

Letter to the Editor

Determination of hydroxyl groups and water content in silica by nuclear magnetic resonance spectroscopy

Sir,

Holík and Matějková¹ recently reported results on the determination of residual hydroxyl groups on silanized silica gel which differed markedly from our results² based on a chemical reaction of hydroxyl groups and/or adsorbed water with a dimethylzinc complex. According to the former authors, the hydroxyl concentration determined by means of hydrogen–deuterium exchange lies between 4 and 8 OH groups per nm² and the water content corresponds to about 1.5–3 H₂O groups per nm². This water content, determined by the displacement of adsorbed water by deuterated trifluoroacetic acid, was in good agreement with thermogravimetric measurements. Our chemical determination² of hydroxyl groups and adsorbed water showed 0.1–1.5 OH groups per nm² and 0.5–2 H₂O groups per nm². Thus the question arises, what is the reason for this discrepancy.

First, the recent paper does not mention any drying of samples prior to the measurements. It is well known that silica gel rehydrates on standing in air and rehydrated samples show a high content of adsorbed or even capillary condensed water. In such cases, concentrations above 8 OH groups per nm² have been found even using chemical methods³. However, a part of this water is lost rapidly by heating of samples at 150–200°C. Also unclear is what is the “water content” measured by means of thermogravimetry¹. Owing to the dehydration of vicinal and/or geminal hydroxyl groups it is almost impossible to distinguish between adsorbed water and hydroxyl groups using thermogravimetry (TG)⁴. Moreover, Holík and Matějková reported neither any TG curves nor the conditions of their TG experiments.

Another possible source of the differences between chemical determinations and the hydrogen–deuterium exchange is well known⁴. On silanized silica surfaces, there may be hydroxyl groups that are inaccessible to the relatively bulky molecules of chemical reagents⁵, although these hydroxyl groups can be determined using deuterium-labelled water, the molecules of which are relatively small and readily permeative. On the other hand, the molecular size of deuterated trifluoroacetic acid, which is recommended by Holík and Matějková for the quantitative exchange of adsorbed water, is comparable with the molecular sizes of other chemical reagents.

The chemical determination of surface hydroxyls is believed to be closely dependent on the sorption properties of the silanized silicas, because the chemical reaction as well as the sorption of relatively bulky solute molecules are sensitive to the accessible hydroxyl groups only. However, there is an additional amount of inaccessible hydroxyl groups shielded by bonded alkyl chains. This is also shown by the results of Holík and Matějková. The relative changes of hydroxyl concentration due to drying, silanization and capping, which they have reported, are surprisingly low —

see, for example, Samples 1–4, because they are superimposed on the “background” of the unknown concentration of these inaccessible hydroxyls.

The feasibility of the two methods should be judged only on the basis of relationships between the hydroxyl concentration and the chromatographic properties of silanized silica gels.

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Science,
Praha 6-Suchbát 2 (Czechoslovakia)*

L. NONDEK

- 1 M. Holik and B. Matějková, *J. Chromatogr.*, 213 (1981) 33.
- 2 L. Nondek and V. Vyskočil, *J. Chromatogr.*, 206 (1981) 581.
- 3 W. Hanke, *Z. Anorg. Allg. Chem.*, 395 (1973) 191.
- 4 K. K. Unger, *Porous Silica (Journal of Chromatography Library, Vol. 16)*. Elsevier, Amsterdam. Oxford, New York, 1979, Ch. 3.1.1.
- 5 R. K. Iler, *J. Chromatogr.*, 209 (1981) 341.

(Received October 28th, 1981)