# Nanoporous silica glass sensibilisation in respect to the gas components detection

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Techniques and technology for a specific surface treatment of the nanoporous (~8 nm) silicate glass is presented and discussed. That treatment is aimed at the achievement of the sample sensitivity to individual chemical components of atmosphere and other gas mixtures. The treatment technology is based on the impregnation of the nanoporous glass plates with solutions of different pH and other colour indicators and dyes. After the solvent evaporation, the indicator molecules remain immobilized in the pores of glass. The immobilized molecules are able of active interaction with ambient gas molecules. Those interactions are specific and they reveal themselves in the samples spectral changes (in visible and infrared wave range), including spectral absorbance and fluorescence. So, it has turned out that a selective detection of the gas mixture components and estimation of its concentration are possible. Physical and chemical interpretations of the observed phenomena are presented.

Keywords: silicate porous glasses, glass surface properties, optical gas sensors, interface molecular interactions, chemical hard and soft acids and bases.

## 1. Introduction

Porous glasses, having pores sizes of hundred nanometers and less, proved to be the most convenient material for numerous applications [1, 2]. Wide prospects are opened by the porous glass surface modification with different passive and active agents in order to impart the required properties to the samples.

Among others, the glasses of the nanoscale porosity present very good prerequisites for the development of optical gas sensors. Firstly, the nanoporous samples with pores of about 10 nm have highly developed surface, a specific surface area being of $100 \text{ m}^2/\text{cm}^2$ and more. That provides a large contacting area with ambient gas and liquid media. Secondly, the nanoscale pores keep the samples transparent to the light in visible and near infra wave range as well as permeable to ambient gases and liquids. So, the obvious prospects for optical sensors developments are opened.

A method of introducing foreign inclusions into porous silicate glass has been invented quite a long time ago [3] but only during the past decade the intensive studies were undertaken, having as an object the organic and inorganic dye molecules

immobilized on the highly developed surface of the porous glass. An idea to impart the gas sensitivity to the nanoporous samples has appeared in the early 1980s [4, 5]. Since then, a rather long list of related papers has been published [6–12]. Nevertheless, many details of the interactions between a modifier, surface, and ambient medium require further investigations.

## 2. Original glass characterization

Our researches have led us to nanoporous sodium-borate-silicate glasses that turned out to be an almost optimum substrate for various molecular species for optical applications.

Original solid glass was a liquated sodium-borate-silica glass Na 7/23 with phase separation produced by a standard technology [1, 2]. The electron probe microanalysis of the original non-porous glass has shown that the $Na_2O$ content approximately equals 6.8%, boron oxide – 26.7%, silica – 66.0%.

Porous samples were produced using a stepwise thermal and chemical treatment according to a well-known Vycor process. A throughout porous structure, permeable to gases and vapours, was formed within a silica framework after an appropriate treatment in aqueous solution of 3 N hydrochloric acid, leaching-out the sodium-borate phase and annealing in air at +550 °C (1 hour) [2]. The $Na_2O$ content decreased to 0.2%, the $SiO_2$ content was about 87.5%.

Phase content was determined with the use of wide-angle X-ray techniques [13]. The silica matrix proved to be predominantly amorphous; the X-ray spectra of samples showed a broad maximum corresponding to the vitreous state of matter. Some additional information was obtained with the use of computer processing of the patterns. The crystallinity grade (silica of low syngony) in accordance with Ruland's method was found to be about 7%.

An appropriate processing of the taken adsorption isotherms in the area of capillary condensation has revealed the pore size distribution in the vicinity of 8 nm, the volume porosity being of 28%. Specific surface area was calculated upon a specific point B of the isotherm curve knee; obtained values were about 100 $m^2/cm^3$ [13].

Nanoporous samples have shown a clear isotherm of IV type (an A-subtype), according to the Gregg's classification [14]. That reveals the long-capillary shape of pores with open ends. The resulting porous structure was characterised by almost monodisperse distribution of pore sizes with maximum at 8.0 nm, the average porosity being about 28 vol%. The found dimensionality value was about 1.8, *i.e.*, the inner structure is essentially plane.

## 3. Spectral measurements

The infrared measurements were made with the use of an up-to-date IR Fourier--transform spectrometer 5DXC (Nicolett, USA) which enabled the reliable measurements on the samples with optical density up to 5 and higher.

Visible absorption spectra of the samples and of the impregnating solutions were run on a spectrophotometer СФ-26 (LOMO Corp., Russia) in the wave range 300–800 nm. In order to compensate the light scattering caused by the porous matrix, a "clean" porous sample was measured as a reference.

The fluorescence spectra were run with the use of a double monochromator ДФС-4 (LOMO Corp., Russia). In case of measurements in steady state, a porous matrix influence on the resulting response was rather negligible.

During experiments the samples were fixed on a holder placed within an evacuable light transparent cell. The gas mixture of desired content was let into that cell and the spectral transmittance or emission were measured.

Before taking the readings, the samples were kept in the analyzed gas mixture sufficiently long (10 min or longer). The reference spectral characteristics referred to the samples kept in normal laboratory atmosphere (relative humidity of 50% at 20 °C).

## 4. Optical characteristics of the samples

The optical properties of the samples were of most interest. The glass pore sizes were much less than the optical wave range 350–700 nm. A general run of the visible absorption spectrum of original porous samples in normal atmosphere demonstrated a monotonic drop in accordance with a well-known Rayleigh law ($\lambda^{-4}$). That corresponds to the light scattering by small irregularities in the glass bulk. Scattering intensity remarkably increases only at approaching to 350 nm.

Infrared spectra of the samples were much more informative. In Fig. 1 the spectra of clean porous glass are presented – optical density versus wave number. Noteworthy is that the majority of the researchers use the samples thoroughly dried and evacuated, usually at elevated temperatures. In contrast to that, our investigations
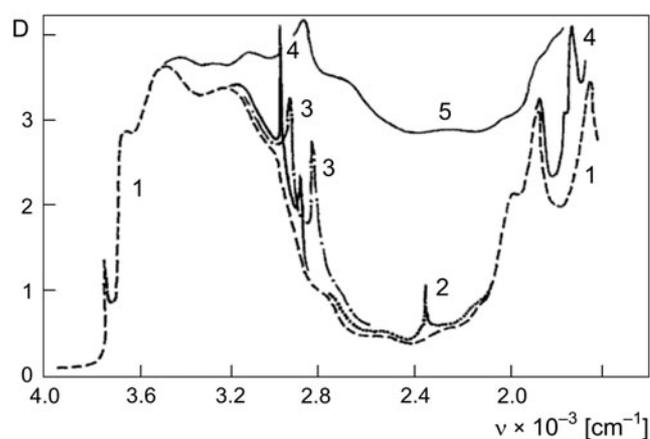


Fig. 1. Infrared absorption spectra of a nanoporous glass sample under different atmospheric conditions: 1 – air with relative humidity of 50% at 20 °C, 2 – air and carbon dioxide (10 vol%), 3 – air and methanol vapour (10 vol%), 4 – air and acetone vapour (10 vol%), 5 – air and ammonia vapour (10 vol%).

implied a spectral behaviour of porous samples in actual humid atmosphere; in these conditions the sample surface was significantly hydrated. Using a computerized Fourier-transform spectrometer, we have succeeded in the infrared spectra measurements of strongly absorbing samples and in the spectral lines attribution, see [13].

Due to highly developed surfaces of the samples, their spectra are effectively influenced by the components of ambient atmosphere, as shown in Fig. 1. Of special importance and interest is the found fact that various gas molecules influence the spectra in different ways. Ammonia vapours act as a spectrum smoothing agent (see spectrum 5) due to the formation of hydrogen bonds covering the surface on the whole, with the participation of $NH_4^+$ ions adsorbed on the Si–OH groups. These are the Brønsted's type sites. At the same time, there is a strong band in the spectrum (with maximum at 3000 cm$^{-1}$) assigned to the vibrations of adsorbed molecular $NH_3$ which reveals the surface sites of the Lewis' type. On the other hand, carbon dioxide, methanol and acetone vapours also produce the distinct peaks (spectra 2−4) attributed to valence and bending vibrations within immobilized molecules. These peaks are slightly shifted in regard to the spectra of isolated molecules. So, the spectral data confirm the concept of two surface adsorption sites known as Brønsted's and Lewis' sites.

The mentioned-above spectral changes turned out to be spontaneously reversible.

## 5. Purpose-aimed glass surface modification

A final purpose of present researches was to achieve samples sensitivity to gases. The infrared spectra discussed above were rather of pure scientific interest because the wave range used is not sufficiently supported instrumentally for applications in practical devices. Much more prospects open here for the compositions containing the chemically sensitive organic and metal-complex species immobilized on the inner surface of the glass nanopores. We have independently invented a method of the required immobilization.

An idea itself to put different dopants into porous silicate glass is obvious, it has appeared rather a long time ago [3]. An essence of our approach consisted in making the immobilized molecules (without porous structure collapsing) to interact directly and actively with molecules from ambient atmosphere. So, we have turned to the well-known chemical indicators of the media content. Firstly, to usual colour pH indicators, such as widely used phenolphthalein, thymol blue, bromocresol purple and others. Our aim was to make the indicator molecules work not in solution but in adsorbed state without solvent.

We have developed a procedure of porous matrix impregnation in solutions of the desired pH indicator after solvent evaporation. The samples were put into the solution and left there for 24 hours or longer until sorption equilibrium. Then the samples were taken out and dried at +50 °C in the air with the purpose to evacuate the residual solvent from the matrix. After such treatment the indicator molecules remained fixed

on the pores surface. The samples produced in this way gain the permeability to gases and inherent colouring in accordance with spectral absorbance of the immobilized indicator.

This procedure was useful for other colour indicators, such as metal-complexes on the basis of Co(II), Pd(II), Cu(II), Ru(II).

## 6. Immobilized colour pH indicators

Using an absorption spectroscopy technique, a correlative spectral analysis has been made on specific colour changes of certain usual acid-base indicators (like phenolphthalein, thymol blue, bromocresol purple and others). The indicator species were investigated both in the solutions and in the immobilized state on the nanopores surface being free of the solvent. Spectral characteristics were run in various acid-base conditions in the liquid solution or in the ambient gas medium.

For example, in Fig. 2**a** the spectra of the initial impregnating phenolphtalein solutions with various pH-values are presented. The pH-value was varied by means of the sodium carbonate addition in the solution. As an optimum composition, the 0.1% water-alcohol solution of phenolphthalein with addition of 2% sodium carbonate was selected.

In that solution, the nanoporous samples were processed and then the solvent was evaporated, so the indicator molecules became immobilized on the nanopore inner surface. Figure 2**b** displays the sample spectra; one can observe broadening and
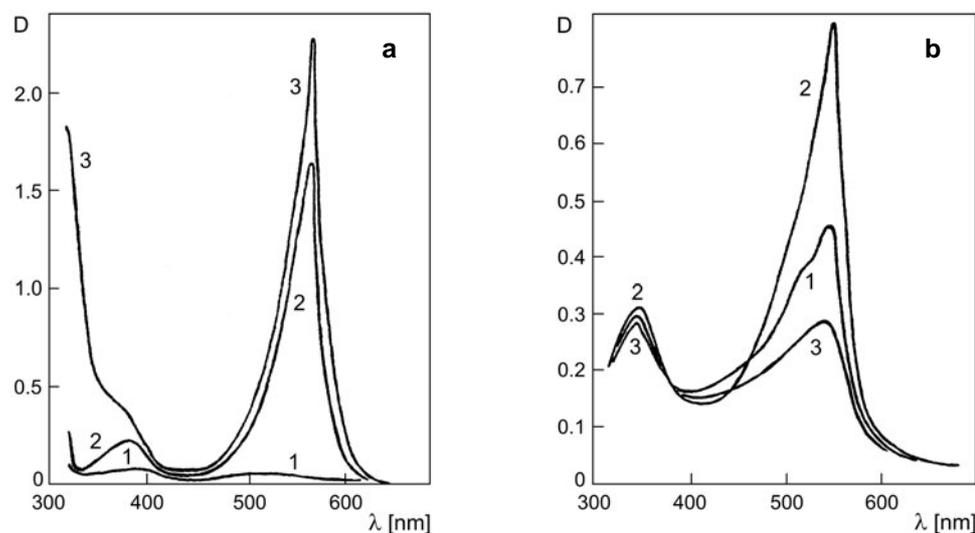


Fig. 2. Absorption spectra of impregnating phenolphtalein solutions (0.1 mas%) of various acidities: 1 – pH 3.5, 2 – pH 9.0, 3 – pH 10.5 – **a**. Absorption spectra of phenolphtalein immobilized within a nanoporous matrix: 1 – in normal atmosphere; 2 – in the presence of ammonia vapours (5 vol%); 3 – in the presence of carbon dioxide (5 vol%) – **b**.

lowering of the absorption band and the maximum's shift to 550 nm. The titration equivalence points are also shifted by about 2 pH units toward the acidic range. Particularly, the colour changes of the samples treated in solutions of the acid-base indicators allowed to determine the surface acidity as pH ≈ 4.5. The main light absorption band appears due to the disconnection of a lactone bridge within the phenolphtalein molecule.

A specific problem in these experiments consisted in the creation of the desired acidity or alkalinity of the ambient gas medium. This problem was solved by means of letting into a cuvette the certain gases, such as carbon dioxide or ammonia within the concentration range of 0–5 vol%. In Figure 2**b** the sample spectra in clear atmosphere (curve 1) and in the atmosphere containing $CO_2$ or $NH_3$ (curves 2 and 3) are shown. One can see that $NH_3$ intensifies the absorption band and $CO_2$ reduces it. The experiments have shown that spectral reaction on these gas components not only remained but sometimes became even more pronounced at elevated temperatures (up to +70 °C).

Similar regularities have been obtained with other indicators from the phenolphtalein row: thymol blue and bromocresol purple. In general, the results obtained may lead to important chemical conceptual conclusions (see below).

Further experiments with gas concentration variations have surprisingly demonstrated that resulting spectral changes are spontaneously reversible in normal conditions with time constant being about 30 s (for $NH_3$) and about 3 min (for $CO_2$). That means that the sample spectra returned back to their initial shape after the removal of active gas components from ambient atmosphere without any additional regeneration procedures (heating, evacuation or others).

The purple samples get coloured more intensively in the presence of ammonia vapours and lose their colour in the atmosphere containing carbon dioxide (see Fig. 2**b**). Hence, the adsorbed molecules play simultaneously a role of spectral indicators, both of the matrix surface state and of the ambient atmosphere composition. As a matter of fact, due to immobilized indicator molecules, the spectral sensitivity of a sample to gases was shifted from an infrared into a visible wave range. Similar effects were discovered for other indication pairs: thymol blue – oxides of nitrogen; bromocresol purple – ammonia vapours, *etc*. Our thermal experiments have shown that the immobilized indicator molecules interact directly with gas molecules, so that dissolving of gas in the layer of adsorbed water has not appear.

## 7. Immobilized metal-complexes as indicators

It has been found that the complexes on the basis of some transition metal ions, being adsorbed, sustain their ability to catch certain gas molecules from ambient air and to build-in them into its coordination sphere. This process is accompanied by clear colour changes of the samples. We have developed some sensitive nano-compositions on this

principle, such as immobilized cobalt(II) ions for water vapours; palladium(II) ions for carbon monoxide; copper(II) for methanol vapours and others.

In Figure 3, the spectra for one of those complexes on the basis of Co(II) are shown. The main absorption band at 700 nm is attributed to an electron transition in the metal ion $^4A_2 \rightarrow {}^4T_{1g}(P)$. The neighbouring bands are assigned to the spin–orbital interaction. The intensity of a combined absorption band drops gradually with an increase in air humidity, so that a humidity sensor may be made on this base. These independent X-ray experiments have shown that within the pores, the crystalline
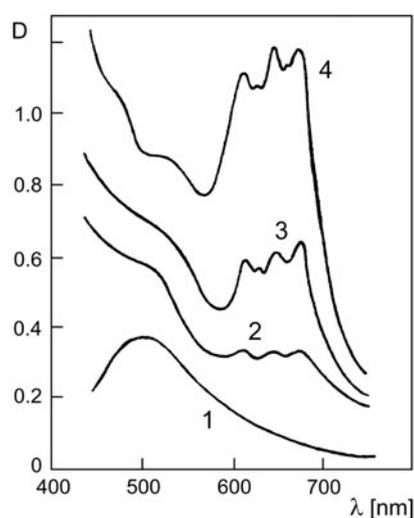


Fig. 3. Absorption spectra of cobalt(II) complexes: 1 – in 1 M of aqueous solution, 2 – immobilized within nanoporous glass in the air of relative humidity of 50% at 20 °C, 3 – the same in the air of relative humidity of 30%, 4 – the same in the air of relative humidity of 5%.
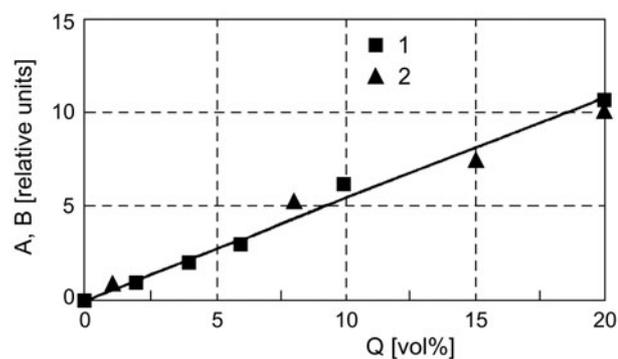


Fig. 4. Sensitivity of the Ru(II) complex fluorescence band to oxygen; 1 – first cycle of measurements, 2 – second cycle.

phases of $CoCl_2 \cdot nH_2O$ exist at any humidity values [11]. In normal atmosphere, a blue dihydrate phase $[CoCl_2 \cdot 2(H_2O)]$ within the pores is stable. At higher humidity these complexes take water molecules and form a metastable phase $[CoCl_2 \cdot 2(H_2O)] \cdot H_2O$.

In all cases the colour changes were spontaneously reversible after the removal of an acting component from the air. One can select a specific indicator for the detection of a certain gas component.

Not only the spectral absorption but also the fluorescence of immobilized molecules may serve for indication of atmosphere content. The polypyridine complexes of ruthenium(II) turned out to be the most promising because of their stability, high reaction ability in excited states and high fluorescence capacity [7, 8].

The fluorescence band at 650 nm is quenched by molecular oxygen, sulphur oxide and others. A lifetime of excited state for the Ru(II) complexes is much longer than that of the most organic fluorophores and these complexes demonstrate high quenching efficiency. The emission intensity is effectively quenched in accordance with the known Stern–Volmer equation:

$$\frac{I_o}{I} = 1 + kC_{O2}$$

The typical experimental diagram for oxygen is shown in Fig. 4.

## 8. Chemical interpretation of results

For the systematization and interpretation of these phenomena, the Lewis' and Pearson's concept about Hard and Soft Acids and Bases (HSAB) has been invoked [15, 16]. According to the HSAB concept, all the Lewis' acids and bases (electrophilic and nucleophilic agents, respectively) may be characterized upon their ability to form stable acid-basic complexes in the course of the electrophilic (nucleophilic) substitution reactions. A characteristic parameter is here a rate of the complex formation.

Due to numerous studies, it has been found that the ions such as $H^+$, $Na^+$, $Ca^{2+}$, $Si^{4+}$, *etc.* and some oxides including $CO_2$ and $SiO_2$ play the role of the hard acids. The ions $Pd^{2+}$, $Ag^+$ as well as neutral metal atoms may be assigned to the soft acids. Such ions as $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and others take an intermediate position.

On the other hand, the hard Lewis' bases are the $OH^-$, $CO_3^{2-}$, $SO_4^{2-}$ ions and the $H_2O$, $NH_3$, $N_2H_4$ molecules. The soft bases are the molecules $CO$, $(CH_3)_2SO$, the $I^-$ ion and others, to the intermediate group belong, for example, the $Br^-$, $SO_3^{2-}$ and $NO_2^-$ ions.

Pearson has formulated the following laconic principle: *Hard acids preferably do compounds with hard bases and soft acids with soft bases; otherwise the stable compounds and strong bonding do not formed* [16].

The Lewis–Pearson's concept is very useful and productive in many cases; however, till now it has a rather qualitative character and needs further evidence. Our experimental results most likely present one of such confirming examples. Indeed, in

T a b l e.  Some parameters and characteristics of prototype spectral gas sensors.

| Immobilized colour indicator | Analyzed gas (vapour) [vol%] | Sensitivity [%$^{-1}$] | Time constant [min] |
|---|---|---|---|
| Phenolphthalein 0.1 mas% | $CO_2$: 0.05–3.0 | 0.1 | 5 |
| Phenolphthalein 0.1 mas% | $NH_3$: 0.001–0.010 | 0.3 | 3 |
| Bromocresol purple, 0.1 mas% | $NH_3$: 0.05–5.0 | 0.4 | 1 |
| Thymolsulfophthalein, 0.1 mas% | $NO_x$: 0.001–0.010 | 0.1 | 2 |
| Cobalt chloride, 1 M | $H_2O$: 5–190 (rel. humid.) | 0.02 | 15 |
| Palladium hloride, 1 mas% | CO: 0.001–0.010 | 0.02 | 15 |
| Copper chloride, 2 M | $CH_3OH$: 0.05–10.0 | 0.07 | 2 |

most cases of the observed interactions, the principle of Pearson mentioned above is obeyed, *i.e.*, substances being opposite in their nature form more stable complexes and *vice versa*.

## 9. Potential gas sensors and analyzers

The observed phenomena open good prospects of possible practical application in gas components detection. For example, the plates made of nanoporous glass impregnated with different indicators might serve within an optronic pair as the sensing elements in spectral optical gas sensors for remote atmosphere monitoring. Some parameters and characteristics of prototype spectral gas sensors are presented in the Table.

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