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**Note**

**Determination of surface hydroxyl groups on silanized silica gels for reversed-phase liquid chromatography**

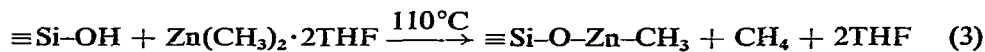
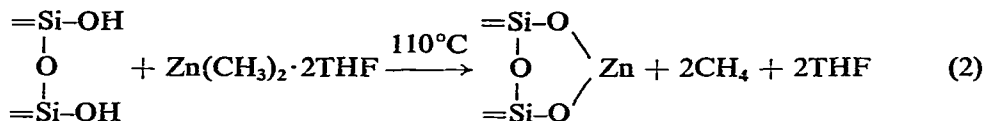
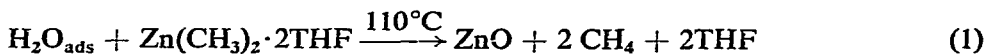
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The chromatographic properties of silica gels used for reversed-phase liquid chromatography (RPLC) are strongly dependent upon the silanization procedure<sup>1,2</sup>. The surface silanol groups of silica gel react only partially with a di- or trichlorosilane and the remaining hydroxyl groups must be “capped” by reaction with a monofunctional reagent such as trimethylchlorosilane, hexamethyldisilazane, etc. The quality of the resulting sorbent can then be checked by a standard chromatographic procedure or adsorption of methyl red<sup>3,4</sup>.

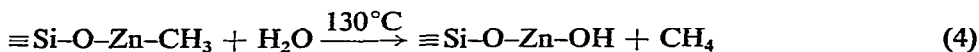
Recently, we developed a direct pulse chromatographic determination of surface hydroxyl groups and/or adsorbed water<sup>5</sup>. This pulse method is based on the reaction between active hydrogen and the dimethylzinc tetrahydrofuran (THF) complex (DMZ), a method proposed earlier by Hanke<sup>6</sup>.



However, the two methods differ substantially in the reaction conditions and the experimental technique. In contrast to Hanke<sup>6</sup>, who used a classical volumetric apparatus and a liquid reagent at ambient temperature, we have utilized<sup>5</sup> the pulse introduction of a gaseous reagent at elevated temperature. Our experimental technique makes it possible to measure even small amounts of evolved methane by means of a gas chromatographic (GC) detector. It is therefore more sensitive, and a complete determination can be performed in minutes using small amounts of sample ( $\approx 10$  mg) and reagent ( $\approx 50$   $\mu$ l).

The method was used successfully for the characterization of different heterogeneous catalysts<sup>7,8</sup>. With this method, Malinowski and co-workers<sup>9</sup> achieved results in good accord with the titration of surface hydroxyl groups by means of alkali-metal naphthenides.

Moreover, a water "retitration" after the DMZ treatment makes it possible to distinguish between the isolated hydroxyl groups, which have reacted with DMZ according to eqn. 3, and the sum of adjacent silanol groups plus adsorbed water, eqns. 1 and 2. When water is introduced onto a sample which has previously been treated with DMZ an additional amount of methane is liberated:



This has been shown by experiments with meta-kaolin<sup>10</sup> bearing mainly isolated hydroxyl groups on its surface<sup>11</sup>.

Despite the important effect of free silanol groups on the chromatographic properties of RPLC sorbents, until now no suitable method for their direct determination has been described. In this paper, we report the determination of such groups and/or adsorbed water on various RPLC sorbents using the above pulse chromatographic method<sup>5</sup>.

#### EXPERIMENTAL

The DMZ reagent was prepared according to Thiele<sup>12</sup>, purified by distillation and stored in sealed glass ampoules. The surface areas of commercial reversed-phase sorbents (I-VII) of different origin taken at random (Laboratorní Přístroje, Prague, Czechoslovakia; Lachema, Brno, Czechoslovakia; Macherey, Nagel & Co., Düren, G.F.R.; E. Merck, Darmstadt, G.F.R.; Shandon Southern Products, Runcorn, Great Britain) as well as of samples VIII and IX (Laboratory of Synthetic Fuels, Prague Institute of Technology) were estimated by the BET method. An unsilanized silica gel having a specific surface area of 454 m<sup>2</sup>/g served as a standard (see ref. 5).

A diagram of the apparatus is shown in Fig. 1. Helium used as carrier gas (20-30 ml/min) was carefully dried by passing it through columns of silica gel and molecular sieve. A 10-50 mg sample was placed into a glass reactor (Fig. 2), which

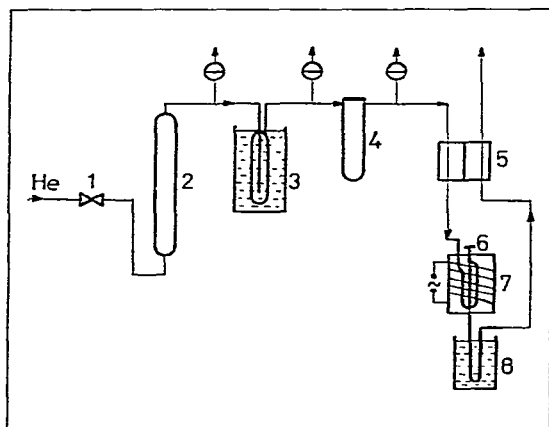


Fig. 1. Schematic diagram of the apparatus: 1 = needle valve; 2 = silica gel column; 3 = cooled molecular sieve column; 4 = flow-meter; 5 = katharometer; 6 = septum cap; 7 = electric oven; 8 = cooling bath.

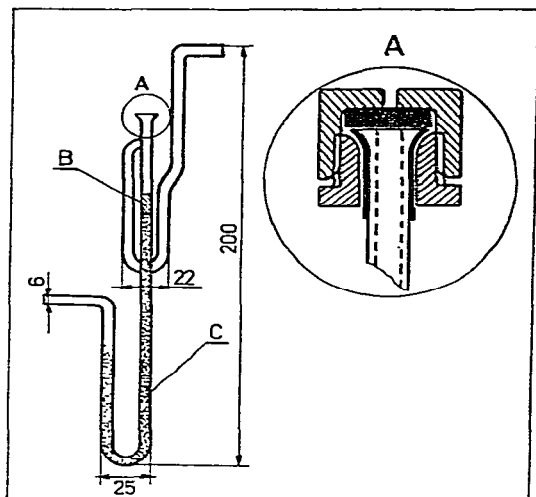


Fig. 2. Diagram of the glass reactor: A = septum in a screw cap; B = examined sample; C = part of the reactor packed with glass spheres.

was packed with small glass spheres. All samples were dried in the reactor (20 ml He/min) for 2 h prior to each measurement. The lower part of the reactor, which was cooled with a mixture of solid  $\text{CO}_2$  and ethanol, served as a trap for unreacted reagent, THF and water. The DMZ reagent was injected in small portions ( $1-2 \mu\text{l}$ ) through a septum. The pulses of methane formed during the surface reaction at about  $110^\circ\text{C}$  were detected by means of a katharometer, which was calibrated after each experiment by using a known amount of methane. Details of the procedure (Fig. 3) are described elsewhere<sup>5</sup>.

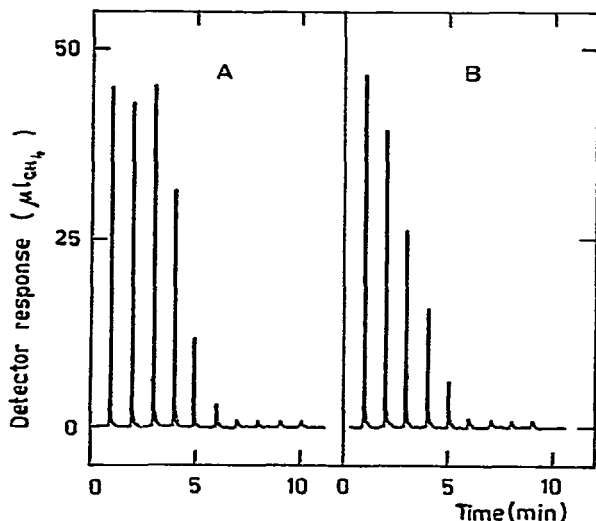


Fig. 3. Typical record of a complete determination for sample IX (6.9 mg): A, "titration" of hydroxyl groups and/or adsorbed water with DMZ ( $110^\circ\text{C}$ ); B, "retitration" with water ( $130^\circ\text{C}$ ).

In the determination of the isolated hydroxyl groups, the sample which had previously been treated with DMZ was flushed with dry helium at 150°C for 2 h. Small amounts of water (1–2  $\mu$ l) were then introduced to the reactor at 130–140°C and the amount of methane liberated, which corresponds to the content of isolated hydroxyl groups according to eqn. 4, was detected by the katharometer. Under standard conditions, the relative error of the determination of total hydroxyl groups and/or water,  $c_t$ , did not exceed 10% provided the peak heights were used for the calculation; that for the concentration of isolated hydroxyl groups,  $c_i$ , is about 25%.

## RESULTS AND DISCUSSION

The results of our experiments are given in Table I as the number of hydroxyl groups per unit area of the sorbent surface (OH per  $\text{nm}^2$ ). The samples examined differ markedly, but all values of  $c_t$  are surprisingly high compared with unsilanized silica gel (sample X). The observed differences may be due to the various silanization procedures used by manufacturers.

TABLE I

### SURFACE CONCENTRATIONS OF SILANOL GROUPS AND/OR WATER ON VARIOUS RPLC SORBENTS

$N_c$  = Number of carbon atoms in bonded alkyl groups.

Sample	$N_c$	Surface area ( $\text{m}^2/\text{g}$ )	Drying temp. ( $^{\circ}\text{C}$ )	Concentration		
				$c_t$ (OH per $\text{nm}^2$ )	$c_i$ (OH per $\text{nm}^2$ )	$c_w$ ( $\text{H}_2\text{O}$ per $\text{nm}^2$ )
I	1	126	150	5.2	1.3	1.95
			185	4.6	1.4	1.60
			210	4.2	1.1	1.55
II	1	535	150	1.4	0.2	0.60
III	8	102	150	2.7	0.5	1.10
IV	18	87	150	2.2	0.1	1.05
V	18	147	150	1.1	0.2	0.45
VI	18	190	150	1.7	0.5	0.60
VII	18	210	150	2.2	0.5	0.85
VIII	18	66	150	2.8	0.6	1.10
IX*	18	66	150	10.0	6.6	1.70
X**	0	454	150	2.4	0.1	—

\* Sample VIII before "capping" with trimethylchlorosilane.

\*\* Untreated silica gel (for comparison see refs. 5, 13).

A polymeric network is believed to be formed during silanization<sup>14</sup>, in which a relatively large amount of water can be trapped. Thus, we have assumed that the relatively high  $c_t$  values are caused mainly by this sorbed water. In order to test this hypothesis we dried the randomly chosen sample I at different temperatures (Table I). The total concentration,  $c_t$ , was found to decrease with increasing temperature of drying, in contrast to the concentration of isolated hydroxyl groups,  $c_i$ .

In the polymeric network, the residual hydroxyl groups are randomly orientated. Therefore, the concentration of geminal and vicinal hydroxyl groups is assumed

to be negligible and the concentration of the water trapped in the surface polymeric layer may approximately be expressed as  $c_w$ :

$$c_w \doteq (c_t - c_1)/2 \quad (5)$$

The highest concentration of isolated hydroxyl groups (6.6 OH per nm<sup>2</sup>) was determined on a silica gel treated with trichlorooctadecylsilane<sup>15</sup> (sample IX). This concentration was strongly reduced by "capping" with trimethylchlorosilane<sup>15</sup> and the resulting sample (VIII) exhibits only 0.6 OH per nm<sup>2</sup>. However,  $c_w$  was reduced only from 1.7 (sample IX) to 1.1 H<sub>2</sub>O per nm<sup>2</sup> (sample VIII).

A poor correlation (correlation coefficient 0.831) has been found between  $c_1$  and  $c_w$  calculated according to eqn. 5 for samples (I–VIII) dried at 150°C. Thus, the efficiency of the capping procedure is characterized by the concentration of isolated hydroxyl groups,  $c_1$ , which is independent of the concentration of adsorbed water,  $c_w$ . On the other hand, the total concentration of hydroxyl groups and/or adsorbed water,  $c_t$ , depends mainly upon the structure of the surface layer formed in the course of silanization.

#### ACKNOWLEDGEMENT

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