

# The nature of silanol groups on the surfaces of silica, modified silica and some silica based materials

Alfred A. Christy

Department of Science, Faculty of Engineering and Science, University of Agder, Serviceboks  
422, N-4604 Kristiansand, Norway

email: alfred.christy@uia.no

**Keywords:** Silica gel, Silanol groups, water adsorption, Near infrared spectroscopy, second derivative profiles

**Abstract.** Silica gel, a material that is produced from the condensation polymerisation of silicic acid, contains surface silanol groups formed during the condensation. The silanol groups on the surface are mostly of free and vicinal silanol groups. These silanol groups can be modified in several different ways. Thermal treatment and hydrothermal treatment can be carried out to alter the concentration proportions between free and hydrogen bonded silanol groups on the surface. They can also be chemically treated with suitable chlorosilanes to modify the silanol groups into polar or non polar materials that can be used in separation science.

This article explores the chemical nature of silanol groups on the surfaces of different materials. Near infrared reflectance spectroscopy was used as the instrumental technique in this study. The silanol groups classifications were made by analyzing the near infrared spectra obtained during the adsorption of water molecules. Absorption of the combination frequencies of water molecules in the region 5500- 5000  $\text{cm}^{-1}$  were used in characterizing the silanol groups on the surfaces. Second derivative technique was employed in the resolution and detailed analysis of these absorptions.

The study reveals that the materials contain free, vicinal and gem silanol groups. Silica gel contains free and vicinal silanol groups, thermally treated silica gel contains fewer vicinal silanol groups compared to the base silica gel, and hydrothermally treated silica gel contains higher concentrations of vicinal silanol groups compared to the base silica gel. Furthermore, the chemically modified silica gel contains vicinal or geminal silanol groups depending on the type of functionality introduced.

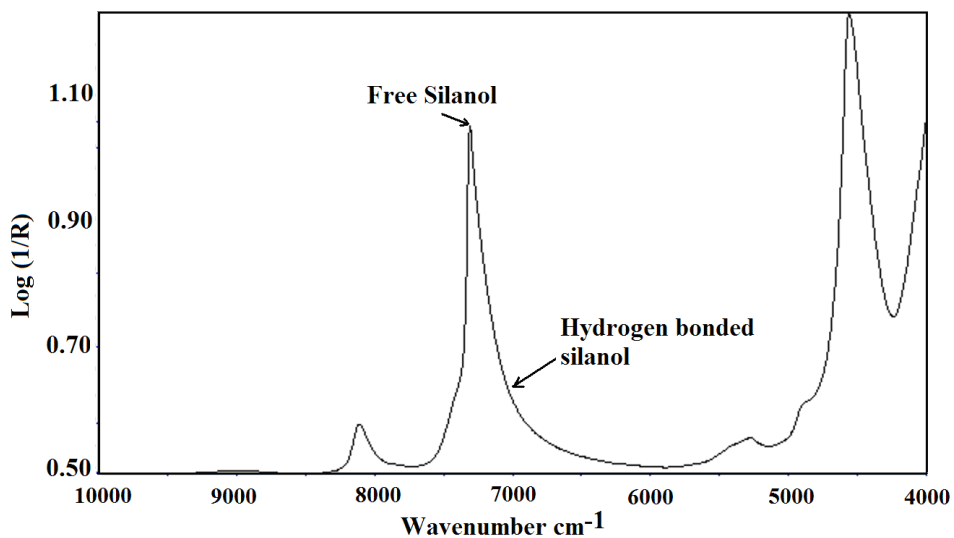
## Introduction

Silica gel, a material used in several different fields including catalysis, separation science and polymers, is prepared by the condensation polymerisation of silicic acid. The material so produced contains free and hydrogen bonded silanol groups on the surface. The surface silanol groups are polarised due to hydrogen bondings and the exhibit three different degrees of acidity. The acidic nature of the silanol groups is responsible for the adsorption properties of silica gel. The polarised silanol groups on the surface can adsorb water molecules and other polarised molecules by hydrogen bonding.

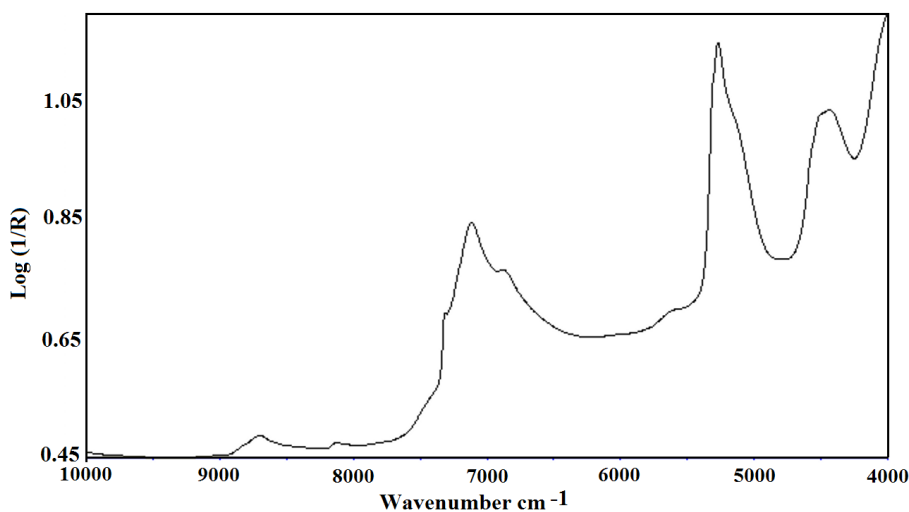
There have been several studies in the literature using mid-infrared and near- infrared spectroscopy dealing with the surface functionalities of silica gel surface and the type of bondings take place when water molecules are adsorbed onto the silica gel surface [1-15]. These studies gave some understanding of the functionalities on the silica gel surface. However, the models presented were not quite clear.

Christy [16] has studied several silica gel samples and their water adsorption evolutions using gravimetry and near infrared transmittance spectroscopy with the help of second derivative techniques and showed that the hydrogen bonded silanol groups adsorb water readily compared to free silanol groups. Furthermore, an equal proportion of free and hydrogen bonded silanol groups are needed for effective water adsorption.

A completely dry silica gel sample gives a very simple near infrared spectrum in the region  $11000\text{-}4000\text{ cm}^{-1}$  (Fig.1). The spectral features change when the sample is exposed to the surroundings (Fig. 2). One can clearly observe that a peak arise in the region  $5300\text{-}5000\text{ cm}^{-1}$  purely from the water molecules adsorbed on the surface. A second derivative operation reveals that there are two different bands in this broad peak and the band at  $5270\text{ cm}^{-1}$  is due to the water molecules adsorbed onto hydrogen bonded silanol groups and the band at  $5314\text{ cm}^{-1}$  is due the water molecules adsorbed onto the free silanol groups on the surface [16]. Even though, the methodology used in this study is not direct, it gives clear picture of the nature of functionalities on silica gel surface.



*Fig. 1 Near infrared spectrum of dry silica gel sample*



*Fig. 2. Near infrared spectrum of the silica gel sample after adsorption of water*

The aim of this article is to provide some information on the surface functionalities of physically and chemically treated silica gel samples. A similar approach used in the study of silica gel samples in reference 16 was used in revealing the surface functionalities of the modified silica gel samples.

## Experimental

**Materials and preparation of the samples.** A silica gel sample with a surface area of 402 m<sup>2</sup> with a silanol number 3.1 was used to illustrate the surface functionalities. The modification of the sample was carried out separately. Some chemically derived silica gel samples were bought from Machery Nagel. These samples were parts of the Chromabond standard development kit. These materials are used in preparing samples for HPLC analysis and to remove interfering components in the analyte. Silica samples with C18, cation exchange SA (SCX), anion exchange SB (SAX) modifications with a particle size of 45 µm and a pore size of 60 Å were used. These samples were not encapped for rest silanol groups.

**Heat treatment.** A ceramic heater (BA electric Bunsen from Electrothermal, UK) controlled by an external power supply was used in heating the samples. The temperature of the sample was measured by using a digital thermometer with a K type thermocouple (Clas Ohlson, UK). A powerful vacuum pump (Edwards, UK) was used in the evacuation of the samples. The sample was heated to 750 °C to eliminate the hydrogen bonded vicinal groups.

**Hydrothermal treatment.** Hydrothermal experiment was carried out in a steel bomb of 25 cm in length and 1 cm in internal diameter. One gram of dry silica gel sample and 0.4 cm<sup>3</sup> of distilled water were added to the bomb and sealed. The bomb was then placed in a chromatographic oven set to 160 °C and left for two hours. The hydrothermally treated sample was removed and evacuated at 200 °C to remove physically adsorbed water from the surface [17].

**Chemically modified silica gel:** These samples were parts of the Chromabond standard development kit. These materials are used in preparing samples for HPLC analysis and to remove interfering components in the analyte. Silica gel with C18, cation exchange SA (SCX), anion exchange SB (SAX) modifications with a particle size of 45 µm and a pore size of 60 Å were used.

**Near infrared (NIR) measurements.** The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer (Perkin Elmer Ltd, UK) equipped with a PerkinElmer transmittance accessory and deuterated triglycine sulphate detector. Each of the samples (around 0.3g) dried as mentioned above, cooled and transferred to a sample cup with an IR transparent window. The near infrared measurements were made using a Perkin Elmer Spectrum One NTS FT-NIR spectrometer (Perkin Elmer Ltd, UK) equipped with a PerkinElmer transmittance accessory and deuterated triglycine sulphate detector. The sample cup containing the silica gel sample was placed directly on the crystal of the transmittance accessory and allowed to equilibrate with the surrounding air, and the near infrared spectrum of the sample was measured in the region 10,000–4000 cm<sup>-1</sup> at a resolution of 16 cm<sup>-1</sup>. A total of 30 scans were made each time.

The reflectance spectra were then converted to log (1/R) format and derivated twice and saved. These spectra were used in the detailed analysis of the silanol groups on silica gel sample. The band positions of the OH combination frequency of water molecules were used in characterising the surface silanol groups on the surfaces of different materials.

## Results and discussion

A near infrared spectrum of the dry silica gel sample used in this study is shown in Fig. 1. The near infrared band assignments for silica gel samples and its derivatives with water

molecules adsorbed is shown in Table 1. The spectrum in Fig. 1 shows the first overtone of the OH stretching vibrations of the free silanol groups at  $7316\text{ cm}^{-1}$ . This peak is not symmetrical and a part of the absorptions in this region arise also from the overtones of the silanol groups involved in hydrogen bondings with their neighbours.

*Table 1 Near Infrared band assignments for silica gel samples and its derivative*

<b>Peak (<math>\text{cm}^{-1}</math>)</b>	<b>Band assignment</b>
9200-7600	CH second overtone and OH combination
7316	Overtone-OH stretchings-
7225- 6860	free silanol groups Silanol groups hydrogen bonded to water molecules Water molecules hydrogen bonded to silanol groups, water molecules hydrogen bonded to other water molecules
5950-5300	First CH overtone
5311	Combination band OH stretching and bending water molecules hydrogen bonded to free silanol groups Water molecules hydrogen bonded to vicinal silanol groups (geminal silanol groups)
5270 (5265)	Water molecules hydrogen bonded to vicinal (and geminal) silanol groups
4579	Combination band OH stretching and siloxane (Si-O-Si) bending
4500-4400	Combination band silanol OH stretching (hydrogen bonded to water molecules)and siloxane (Si-O-Si) bending

**water molecule hydrogen bonded to vicinal silanol groups**

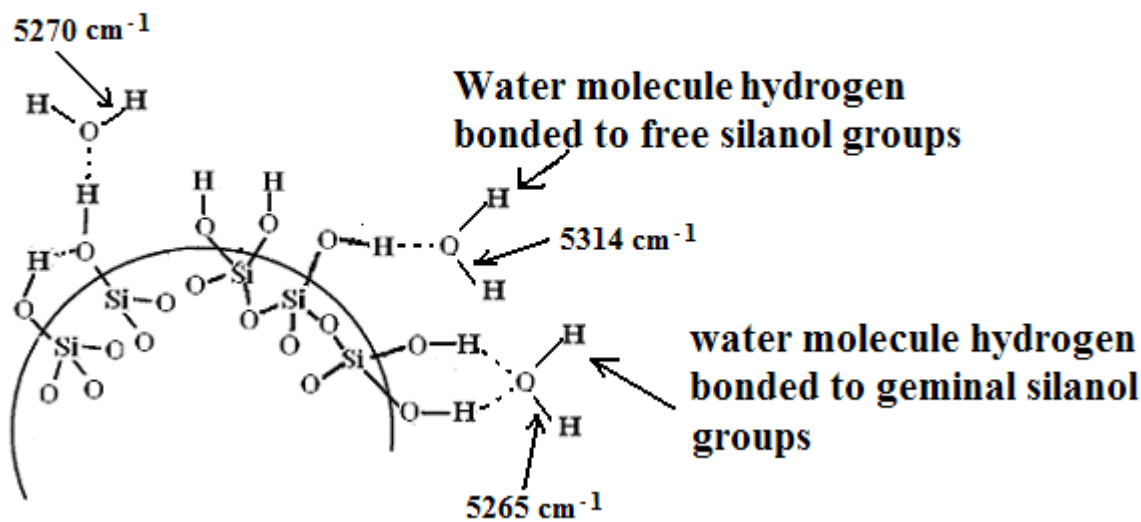


Fig. 3. The combination frequency of O-H stretching and bending absorptions of water molecules hydrogen bonded to different surface silanol groups. The figure was modified from Ref. 18.

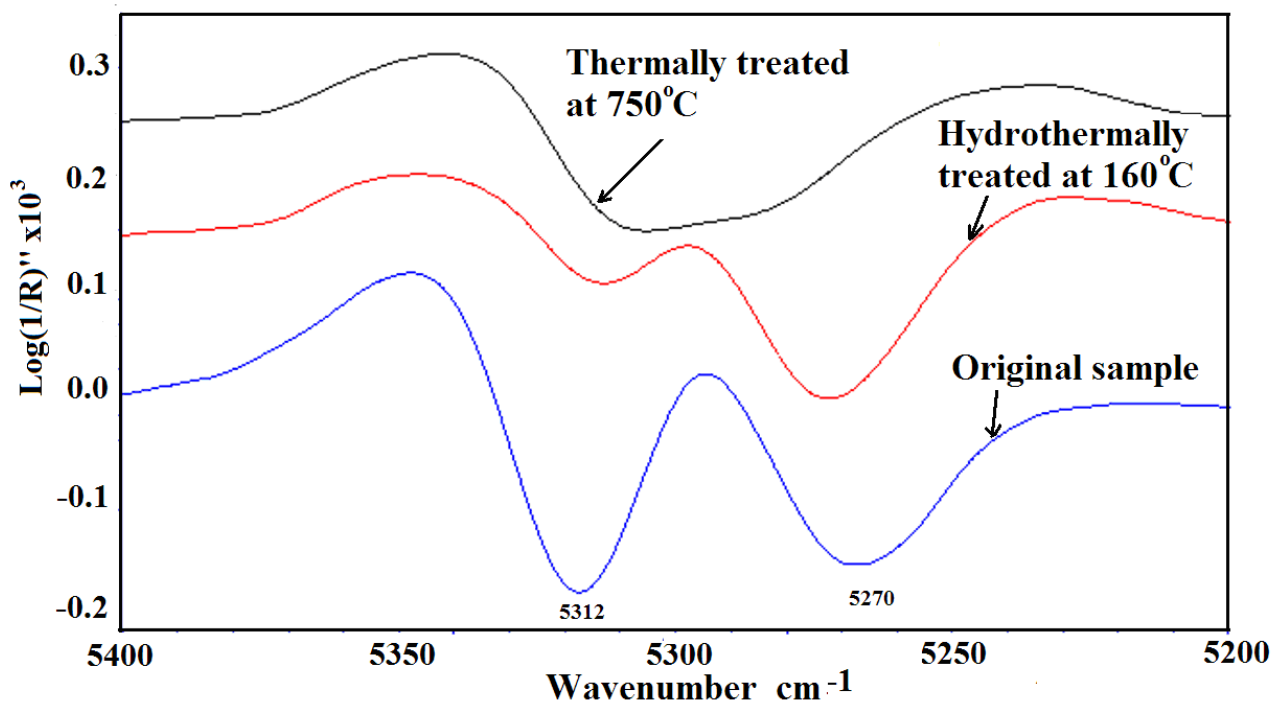


Fig. 4. Second derivative profiles of the near infrared spectra of silica gel sample and treated silica gel sample in the region 5400-5200  $\text{cm}^{-1}$ . Spectra are scale adjusted for clarity

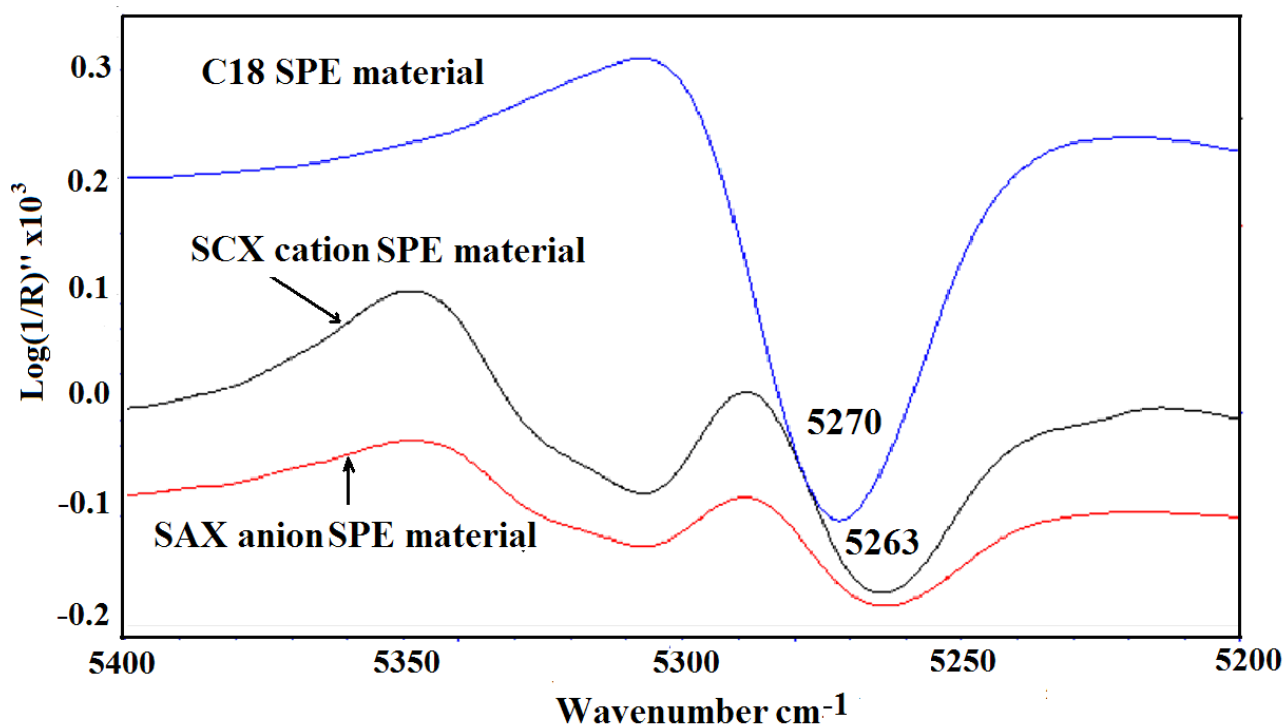


Fig. 5. Second derivative profiles of the near infrared spectra of chemically modified silica gel samples in the region  $5400\text{-}5200\text{ cm}^{-1}$ . Spectra are scale adjusted for clarity

Silica gel surface functionalities and the absorptions arising in the near infrared region are illustrated in Fig. 3. These details can be used in characterising the surface functionalities of the modified silica gel samples. Second derivative profiles of the near infrared spectra measured on the thermally treated, hydrothermally treated and chemically modified silica gel samples with adsorbed water molecules are shown in Fig. 4 and 5. The OH combination absorptions of the samples clearly show the differences that have taken place during the thermal treatment and hydrothermal treatment of the silica sample. The thermal treatment

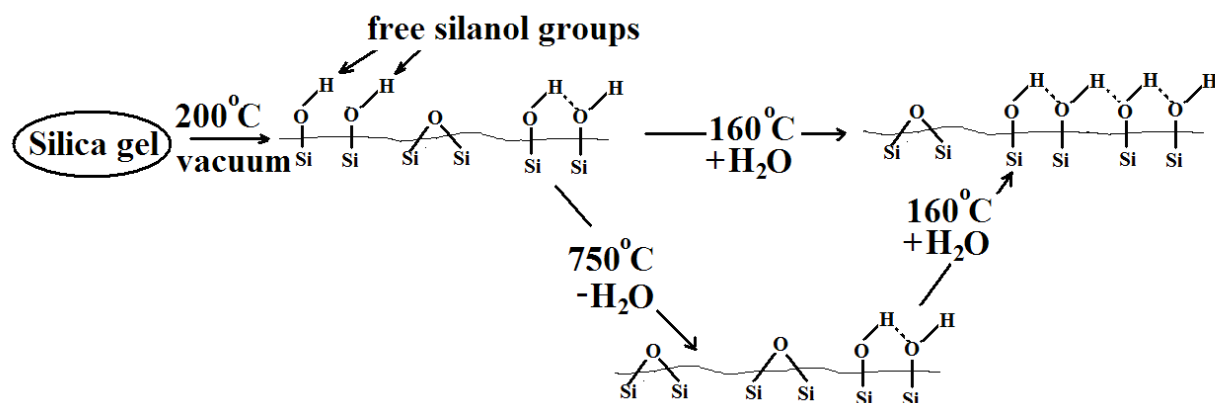


Fig. 6. Figure illustrating the changes taking place during the physical treatment of the silica gel sample. Figure modified from Ref. 17 with permission from Ind. & Eng. Chem. Res.

eliminates most of the hydrogen bonded silanol groups and hydrothermal treatment increases the relative concentration of the hydrogen bonded silanol groups. The identity of the hydrogen bonding in these treated samples is confirmed from the absorption at  $5270\text{ cm}^{-1}$  as vicinal OH groups. A figure illustrating the changes during these physical treatments of the silica gel sample is given in Fig. 6.

The OH combination absorptions arising from the chemically treated samples shown in Figure 5 show that the C18 chemically modified sample contains no free silanol groups on the surface. In contrast, the cationic and anionic modified samples contain both free silanol groups and hydrogen bonded silanol groups in the samples. These spectra clearly show that there are rest silanol groups on the surfaces of all the chemically modified silica samples. The absorptions arising from the water molecules adsorbed onto the hydrogen bonded silanol groups on the surface of the C18 modified silica sample indicates that the rest silanol groups are of vicinal type at the same time the absorptions of the anionic and cationic modified samples indicate that the hydrogen bonded silanol groups are of geminal type.

## Conclusion

The use of near infrared spectroscopy and second derivative techniques in identifying rest silanol groups on physically and chemically modified silica gel samples are summarized in this article.

Near infrared reflectance accessory provides an easy sampling technique that requires almost no sample preparation. Second derivative techniques resolve the bands of the water OH combination absorption peaks effectively and reveal indirectly the positions of the bands related to specific types of silanol groups on the silica surface.

The presence of free silanol groups are confirmed by the absorption near  $5314\text{ cm}^{-1}$ . The presence of vicinal silanol groups are confirmed by the absorption near  $5314\text{ cm}^{-1}$  and the presence of geminal silanol groups are confirmed by the absorption near  $5263\text{ cm}^{-1}$ . The presence of free silanol groups are confirmed by the absorption near  $5314\text{ cm}^{-1}$ .

## References

- [1] J.H. Anderson, K.A. Wickersham, Near infrared Characterization of Water and Hydroxyl Groups on Silica Surfaces, *Surf. Sci.* 2 (1964) 251-260.
- [2] M.J.D. Low, N. Ramasubramanian, Infrared Study of Nature of Hydroxyl Groups on Surface of Porous Glass, *J. Phys. Chem.* 70, 9 (1966) 2740-2748.
- [3] C.G. Armistead, A. J. Tyler, F. H. Hambleton, S. A. Mitchell, J. A. Hockey, Surface Hydroxylation of Silica, *J. Phys. Chem.* 73, 11(1969) 3947-3953.
- [4] K. Klier, J.H. Shen, A.C. Zettlemyer, The Surface Hydroxylation of Silica, *J. Phys. Chem.* 77, 11 (1973) 1458-1465.
- [5] R.P. W. Scott, S. Traiman, Solute –Solvent Interactions on the Surface of Silica- Gel. 3. Multilayer Adsorption of Water on the Surface of Silica-Gel, *J. Chromatogr.* 196, (1980) 193-205.
- [6] J. Stone, G.E. Walrafen, Overtone Vibrations of OH Groups in Fused Silica Optical Fibers, *J. Chem. Phys.* 76, 4 (1982) 1712-1722.
- [7] S.G. Bush, J.W. Jorgenson, M.L. Miller, R.W. Linton, Transmission Near-infrared Technique for Evaluation and Relative Quantitation of Surface groups on Silica, *J. Chromatogr.* 260 (1983) 1-12.
- [8] S.G. Bush, J.W. Jorgenson, Confirmation and Application of Transmission Near-infrared Absorption Technique for Absolute Quantitation of Functional-Groups on Silica-gel, *J. Chromatogr.* 503(1990) 69-91.
- [9] H. Yamauchi, S. Kondo, The Structure of Water and Methanol Adsorbed on Silica Gel by FT-NIR spectroscopy, *Colloid. Polym. Sci.* 266 (1988) 855-861.
- [10] B.A. Morrow, A.J. McFarlan, Infrared and Gravimetric Study of an Aerosil and a Precipitated Silica using Chemical and H/D Exchange Probes, *Langmuir* 7 (1991)1695-1701.

- [11] E.D. Lipp, Near-infrared Spectroscopy of Silicon-Containing Materials, *Appl. Spectrosc. Rev.* 27, 4 (1992) 385-408.
- [12] H.P. Boehm, Chemical Identification of Surface Groups, in: D. D. Eley (ed.), *Advances in Catalysis*, Academic Press, New York, 1966, pp. 179-274.
- [13] P. Hoffman, E. Knozinger, Novel Aspects of IR Fourier Spectroscopy, *Surf. Sci.* 188 (1987) 181-198.
- [14] B.A. Morrow, I.A. Cody, L.S.M. Lee, Infrared Studies of Reactions on Oxide Surfaces .7. Mechanism of Adsorption of Water and Ammonia on Dehydroxylated Silica, *J. Phys. Chem.* 80 (1976) 2761-2767.
- [15] A. Burneau, O. Barres, J.P. Gallas, J.C. Lavalley, Comparative-Study of the Surface Hydroxyl-Groups of Fumed and Precipitated Silicas .2. Characterization by Infrared-Spectroscopy of the Interactions with Water, *Langmuir*, 6 (1990) 1364-1372.
- [16] A. A. Christy, New Insights into the Surface Functionalities and Adsorption Evolution of Water Molecules on Silica Gel Surface: A Study by Second Derivative Near Infrared Spectroscopy, *Vib. Spectrosc.*, 54, 1 (2010) 42-49.
- [17] A. A. Christy, Effect of Hydrothermal Treatment on Adsorption Properties of Silica Gel, *Ind. & Eng. Chem. Res.* 50 (9) (2011) 5543-5554.
- [18] A.A. Christy, The Nature of Rest Silanol Groups on the Surfaces of Silica Based Solid Phase Extraction Materials, *Adv. Mat. Res.*, 650 (2013) 66-71.