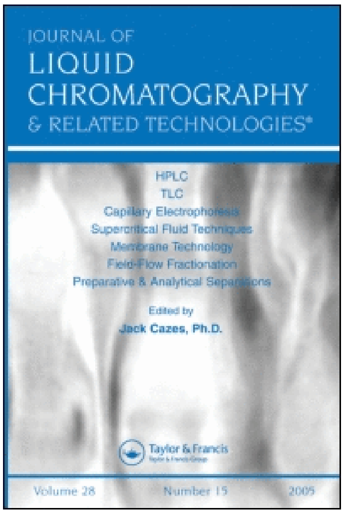

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DETERMINATION OF SURFACE SILANOLS OF SILICA GELS AND HPLC BONDED PHASES

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ABSTRACT

A rapid method determining the surface silanols of silica gels and HPLC bonded phases involves a titration of silica gel with sodium hydroxide, in a medium of any of the following 10% aqueous salts: sodium chloride, sodium nitrate, sodium sulfate, potassium chloride, potassium nitrate and potassium sulfate. The silanols are quantified as m eq/g. It is possible to determine cation exchange capacity of a cation-exchanger due to an acid as an end group and surface silanols separately.

INTRODUCTION

Silanols or hydroxyl groups on the silica gel surface are the major centers of solute absorption

(10). Characterization and quantification of the silanols have been done by using adsorption methods (3, 9, 12) and spectroscopic techniques such as solid-state nuclear magnetic resonance (2, 7, 10), reflectance (4, 6) and transmission (5, 11) infrared spectroscopy. The present investigation is directed to analyze the silanols on the silica gel surface by direct titration with 0.01 N NaOH in the presence of any of the following 10% aqueous salts: NaCl, KCl, $NaNO_3$, KNO_3, K_2SO_4 and Na_2SO_4.

EXPERIMENTAL

Materials

Sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, potassium sulfate, sodium sulfate and standard solution of 0.01 N NaOH were purchased from EM Science (Cherry Hill, NJ). Partisil-10 C-1 300, Partisil-10, Partisil-5, PartiSphere-5, Partisil-10 SCX, Partisil-5 SCX, PartiSphere-5 SCX, PartiSphere-5 WCX, Partisil-5 ODS-3 and Partisil-5 C-8 were supplied by Whatman Inc. (Clifton, NJ). Nucleosil SA was purchased from Machery-Nagel GMBH & Co., Inc. (Durwn, Germany), Vydac Cation-Exchanger was obtained from Separations group Inc. (Hesperia, CA).

Preparation of Solutions

Solution of sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, sodium sulfate and potassium sulfate were prepared by dissolving 10 g of each in 100 mL of water.

Titration of Materials

Titration of various kinds of silica gels was carried out by suspending 0.5 g of the materials in 10 mL of 10% solutions of NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4. In the case of reverse phases such as Partisil-10, Partisil-10 ODS-3, Partisil-10 C-8, the titrations were performed by suspending 0.5 g of the bonded phases in 10 ml of 10% solutions of NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4 containing 3 mL of isopropanol. Partisil-10 SCX, Partisil-5 SCX, PartiSphere-5 SCX, PartiSphere-5 WCX, Nucleosil SA and Vydac Cation-Exchanger were titrated by suspending 0.5 g of the materials in 10 mL of water in order to calculate cation-exchange capacity due to $-SO_3H$ or-COOH groups. The surface silanols of these materials were quantified by continuing the titrations of the same suspensions in presence of 10% NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4. The titrations were performed to pH 9. The pH was measured with a high pH (Beckman) glass electrode and a calomel reference electrode.

Specific Surface Area

The specific areas were measured by low-temperature nitrogen adsorption technique (1).

RESULTS AND DISCUSSION

Silanols on the surface of silica gel and its various bonded phases have been quantified as meq/g by titrating the aqueous suspensions in presence of any of the following salts: NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4. The reactions in all these cases can be represented by following equation

$$\begin{array}{l} \text{Si-OH} + \text{MX} \rightleftharpoons \text{Si-OM} + \text{HX} \\ \qquad\qquad\qquad\qquad\qquad \downarrow 0.01\ \text{N NaOH} \\ \qquad\qquad\qquad \text{Si-OM} + \text{NaX} + H_2O \end{array}$$

Where MX is NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4

(eq. 1).

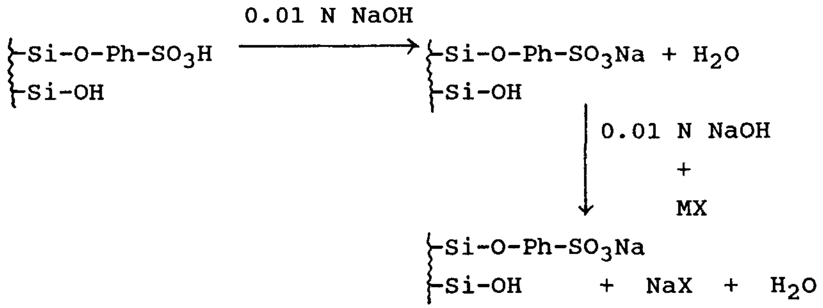
The surface hydroxyl or silanol groups of the silica gel are not titrable as such in aqueous suspensions but the addition of 10% salts increase their ionization enough to titrate with dilute alkali such as 0.01 N NaOH. Table 1 shows the results of

TABLE 1. Cation Exchange Capacity of Silica Gel and Various HPLC Bonded Phases*

Silica Gels	Cation-Exchange Capacity (meq/g)	Surface Areas m^2/g
Group-1		
Partisil-10	0.280	400
Partisil-5	0.300	400
Partisil-10(300)	0.220	300
PartiSphere-5	0.150	170
K-6	0.370	500
Group-2		
Partisil-10 C-1	0.0016	
Partisil-10-ODS-3	0.006	
Partisil-10 C-18	0.002	
PartiSphere-5-ODS-3	0.0014	
Group-3		
Partisil-10 SCX	0.290 (Due to $-SO_3H$ group) 0.280 (Due to residual silanols)	
Partisil-5 SCX	0.240 (Due to $-SO_3H$ group) 0.286 (Due to residual silanols)	
PartiSphere-5 SCX	0.168 (Due to $-SO_3H$ group) 0.160 (Due to residual silanols)	
PartiSphere-5 WCX	0.09 (Due to -COOH group) 0.12 (Due to residual silanols)	
Nucleosil SA	0.022 (Due to $-SO_3H$ group) 0.158 (Due to residual silanols)	
Vaydac Cation Exchanger	0.024 (Due to $-SO_3H$ group) 0.154 (Due to residual silanols)	

* The titrations were performed in 10% aqueous NaCl.

analysis of various kinds of silica gels and bonded phases. The Group-1 represents different kinds of silica gels. The higher values of Partisil-10, Partisil-5 and K-6 silica gels are due to their larger surface areas. Group-2 represents the cation-exchange capacity of residual silanols of some of the reverse phases such as Partisil-10 C-1, Partisil-10-ODS-3 and Partisil-10 C-8. It is possible to determine cation-exchange capacity due to acid groups and silanols in cation-exchangers separately (Group-3) by titrating the bonded phases against 0.01 N NaOH in absence and presence of 10% salt solutions as shown in the eq. 2.



$$\begin{tikzcd}
\begin{array}{l}\text{-Si-O-Ph-SO}_3\text{H}\\ \text{-Si-OH}\end{array} \arrow[r, "0.01\ \text{N NaOH}"] & \begin{array}{l}\text{-Si-O-Ph-SO}_3\text{Na} + \text{H}_2\text{O}\\ \text{-Si-OH}\end{array} \arrow[d, "0.01\ \text{N NaOH} + \text{MX}"] \\
 & \begin{array}{l}\text{-Si-O-Ph-SO}_3\text{Na}\\ \text{-Si-OH} + \text{NaX} + \text{H}_2\text{O}\end{array}
\end{tikzcd}$$

(eq. 2)

Where MX is NaCl, KCl, $NaNO_3$, KNO_3. Na_2SO_4 and K_2SO_4. Partisil-5 SCX and Partisil-10 SCX have higher cation exchange values which may be due to the generation of extra silanols on the surface of the bonded phase when trichlorosilane or trialkoxysilane are used as condensing reagents. the chloro or alkoxy groups have the tendency to undergo hydrolysis under acidic conditions to give rise hydroxy groups. All the titrations in the Table-1 were performed in the presence of NaCl. Identical results were obtained whensalts other than NaCl were used.

Figure 1 shows a plot of volume of base added against specific surface by nitrogen. A straight line was obtained, the equation for which is

$$S = 31V - 41$$

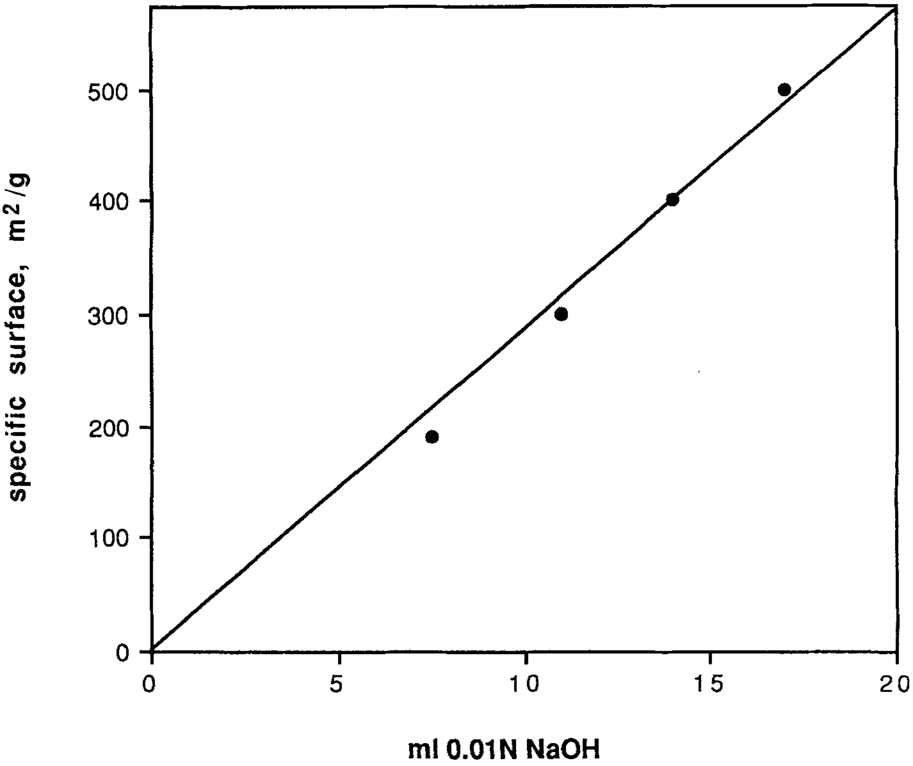


Figure 1. Specific area determined by nitrogen adsorption. Titrations at 25°C of 0.5 g of silica gels in 10 mL of 10% sodium chloride.

where S is specific surface in square meters per gram and V is volume in milliliters of 0.01 N NaOH required for 0.5 g of silica gel. Thus, with a simple titration, the specific surface of bonded and unbonded silicas can be determined.

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