



## Determination of accessible silanols groups on silica gel surfaces using microcalorimetric measurements

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### ABSTRACT

The calorimetric measurements of methanol and hexane heats of immersion were carried out on different silica gels. Based on the difference in immersion heats, a methodology for the determination of the number of silanols on the surface is presented. The calculated concentration of residual silanols on the silica gel surface agreed with data found in the literature. The proposed methodology, based on a calculation of possible hydrogen bond formation, was also tested on the series of bonded stationary phases with different coverage densities. A very good correlation between the calculated number of accessible residual silanols and the coverage density of bonded ligands was observed.

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### 1. Introduction

Silica gel is the most important material utilized in liquid chromatography as an adsorbent or the support for bonded stationary phases. The most important advantages of these packing materials are its chemical stability and porous structure which assures rapid mass transfer, good loadability, and high reproducibility [1]. Even after the derivatization of silica gel, residual silanols are always present on the surface of the material. The presence of residual silanols can have a negative influence on the separation of polar analytes, especially basic compounds and biopolymers [2].

During the elution process solvents from the mobile phase adsorb on the silica and modified silica surfaces. Water adsorbs preferentially on the residual silanols which can be divided into two groups: isolated silanols and geminal silanols and on the siloxanes [3–5]. The most active are geminal silanols but their concentration on the surface is the lowest (10–12%) and isolated silanols (60–65%). Siloxanes make the rest [6–8]. Residual silanols may participate in the retention of solutes [9–11]. From the amount of residual silanols – which are not bonded with silanes – only about 5% exist as a polar strong adsorption center. This effect is caused by the shielding properties of the methyl group connected to the silicon atom in the silanes bonded to the surface [5,12].

When the stationary phase is in contact with the mobile phase, interactions of organic solvent with the silanols are also possible [13,14], but they preferentially solvate chemically bonded organic ligands. This phenomenon has been a topic of many previous investigations [15–18].

The microcalorimetric measurement of the thermal effect accompanying wetting of the surface by organic solvent is another method that can give useful information about solvent interactions with silica and modified silica surfaces [19–22]. In addition, the temperature strongly influences the solvation processes [23].

The measured heat of immersion is generated by both specific and non-specific interactions. In the case of methanol, acetonitrile and hexane, all solvents may interact with the silica surface due to non-specific mechanisms (van der Waals forces and London forces) but only methanol and acetonitrile exhibit the ability for specific polar interactions (hydrogen bonding and dipole–dipole). In this case the heat of adsorption is higher for alcohols than for hydrocarbons [24,25]. Thus, microcalorimetric measurements may be used to determine the possibility of polar interactions of some solvents with the surface silanols.

In previous work [19,26] the microcalorimetric study of solvent adsorption was compared with excess isotherm measurement in chromatographic systems and the use of microcalorimetric measurements for the determination of the polarity of bonded stationary phases. The goal of the present study was to determine the number of the accessible residual silanols using microcalorimetric investigation. Based on the heat of hexane and methanol adsorption, the thermal effect connected with hydrogen bond creation

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**Table 1**  
Properties of the silica gels.

Material	Mean particle size ( $\mu\text{m}$ )	Particle shape	Specific surface area ( $\text{m}^2/\text{g}$ )	Mean pore diameter ( $\text{\AA}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )
Kromasil 100	5	Spherical	313	100	0.87
Kromasil 300	10	Spherical	112	300	0.83
Microsolv Technology	4.2	Spherical	350	100	0.9
LiChrospher Si 100	5	Spherical	400	100	1.25
Silpearl	6.8	Spherical	612	46	0.67
SG 7/G	7.5	Spherical	361	200	2.1
Lichrosorb Si 60	7	Irregular	300	60	0.75

was obtained. From these measurements it is possible to calculate the number of residual silanols accessible for hydrogen bond creation during chromatographic elution.

## 2. Experimental

### 2.1. Instruments

The calorimetric measurements were carried out using a home-made microcalorimeter with a Tian-Calvet isothermal design. The measurement temperature was  $37^\circ\text{C}$  [27].

The degree of the surface coverage by octadecyl ligands ( $\alpha_{\text{RP}}$ ) was calculated on the basis of the carbon percentage determined with a Model 240 CHN analyzer (Perkin Elmer, Norwalk, USA). Calculations were done according to methodology proposed by Berendsen and de Galan [28].

### 2.2. Methods

The study of the immersion heats was carried out using a Tian-Calvet calorimeter. Before measurement the sample consisting of 300 mg of the bonded stationary phase was dried at 373 K under vacuum. The silica material was placed into the microcalorimeter in a vessel and  $5\text{ cm}^3$  of the solvent was added. The adsorbent and solvent were separated using a membrane. After a constant temperature in the calorimeter was reached (18 h), the membrane was broken and the silica material was immersed in the solvent. The heat of the immersion was measured.

Elemental analysis is the common method used to characterize the composition of stationary phases. Determination of the carbon percentage enables one to calculate the coverage density of the stationary phase. In this case, the Berendsen equation is used [28]:

$$\alpha_{\text{RP}}^{\text{I}} = \frac{10^6 P_{\text{C}}}{1200 n_{\text{C}} - P_{\text{C}}(M_1 - n_{\text{X}})} \times \frac{1}{S_{\text{BET}}} \quad (1)$$

$\alpha_{\text{RP}}^{\text{I}}$ , coverage density ( $\mu\text{mol}/\text{m}^2$ );  $P_{\text{C}}$ , percent of carbon (%);  $n_{\text{C}}$ , number of carbon atoms in the ligand;  $M_1$ , molar mass of the ligand;  $n_{\text{X}}$ , number of reactive functional groups in on the silane;  $S_{\text{BET}}$ , specific surface area ( $\text{m}^2/\text{g}$ ).

### 2.3. Materials

Five sources of silica gel were used in the study: Kromasil 100 and Kromasil 300 (Akzo Nobel, Bohus, Sweden), Microsolv Technology (Eatontown, NJ, USA), Silpearl (Glaswork, Czech Republic), SG 7/G (Slovak Academy of Sciences, Slovakia) Lichrosorb and LiChrospher from Merck (Darmstadt, Germany). The solid support of the in-house made phases was Kromasil 100. Parameters of the silica gels used in the study are listed in Table 1.

Six chromatographic columns were studied. All the columns were prepared from the same batch of silica particles. The silica gel was chemically modified with chlorodimethyloctadecylsilane and chlorotrimethylsilane (Wacker GmbH, Munich,

Germany). Morpholine was purchased from Sigma–Aldrich Chemie (Steinheim, Germany).

All solvents were HPLC grade, purchased from J.T. Baker (Deventer, The Netherlands). Water was purified using a Milli-Q system (Millipore, El Paso, TX, USA). Changing of the proportion of octadecyldimethylchlorosilane and an activator (morpholine) during synthesis, the series of stationary phases with different densities of octadecyl ligands was obtained. Properties of these stationary phases were presented in the previous works [29].

The characteristics of the stationary phases are listed in Table 2. All eluents were degassed in an ultrasonic bath under vacuum.

## 3. Results and discussion

### 3.1. Determination of accessible silanols on silica surface

Solvents adsorb on the silica surface, but the mechanism of the adsorption depends on the properties of the solvent molecules. In the case of hexane, it can interact with the silica surface only due to nonspecific dispersive forces. Methanol can interact using dispersive forces and hydrogen bonds. The energy of hydrogen bonds ( $E_{\text{H}}$ ) is on the order of magnitude of 20 kJ/mol whereas the energy of dipole–dipole interactions is in the range 0.6–2 kJ/mol. The energy of dispersive London forces is also about 2 kJ/mol [25]. The energy of hydrogen bonds is at least 10 times higher than energy of dispersive interaction.

All of the solvents may act with the silica surface due to non-specific interactions (van der Waals forces, London forces) but only methanol has specific polar interactions (hydrogen bonding and dipole–dipole). In this case the heat of adsorption is higher for alcohols than for hydrocarbons [24,25]. Data are listed in Table 3.

The heat of hydrocarbon immersion (normal alkanes) on the silica gel surface in principle, is independent of the chain length [24] (0.065 and 0.066 J/m<sup>2</sup> for hexane and heptane, respectively). It is also almost constant for water and alcohols [19] (0.17, 0.18, 0.17, 0.16 J/m<sup>2</sup> for water, methanol, ethanol, and 2-propanol, respectively). Fig. 1 summarizes the differences between the two classes of compounds.

The heat of hexane immersion depends only on the dispersive forces. In the case of methanol, the thermal effect is a sum of dispersive forces and polar interactions.

$$\Delta H_{\text{T}} = \Delta H_{\text{D}} + \Delta H_{\text{S}} \quad (2)$$

**Table 2**  
Coverage density of stationary bonded phases.

Phase code	Carbon load ( $P_{\text{C}}$ ) (%)	Coverage density ( $\alpha_{\text{RP}}$ ) ( $\mu\text{mol}/\text{m}^2$ )
# 1 (C18)	2.42	0.33
# 2 (C18)	7.55	1.11
# 3 (C18)	10.88	1.68
# 4 (C18)	17.27	2.95
# 5 (C18)	18.70	3.27
# 6 (C1)	4.21	4.08

**Table 3**  
Heats of methanol and hexane immersion on the tested materials (raw data).

Material	Heat of methanol immersion (J/g)	Heat of hexane immersion (J/g)
Silica gels		
Kromasil 100	63.21	14.81
Kromasil 300	24.02	5.40
Microsolv technology	73.05	18.33
LiChrospher Si 100	85.58	17.17
Silpearl	69.54	24.43
SG 7/G	69.54	24.43
Lichrosorb Si 60	66.17	21.19
Octadecyl stationary phases		
# 1 (C18)	46.02	14.79
# 2 (C18)	34.40	12.76
# 3 (C18)	25.92	12.55
# 4 (C18)	14.65	9.55
# 5 (C18)	14.19	9.38
# 6 (C1)	11.00	7.60

where  $\Delta H_T$  is the total thermal effect observed ( $\text{J/m}^2$ ),  $\Delta H_D$  is a thermal effect connected with dispersive forces interactions ( $\text{J/m}^2$ ) and  $\Delta H_S$  is a heat of specific interactions ( $\text{J/m}^2$ ).

If it is assumed that the  $\Delta H_T$  value is represented by the heat of methanol immersion and the  $\Delta H_D$  is the heat of hexane immersion, then the contribution of the polar heat interactions ( $\Delta H_S$ ) may be calculated.

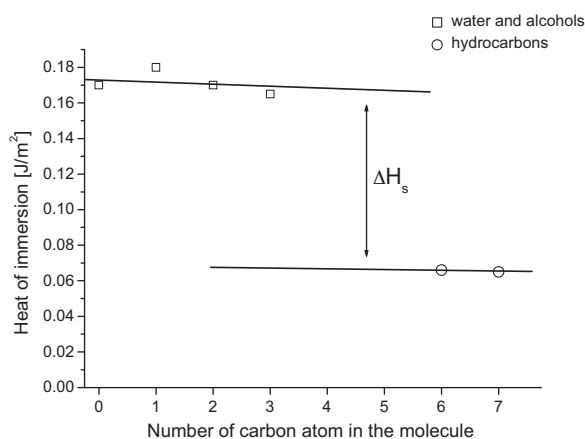
Then, the concentration of the silanols on the surface may be calculated from the following equation:

$$\alpha_{\text{OH}} = \frac{\Delta H_S}{E_H} \quad (\text{mmol/m}^2) \quad (3)$$

where  $\alpha_{\text{OH}}$  is a concentration of surface silanols and  $E_H$  is the energy of hydrogen bond ( $\text{kJ/mol}$ ). Concentration of silanols may be next recalculated to  $\mu\text{mol/m}^2$ .

The energy of hydrogen bond formed between oxygen and hydroxyl group ( $\text{O}-\text{H}\cdots\text{O}$ ) is in the range 19–21  $\text{kJ/mol}$  [25]. The results obtained are presented in Table 4 and they are in agreement with data found in the literature. Data presented in the literature do not correspond to all of investigated samples. It is shown to compare the oldest results and these obtained using the presented methodology.

The concentrations of residual silanols on the silica surfaces presented in the literature are changing. These values depend on methodology in which it was measured. At this time it is difficult to choose the best one. The methodology reported here gives the results which are consistent with data presented in literature. However, the average equals 7.51. Measured values of surface silanol



**Fig. 1.** Changes of hydrocarbon and alcohol heat of immersion on the silica gel surface.

**Table 4**  
Calculated concentrations of silanols on the silica gel surface in the present study and presented in the literature. Literature data do not corresponds to following silica gels.

Silica gel	Measured concentration of silanols ( $\mu\text{mol/m}^2$ )	Concentration of silanols on different silica gels presented in the literature ( $\mu\text{mol/m}^2$ )
Kromasil 100	7.73	
Kromasil 300	8.06	7.1 [30]
Microsolv Technology	7.81	7.6 [31]
LiChrosorb Si 60	7.50	7.6–7.8 [32]
LiChrospher Si 100	8.55	$8 \pm 0.1$ [3,33]
Silpearl	6.13	$8.44 \pm 0.1$ [34,35]
SG 7/G	6.26	6.21 [36,37]

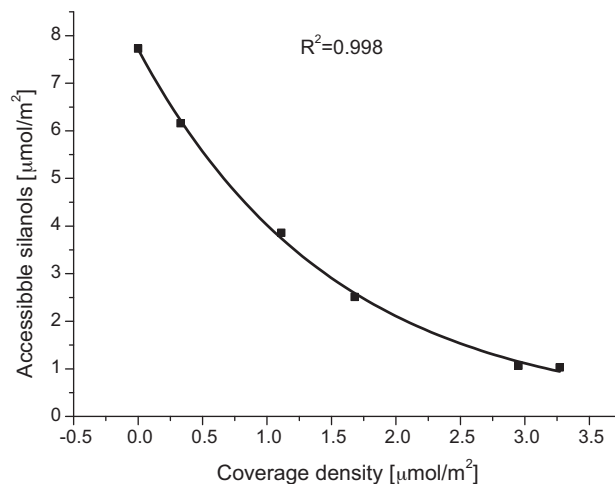
concentration are in the range typical for silica gel measured in different methods, with average 7.43. It suggests that the methodology may be used for investigation of silanol groups on silica surfaces. Additionally, it can make a compromise between different methods, commonly used by many of authors.

### 3.2. Determination of accessible silanols on chemically bonded phases

A similar calculation may be done for determining the number of residual accessible silanols in the structure of the bonded stationary phase. First of all, the term residual accessible silanols must be defined. Not all of the residual silanols present in the stationary phase are accessible. This accessibility means the possibility for interaction with the solute or with mobile phase components. As was mentioned in the previous work, residual silanols are solvated by water or methanol molecules via hydrogen bonding [29]. In the case of a solute which can be a donor or acceptor of a hydrogen bond, competition between the solvent and the solute for interaction with residual silanols is observed. As results tailing peaks are observed, especially for elution of amines. Thus, the number of accessible residual silanols is equal to the number of hydrogen bonds created between the solvent and the stationary phase.

The calculated number of residual silanols for a series of stationary phases is presented in Fig. 2. The correlation coefficient ( $R^2$ ) of this dependence is equal 0.998.

The decrease of the accessible silanol concentration is caused by two effects. Firstly, the organic ligands bonded to the silica surface reduce number of residual silanols. The number of reduced silanols is equal to the coverage density of bonded ligands.



**Fig. 2.** Changes of the concentration of accessible silanols with surface coverage density of organic ligands.

Additionally, ligands possess two methyl groups connected to a silicon atom. These groups shield some part of the surface and block some residual silanols. Thus, the decrease of the accessible silanol number is non-linear. As was mentioned by Nawrocki [5], for high coverage stationary phases only about 5% of residual silanols are a strong polar adsorption center. From the data obtained for the stationary phase with the highest coverage density ( $\alpha_{RP} = 4.08 \mu\text{mol}/\text{m}^2$ ), the number of accessible silanols equals  $0.54 \mu\text{mol}/\text{m}^2$ . If it is assumed that the total concentration of silanols on the silica surface is  $7.73 \mu\text{mol}/\text{m}^2$ , then the calculated number of residual silanols able to hydrogen bond are about 15% of residual silanols present on the stationary phase surface.

As determined in previous papers [29,38] for high coverage bonded stationary phases, the free volume between bonded ligands is low and penetration of solvent molecules to the silica surface is hampered. If one extrapolates the plot in Fig. 2 to a stationary phase which is dense enough to block and shield all of the residual silanols, the heat of methanol and hexane immersion should be the same and thus the number of accessible silanols equals zero.

These results confirm the effectiveness of the methodology described in this study for the determination of the number of residual silanols on unmodified and chemically modified silica.

#### 4. Conclusions

This study presents a calorimetric method for the determination of the number of accessible silanols. Based on the difference in thermal effects of surface immersion of methanol and hexane the number of hydrogen bonds created was calculated. This method may be used for silanol determination on bare silica gel. It gives results similar to data presented in the literature. The presented methodology may be also used for bonded stationary phase characterization by determining the number of silanols which are available for hydrogen bond interactions during chromatographic elution.

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