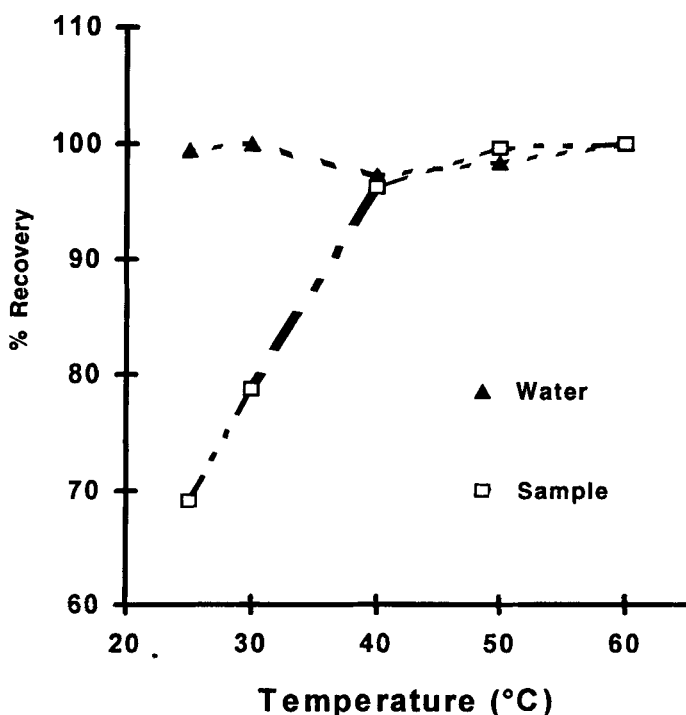


FIGURE 1 The effect of temperature on Karl Fischer titration of silanol (open squares) and water (solid triangles).

nearly 100%, because the concentration of the titrant (CONC value) has been determined using the same reaction time (20 min).

On the basis of the shape of the curves Figure 1, the temperature used in the Karl Fischer titration of silanols must be between 50° to 60°C to achieve complete methoxylation reaction of the silanol group in a reasonably short time.

The reaction time of water and the sample between 5 to 60 min were further studied at 50°C, as shown in Figure 2. As can be seen, the titration result of the water (solid triangles) decreases with increasing waiting time as a consequence of volatilizing. In the same time period, the titration result of a sample of low molecular weight polysiloxane (open squares) increases during the first 15 min, then stabilizes between 15 to 30 min, decreasing after 30 min. Using the data from the water titration, the loss of water during the reaction time can be compensated, as shown by the closed square in

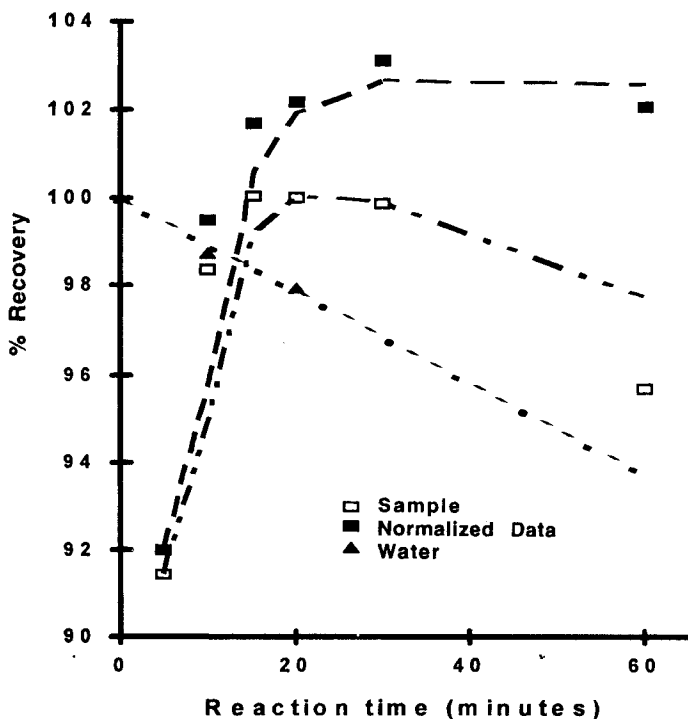


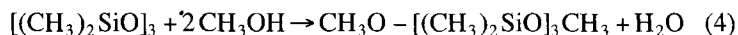
FIGURE 2 The effect of reaction time on Karl Fischer titration of water (solid triangles) and silanol (solid and open squares) at 50°C.

Figure 2. The optimum waiting time with regard to the sample for a methoxylation reaction of the silanol group is achieved after 20 min at a temperature of 50°C. It should be noted that all of these values are normalized to the result obtained after 20 min reaction time. The maximum values of the normalized data are clearly over 100%, since the concentration of the titrant was determined using the reaction time of 0 min instead of 20 min. These optimized values were applied during the analytical evaluation of the Karl Fischer titration method.

Functional groups of silicon were identified by characteristic IR bands. To isolate the sample, water was added to the titrated sample to separate the product from the titration solution. The product remained in the top layer, and it was then examined by FT-IR. Typical spectra obtained from an untreated and an extracted sample are shown in Figure 3. The broad band at around 3300 cm^{-1} in Figure 3 corresponds to associated SiOH groups. Within the spectrum of the extracted sample (spectrum B), the SiOH band is absent and another peak at 2835 cm^{-1} has appeared corresponding to the methoxy group (OMe) in the sample. It is therefore evident that the SiOH groups in the sample have been fully methoxylated during the titration procedure.

Possible Interference in Karl Fischer Titration

Karl Fischer titrant used in this study contained 2-methoxyethanol or diethylene glycol monoethyl ether as a solvent. Other constituents were iodine, sulfur dioxide and imidazole. The solvent consisted of methanol, sulfur dioxide and imidazole. Several functional groups react with the components of KF solutions causing quantitative interference with this determination. This applies to the generally known interfering groups in the Karl Fischer titration, such as ketones, aldehydes, amines and vinyl groups. Other possible reactions of methanol with silanol or siloxane have been reported which may interfere with the KF analysis: condensation of silanol and cleavage of cyclic trimer siloxane,^[16,17] if present, producing water as follows:



The condensation of silanol (reaction 3) occurs in an acidic or basic medium. Although the titration system contains sulfur dioxide, which forms a strong acid such as CH_3HSO_4 , in this system the imidazole base

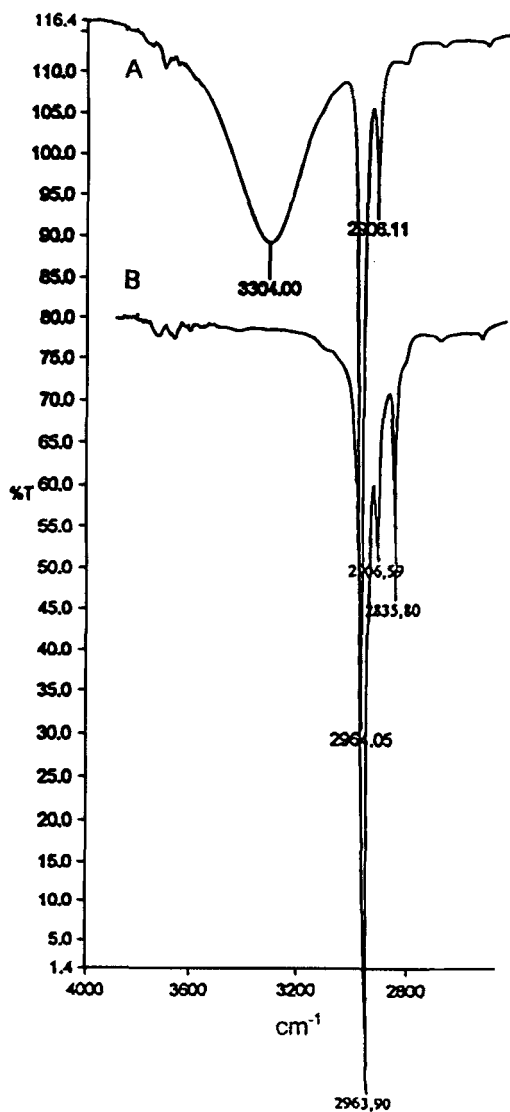


FIGURE 3 FTIR-spectra of silanol-terminated low molecular weight polysiloxanes: A = untreated and B = extracted from the titration cell after titration.

buffers the solution to the neutral region, obviously preventing or slowing the condensation reaction. If condensation had occurred, the stoichiometry of the system would have been 2 moles of silanol for 1 mole of water and the titration results of silanol should have been much lower than the determined values. The tests for the analytical evaluation showed clearly that the condensation process does not occur or occurs very slowly and does not interfere with the analysis.

The only reported and discernable interfering siloxane is the cyclic trimer siloxane,^[16] which may cause problems if it exists in a high amount in the sample.

Analytical Evaluation

The developed Karl Fischer titration method for silanol determination was evaluated (validated) in terms of accuracy, precision, and linearity.^[18] In this case, where the procedure is not specific, that is, the determination is based on chemical reactions which may be subject to interference from other chemical (side) reactions, the importance of accuracy is evident. Linearity of the method is needed to ensure that all the reagents used during the analysis are sufficient for the sample size to achieve complete reaction and the correct results. Also, reaction time can be dependent on sample size.

Tables I and II present data from the determinations of precision and accuracy, respectively. The test for the precision by an analyst was performed by assaying five times in duplicate (10 single determinations) a sample of silanol-terminated low molecular weight polysiloxane. The standard deviation of the Karl Fischer titration procedure was $\pm 0.04\%$ (0.90% RSD). The accuracy of the method was checked by comparing the titration results to the FT-IR assay results. Six lots of low molecular weight polysiloxanes, in which the silanol content was between 3 to 4 wt % were analyzed in duplicate. The Karl Fischer procedure provided similar quantitative results, deviating only by $\pm 0.1\%$ from the FT-IR results. The small bias means complete methoxylation of silanol groups and excludes the possibility of a condensation reaction. These results are contrary to previously reported observations of incomplete reactions and condensations of silanols in the Karl Fischer titration.^[16]

The linearity of the titration method was checked at a concentration range of 40 to 175% of the sample concentration used in the evaluation of precision and accuracy of the method. The equation corresponding to the

TABLE I Precision of the Karl Fischer titration procedure

<i>Sample No.</i>	<i>Result (%)</i>	<i>Mean (%)</i>	<i>RSD (%)</i>
1/1	3.86		
2/1	3.90	3.88	0.75
1/2	3.84		
2/2	3.77	3.80	1.36
1/3	3.82		
2/3	3.77	3.80	0.87
1/4	3.82		
2/4	3.81	3.82	0.17
1/5	3.80		
2/5	3.91	3.85	2.13
Mean (%):		3.83	
SD:		0.04	
RSD (%):		0.90	

Sample: silanol-terminated low molecular weight polysiloxane.

obtained graph can be expressed as $y = 0.0078x - 0.0015$, where x is the weight of the sample (mg) and y is the corresponding consumption of the titrant (mL). The correlation coefficient (R) was 0.9981. When it is taken into account that the sample contained about 4% of silanol and the titrant concentration was 5 mg water/mL, the stoichiometry of the method was calculated to be 1 mole of silanol for 1 mole of water.

CONCLUSIONS

The proposed Karl Fischer procedure allows for a simple and convenient manner to quantitate silanols (total hydroxyl content) in silanol-terminated low molecular weight polysiloxanes. This procedure has proven to be

TABLE II Accuracy of the Karl Fischer titration procedure

<i>Lot No.</i>	<i>Hydroxyl content (%)</i>		<i>Deviation (KF-FTIR)</i>
	<i>KF titration</i>	<i>FTIR</i>	
1	3.23	3.28	-0.05
2	3.65	3.72	-0.07
3	3.41	3.47	-0.06
4	4.08	3.97	0.11
5	4.05	3.94	0.11
6	4.08	4.04	0.04

Samples: silanol-terminated low molecular weight polysiloxanes.

advantageous in routine work since the solvents/chemicals needed are easily handled, and the titrant concentration may be easily determined using water as a standard. The validation showed that the procedure is precise and the results are comparable to those analyzed by FT-IR.

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