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Effects of Different Treatments on Purity of Silica from Soluble Sodium Silicate*

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ABSTRACT

Noncrystalline silica was obtained with low iron, sodium, and nitrate ions concentrations from soluble sodium silicate (water glass) and nitric acid solution. Extractions with nitric acid solution and/or deionized water and/or dialysis were carried out to eliminate soluble metal ions. Products were dried in a microwave oven and characterized by chemical analysis, XRD, and IR. Dialysis seems to be the best treatment for the elimination of sodium and nitrate ions. Silica purified by nitric acid and water extractions followed by dialysis yields the purest silica sample.

Key Words. Silica; Soxhlet extraction; Dialysis

INTRODUCTION

On account of its abundance in nature and its capability of different material applications, silica has been used since the beginning of civilization (1). Silica multimode fiber-optic with an acrylate primary coating acts as an intrinsic sensor of microwave power (2). Aerogels of silica are used as Cherenkov radiation detectors in nuclear reactors (3). Aerogels are also on the

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verge of commercialization as insulating glazing materials (4). Purified silica is used in manufacturing integrated-circuit sealants, quartz glass, optical glass (5), and pigments (6). High-purity silica is useful as a filler of integrated-circuit sealing resins, electronic parts, and glass for semiconductor-manufactured devices (7). The majority of silica applications requires low metal ions content to improve material performance. For instance, silica for optical fiber as well as for luminescent materials is low in sodium content and must not contain iron, which is a luminescent poison.

Silica precipitation from aqueous alkali metal silicate solution (water glass) with mineral acid solution is one method to obtain amorphous silica (8–14). Colloidal silica is prepared from freshly precipitated silicic acid with hydrochloric acid solution and dechlorination treatment made by addition of sodium hydroxide solution (15). Silica gel with spherical particles can be manufactured by spray drying a mixture of silica sol with aqueous alkali metal silicate solution (16). Another method for manufacturing high-purity silica is the treatment of husk with fluoridric acid solution (17). High-purity silica is also manufactured by reacting alkali metal silicates with a mineral acid, feeding the resulting granular silica gel slurry to the top of a vertical column, and purifying the slurry by injecting water into the bottom of the column (18). Aqueous alkali silicate solution is directly poured into a mineral acid to elute impurities to the mineral acid solution and to precipitate silica which is washed with mineral acid to give a high-purity product (15). An alternative method for silica purification is reverse electrodialysis (19).

Although high-purity silica can be obtained conventionally by silicon tetrachloride oxidation (1, 20), and more recently by sol–gel techniques from silicon alkoxides (21), free-metal ion silica may be alternatively obtained by an adequate treatment of precipitated silica from soluble silicate solutions. Many silica purification processes are known to use the association of two separation steps, such as washing and centrifugation, or sodium ethylenediaminetetraacetate salt complexing to eliminate ions.

This paper deals with the preparation of and purification methods for noncrystalline silica with low sodium, iron, and aluminum contents from soluble sodium silicate solution. Acidic and water extractions and dialysis purification methods were investigated for precipitated silica, and the products were characterized by using x-ray powder diffraction (XRD), infrared spectroscopy (IR), flame photometry and atomic absorption (AA) analyses, and scanning electron microscopy (SEM) with chemical analysis by wavelength-dispersive spectroscopy (WDS).

EXPERIMENTAL PROCEDURE

The semi-alkaline soluble sodium silicate, molar ratio SiO_2:Na_2O = 3.30 (water glass H300 NDL), used in this work was supplied by ICI Brasil Ltda, now Gessy Lever-Crosfield Division/Brazil. Silica was obtained by adding a

nitric acid solution to a soluble sodium silicate solution previously diluted with deionized water. The acid solution addition was made under moderate stirring in a Kettler flask containing sodium silicate at 80°C under reflux. A gel was obtained after 1 hour under these conditions.

Extraction with nitric acid solution and/or deionized water and/or dialysis was performed for the elimination of soluble metal ions. A Soxhlet extractor was employed for the extraction treatment. A sintered glass plate was used to fix the gel. Different sample treatments are identified in Fig. 1. The products

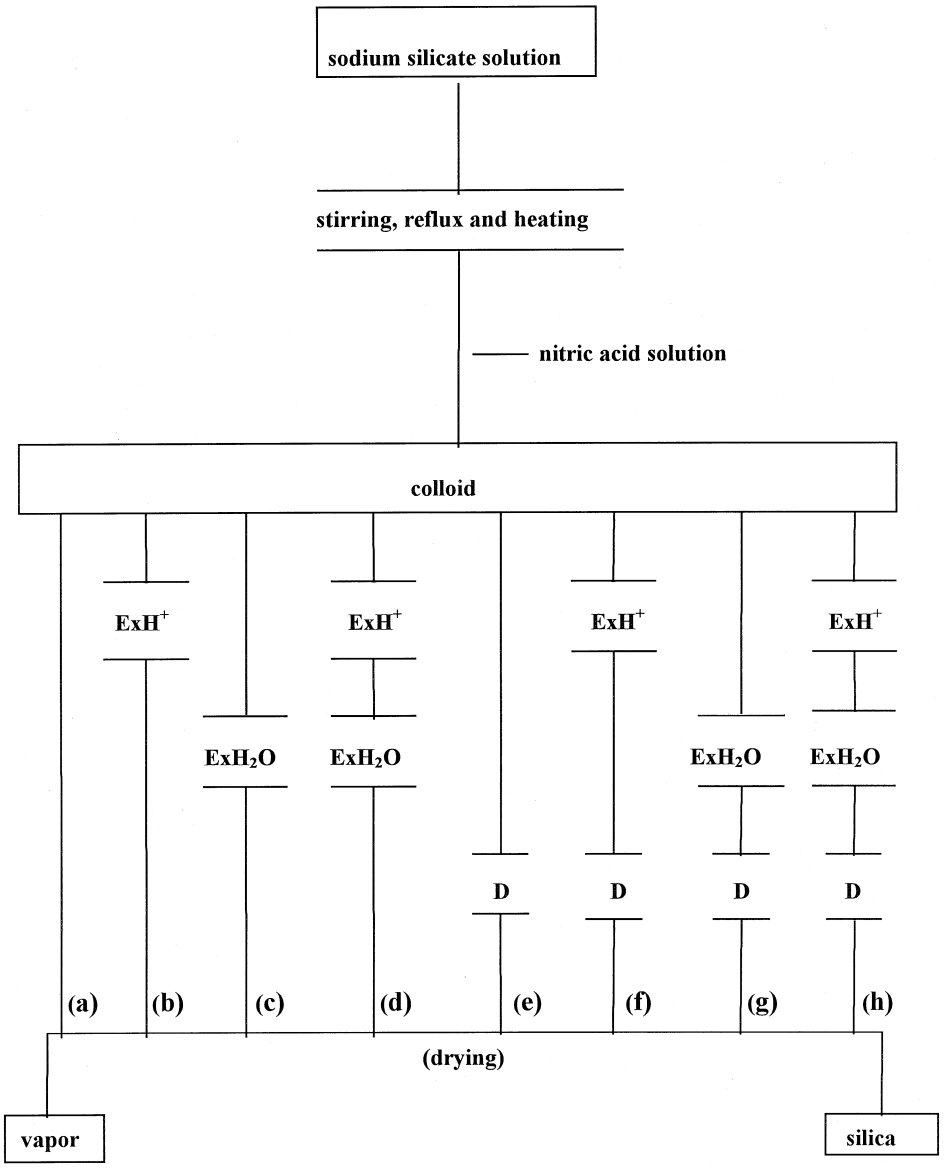

FIG. 1 Flow diagram for silica treatments including sample identifications (a)–(h).

were dried in a modified (22) microwave oven (White Westinghouse model EM 900).

Sodium and iron analysis were carried out by flame photometry and atomic absorption spectrophotometry with a flame photometer (Micronal model B262) and a spectrophotometer (Varian Intralab model AA-1475), respectively. Silica samples for chemical analysis were systematically milled in an agate mortar and dried in an oven at 150°C for 4 hours. Then they were digested with a mixture of water, concentrated nitric acid, and 40% fluoridric acid at (1:5:25). A calibration curve for sodium was obtained for the 0 to 15 $\times 10^{-3}$ g·dm^{-3} range from a 50 $\times 10^{-3}$ g·dm^{-3} sodium chloride (Merck pa) stock solution. The calibration curve for iron was obtained for the 2 to 10 $\times 10^{-3}$ g·dm^{-3} range from iron chloride (Titrisol-Merck) at a concentration of 1.000 g·dm^{-3}.

Characterizations were carried out by XRD in a diffractometer (Carl Zeiss model HGZ 4B) by using Ni-filtered CuKα radiation generated at 20 mA and 36 kV. Samples were milled with 10% (w/w) tungsten as an internal standard for intensity comparison, normalized to the most intense 110 reflection. Vibrational infrared spectra were obtained from a spectrophotometer (Nicolet FT-IR model Impact 400) in the 4000–400 cm^{-1} wavenumber range. The 1550–1260 cm^{-1} region was expanded in absorbance to integrate the nitrate group band [ν_3(E), D_{3h} point group]. Pellets of samples were prepared by diluting them in KBr at a proportion of 1:93 (w/w) for IR spectroscopy. The SEM micrograph of one sample (**h**) was obtained in a scanning electron microscope (Jeol JSM T33A). Chemical analysis with a wavelength dispersive spectroscopy (Microspec WDS) microscope (Stereoscan 440) was carried out for aluminum and iron in some samples (**e, f, g,** and **h**), and for sodium in all samples.

RESULTS AND DISCUSSION

The SEM micrograph of the representative sample in Fig. 2 shows that powder morphology and size are irregular. The silica particles are aggregates with particle sizes between 1 and 10 μm. This particle size range is adequate for plate chromatography applications. Silica particle size in this range was also obtained by using sulfuric acid for precipitation (13). Elimination of crystalline impurities of samples is evidenced by x-ray diffraction. The XRD patterns for unpurified powder samples show sodium nitrate interplanar distance, d_{hkl}, of 3.04, 2.31, 3.89, and 1.90 (JCPDS 4-0787). The purification efficiency for silica is related to any remaining sodium nitrate by comparing the relative peak intensities of reflection shown in Table 1 that refer to the different sample treatments (**a, b, c,** and **d** processes). By comparing the relative peak intensities of any sodium nitrate reflection, it is possible to assay purification ef-

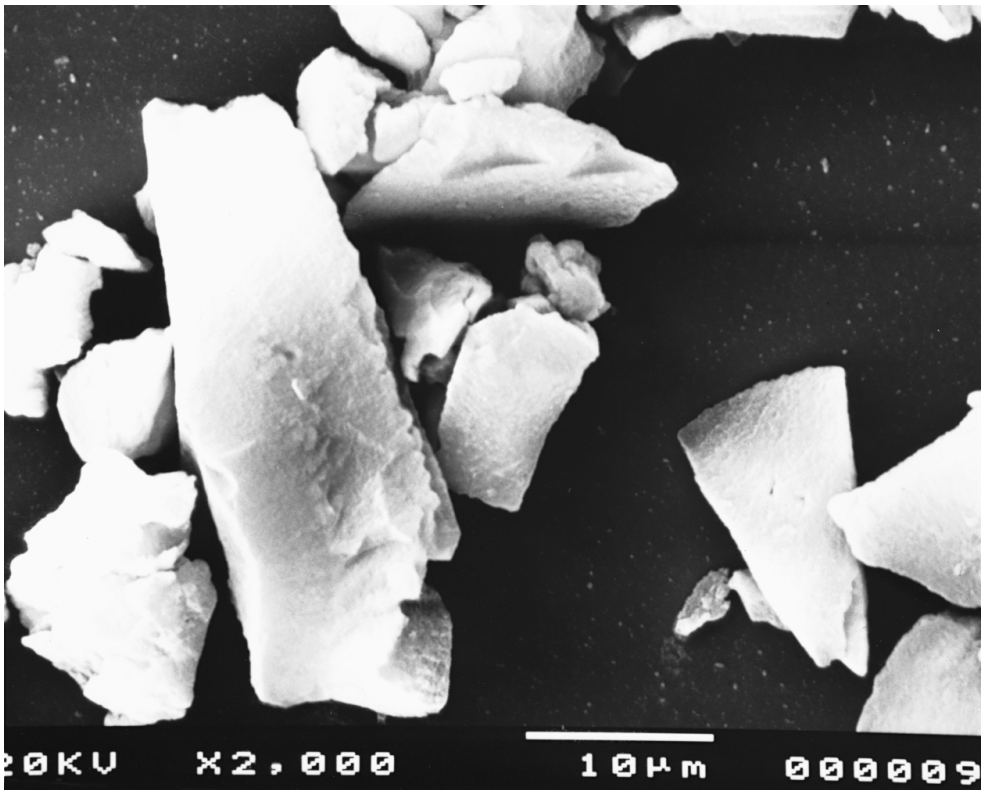

FIG. 2 SEM micrograph of silica treated by acid solution, water extractions, and dialysis (**h**).

ficiency. Among the **b, c,** and **d** processes, the least efficient in sodium nitrate elimination is acid solution extraction (**b**) due to the salting out effect. Water extraction (**c**) eliminates a small amount of the sodium nitrate salt but not as much as acid solution extraction. Water extraction treatment after nitric acid solution (**d**) is more efficient than the other treatments in which only one extraction is used (**a** and **b**). All other process (**e, f, g,** and **h**) are good methods because salt x-ray reflections are not observed in any x-ray diffractograms. Dialysis alone (**e**) or dialysis after any other extraction step (**f, g,** and **h**) results

TABLE 1
Sodium Nitrate XRD Results as a Function of Purification Processes

Sample	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0	d_{hkl}	I/I_0
a	3.04	100%	2.31	21%	2.80	16%	1.88	12%
b	3.04	69%	2.31	13%	1.90	12%	2.80	11%
c	3.04	60%	2.31	12%	2.80	9%	1.88	8%
d	3.04	42%	2.31	11%	2.80	9%	1.90	8%

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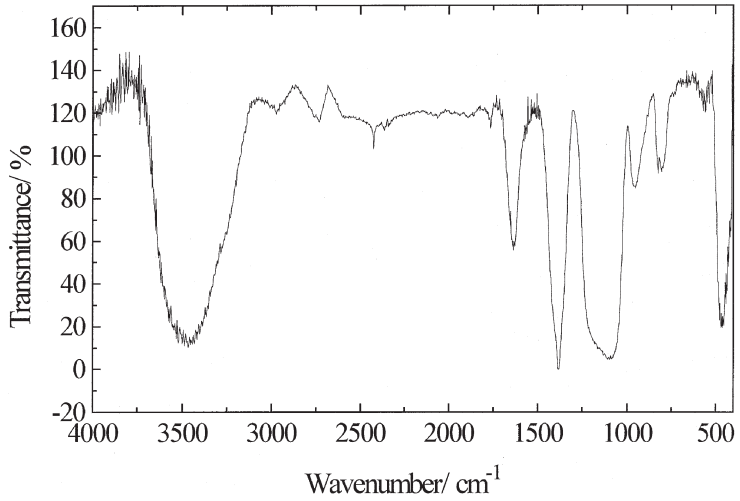

FIG. 3 IR spectrum of silica treated by water extraction (**c**).

in sodium nitrate elimination from silica samples. In addition, all x-ray powder diffractograms do not show reflections assigned to silica. The temperature reached on solid samples under microwave oven heating does not allow powder crystallization. Microwaves provide the only method of heating that does not use thermal conduction and which penetrates several centimeters deep, dissipating the energy carried to the bulk sample. Polar molecules, especially water, heat under microwave activation and evaporate from the bulk to the surface of a sample (23). Also in this process, silanol groups can form polycondensation products which give a smooth surface (28). The microwave drying process is homogeneous and fast.

Nitrate ion excess in powder samples can be detected by IR measurements. The IR spectra in Figs. 3 and 4 are typical of noncrystalline silica, including nitrate ion bands. The band assignments from the spectrum of Fig. 4 are described. Asymmetric stretching Si—O and Si—O—(Si) vibrations occur in the 1233–1041 cm^{-1} wavenumber range (24, 25). This range is larger than that for cristobalite bands due to the noncrystallinity of silica. Spectra do not display the typical 625 cm^{-1} cristobalite band (24), indicating that there is no tendency for silica crystallization upon microwave oven drying. Si—O^- asymmetric and SiO symmetric stretchings appear in 957 and 803 cm^{-1}, respectively. Deformation (24–26) O—Si—O appears at 464 cm^{-1}. All the spectra show typical water molecule stretching bands in the 3622–3323 cm^{-1} region. The water molecule deformation band generally observed at ca. 1625 cm^{-1} appears at ca. 1637 cm^{-1} for any treatment. This shift to a larger wavenumber can be attributed to the presence of H_3O^+ ions (25) in the silica samples.

The ionic nitrate group (NO_3^-, D_{3h} symmetry) band frequency attributions (27) are: $\nu_3(E) = 1385\ cm^{-1}$, asymmetric stretching; $\nu_2(A_2) = 826\ cm^{-1}$,

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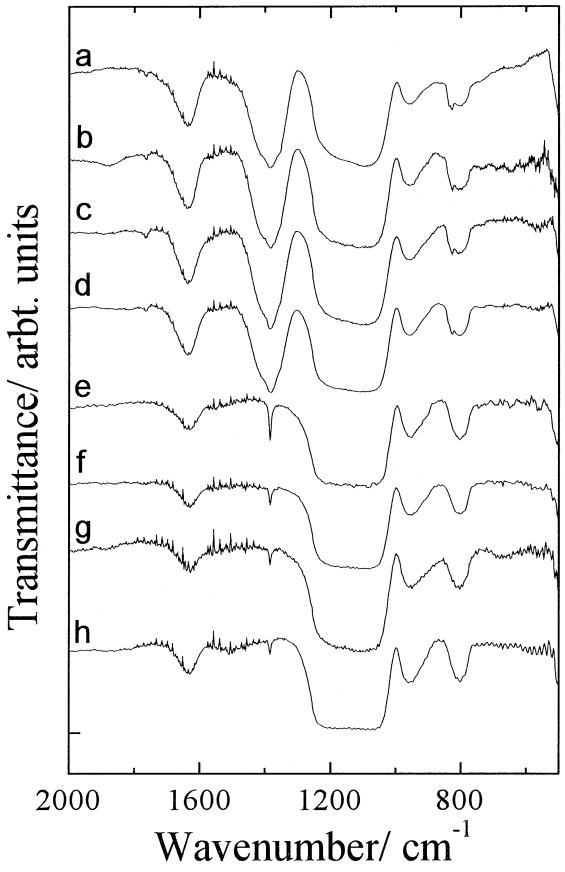

FIG. 4 IR spectra of samples submitted to different treatments. (See sample identifications in Fig. 1.)

bending out of plane; and ν_4(E) = 730 cm^{-1}, bending in plane. Elimination of nitrate ions by extractions and dialysis can be observed by powder pellet IR spectra following the ν_3 in 1385 cm^{-1} and the ν_2 in 826 cm^{-1} bands. Qualitative analysis can be done from the spectra in Fig. 4 which clearly shows the ν_3 intensity variation as a function of treatments. Among all bands, ν_3 is the highest one for the samples without dialysis (**a, b, c,** and **d**) and the lowest one for the sample including dialysis as a purification method (**e, f, g,** and **h**). Also, ν_2 appears as a shoulder in the SiO symmetric stretching band especially when samples were not treated by dialysis (**a, b, c,** and **d**). To verify the purification method efficiency, expanded IR spectra were used to integrate the ν_3 nitrate ion band. The integration band values are plotted as a histogram in Fig. 5. The silica samples treated by water extraction, nitric acid extraction, and nitric acid extraction before water extraction (**a, b, c,** and **d** processes) have more nitrate ion content than the other treatments. When silica gel is treated by dialysis, or by any other method followed by dialysis (**e, f, g,** and **h** processes), it is ob-

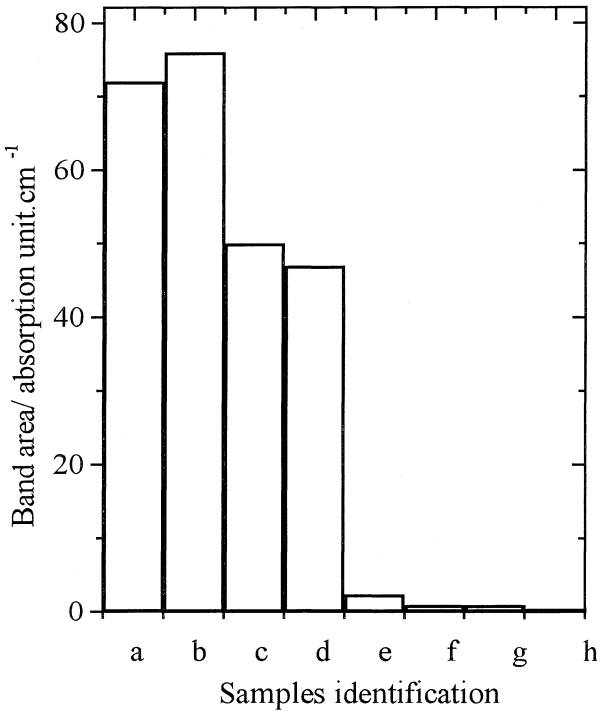

FIG. 5 Nitrate ion band (ν_3) area as a function of purification process.

served that the powders have a low amount of nitrate ions. The iron content of silica samples obtained from atomic absorption is in the 0.1–0.2 $\mu gFe \cdot g^{-1}$ range, no matter what the sample treatment. The contribution of analytical reagents is 0.03–0.06 $\mu gFe \cdot g^{-1}$ of sample. Results of iron and aluminum analyses from WDS of samples that could be adequately prepared are presented in Table 2. The topographical artifacts of specimen prepared for WDS experi-

TABLE 2
Sodium, Iron, and Aluminum WDS Analysis Results for Silica Samples

		Ion concentration/($g \cdot g^{-1}$ sample)	
Sample	$[Na] \times 10^{-3}$	$[Fe] \times 10^{-5}$	$[Al] \times 10^{-4}$
a	55	—	—
b	45	—	—
c	43	—	—
d	47	—	—
e	0.55	6.7	2.0
f	0.60	5.9	2.1
g	0.39	9.3	1.5
h	0.35	1.9	9.6

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ment may arise from absorption and blockage of x-rays. Better specimens were created with dialyzed silica samples. The iron content value of sample (**h**), which underwent acid and water extractions and dialysis, was compared with the atomic absorption result. This sample presented the lowest value of iron. Therefore, aluminum concentration in silica samples is higher than that of iron.

The efficacy of sodium ion elimination by using different treatments can be observed in Fig. 6 and it is confirmed by WDS results. The water extraction treatment (**a, b, c,** and **d**) removes part of the sodium nitrate from silica gel. Extraction with nitric acid solution (**b**) is more efficient than with water (**a, c,** and **d**) because silica pores can be closed by boiling water during the extraction process and that traps sodium within the pores. Water usually promotes coarsening due to high silica solubility (1, 28). Acid or acid followed by water extraction showed similar purification results for sodium ion content in silica. Dialysis, dialysis after acid solution extraction, and dialysis after water extraction (**e, f,** and **g**) are effective processes for sodium ion elimination. The silica retains a low sodium ion content when the gel is treated by dialysis. Water or acid extraction before dialysis treatment is slightly more efficacious than dialysis treatment alone. Dialysis performance for sodium ion withdrawal is probably related to the treatment time. Extractions by nitric acid solution and

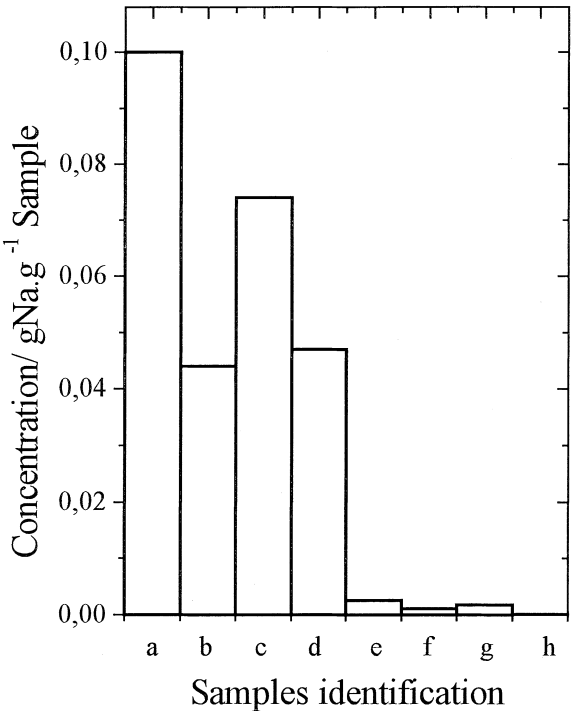

FIG. 6 Sodium ion contents as a function of purification process. (See sample identifications in Fig. 1.)

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water followed by dialysis (**h**) procedures are the most effective treatments for silica gel purification. In the latter case the sodium ion content is 99 μg sodium per gram of silica.

Figure 7 shows a schematic system representation to explain the effectiveness of salt elimination by hot extraction only. The sodium nitrate particles,

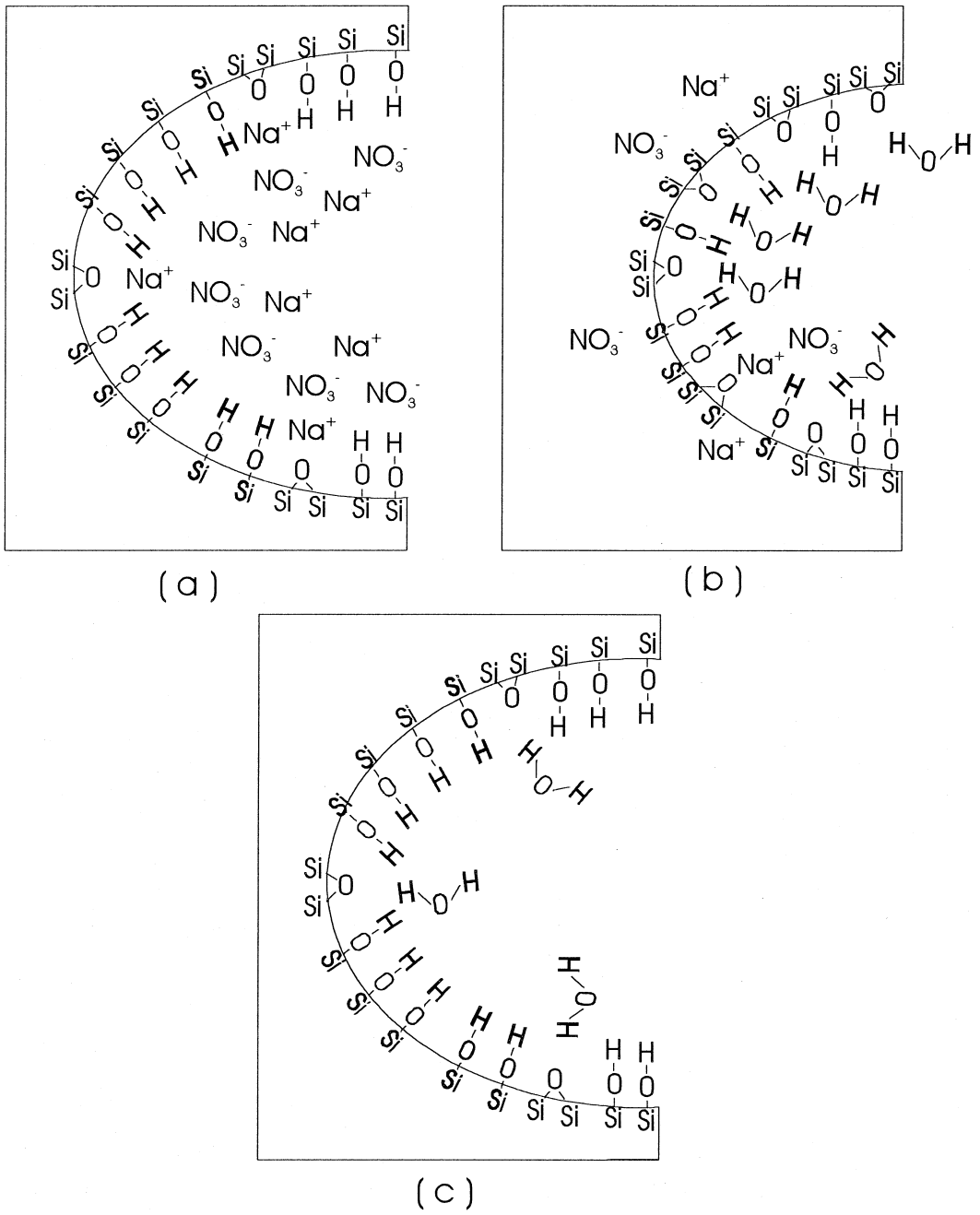

FIG. 7 Schematic representation of impurities at silica surface: (a) without treatment; (b) hot water extraction treatment; (c) dialysis treatment.

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for example, are deposited upon the surface of silica pores (Fig. 7a). Extractions by acid solution and water eliminate part of the sodium nitrate of silica pores, but silica polymerization probably occludes the remained ions (Fig. 7b) due to heating during the extraction of sodium ions by hot acid solution and water. Dialysis is a nondrastic method for the elimination of impurities and the microstructure probably does not change with sodium ion migration by deionized water without the closing of pores (Fig. 7c).

CONCLUSIONS

Heating of silica powder samples in a microwave oven does not allow for crystallization. Dialysis is the best treatment for sodium and nitrate ions eliminations. Although all samples treated by dialysis are of high purity, the best is silica purified by nitric acid and water extractions before dialysis because it has ca. 0.2 ppb iron, ca. 1 ppb aluminum, and ca. 1 ppb sodium. The silica particles are aggregates with particles sizes of 0.2 to 5 μm. Silica samples treated by nitric acid and water extractions before dialysis have been successfully used for the preparation of luminescent materials and are also adequate for chromatography application.

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