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Silica and silica–titania sol–gel materials: Synthesis and analytical application

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A B S T R A C T

This review describes last decade progress in the synthesis of sol–gel materials with analytically relevant properties and their application for the determination of metal ions, non-metal and organic compounds. The following types of materials are discussed: silica sol–gel materials doped with various analytical reagents, organofunctional silica sol–gel materials, and silica titania sol–gel materials. The variety of obtained materials allows their application for a wide range of analytical systems: electrochemical sensors, solid phase spectrophotometrical and SIA determination, and also for test determination including the employment of "length-of-stain" indicator tubes. This review surveys the results of studies on mentioned above subjects and summarizes the works accomplished in the field by author's team in Moscow State University.

1. Introduction

Sol–gel process first described 150 years ago is still receiving great attention as one of the easiest ways to develop modified materials (materials with required properties). Sol–gel materials are characterized by durability and stability; many of them are optically transparent. Currently, silica based sol–gel materials are the most widespread ones. Sol–gel materials on the base of other oxides—e.g. titanium, zirconium, aluminum oxides—have not been used extensively so far. Sol–gel monoliths, thin films, mono- and polydisperse powders can be obtained by sol–gel technology. The most noticeable feature of sol–gel process is the variety of possible modifications. Such modification can be achieved by incorporating analytical reagents, enzymes, etc., by using appropriate functionalized alkoxysilanes (containing amino, phenyl, pyridine, mercapto, and other groups), by employing both silica and titania precursors. These modified materials can be then utilized for spectroscopic and electrochemical sensors construction [1–12].

New sol–gel materials have been synthesized and studied at Moscow State University (MSU) analytical chemistry division during the last decade. These materials have been utilized for solid spectrophotometrical and test determination of different compounds, for electrochemical sensors development, and for SIA determination as well. This review covers the results achieved by author's team [13–27] and is organized as follows:

2. Synthesis and characterization
    2.1 Silica materials doped with analytical reagents.
    2.2 Functionalized silica materials
    2.3 Silica–titania and titania materials
3. Application
    3.1 Electrochemical sensors
    3.2 Solid phase spectrophotometrical determination
    3.3 SIA
    3.4 Test determination.

2. Synthesis and characterization

General scheme of sol–gel materials synthesis includes sol (colloid suspension) preparation, for example, alkoxysilanes hydrolysis (mainly tetraethoxy- or tetramethoxysilanes); gel formation; and following drying of gel (xerogel formation) if necessary (Fig. 1). The reactions are presented below:

Hydrolysis

$$\equiv\text{Si–OR} + \text{H}_2\text{O} \leftrightarrows \text{Si–OH} + \text{ROH} \quad (1)$$

Condensation

$$\equiv\text{Si–OR} + \text{HO–Si}\equiv \leftrightarrows \equiv\text{Si–O–Si}\equiv + \text{ROH} \quad (2)$$

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \leftrightarrows \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O} \quad (3)$$

Hydrolysis results in significant increase in concentration of alkoxysilane molecules containing silanol groups and leads to "silanol-ether" and "silanol-silanol" condensation reactions. Consequently,

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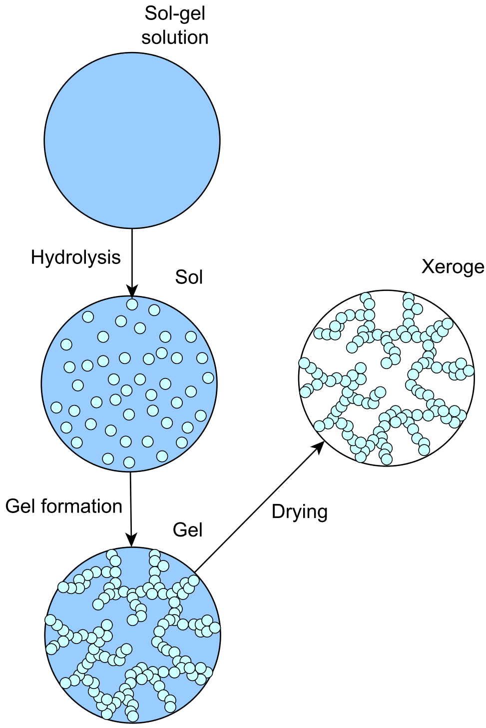

Fig. 1. The stages of silica sol–gel materials synthesis.

the structure of cross-linked siloxane bonds is formed. Structural properties of sol–gel materials depend on the conditions of sol–gel process (hydrolyzing mixture composition, catalyst nature, pH) and drying mode essentially [1–4].

Using the new catalyst that accelerates the gel forming process and microwave drying of wet gels that has been proposed in our lab we have developed a fast way of xerogel powders fabrication. Depending on microwave irradiation power it takes from several minutes to 2 h for wet gels to dry. The increase of microwave irradiation power from 300 to 1000 W leads to increase of surface area from 490 to 960 m^2/g [13–15]. New catalyst and microwave drying have been employed to get silica materials doped with analytical reagents, functionalized silica materials, and silica–titania materials (Fig. 2.).

2.1. Silica materials doped with analytical reagents

For the first time analytical reagent (Rhodamine 6G) was immobilized using sol–gel process in 1984 [28]. In 1990 Avnir et al. [29] basing on the existing data concluded that various compounds incorporated in sol–gel materials could undergo chemical reactions and, therefore, those analytically important reactions can be carried out in the materials. That motivated synthesis and characterization of modified sol–gel materials. Numerous studies have proven that conclusion is right.

Sol–gel technology has been employed to get monoliths and films modified with acid-base and ox-red indicators [30–36], complexing organic reagents [29,37–44]. Sol–gel technology can also be used for easy immobilization of biomolecules (proteins, enzymes, antibodies), and interesting results of such immobilization are discussed in reviews [11,12].

The reactions of acid-base indicators incorporated in sol–gel materials have been studied in detail. The acidity constants values of immobilized porphyrins, azo-, sulfophthalein and phthalein compounds have demonstrated that the acidic properties of these indicators are enhanced due to immobilization [31,33].

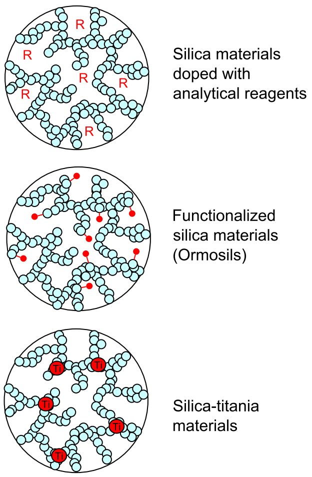

Fig. 2. Three types of silica sol–gel materials modification.

Complexing reactions in sol–gel matrix have been studied to a lesser extent. Only 4 systems have been presented explicitly: iron(II)–1,10-phenanthroline (Phen) [4], nickel–dimethylglyoxime [37], copper(II)–eriochrome cyanine (ECC) [42], aluminum–morin [43]. The reagents retention has been noted to depend significantly on the materials porosity [37,42].

Sol–gel films and monoliths doped with various reagents have been used for electrochemical and spectroscopic determination of organic and inorganic substances [3–12,29–44]. The most noticeable disadvantage of monoliths application is the sorption equilibrium time duration (up to several days).

We have synthesized silica xerogel powders doped with analytical reagents for determination of metal ions, non-metallic compounds, and organic substances.

The following complexing reagents were immobilized in sol–gel materials: hydroxyquinolines (8-hydroxyquinolines (8-HQ), 5,7-dibrom-8-hydroxyquinolines (Br-8-HQ)); oximes (dimethylglyoxime, furyldioxime, benzyldioxime); derivatives of triphenylmethane and xanthene (chrome azurol S (CA), sulfochrome (SC), ECC, xylenol orange (XO), crystal violet); azo compounds (PAR, PAN, TAN, sulfochlorophenolazorhodanine (SCPAR), brombenzothiazo (BBT), lumogallion (LG), cadion, zincon, hexacycloazochrome (HCAC), sulfarsazene); phenanthrolines (Phen, batophenanthroline (bPhen)); diphenylcarbazone (DPC) [16–21].

Previously, the sol–gel monoliths and films durability has been shown to increase in presence of surfactants, but their influence on physicochemical properties of sol–gel materials has not been investigated thoroughly [6,34]. We have made an important observation while characterizing sol–gel materials modified with both complexing reagents and surfactants (cetylpyridinium chloride (CPC), sodium dodecylsulfate (SDS), Triton X-100). In presence of CPC derivatives of triphenylmethane (CA, SC, ECC) are better retained, and that might be attributed to ion associate formation. Retention does not change significantly in presence of SDS and Triton X-100 [19].

The spectrophotometric characteristics of these reagents entrapping in silica xerogels and their metal complexes have been studied.

Immobilization on xerogels results in increase of complexing reagents acidic properties. This is probably connected with interactions of labile protons of reagents with deprotonated silanol groups of the silica matrix. As a result, the dissociation of immobilized reagents becomes easier. The difference between acidity constant values in solution and in xerogel for some reagents are given in Table 1.

Table 1
Acidity constants of some reagents in solution and in xerogel ($n=3$, $P=0.95$).

Reagent	pK_a in solution	pK_a in xerogel	ΔpK_a
4-(2-Pyridilazo)resorcin	5.5	4.9 ± 0.3	0.6 ± 0.3
Brombenzothiazo	13.3	10.9 ± 0.5	2.4 ± 0.5
Lumogallion	5.7	4.8 ± 0.3	0.9 ± 0.3
Xylenol Orange	10.4	9.0 ± 0.4	1.4 ± 0.4

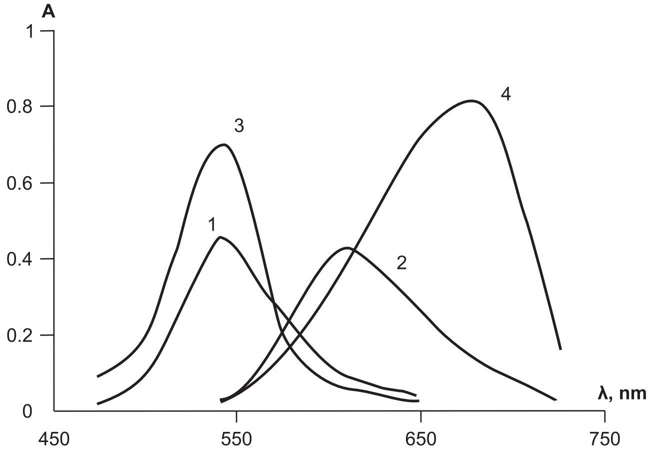

Fig. 3. Absorption spectra of silica xerogels doped with 4-(2-pyridilazo)resorcin (1), chrome azurol (2), 4-(2-pyridilazo)resorcin and cetylpyridinium chloride (3), chrome azurol and cetylpyridinium chloride (4) after their reaction with Zn (1 and 3) or Fe(III) (2 and 4). Concentration of complexing reagents is $1.1 \cdot 10^{-4}$ M, concentartion of metal ions is 4 ppm [19].

The interaction of metal ions with immobilized reagents is described by the following equation:

$$\mathrm{Me}^{n+} + \overline{n\mathrm{HR}} = \overline{\mathrm{MeR}_n} + n\mathrm{H}^+ \qquad (4)$$

where the line denotes the compound in a xerogel phase.

We have suggested using the equilibrium-shift method to describe heterogenic complexing reactions. Complexes compositions and equilibrium constants values have been determined for interactions in the following systems: immobilized ECC–Cu(II), Fe(III); immobilized XO–Al, Zr; immobilized PAN–Cu(II), Ni, Fe(III), Mn(II); immobilized PAR–Pb, Co(II), Zn; immobilized BBT–cadmium(II); immobilized HCAC–lead(II); immobilized SCPAR–silver; immobilized LG–molybdenum(VI); immobilized 8-HQ and Br-8-HQ—cerium(IV); immobilized zincon–copper(II); immobilized CA and SC–Al(III), Cu(II), Fe(III); immobilized Phen and bPhen–iron(II); immobilized DPC–mercury.

For all the studied systems the ratio metal ion:reagent is lower than in solution, and this might be caused by steric complications due to reagent immobilization. Complexes with 1:3 metal ion:-reagent composition have been proven to be formed in xerogels only for cerium(VI) complexes. In all other cases complexes with 1:1 and 1:2 compositions have been observed. Interaction pH intervals of metal ions with complexing reagents are shifted towards bigger values compared with those in solution, and that might be a consequence of complexing reactions complications in xerogels.

It is worth noting that metal ions complexing with sol–gel materials containing CPC along with complexing reagents is accompanied by significant increase in light absorbance intensity, and for some systems, even in reaction contrast (Fig. 3).

The kinetics of these heterogeneous reactions has been studied. Equilibrium time is 15–30 min, and half reaction time is 2–10 min.

For organic substances determination we have synthesized xerogels doped with Cu(II), Co(II,III), and Fe(III) salts [16,22]. IR-spectroscopy data show that metal ions interact with silanol groups. Cobalt ions are also oxidized by atmospheric oxygen from Co(II) to Co(III) [22].

Copper(II) has been employed as immobilized reagent for interaction with ammonia, methyl- and diethylamine, pyridine, papaverine, picoline, EDTA, and PAR. Cobalt(III) has been immobilized in sol–gel matrix to study its interaction with ammonia, methyl- and diethylamine, pyridine, papaverine, picoline, 1-nitroso-2-naphthol (1N2N), and 2-nitroso-2-naphthol (2N2N). Interactions between immobilized iron(III) and phenyl-, methyl-, bromomethyl-, n-, and iso-butylhydroxamic acids have been studied [16].

The interaction of inorganic and organic substances with immobilized metal ions is described by the following equation:

$$n\mathrm{HR} + \overline{\mathrm{Me}^{n+}} = \overline{\mathrm{MeR}_n} + n\mathrm{H}^+, \qquad (5)$$

where the line denotes the compound in a xerogel phase.

For all the studied systems the ratio metal ion:reagent was the same as in solution (e.g. 1:3 for immobilized cobalt(III)–1N2N, 2N2N; 1:1 for immobilized copper(II)–PAR; 1:2 for immobilized iron(III)–hydroxamic acids). That can probably be explained by the presence of rather large pores in xerogels, which allow easy complexing. As in the case of ion metals interactions with immobilized complexing reagents pH intervals are shifted towards bigger values.

Equilibrium constants of heterogenic reactions in both cases (immobilized reagents and metal ions) change symbate with stability constants of corresponding complexes in solution or extraction constants. For example, the following dependence has been determined between equilibrium constants(K) of metal ions and PAN heterogenic reactions and corresponding extraction constants(K_{ex}):

$$pK = 2{,}8 + 0{,}5\ pK_{ex},\ R^2 = 0{,}991.$$

Oxidation-reduction reactions involving the sol–gel incorporated reagents have been investigated through example of the Mo,P heteropolycompounds (Mo,P HPC), well-known analytical reagents for determination of various reductants.

We have synthesized xerogels doped with various Mo,P heteropolycompounds (Mo,P HPC), with and without the reduction catalyst (copper(II)) [14,23,24].

Properties of xerogels doped with Mo,P HPC and their interactions with ascorbic acid, hydrazines, hydroquinone, iron(II), and tin(II) have been studied. The modified xerogels can undergo up to 30 cycles of oxidation-reduction. The addition of copper(II) accelerates the reaction significantly. Results for the interaction with ascorbic acid are given in Table 2.

The formal redox potential of Mo,P heteropoly acid is +0,751 V at pH 3,6 which indicates that oxidating ability is enhanced after entrapping in silica sol–gel materials [24].

Azocoupling and oxidative condensation reactions in sol–gel materials have been studied using xerogels doped with reagents entering the reactions of azo or oxidative coupling (1-naphthol,

Table 2
Copper(II) influence on the ascorbic acid interaction with silica xerogels doped with Mo,P heteropolycompounds [23].

Xerogel doped with Mo, P HPC	Equilibrium time, min	Half-reaction time, min
Without copper(II)	60	20
With immobilized copper(II)	20	2.5

2-naphthol), 2,7-dihydroxynaphthalene (2,7-DON) [25], and 4-aminoantipyrine (4-AAP) [16].

The conditions for aniline and its derivatives interaction with the diazocoupling product of reaction between aniline and phenolic compounds (1-naphthol, 2-naphthol, 2,7-dihydroxynaphthalene (2,7-DON)), included in xerogels have been determined. Xerogel modified with 1-naphthol has turned out to show the best performance. It interacts with aniline and its alkyl derivatives in pH interval of 8,4-9,2 [25].

Phenol and its chlorated derivatives (3-chlorophenol, 2,4-, 2,6-diclorophenol, 2,4,5-, 2,4,6-trichlorophenol) react with 4-aminoantipyrine modified sol–gel materials in presence of potassium hexacyanoferrate. The optimal pH interval is 7.0–7.5 [16].

The kinetics of these heterogeneous reactions has been studied; equilibrium time is 20–25 min [16,25]

In order to further investigate the analytic possibilities of sol–gel materials we developed methods of amino-functionalized silica sol–gel materials and silica–titania sol–gel materials.

2.2. Functionalized silica materials

Sol–gel materials can be modified by using functionalized alkoxysilanes, containing alkyl, amino, vinyl, epoxy, mercapto, and other groups. Organically modified silicate (Ormosil) materials are prepared by the sol–gel process using both alkoxysilane and its derivatives. This method of preparation gives these modified materials greater flexibility [10]. Employment of Ormosils is a simple way to change physical and chemical properties of sol–gel materials and get the desired matrix [11]. Thus, the variety of sol–gel sensors and biosensors is even more increased [4,11]. Functionalized silica sol–gels have been used for metal ions determination. Sol–gel monoliths grafted with pyridine have been utilized for Cr(VI) determination [45]. Amino-functionalized sol–gels and sol–gels grafted with diethylenetriamine have been employed for optical determination of copper [37,46]. Ormosils with thiol groups have been used for sol–gel layers with dispersed metals [47,48]. Sensors for BOD determination have been constructed with the use of whole microorganisms cells incorporated in poly(vinyl alcohol)-functionalized silica sol–gel [49–53].

Using the described above method for xerogel powders fabrication we synthesized sol–gel materials with amino groups (0.5–15%vol). The ratio tetraethoxysilane: 3-aminopropyltriethoxysilane has been varied to obtain different materials. Those xerogel powders have been used as sorbents. In order to utilize them for polyphenol compounds determination we have investigated the sorption of quercetin and the product of its oxidative coupling with 3-methylbenzothiazolinone-2-hydrazone (MBTH). Sorption rate increases with the increase of amino group concentration, and starting from 10% it becomes quantitative ($R = 96 \pm 1\%$). Sorption equilibrium time is 15 min for quercetin, and 5 min for the product of oxidative coupling [53].

The Ormosils have been used for developing of quercetin SIA-BIS determination procedure.

2.3. Silica–titania and titania materials.

At the present time titania sol–gel materials are not yet widely used for inorganic and organic compounds determination. Some examples of titania and silica–titania are present in literature [54–60]. Titania containing sol–gel materials have been used for amperometric [55–58] and spectroscopic [59,60] determination. Titania sol–gel films doped with hemoglobin [55], glucose oxidase [56], and tyrosinase [57,58] have been employed to construct amperometric sensors for determination of corresponding substrates. These matrixes have provided a biocompatible microenvironment for retaining the native structure and activity of the entrapped protein and enzymes and a very low mass transport barrier to the substrates. SiO_2–TiO_2 composites have been used as fluorimetric sensor for hydrogen peroxide as its phosphorescence is quenched by H_2O_2[59]. The fabrication and characterization of a pH sensor based on titania sol–gel films doped with different organic dyes(brilliant green, rhodamine 6G, rhodamine B and coumarin) is described [60].

We have suggested utilizing the color reaction between silica–titania sol–gel materials and analyte for rapid determination of ascorbic acid, polyphenols and hydrogen peroxide [26,27].

Silica–titania sol–gel materials have been obtained using earlier developed procedure. To obtain materials with different content of titanium(IV) the ratio of tetraethoxysilane and titanium(IV) tetrabutylate in the hydrolyzed mixture has been varied from 95:5 to 0:100 vol%. The materials have been dried at 800 W microwave irradiation to get xerogel powders.

We have studied the interaction of silica–titania sol–gel materials with ascorbic acid and phenolic compounds (catechol, quercetin, dihydroquercetin, rutin, gallic, caffeic, and ferulic acids), hydrogen peroxide. When the silica–titania sol–gel materials contact with a solution of these compounds through a complexing reaction, it leads to the coloration of powders or films, respectively. For example, the adsorption spectra of the silica titania xerogels after contact with ascorbic acid and phenolic compounds are presented in Fig. 4. Two absorption maxima are observed in the spectra: at 390 and in the range 470–520 nm.

In the IR spectra a wide absorption band corresponding to covalent vibrations of OH-bonds has been observed at 3700–2600 cm^{-1}. Therefore, the complexing reaction between silica–titania xerogels and analytes can be described by the following scheme for ascorbic acids and phenolic compounds [26]:

$$\equiv \text{Ti–OH} + n\text{HR} \leftrightarrows \equiv \text{TiR}_n + n\text{H}_2\text{O} \tag{6}$$

and by another scheme for hydrogen peroxide [27]:

$$\equiv \text{Ti–OH} + n\text{H}_2\text{O}_2 \leftrightarrows \equiv \text{Ti(O2H)}_n + n\text{H}_2\text{O} \tag{7}$$

We used the equilibrium-shift method to describe heterogenic complexing reactions. For all the studied compounds the complex composition was 1:1. According to the calculated complexation constants, the stability of the complexes of titanium(IV)

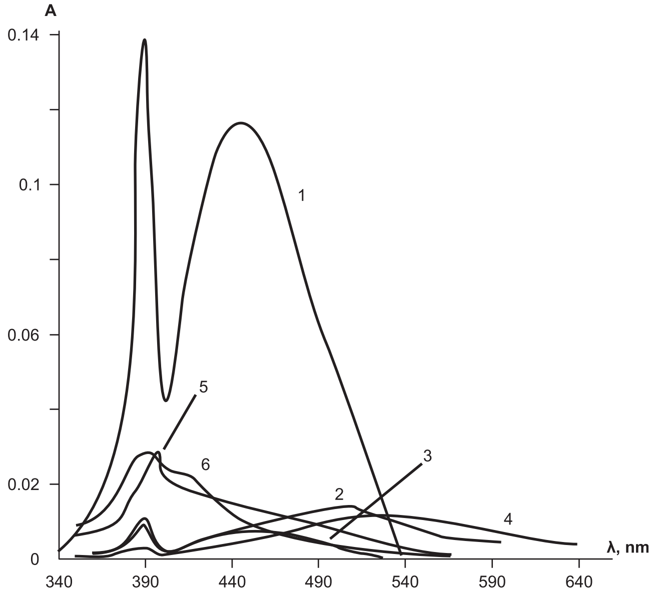

Fig. 4. Absorption spectra of silica–titania xerogel (5 vol %) after the interaction with. $5 \cdot 10^{-5}$ M solutions of caffeic acid (*1*), quercetin (*2*), rutin (*3*), dihydroquercetin (*4*), gallic (*5*) and ascorbic acid (*6*) [26].

incorporated into xerogels reduces in the row: dihydroquercetin > gallic acid > ascorbic acid, hydrogen peroxide > catechol > quercetin > caffeic acid > rutin > ferulic acid. Low sensitivity of the xerogels towards ferulic acid could be explained by the involvement of one hydroxyl and one methoxy group in the complexing reaction compared with two hydroxyl groups for all the other studied compounds. Evidently, such complexes are less stable.

Kinetics of heterogeneous complexing reactions has been studied. The equilibrium time for all the studied compounds does not exceed 10 min. Catechol, dihydroquercetin, and hydrogen peroxide react most rapidly (half reaction time is less than 30 s).

Silica–titania sol–gel films and powders have been employed for solid spectroscopic determination of ascorbic acid, phenolic compounds (catechol, quercetin, dihydroquercetin, rutin, gallic, caffeic, and ferulic acids), and hydrogen peroxide. Test determination of hydrogen peroxide has been also performed with the use of silica–titania xerogel powders.

3. Application

3.1. Electrochemical sensors

Modified sol–gel materials offer great possibilities and are coming into wide use in electrochemical analytical methods, mainly in voltammetry. Three stages can be marked out in developing of voltammetric electrodes based on sol–gel materials: standard graphite or metal electrodes modification with modified sol–gel layers, creating electrodes made of new composite silicon–carbon materials, and production of planar disposable electrodes as a result of sol–gel layer polymer materials modification.

Electrodes of first two types are widely acknowledged as suitable for metal ions determination. Lundgren and Murray [61] were first to use the sol–gel technology for the modification of graphite and carbon paste electrodes. They have created electrodes for copper(II), iron(II), mercury(II), nickel and lead using graphite electrodes covered with sol–gel layers modified with thiosemicarbazone, neocupferron, 4,7-dimethyl-1,10-phenantroline, dimethylglyoxime, diphenylcarbazone and other reagents [62–66].

Glassy carbon electrode coated with sol–gel films doped with enzymes (tyrosinase [67], glucose oxidase [68], HRP [69]) have been used for the determination of phenols, glucose, and hydrogen peroxide, respectively. Sol–gel film functionalized with pyridine is characterized by ion-exchange possibility, and that has allowed creating an electrode for chromium(VI) determination [70]. For the determination of ascorbic and uric acids glassy carbon electrodes have been coated with sol–gel films with incorporated methylene blue dye [71]. Gold electrode, covered with imprinted sol–gel layer has been proposed for bisphenol A determination in different samples [72]. Platinum electrode has been covered by sol–gel layer modified by entrapped HRP and successfully applied for the hydrogen peroxide determination [73].

Other works have also contributed to this approach [74–76] and have clarified the advantages of using the carbon powder as a part of silicon–carbon sol–gel materials to create the electrodes. Wide range of electrodes for the biomolecules (phytohormones, glucose, L-cysteine, glutathione, insulin, and dopamine) determination have been created using the described approach [47,48,68,77–80]. Some of them are biosensors based on the proteins (enzymes and antibodies) incorporation in the sol–gel matrix. Other electrodes have been obtained by inserting ruthenium complexes [79], metallic nickel and octacyanomolybdate(IV) [80] into the sol–gel layer. It is worth mentioning that Ormosils also can be applied this way; the examples of using the Ormosil containing thiol group for the creation of the sol–gel layers with dispersed metals are described (with dispersed silver [47], with dispersed copper[48]).

Wang has suggested using the screen-printing technology to obtain the planar sol–gel electrodes [82]. They are mainly used for the biologically active substances, such as dopamine, insulin, glutathione, urea and others [63,64,81]. These electrodes are not being widely used for the inorganic compounds determination currently. The possibility of their application for copper(I), iron(II), and selenium determination is described as well [65,66].

We have developed the procedure for sol–gel electrodes production through the example of the electrodes for iron(II,III) [83] and selenium (VI) [84] determination. We have tested two different approaches to get the electrochemically sensitive layers: putting the sol–gel layer on a carbon containing ink (for iron(II,III) determination) and incorporating carbon powder particles into sol–gel film (for selenium (VI) determination).

To select the sensitive voltammetric iron determination conditions sol–gel electrodes modified with 1,10-phenantroline, 2,2'-dipyridyl, chromazurol, and eriochrome cyanine have been studied. The currents of iron complexes electrotransformation have been better expressed and have had bigger value when the sol–gel electrodes modified with 1,10-phenantroline and 2,2'-dipyridyl have been used, so they have been chosen for further investigation. The maximum of analytical signal has been obtained when pH is 4,5–5,0. Analytical signal of iron has had the maximal value with the concentrating potential ranging from $-0{,}3$ to $-0{,}5$ V. Analytical signal of iron changes linearly with the increase of concentrating stage duration up to 180 s.

Thus, the following conditions have been chosen for the stripping voltammetric iron determination with the use of sol–gel electrodes modified with 1,10-phenantroline and 2,2'-dipyridyl: 0,1 M acetic buffer as a background electrolyte, concentrating potential from $-0{,}3$ to $-0{,}5$ V, concentrating stage duration 10–120 s depending on iron(II) concentration in the solution. The procedures for iron voltammetric determination have been proposed, the analytical range is 50–300 ppb for 30 s of concentrating stage duration. These procedures have been applied to iron determination in natural waters [83].

Another type of planar electrodes implies inserting graphite particles into the sol–gel layer instead of putting the latter on the carbon-containing ink, so that the conductor is embedded into the sol–gel matrix itself. O-diamines (2,3-diaminonaphtalene, o-phenylenediamine, 3,3'-diaminobenzidine) have been used as analytical reagents, as they are known to be the most sensitive and selective reagents for the selenium (VI) determination. 2,3-Diaminonaphtalene has turned out to be the best reagent in given conditions. The analytical range is 0.1–20 ppb for 10 s of concentrating stage duration.

The selectivity of planar electrodes has been discovered to be very high. Surfactants and humic acids present in natural waters also do not show significant interference during the selenium (VI) determination. We have developed the procedures for selenium (VI) determination in natural waters [84].

Sol–gel sensors containing enzymes have been proposed for amperometric detection in FIA [58,85,86].

3.2. Solid phase spectroscopic determination

Modified sol–gel layers and monoliths are have been actively used for solid spectrophotometric determination of different substances since early 1990s [2–4]. Numerous studies have proven that enzymes and other biomaterials [5,11,12,87–93], acid-base indicators [30–32,94], and organic complexing reagents [29,40–43,45,95,96] incorporated into silica sol–gel materials are still able to undergo the chromogenic reactions typical for them in solution.

Using the new way of fast preparation of modified sol–gel materials powders has significantly widened the range of immobilized analytical reagents. Sensitive and simple procedures based on the described above materials have been developed for Ag(I), Cd, Fe(III), Mn(II), Mo(VI), Ni, Pb, Zn, chlorides, fluorides, hydrazines, hydrogen peroxide, iodides, ascorbic acid, anilines, naphthols, esters, phenols, and polyphenolic compounds determination [16–19,21–27].

These procedures are rapid; it takes only 5–20 min to reach the sorption equilibrium.

The high selectivity is gained by proper reagents choice and heterogenic reactions conditions selection. In some cases, the selectivity can also increase because of immobilization itself.

The characteristics of developed procedures are presented in Table 3. Those procedures have been successfully applied to analysis of various samples: environmental, food, sanitary, and pharmaceutical samples (Table 4).

3.3. SIA

In recent years, the sequential injection analysis (SIA) has become an important analytical technique. Method developed by Ruzicka and Marshall in 1990 [97] is based on forward, reversed and stopped flow of the carrier stream. It offers several advantages: the instrumental set-up is very flexible, the components wear out less, and the process can be efficiently controlled.

The coupling of monolithic column with sequential injection technique (SIA), as a new possibility of implementation of a separation step in SIA has been described. Monolithic columns have been developed based on new sol–gel materials obtaining from alkoxysilanes in the presence of water-soluble polymers (e.g. poly(ethyleneoxide) or polyethylene glycol (PEG)). Due to the presence of macropores these columns can be coupled with the SIA system without loss of performance. A novel reversed-phase sequential injection chromatography technique has been optimized and validated for pharmaceutical analysis [98].

The last modification of this method is a bead injection technique that combines the use of beads within a flowing stream of solution in a flow injection system. Detection can be done directly on the beads—bead injection spectroscopy (BIS). Beads are utilized as a renewable sensing layer containing suitable groups for preconcentration of analyte or its derivatives. Sol–gel materials, that can be utilized as beads, are not being widely used for SIA currently.

We have investigated the possibilities of Ormosils with amino groups as beads for BIS quercetin determination after its oxidative coupling with MBTH in the presence of cerium(IV) [99]. Ormosils with amino groups have been found to be most appropriate for determination of quercetin. Also, sol formation in presence of 1–2%vol PEG gives lighter beads, which lessens the sedimentation. The analytical range is 24–150 ppm, throughput is 24 samples/h. The procedure has been used for quercetin determination in pharmaceuticals [53].

The sol–gel materials application to SIA might give new opportunities for bead injection.

3.4. Test determination

The development of simple and rapid methods for on-site determining inorganic and organic substances in environmental, food, beverages, and pharmaceutical samples has remained an important problem. This can be accomplished using different approaches, and one of them is test determination. Test methods for analysis of various samples are being under intensive development and widely used. Many companies are producing test tools—paper test strips, dropping bottle, ampoules, tablets made from dry reagents, etc. Generally, most test-methods are based on chromogenic reactions and provide the possibility of visually observed analytical signal.

We have elaborated test-methods suitable for both large scale and reliable analysis of various liquid samples. These methods are based on using various sol–gel materials which serve as indicator powders. In the first case an analytical signal is color of indicator powder, in the second one—the length of colored zone in an indicator tube.

Table 3
Characteristics of solid phase spectrophotometric determination of various analytes using silica–titania and modified silica xerogels.

Analyte	Xerogel type	Analytical range, ppm	LOD, ppm	Ref.
Metal ions				
Ag(I)	Silica with sulfochlorophenolazorodanine	0.5–8	0.1	[17]
Cd	Silica with bromobenzothiazo	0.02–0.2	0.01	[17]
Fe(III)	Silica with chrome azurol and cetylpyridinium chloride	0.08–5.0	0.04	[16]
Mn(II)	Silica with 1-(2-pyridilazo)naphthol	0.07–2.0	0.05	[16]
Mo(VI)	Silica with lumogallion	0.2–6	0.2	[16]
Ni	Silica with 1-(2-pyridilazo)naphthol and cetylpyridinium chloride	0.1–2.0	0.04	[18]
Pb	Silica with chrome pyrazol I	0.01–4.0	0.005	[17]
Zn	Silica with 4-(2-pyridilazo)resorcin and cetylpyridinium chloride	0.1–4.5	0.06	[19]
Non-metal compounds				
Chlorides	Silica with diphenylcarbazone	1.0–30	0.5	[21]
Fluorides	Silica with xylenol orange	0.5–10	0.3	[21]
Hydrazines	Silica with Mo,P heteropolycompounds	0.2–20	0.1	[24]
Hydrogen peroxide	Silica–titania	0.6–15	0.2	[27]
Iodides	Silica with starch	100–800	10	[16]
Organic compounds				
Anilines	Silica with 1-naphthol	0.05–10	0.02	[25]
Ascorbic acid	Silica with Mo, P heteropolycompounds and copper(II)	1.0–50	0.3	[23]
	Silica–titania	6–110	2	[26]
Esters	Silica with Fe(III) salts	17–450	11	[16]
Naphthols	Silica with Co(III) salts	0.1–4.0	0.05	[22]
Phenols	Silica with 4-aminoantipyrine	0.03–0.5	0.01	[16]
Caffeic acid	Silica–titania	0.2–2	0.07	[26]
Dihydroquercetin	Silica–titania	1.2–200	0.4	[26]
Gallic acid	Silica–titania	3–500	1	[26]
Quercetin	Silica–titania	63–300	21	[26]
Rutin	Silica–titania	36–500	12	[26]

Table 4
Results of solid phase spectrophotometric (SPS) and indicator tubes (IT) determination of metal ions, non-metal and organic compounds in environmental, food, pharmaceutical, and sanitary samples.

Analyte	Sample	Method	Found		Reference
			Developed method	Independent method	
Environmental analysis					
Cu	Mineral fertilizer	IT	(50 ± 5) ppm	(54.0 ± 0.1) ppm (AAS)	[20]
Ni	Technological solution	IT	(62 ± 3) %	65% (AAS)	[18]
Zn	Soil extract	SPS	(55 ± 2) ppm	53 ppm (VA)	[19]
Phenols	Waste water	SPS	$(3.6 \pm 0.3) \cdot 10^{-5}$ M	$(3.8 \pm 0.1) \cdot 10^{-5}$ M (S)	[16]
Food analysis					
Al	Coca-Cola, aluminum can	IT	(0.50 ± 0.06) ppm	0.55 ppm (S)	[16]
Al	Fanta, aluminum can	IT	(1.2 ± 0.1) ppm	1.1 ppm (S)	[16]
Cl^-	Mineral water	IT	(130 ± 20) ppm	130 ppm (T)	[21]
Cu	Pea	IT	(6.5 ± 0.5) ppm	6.3 ppm (AAS)	[16]
Cu	Grapes	IT	(4.5 ± 0.3) ppm	4.4 ppm (AAS)	[16]
Fe(III)	Mineral water	IT	(0.10 ± 0.05) ppm	0.13 ppm (S)	[16]
Fe(III)	Grapes	SPS	(6.3 ± 1.3) ppm	6.5 ppm (S)	[16]
F^-	Mineral water	SPS	(1.8 ± 0.5) ppm	2.0 ppm (I)	[21]
Zn	Milk	SPS	(2.7 ± 0.2) ppm	2.5 ppm (VA)	[19]
Zn	Beef	SPS	(60 ± 4) ppm	60 ppm (AAS)	[19]
Zn	Pork	SPS	(13 ± 2) ppm	10.5 ppm (AAS)	[19]
Ascorbic acid	Soft beverage	SPS	(22 ± 1) ppm	20 ppm (S)	[23]
Pharmaceutical and sanitary analysis					
Sn(II)	Reagent for radiopharmaceutical	IT	(60.2 ± 0.3) μg/vial	60.0 μg/vial (S)	[24,100]
Hydrogen peroxide	Antiseptic solution 1	IT	(73 ± 2) ppm	73.5 ppm(T)	[27]
	Antiseptic solution 2	SPS	(10.1 ± 0.5) ppm	10.0 ppm (T)	[27]
Ascorbic acid	Drug "Antigrippin"	SPS	(264 ± 44) mg/pill	300.0 mg/pill (PD)	[26]
Dihydroquercetin	Predrug " Dihydroquercetin "	SPS	(28.9 ± 0.4) mg/pill	25.0 mg/pill (PD)	[26]
	Predrug "Kapilar"	SPS	(9.2 ± 0.8) mg/pill	10.0 mg/pill (PD)	[26]

S—spectrophotometry, AAS—atomic absorption spectroscopy, VA—voltamperometry, I—ionometry, T—titrimetry, PD—producer's data.

Table 5
Characteristics of test determination of various analytes using silica–titania and modified silica xerogels.

Analyte	Xerogel type	Method	Analytical range, ppm	Reference
Metal ions				
Cd	Silica with bromobenzothiazo	Visual	0.001–0.05	[17]
		Indicator tube, pumping	0.1–3	[17]
Co(II)	Silica with 4-(2-pyridilazo)resorcin and cetylpyridinium chloride	Indicator tube, dipping	0.1–10	[16]
Cu(II)	Silica with bromobenzothiazo	Visual	0.004–1.5	[17]
	Silica with chrome azurol and cetylpyridinium chloride	Visual	0.05–4	[16]
	Silica with 1-(2-pyridilazo)naphthol, zincon, and cetylpyridinium chloride	Indicator tube, dipping	0.3–10	[16]
Fe(III)	Silica with chrome azurol and cetylpyridinium chloride	Visual	0.1–4	[16]
		Indicator tube, dipping	0.3–25	[16]
		Indicator tube, pumping	0.5–5	[16]
Mn(II)	Silica with 1-(2-pyridilazo)naphthol	Visual	0.5–5	[17]
Ni	Silica with 1-(2-pyridilazo)naphthol and cetylpyridinium chloride	Indicator tube, dipping	0.3–30	[18]
		Indicator tube, pumping	0.1–20	[18]
Sn(II)	Silica with Mo,P heteropolycompounds	Indicator tube, pumping	6–60	[24]
Non-metal compounds				
Chlorides	Silica with diphenylcarbazone	Visual	3–20	[21]
		Indicator tube, dipping	20–200	[21]
Fluorides	Silica with xylenol orange	Visual	1–10	[21]
Hydrazines	Silica with Mo,P heteropolycompounds	Visual	0.3–3	[24]
		Indicator tube, pumping	0.02–1	[24]
Hydrogen peroxide	Silica–titania	Indicator tube, dipping	3000–19000	[27]
Iodides	Silica with starch	Indicator tube, dipping	10–800	[16]
Organic compounds				
Anilinies	Silica with 1-naphthol	Visual	0.05–10	[25]
Ascorbic acid	Silica with Mo,P heteropolycompounds and copper(II)	Visual	10–400	[23]
Esters	Silica with Fe(III) salts	Visual	0.01–1	[16]
Phenols	Silica with 4-aminoantipyrine	Visual	0.001–0.5	[16]

Analytical reagents used for preparing indicator powders have to be as sensitive and selective as possible. In addition their reactions with analytes have to be rapid and yield contrast color changes. It is important that both the reagent and the reaction product should not be washed out of the indicator powder with the test solution.

We have developed analytical procedures for Cd, Cu(II), Fe(III), Mn(II), chlorides, fluorides, hydrazines, anilines, ascorbic acid, esters, and phenols colorimetric test determination with the use of silica xerogels doped with analytical reagents as indicator powders (see Table 5) [16–18,21,24,25]. The criteria to choose the sol–gel material for test determination are high contrast of reaction, satisfactory selectivity, and high speed of heterogenic equilibrium achievement between powders and analyte solution [16].

The principal difference and the main advantage of indicator tubes method is the analytical signal measured in length of colored zone and not the intensity of color itself. This makes the measurement much more simple and precise. One of the significant "length-of-stain" indicator tubes characteristics is the RSD value, which equals 2–15%. This value can be compared with the ones for instrumental analysis methods. Using silica xerogels doped with 1-nitroso-2-naphthol, alizarin, and 1,10-phenanthroline Lev et al. [34,38,39] have developed indicator tubes for cobalt(II), pH, and iron(III). The injection of the analyte solutions into the indicator tube can be performed by two methods: by rising of the liquid induced by capillary force ("dipping mode") or by forced pumping through the tube ("pumping mode"). The first mode provides faster and simpler analysis, and the second one ensures more sensitive determination due to bigger volumes of analyte solutions used for analysis.

Using doped silica and silica–titania xerogels we have developed indicator tubes for Cd, Co(II), Cu(II), Fe(III), Ni, Sn(II), chlorides, hydrazines, hydrogen peroxide, and iodides determination [16–18,21,24,27]. The analytical characteristics of indicator tube determination are given in Table 5.

Developed test tools based on various sol–gel materials have been used for environmental, food and beverages, sanitary, and pharmaceutical analysis. The results of such application are given in Table 4.

The obtained results demonstrate the main features of the test determination with the use of the indicator tubes: high reproducibility, sensitivity, and also fast and simple utilization (time of analysis equals 2–10 min).

4. Conclusion

The silica and silica–titania sol–gel materials can be used for various sensing systems, and their versatility presents great perspectives for analytical chemistry. In this review both synthesis and application of silica and silica–titania sol–gel materials have been discussed. Summarizing all the work performed under authors supervision in MSU two main ways of sol–gel materials application can be outlined: using these new materials as a matrix for different analytical reagents and then utilizing it as a part of a highly sensitive sensor system (electrochemical, optical), or preparing novel tools for simple and fast test determination (indicator powders, indicator tubes). The procedures have been developed for numerous metal ions, non-metal and organic compounds determination for both types of sol–gel materials application, and they have been successfully used for environmental, food, sanitary, and pharmaceutical samples analysis. The works accomplished by author's team have made a significant input in sol–gel chemistry investigation, and, hopefully, this field is still open for future studies and innovative solutions.

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