

## SHORT COMMUNICATION

**Surface resistivity of different silylated glasses**

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**1. Introduction**

The reaction of silanes with glass surfaces has been known for a long time but recently has regained interest due to its application in the preparation of capillary columns for gas chromatography (see, for example, [1-4]).

Walker [5] was the first to use this reaction for the purpose of fabricating liquid membrane ion-sensitive microelectrodes, in which a column of a hydrophobic liquid sensor is lodged in the open tip of a glass micropipette. This application has been exploited by others (see, for example, [6-8]). Microelectrodes are now widely used for extra- and intracellular measurements of the activity of ionic species in biological tissues [9-11]. Typically, for intracellular measurements it is necessary to use microelectrodes with fine tips of i.d.  $\leq 0.5 \mu\text{m}$ .

As in the preparation of a chromatographic column, the silylation of microelectrode surfaces is done, on one hand, to avoid the adsorption of water on the glass surfaces and on the other, to replace polar (hydrophilic) surface OH groups by non-polar organic (hydrophobic) O-Si(R)<sub>3</sub> groups. In addition, such a treatment increases the surface resistivity of the glass [12, 13]. Consequently, any surface conductance leakage would be prevented. This leakage tends to short-circuit the e.m.f. that is generated by the ionic activity differences between the external solution and the reference solution within the microelectrode.

Using reaction conditions potentially applicable to the fabrication of liquid membrane ion-sensitive microelectrodes several different silanes have been compared and tests made of the effect of reaction duration and temperature, and pretreatment of the glass surface particularly for N,N-trimethyl-

(dimethylamino)silane (TMDMAS) [14, 15]. The silylation of the surface was examined by measuring the hydrophobicity [14] or the surface resistivity [15, 16]. It was also shown that after silylation, surface resistivity of Pyrex and aluminosilicate glasses increased in that order [15]. With a view to adding to our understanding of silylation we now report a more extensive comparison of different silicate glasses and also a comparison of different methods of carrying out the reaction.

**2. Experimental approach****2.1. Silylation methods**

Silylation was carried out on capillary tubes i.d.  $\approx 1 \text{ mm}$ . Two of the methods used are employed in the fabrication of ion-sensitive microelectrodes: these are the Tsien and Rink oven method [8] and the Coles and Tsacopoulos vapour flow method [7].

In the oven method, a drop of silane is added to a heated petri dish containing a batch of capillaries. In the vapour flow method, a capillary is held in the centre of a heating coil and silane vapour is entrained by a flow of dry nitrogen into the capillary (see Munoz *et al.* [15] for details).

In another method, used principally by surface chemists, the silylation process is carried out at the desired temperature in a sealed ampoule that contains the capillaries and the reagent (see, for example, [14, 17]).

To estimate the performance of each method, we measured the surface resistivities of the following glasses: soda-lime hematocrit from Becton Dickinson Labware, Oxnard, CA 93 030, Ref. 1021F), the borosilicate Pyrex (Code 7740,

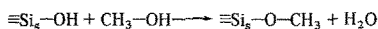
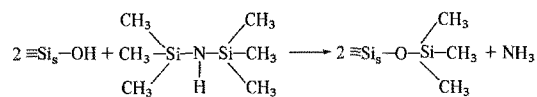
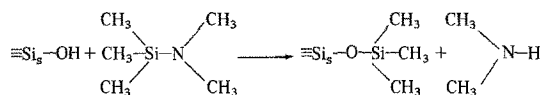
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Corning, USA), aluminosilicate (A41, Glass Works, Newcastle upon Tyne, NE15 8SX, UK) and fused silica (Heralux, Heraeus Quarzschmelze, D-6450 Hanau, FRG). The silane TMDMAS (Fluka, 9470 Buchs, Switzerland) was chosen to treat each type of glass using all three methods.

All the capillaries were acid leached in concentrated  $\text{HNO}_3$  (Merck, 60%) for 24 h, rinsed with distilled water and then dried overnight at  $80^\circ\text{C}$  in an oven.

Five capillaries were simultaneously treated with TMDMAS at  $250^\circ\text{C}$  by each method, except for the vapour flow method where the tubes were treated successively. The treated capillaries were then rinsed with diethylether and dried again overnight at  $80^\circ\text{C}$ .

In order to see if better results could be obtained with another silane Pyrex capillaries were treated with hexamethyldisilazane (HMDS). Other Pyrex capillaries were esterified with methanol. In this manner, the utility of silane surface treatments, under the same conditions, was checked. The following reactions show schematically the above mentioned surface treatments.



## 2.2. Method and results of surface resistivity measurements

The surface resistivity of the treated capillaries was measured as described by Munoz *et al.* [15]. Briefly, at each end of the treated capillaries a liquid column of KCl (1M) was introduced in such a manner as to allow the formation of a bubble at the centre of the tube. The length of the bubble was then adjusted to 100–600  $\mu\text{m}$  long as measured under a microscope. Two chlorided silver wires were inserted into the electrolyte column at each end of the capillary (again, see Munoz *et al.* [15]). This method

was improved by connecting five capillaries in parallel for resistivity measurements as shown in Fig. 1 which also shows the electrical circuit used for resistivity measurements.

The surface resistivities were calculated using the measured values of the resistances, the length of the bubbles and the internal diameter of the tubes (see Equation 1). The bubble length was remeasured after each electrical measurement.

$$\sigma = \pi V_{\text{in}}/V_{\text{out}} R_{\text{ref}} \sum_i d_i/l_i \quad (1)$$

where  $V_{\text{in}}$  is applied voltage (38 V),  $V_{\text{out}}$  is measured voltage,  $d_i$  is internal diameter of the  $i$ th capillary and  $l_i$  is its bubble length.  $R_{\text{ref}}$  is the feedback resistance (see Fig. 1). All the results are given in Table 1.

## 3. Conclusion

From the results obtained several conclusions may be drawn. As shown in Table 1, for a given type of glass, similar surface resistivity values were obtained for all three silylation methods used. On the contrary, as confirmed by all three methods, the surface resistivity is a function of the glass employed. Results show that the resistivity increased in the following manner: soda-lime, borosilicate, aluminosilicate and fused silica. Thus, the addition of oxides, particularly the alkali oxides, to pure silica increases the surface conductivity of the treated glass, even if it has been previously leached for 24 h in concentrated  $\text{HNO}_3$ . The same increasing order is found when the ratio of surface resistivities of silylated to the non-silylated glasses is calculated:  $1.5 \times 10^2$ ,  $6 \times 10^3$ ,  $5.8 \times 10^4$ ,  $1.2 \times 10^5$ .

Tests with Pyrex, to see the influence of reaction time, confirm that the surface resistivity reaches its limiting value within the first minutes of the reaction. Prolonged reaction times, even after several hours, only slightly increased this value.

The results confirm that the main role of the silylation reaction in the fabrication of electrodes would be to avoid the formation of a continuous conductive film at the surface of the glass [12, 13]. The hydrophobicity of the glass surface increases greatly with the effectiveness of the silylation reaction [17] and silylating reagent [14]. But it appears that once a certain level of

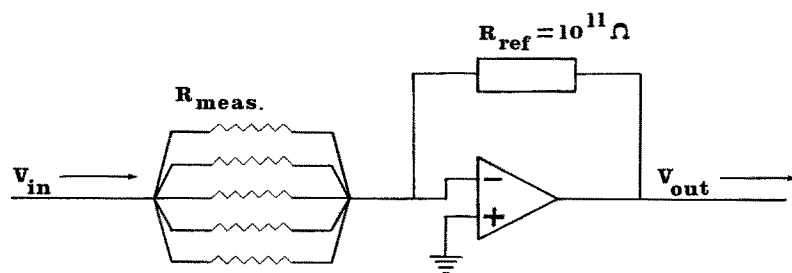


Fig. 1. A current-to-voltage converter based on an operational amplifier (AD 515 LH, Analog Devices) was used for resistivity measurements.

hydrophobicity is reached a limiting surface resistivity value is obtained. Increased silylation, although it could increase hydrophobicity, increased the surface resistivity only slightly. The reaction of the Pyrex glass with a silane (HMDS) more reactive than TMDMAS gave only a slight improvement in the surface resistivity (see Table 1), whereas the hydrophobicity greatly increased (see Deyhimi and Coles [14]).

It is now accepted [1, 2] that due to steric hindrance, only half of the surface hydroxyl groups can be silylated. However, better results are found with silanes, either for hydrophobicity or surface resistivity, compared to those

obtained with methanol. This is true, even if there is no steric hindrance in the reaction of MeOH with surface hydroxyl groups, and even if, in this reaction the surface coverage approaches completion (see, for example, [1, 2]).

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Table 1. Surface resistivity of several types of glass: soda-lime, Pyrex, aluminosilicate and fused silica.

Glass	Treatment*	Silylation Method†	$\sigma(\Omega)$ (Mean $\pm$ S.D.)‡
Soda-lime	Untreated	—	$(2.9 \pm 2.3)10^{11}$
	DMATMS	C + T	$(2.6 \pm 1.6)10^{13}$
		T + R	$(5.2 \pm 4.8)10^{13}$
Pyrex	Untreated	—	$(1.3 \pm 0.6)10^{12}$
	CH <sub>3</sub> OH	SA	$(1.0 \pm 0.8)10^{14}$
	DMATMS	C + T	$(8.5 \pm 1)10^{15}$
		T + R	$(6.8 \pm -)10^{15}$
		SA	$(8.1 \pm 0.9)10^{15}$
	DMATMS	SA (2h)	$(3 \pm 1)10^{15}$
		SA (25h1/2)	$(2.1 \pm 2.5)10^{16}$
Aluminosilicate	HMDS	SA	$(1 \pm 0.8)10^{16}$
	Untreated	—	$(3.8 \pm 2.5)10^{11}$
	DMATMS	C + T	—
		T + R	$(2.5 \pm 2.7)10^{16}$
		SA	$(1.9 \pm -)10^{16}$
		Fused silica	Untreated
DMATMS	C + T		$(2.3 \pm 0.4)10^{17}$
	T + R		$(1 \pm -)10^{17}$
		SA	—

\* Untreated means: the glass was only acid-leached in concentrated HNO<sub>3</sub> for 24 h, rinsed and dried overnight at 80° C. T = 250° C and reaction time = 15 min when not specified.

† References for silylation methods are: C + T [7, 15], T + R [8] and SA [14, 17].

‡ The mean value of measured surface resistivities for five tubes ( $\pm$  S.D. when individual measurements were made).

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