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Dedicated to the 90th birthday of Academician Yu.A. Zolotov

Complex Formation in the Modified Xerogel Phase: Study and Application in Analysis

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Abstract—The review summarizes the author's results concerning the complex formation in the phase of modified xerogels synthesized by the sol–gel process for application as sensor materials. The results of studying the complex formation (pH ranges of reactions, light absorption maxima and compositions of complexes, and equilibrium constants) are presented and discussed for 87 systems of two types, that is, immobilized ligand (organic analytical reagent)–metal ion and immobilized metal ion–organic or inorganic compound. The approach proposed by the author to describe the complex formation in the modified xerogel phase is presented. The results of applications of modified xerogels as sensor materials are considered, including their use for determining metal ions; organic compounds; hydrogen peroxide; chloride, fluoride, and oxalate ions in food and hygienic products, pharmaceuticals, biological fluids, and environmental media.

Keywords: sol–gel process, doped silica-based xerogels, silica–titania xerogels, complex formation in heterogeneous systems, equilibrium shift method, sensor materials

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INTRODUCTION

Many analytical methods are based on complex forming reactions. In spectrophotometric analytical methods, metal ions are determined after the formation of colored complexes with organic analytical reagents, while inorganic and organic compounds are determined after the formation of colored complexes with metal ions; determination of anions is often based on the destruction of colored compounds in the presence of these anions due to competitive complexation. The complex forming reactions in heterogeneous systems with the use of sensor materials that change their properties in the presence of analytes improves the metrological characteristics of quantitative analysis and, what is highly important, makes field determinations more convenient. Development of such materials is of considerable interest.

As a result of our studies, xerogels, sensor materials based on silica and titania obtained by a sol–gel process, were implemented in the practice of chemical analysis; methods for determination of metal ions, anions, and organic compounds in various specimens were developed.

This review summarizes the results of studying the complexation in a modified xerogel phase and briefly demonstrates the potential of analytical application of modified xerogels.

Given below are the heterogeneous complex forming reactions taking place in the modified xerogel phase, namely, the metal ion reaction with immobilized analytical reagents (reaction 1, below referred to as (1)) and the reaction of organic and inorganic complex forming agents with immobilized metal ions (2):

$$n\overline{\mathrm{L}} + \mathrm{Me}^{n+} = \overline{\mathrm{MeL}_n}\,, \quad (1)$$

$$\overline{\mathrm{Me}^{n+}} + n\mathrm{L} = \overline{\mathrm{MeL}_n}. \quad (2)$$

Xerogels doped with ligands, analytical reagents, have been used to determine metal ions (1); metal ions immobilized in xerogels in xerogels have been used to determine compounds that can function as ligands (2); immobilized ligands and metal ions under competitive complexation conditions have been proposed for determination of anions and cationic surfactants.

SYNTHESIS OF MODIFIED XEROGELS

Studies of the effect of conditions of synthesis on the product characteristics resulted in the development of a new fast method for the synthesis of materials with specified physicochemical properties. The method is based on hydrolysis of tetraethoxysilane, gelation, and drying of wet gels in a microwave (MW) field [1–4].

The general view of the IR spectra of silica xerogels, representing broad rounded peaks, attests to their amorphous state and high water content. The spectra exhibit intense lines at 478, 656, and 1000–1400 cm^{-1}, corresponding to symmetrical and asymmetrical vibrations of silicon–oxygen bonds. The band at 1620 cm^{-1}, which is present in the spectra of both xerogels dried by heating and xerogels obtained under MW irradiation, indicates the presence of physically adsorbed water. The absence of bands corresponding to the Si–O–C, C–O, C–C, and C–H vibrations in the xerogel spectra means that hydrolysis has proceeded to completion under the chosen conditions and that ethanol has been completely removed by drying [1, 5].

The materials were endowed with important analytical properties using the following techniques:

— introduction of modifying agents (analytical reagent or metal ion) during preparation of the sols to prepare silica-based materials doped with analytical reagents [1, 2, 4, 6–10] or metal ions [1, 2, 11, 12];

— simultaneous use of silica and titania precursors to obtain mixed silica-titania materials [2, 3, 13–20];

— combination of the above approaches: introduction of iron(III) during sol preparation from a mixture of silicon and titanium precursors [5].

In some cases, the synthesized xerogels were additionally modified with a desired reagent via adsorption.

Silica-based xerogels doped with a variety of analytical complexing reagents (L) have been prepared. These reagents include oximes: dimethylglyoxime (DMG), furyldioxime (FD), benzyldioxime (BD); azo compounds: 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN), Brombenzthiazo (BBT), Zincon (ZNC), Arsenazo 1 (AR1), Lumogallion (LG), sulfochlorophenolazorhodanine (SCPAR); hexaoxacycloazochrome (HOCAC); triphenylmethane derivatives: chrome azurol (CAZ), xylenol orange (XO), eriochrome cyanine (ECC), sulfochrome (SC); 1,10-phenanthroline (Phen), bathophenanthroline (BPhen), 2,2-bipyridine (BP), diphenylcarbazone (DPCon), crystal violet (CV), Chrompyrazole 1 (CP1) [1, 2, 6–10]. Below these materials are designated by L–Si.

Studies of the simultaneous complexation of L and various types of surfactants, including cationic (cetylpyridinium chloride (CPC)), anionic (sodium dodecyl sulfate), and non-ionic ones (Triton X-100), showed that in the case of DMG, some azo derivatives, and triphenylmethane derivatives, CPC has a considerable effect on the properties of sensor materials. Xerogels doped with organic analytical reagent + CPC mixtures were prepared, in particular, DMG–CPC–Si, PAN–CPC–Si, PAR–CPC–Si, BBT–CPC–Si, ZNC–CPC–Si, CAZ–CPC–Si, ECC–CPC–Si, SC–CPC–Si. The incorporation of CPC into silica-based sol–gel materials, together with a complexing reagent, substantially enhanced the retention of the complexing reagent by the silica matrix, apparently, due to the formation of ion associates [8–10].

Silica-based xerogels were doped with copper(II) (Cu–Si), cobalt(III) (Co–Si), iron(III) (Fe(III)–Si), and vanadium(V) (V(V)–Si) [1, 11, 12].

In order to elucidate the causes for efficient retention of metal ions by xerogels, cobalt- and iron-doped xerogels were examined by IR spectroscopy. In the IR spectrum of the cobalt-doped xerogel (Co–Si), the absorption band at 3749 cm^{-1}, corresponding to free silanol groups, decreased in intensity compared to that for non-modified xerogel, and an intense band appeared at 955 cm^{-1}, probably due to Co–O bond vibrations. The decrease in the intensity of the 3749 cm^{-1} band may be attributable to the fact that ion exchange reactions take place during gel maturation [11]. The IR spectrum of iron(III)-doped silica xerogel (Fe(III)–Si) exhibited a band at 800 cm^{-1} corresponding to silicon–oxygen bending modes. This suggests that the iron ions in xerogels are bound via the silanol groups of the silica matrix [12].

The assumption that the metal ions are held due to the interaction with xerogel silanol groups is also supported by the fact that the hydrolytic stability region for copper(II)-, cobalt(II)-, and iron(III)-doped xerogels in acidic solutions is restricted by pH 2. This value is rather close to the isoelectric point of silica gel, after which the silanol groups are protonated.

A method for the synthesis of films and xerogels of silica–titania sol–gel materials (Si–Ti) by co-hydrolysis of titanium and silicon alkoxides and gelation has been developed [2, 3, 13–20].

The IR spectra of silica–titania xerogels exhibited absorption bands at 400–600 cm^{-1} (Ti–O–Ti stretching modes) and at 1110 cm^{-1} (Si–O–Si modes). An increase in the titania content led to broadening of the absorption bands corresponding to vibrations of bonds in the titania chain and decrease in the peaks corresponding to bond vibrations in the silicon chain [13].

Iron(III)-doped silica–titania xerogels were prepared (Fe(III)–Si–Ti) [5].

Silica–titania xerogels were modified via adsorption of catechol (Si–Ti/Cat), caffeic acid (Si–Ti/CA), pyrocatechol violet (Si–Ti/PCV), and eriochrome cyanine (Si–Ti/ECC) [17–20].

COMPLEX FORMATION IN THE MODIFIED XEROGEL PHASE

All of the above-mentioned systems for modified xerogel synthesis were chosen for subsequent use in

Table 1. Light absorption maxima of complex compounds in the xerogel phases with immobilized ligands and in solutions [1–3, 6–10]*

Ligand (L)	Metal	λ_{max}, nm	
		solution	xerogel (L–Si)
Dimethylglyoxime	Ni(II)	450	550
Dimethylglyoxime + CPC	Ni(II)		550
1-(2-Pyridylazo)-2-naphthol	Cu(II)	550	560
	Ni(II)	565	570
	Fe(III)	775	580, 750
	Mn(II)	564	580
1-(2-Pyridylazo)-2-naphthol + CPC	Ni(II)	570	575
4-(2-Pyridylazo)resorcinol	Pb	536	540
	Co(II)	510	520
	Zn	520	515
	Cd	500	525
4-(2-Pyridylazo)resorcinol + CPC	Cd	520	535
	Co(II)	520	545
	Zn	515	540
Lumogallion	Mo(VI)	510	515
Brombenzthiazo	Cd	560, 590	570, 620
	Cu(II)	580	590
Brombenzthiazo + CPC	Cu(II)	630	625
Zincon	Cu(II)	600	625
Zincon + CPC	Cu(II)	610	625
Chrome azurol	Fe(III)	580	610
	Al	540	530
	Cu(II)	580	580
Chrome azurol + CPC	Fe(III)	635	675
	Al	630	525
	Cu(II)	615	635
Sulfochrome	Fe(III)	540	590
	Al	540	535
	Cu(II)	540	600
Sulfochrome + CPC	Fe(III)	625	600
	Al	615	540
	Cu(II)	590	620
Eriochrome cyanine	Fe(III)	530	520
	Cu(II)	560	610
Eriochrome cyanine + CPC	Fe(III)	635	535
	Cu(II)	630	620
Xylenol orange	Fe(III)	550	555

Table 1. (Contd.)

Ligand (L)	Metal	λ_{max}, nm	
		solution	xerogel (L–Si)
Xylenol orange	Al(III)	555	550
	Zr(VI)	535	550
Arsenazo I	Al(III)	600	580
Sulfochlorophenolazorhodanine	Ag(I)	510	505
Hexaoxacycloazochrome	Pb	640, 720	640, 715
Diphenylcarbazone	Hg(II)	565	560
1,10-Phenanthroline	Fe(II)	512	480
Bathophenanthroline	Fe(II)	533	505
8-Hydroxyquinoline	Ce(IV)	495	475
5,7-Dibromo-8-hydroxyquinoline	Ce(IV)	505	480

* CPC is cetylpyridinium chloride.

analysis as sensor materials that change their spectrophotometric characteristics after the reaction with analytes, particularly, upon the reactions of immobilized ligands with metal ions or immobilized metal ions with potential ligands.

The materials were optically transparent in thin layers (1–2 mm), which allowed the use of solid-phase spectrophotometry as the key method for studying the complex formation in the modified xerogel phases.

The absorption maxima of complexes and the optimal pH ranges were determined for 87 systems involving modified xerogels. For determining the compositions of complexes formed in modified xerogel phase and the equilibrium constants of heterogeneous reactions, we developed the equilibrium shift method [1, 11–16, 19]. The study revealed characteristic features of the heterogeneous complexation reactions involving modified xerogels. The results of studying the complex formation in the modified xerogel phase involving immobilized ligands and immobilized metals are presented below.

Immobilized analytical reagents (ligands) (L–Si) react with metal ions present in the solution as shown in Scheme 1 [1, 2]. The equilibrium constant of this heterogeneous reaction is given by

$$K_{\mathrm{L}} = \frac{\left[\overline{\mathrm{MeL}_n}\right]}{\left[\mathrm{Me}^{n+}\right]\left[\overline{\mathrm{L}}\right]^n}. \qquad (3)$$

The light absorption maxima for the complexes formed in the modified xerogel phase were determined for 47 systems (Table 1). For most of studied systems, the positions of absorption maxima of the complexes in the modified xerogel phase nearly coincided with the absorption maxima of these complexes in solution. This apparently indicates that the complexes formed in the xerogel phases have the same composition as those formed with non-immobilized ligands. Considerable short-wavelength shifts of the absorption maxima induced by the complexation in the modified xerogel phase in comparison with those in solutions (iron(II)–Phen–Si and iron(II)–BPhen–Si, cerium(IV)–Ox–Si, and cerium(IV)–DBOx-Si systems) are probably attributable to a different composition of complexes that are formed in the xerogel [1]. It is noteworthy that the complexation in the modified xerogel phase in the presence of CPC, like that in solutions, is accompanied by a significant increase in the light absorption intensity. An increase in the contrast of the solid-phase photometric reactions was revealed for zinc–PAR, cobalt–PAR, copper–BBT, copper–CAZ, and iron–CAZ systems in the presence of CPC [8–10].

Study of the effect of acidity on the reactions of immobilized ligands with metal ions provided the conclusion that the conditions for the formation of complexes in xerogels and in solutions are generally similar (Table 2). However, there are a number of obvious differences. For most immobilized reagents, the lower boundary of the optimal pH range of complex formation is shifted to higher pH compared to that in solutions. A considerable difference between the optimal acidity values was found for the formation of ion associates of crystal violet with CdI_4^{2-} and Chrompyrazole 1 with PbI_4^{2-} in xerogels and solutions. Higher acid concentration for the reactions in xerogels is apparently due to the fact that some acid is consumed for the protonation of the silanol groups of the xerogel silica matrix. Interesting results were obtained for the cadmium–BBT–Si system: in the xerogel phase, complexation took

Table 2. pH ranges of the formation of complex compounds in xerogels with immobilized ligands and in solutions [1–3, 6–10]*

Ligand (L)	Metal	pH range	
		solution	xerogel (L–Si)
Dimethylglyoxime	Ni(II)	8–9	8–10
Dimethylglyoxime + CPC	Ni(II)		8–10
1-(2-Pyridylazo)-2-naphthol	Cu(II) Ni(II) Mn(II)	3–8 5–10 8–10	4.8–8.0 5.2–9.0 8.0–9.0
1-(2-Pyridylazo)-2-naphthol + CPC	Ni(II)	5.5–9.0	5.0–9.0
4-(2-Pyridylazo)resorcinol	Pb Co(II) Zn Cd	8.0–10.0 5–9 5–6.5 9.8–10.4	8.5–9.2 6.0–7.6 8–9 7.4–8.6
4-(2-Pyridylazo)resorcinol	Cd Co(II) Zn	8.5–9.5 6–9 9–10	8–10 5–10 8–9
Lumogallion	Mo(VI)	1–4	3–5.8
Brombenzthiazo	Cd Cu(II)	3% NaOH 9–10	8.8–9.2 8–10
Brombenzthiazo + CPC	Cu(II)	7–9	7.0–9.5
Zincon	Cu(II)	5.2	4.5–5.5
Zincon + CPC	Cu(II)		4.5–6.0
Chrome azurol	Fe(III) Al Cu(II)	5–6 6.5 5–7	3.5–5.0 6–6.5 4–6
Chrome azurol + CPC	Fe(III) Al Cu(II)	5–6 6.5–7.0 4–7	3–4 6.5–8.0 4–5
Sulfochrome	Fe(III) Al Cu(II)	4–5 7–8 4–6	3–4 7–8 3–4
Sulfochrome + CPC	Fe(III) Al Cu(II)	5–6 7–8 3–6	2.5–4.0 7.5–8.5 3–4
Eriochrome cyanine	Fe(III) Cu(II)	7–8 5–6	7.5–8.0 4–5
Eriochrome cyanine + CPC	Fe(III) Cu(II)	7.0–7.8 4	7.5–8.5 4–5
Xylenol orange	Fe(III)	1–8	1–4
Sulfochlorophenolazorhodanine	Ag(I)	1.0–7.0	2.0–7.0
1,10-Phenanthroline	Fe(II)	2.0–8.0	2.0–7.4

* CPC is cetylpyridinium chloride.

Table 3. Compositions of complexes (M : L) in xerogel phases with immobilized ligands and in solution [1, 2]*

Ligand (L)	Metal	Composition of complexes (M : L)	
		solution	xerogel (L–Si)
1-(2-Pyridylazo)-2-naphthol (PAN)	Cu(II) Ni(II) Fe(III) Mn(II)	1 : 1 1 : 2 1 : 2 1 : 2	1 : 1 1 : 2 1 : 2 1 : 2
1-(2-Pyridylazo)-2-naphthol PAN + CPC	Ni(II)	1 : 2	1 : 2
4-(2-Pyridylazo)resorcinol	Pb Co(II) Zn Cd	1 : 1 1 : 2 1 : 2 1 : 2	1 : 1 1 : 2 1 : 2 1 : 2
4-(2-Pyridylazo)resorcinol + CPC	Cd Zn	1 : 2 1 : 2	1 : 2 1 : 2
Lumogallion	Mo(VI)	1 : 1	1 : 1
Brombenzthiazo	Cd	1 : 2	1 : 2
Chrome azurol	Fe(III) Al Cu(II)	1 : 1 1 : 1 1 : 1	1 : 1 1 : 1 1 : 1
Chrome azurol+ CPC	Fe(III) Al Cu(II)	1 : 2 1 : 3 1 : 3	1 : 2 1 : 2 1 : 2
Sulfochrome	Fe(III) Al Cu(II)	1 : 1 1 : 1 1 : 1	1 : 1 1 : 1 1 : 1
Sulfochrome + CPC	Fe(III) Al Cu(II)	1 : 3 1 : 3 1 : 3	1 : 2 1 : 2 1 : 2
Eriochrome cyanine	Fe(III) Cu(II)	1 : 1 1 : 1	1 : 1 1 : 1
Eriochrome cyanine + CPC	Fe(III) Cu(II)	1 : 3 1 : 2	1 : 2 1 : 2
Sulfochlorophenolazorhodanine	Ag(I)	1 : 0.5; 1 : 1; 1 : 2	1 : 1
Hexaoxacycloazochrome	Pb	1 : 1	1 : 1
1,10-Phenanthroline	Fe(II)	1 : 3	1 : 2
Bathophenanthroline	Fe(II)	1 : 3	1 : 2
8-Hydroxyquinoline	Ce(IV)	1 : 4	1 : 3
5,7-Dibromo-8-Hydroxyquinoline	Ce(IV)	1 : 4	1 : 3

* CPC—cetylpyridinium chloride.

place quantitatively even at pH 9, while in solution, the reaction occurred only at pH 11. Apparently, the main cause is significant increase in the acidity of BBT upon incorporation into xerogels [1].

The notion of distribution ratio of a metal ion (D_{Me}) was introduced to describe the complex formation involving immobilized ligands (1) [1]

Table 4. Equilibrium constants ($\log K_L$) of the heterogeneous complexation reactions involving xerogels with immobilized ligands [1, 2]

Xerogel (L–Si)	Metal	$\log K_L$
1-(2-Pyridylazo)-2-naphthol	Cu(II) Ni(II) Fe(III) Mn(II)	1.5 4.2 4.4 4.5
4-(2-Pyridylazo)resorcinol	Pb Co(II) Zn	2.7 5.2 6.1
Lumogallion	Mo(VI)	3.4
Brombenzthiazo	Cd	5.5
Sulfochlorophenolazorhodanine	Ag(I)	4.5
Hexaoxacycloazochrome	Pb	2.6
8-Hydroxyquinoline	Ce(IV)	11.9
5,7-Dibromo-8-hydroxyquinoline	Ce(IV)	11.2

$$\mathrm{D_{Me}} = \frac{\left[\overline{\mathrm{MeL}_n}\right]}{\left[\mathrm{Me}^{n+}\right]}.$$

Hence, (3) can be written as

$$K_\mathrm{L} = \frac{\mathrm{D_{Me}}}{[\mathrm{L}]^n}. \tag{4}$$

The $\mathrm{D_{Me}}$ values were found experimentally from the difference between the initial metal ion concentration and residual concentration after the contact with a modified xerogel. The equilibrium concentrations of metal ions were determined by atomic absorption or extraction-and-photometry techniques using calibration curves plotted in advance. In neutral and weakly alkaline media, metal ions are extracted to the modified xerogel phase not only via the reaction with the immobilized reagent, but also due to reaction with the silica silanol groups. The contribution of these ion exchange reactions to the retention of metal ions was taken into account by determining the metal ion retention by non-modified xerogels at particular pH values. In view of the above, $\mathrm{D_{Me}}$ values for specially synthesized modified xerogels with various contents of immobilized ligands were determined. The experimental data plotted as $\log \mathrm{D_{Me}}$ vs. $\log[\mathrm{L}]$ were approximated by straight lines; the compositions of the resulting complexes (n) were found from the slopes of these lines, and the conditional equilibrium constants of the reactions were determined from the y-axis intercept.

The compositions of complexes (n) formed in the modified xerogel phase are summarized in Table 3; and the conditional equilibrium constants of heterogeneous complexation reactions (K_L) for some of the complexes are given in Table 4.

In relation to 43 systems containing immobilized ligands of various classes, it was ascertained that in systems that tend to form 1 : 1 and 1 : 2 complexes in solutions, the composition of complexes did not change when they were formed in the immobilized state in xerogels. An exception was the SCPAR–silver(I) system, probably due to different compositions of complexes. In the systems that tend to form 1 : 3 and 1 : 4 complexes in solutions, the number of ligands coordinated around the central atom upon complexation in xerogels was smaller. These results are in good agreement with the above data on the positions of the light absorption maxima of complexes formed in modified xerogels [1].

The non-covalent immobilization method that we developed for incorporation of ligands (organic analytical reagents) into silica-based xerogels ensures reliable attachment of the ligands. In addition, what is very important, the ligands preserve the ability to form complexes with metal ions. Xerogels doped with organic analytical reagents were used as sensor materials to determine metal ions.

Metal ions immobilized in copper(II)-, cobalt(III)-, iron(III)-, and vanadium(V)-doped xerogels and in mixed silica–titania xerogels react with inorganic and organic compounds capable of complex formation according to Scheme 2 [1, 11–16, 19]. The equilibrium constant for this heterogeneous reaction is given by

$$K_\mathrm{Me} = \frac{\left[\overline{\mathrm{MeL}_n}\right]}{\left[\overline{\mathrm{Me}^{n+}}\right][\mathrm{L}]^n}. \tag{5}$$

In relation to 40 systems, it was found that after the contact of modified xerogels with inorganic or organic compounds, potential ligands, colored compounds were formed in the xerogel phases [1, 11–16, 19]. The light absorption maxima of the colored complexes in the xerogel phase in comparison with those in solutions are given in Table 5. For most of the compounds, considerable blue shifts were observed, which is apparently attributable to the decrease in the number of coordinated ligands in xerogels caused by steric restrictions.

The IR spectrum of the silica-based xerogel doped with iron(III) after the contact with salicylhydroxamic acid exhibited an absorption band at 470 cm^{-1}, which correspondsed to the Fe–N bond, characterizing the formation of iron complexes with hydroxamic acids [12].

Study of the effect of acidity on the reactions of immobilized metal ions with inorganic and organic compounds led to the conclusion that conditions of complex formation in xerogels and in solutions differ insignificantly (Table 6).

Table 5. Light absorption maxima of complexes in xerogel phase with immobilized metal ions and in solutions [1, 11–16, 19]

Immobilized metal ion	Ligand	λ_{max}, nm	
		solution	xerogel
Xerogels doped with metal ions (M–Si)			
Copper(II)	Ammonia	640	600
	Methylamine	690	640
	Diethylamine	700	680
	Pyridine	630	605
	Picoline	640	600
	Ethylenediaminetetraacetate	740	735
	4-(2-Pyridylazo)resorcinol	510	500
Cobalt(III)	Ammonia	650	615
	Methylamine	640	610
	Pyridine	550	495
	Picoline	550	505
	Aniline	640	610
	1-Nitroso-2-naphthol	317, 410	320, 415
Iron(III)	Salicylhydroxamic acid	530	450
	Phenylhydroxamic acid	510	470
	Methylhydroxamic acid*	500	460
	Ethylhydroxamic acid*	500	460
	Butylhydroxamic acid*	510	430
	Isobutylhydroxamic acid *	510	460
	Bromomethylhydroxamic acid*	495	450
	Thiophenylhydroxamic acid*	530	470
Iron(II)**	1,10-Phenanthroline	505	510
Vanadium(V)	Salicylhydroxamic acid	620	550
Mixed silica–titania xerogels (Si–Ti)			
Titanium(IV)	Hydrogen peroxide	410	420
	Ascorbic acid	440	390
	Gallic acid	370	400
	Caffeic acid	380	410
	Rutin		450
	Quercetin		500
	Dihydroquercetin		530
	Catechol		450
	Salicylate	400	410
	Salicylamide		410
	Methylsalicylate		410
	Pyrocatechol violet	600	640
	Pyrocatechol violet + CPC	620	670
	Eriochrome cyanine	485	570
	Eriochrome cyanine + CPC	560	510
	Chrome azurol	485	550
	Chrome azurol + CPC	565	505

* Prepared in situ by hydroxamation of the corresponding esters.

** Prepared by reduction in the presence of antioxidants.

Table 6. pH ranges of the formation of complex compounds in xerogels with immobilized metal ions and in solutions [1, 11–16, 19]

Immobilized metal ion	Ligand	pH range	
		solution	xerogel
Xerogels doped with metal ions (M–Si)			
Copper(II)	4-(2-Pyridylazo)resorcinol	0.1–1 M H_2SO_4	3–5
Cobalt(III)	1-Nitroso-2-naphthol	>4	5–9
Iron(III)	Salicylhydroxamic acid	0–2	1–4
	Phenylhydroxamic acid	1–7	2.5–5.5
Iron(II)*	1,10-Phenanthroline	1–5	2–3
Vanadium(V)	Salicylhydroxamic acid	2–3.5	0.5–2
Mixed silica-titania xerogels (Si–Ti)			
Titanium(IV)	Hydrogen peroxide	0.5–1 M H_2SO_4	3–10
	Ascorbic acid	3.5–6	4–7
	Gallic acid	3.3–5.8	4–7.5
	Caffeic acid	3–5.5	4.5–7.5
	Rutin	3–8	6–8
	Quercetine	3–6	6–8
	Dihydroquercetine	3.5–5.8	4.5–7.5
	Salicylate	<2.5	1.5–2.5
	Salicylamide		1.5–2.5
	Methylsalicylate		7–8
	Pyrocatechol violet		6.5–7.5
	Eriochrome cyanine		1–2
	Chrome azurol		2–3.5

* Prepared by reduction in the presence of antioxidants.

The notion of degree of complexation of the immobilized metal ion (**Φ_{Me}**), defined below, was introduced to study the complexation involving immobilized metal ions (Scheme 2) [1]:

$$\Phi_{Me} = \frac{\left[\overline{MeL_n}\right]}{\left[\overline{Me^{n+}}\right]}.$$

Therefore, (5) can be written as

$$K_{Me} = \frac{\Phi_{Me}}{[L]^n}. \qquad (6)$$

The Φ_{Me} value was found experimentally after identification of the absorption maximum of the complex formed in the modified xerogel phase and choice of the optimal pH value for the complex formation in the modified xerogel.

This was done by studying the dependence of absorbance of modified xerogels on the concentration of inorganic or organic compound, potential ligand, in the solution. Φ_{Me} was calculated as

$$\Phi_{Me} = \frac{A_i}{A_{exc} - A_i},$$

where A_i is the xerogel absorbance at the absorption maximum of the reaction product after a contact with a particular ligand concentration, and A_{exc} is the xerogel absorbance at the absorption maximum of the reaction product after a contact with excess ligand, which hence contains completely complexed immobilized metal ion. The equilibrium concentrations of ligands ([L]) in solutions after a contact with xerogels containing metal ions were determined by spectrophotometry using calibration dependences plotted in advance.

Using the least squares method, the resulting experimental data plotted as $\log\Phi_{Me}$ vs. log[L] were approximated by straight lines; the compositions of the resulting complexes were found from the slopes of these lines, and the conditional equilibrium constants of the reactions were determined from the *y*-axis intercepts.

The metal to ligand ratios in the complex compounds formed in the modified xerogel phase and the

Table 7. Compositions of complexes (M : L) in the xerogel phase with immobilized metal ions and in solution and equilibrium constants ($\log K_{\mathrm{Me}}$) of heterogeneous complexation reactions in xerogels with immobilized metal ions [1, 11–16, 19]

Immobilized cation	Ligand	Composition of complexes (M : L)		$\log K_{\mathrm{Me}}$
		solution	xerogel	
Metal ion-doped xerogels (M–Si)				
Copper(II)	4-(2-Pyridylazo)resorcinol	1 : 1	1 : 1	2.2
Cobalt(III)	1-Nitroso-2-naphthol	1 : 3	1 : 3	11.8
Iron(III)	Salicylhydroxamic acid	1 : 3	1 : 1	2.7
	Phenylhydroxamic acid	1 : 2	1 : 2	6.8
Mixed silica–titania xerogels (Si–Ti)				
Titanium(IV)	Hydrogen peroxide	1 : 1; 1 : 2; 1 : 3; 1 : 4	1 : 1	3.4
	Ascorbic acid	1 : 1; 1 : 2; 1 : 3	1 : 1	3.4
	Gallic acid	1 : 2; 1 : 3	1 : 1	3.7
	Caffeic acid	1 : 1	1 : 0.5	2.5
	Rutin	1 : 1	1 : 1	2.2
	Quercetin	1 : 1; 1 : 2	1 : 1	3.2
	Dihydroquercetin		1 : 1	4.3
	Catechol	1 : 1	1 : 1	3.4
	Salicylate		1 : 0.5	2.0
	Salicylamide		1 : 1	2.9
	Methylsalicylate		1 : 1	3.4
	Pyrocatechol violet		1 : 1	4.1
	Eriochrome cyanine		1 : 1	3.1
	Chrome azurol		1 : 1	3.1

conditional equilibrium constants of the heterogeneous complexation reactions are summarized in Table 7. In relation to the studied 18 systems, it was found that in most cases, complexes with 1 : 1 metal to ligand ratio were formed in the modified xerogel phase; this may be attributable to steric restrictions to the complex formation in the modified xerogels [1, 11–16, 19]. For salicylic acid–Si–Ti and caffeic acid–Si–Ti systems, formation of complexes of a different composition was detected, resulting from the interaction of simultaneously two titanium atoms in the silica-titania xerogels [15].

In the case of polyphenols, the stability of complexes decreased in the following sequence: dihydroquercetin > gallic acid > catechol > quercetin > dopamine > caffeic acid > rutin [13]. The salicylic acid complexes are less stable than complexes formed by its derivatives. In the case of triphenylmethane dyes, the stability of complexes decreases in the following order: pyrocatechol violet > chrome azurol > eriochrome cyanine (Table 7) [19].

The non-covalent immobilization methods that we developed for incorporation of metal ions into silica-based xerogels and methods for the synthesis of mixed xerogels based on silica and titania ensure reliable attachment of metal ions. Furthermore, what is very important, immobilized metal ions preserve the ability to form complexes with potential ligands. Xerogels modified with metal ions were used as sensor materials to determine hydrogen peroxide and organic compounds.

Competitive complexation was studied in systems based on immobilized analytical reagents (L–Si) and silica–titania xerogels (Si–Ti).

The reactions were carried out for the following systems based on immobilized ligands: AR1–Si–zirconium(IV)–fluoride, AR1–Si–aluminum–fluoride, Alizarin red–Si–zirconium(IV)–fluoride, XO–

Si–zirconium(IV)–fluoride, XO–Si–aluminum–fluoride, DPCon–Si–mercury(II)–chloride. An increase in the concentration of halide ions (An) leads to bleaching of the xerogel color as a result of the following reaction:

$$\overline{\mathrm{L}} + \mathrm{An} + n\mathrm{Me}^{n+} = \overline{x\mathrm{MeL}} + (n - x)\mathrm{MeAn}.$$

The organic ligand-doped xerogel–metal ion systems were used to determine fluoride and chloride ions [1–3, 7].

The silica–titania xerogels modified by catechol (Si–Ti/Cat), caffeic acid (Si–Ti/CA), and pyrocatechol violet (Si–Ti/PCV) were used to determine fluoride ions [17, 18]; the silica–titania xerogels modified by eriochrome cyanine (Si–Ti/ECC) were used to determine oxalate ions [19]. In the presence of these anions, the colored complexes of immobilized titanium(IV) formed earlier decomposed according to the reaction

$$\overline{\mathrm{TiL}} + \mathrm{An} = \overline{\mathrm{TiAn}} + \mathrm{L}.$$

The addition of CPC to silica–titania xerogels modified with triphenylmethane derivatives (Si–Ti/PCV, Si–Ti/ECC, Si–Ti/CAZ) markedly increased the absorbance of xerogels (hyperchromic effect). This is apparently indicative of the formation of ternary compounds TiLCPC in the silica–titania xerogel phase. This effect underlies the determination of cationic surfactants [20].

ANALYTICAL APPLICATION OF MODIFIED XEROGELS

Xerogels doped with organic analytical reagents or containing metal ions capable of complex formation were used in analysis as sensor materials for solid-phase spectrophotometric (SPS) and visual colorimetric (visual) determinations and in indicator tubes (IT). Sol–gel films modified with analytical reagents were employed as sensing zones of printed electrodes for metal ion determination using inversion voltammetry [1–3, 5–22].

Criteria for the choice of systems for the development of SPS methods include high molar absorption coefficient of the colored compound formed in the modified xerogel phase, relatively high selectivity, and high rate of attainment of heterogeneous equilibrium in the sensing material–analyte solution system. A key requirement to the indicator powders for visual determination is also a high contrast of the reaction [1–3, 5, 7–9, 11–20].

The IT method is based on proportionality between the length of the colored zone of the sensing material in the indicator tube and the analyte concentration. The major advantage of this approach is the possibility of reliable fast assay of the compound content from the easily measurable colored length rather than the degree of color change or tint (as in most fast assays).

Our studies on the use of modified xerogels as indicator powders resulted in the development of the IT method for analysis of solutions. The requirements to heterogeneous reactions were formulated: it was shown that the determination sensitivity depends on the content of the reagent in the sensing material, geometric dimensions of the indicator tube, and determination conditions [1–3, 6, 7, 9, 10, 14, 21].

Brief information on the use of modified xerogels for determination of metal ions or inorganic and organic compounds in various samples is given below.

Metal ion determination. Determination is based on heterogeneous complexation reactions with immobilized analytical reagents in silica-based xerogels and sol–gel films. Studies of the effects of the content of immobilized analytical reagents in modified xerogels, conditions of analytical reactions, and the method of detection of the analytic signal resulted in the development of SPS, visual, and IT determination procedures [1–3, 6–10, 21]. Sol–gel films doped with Phen, BP, CAZ, and ECC were studied as indicator zones of planar electrodes for inverse voltammetry (IVA) determination of iron in various samples [22, 23].

The analytes, the sensor materials, and analytic signal detection methods are summarized in Table 8 [1–3, 6–10, 21–23].

Determination of organic compounds and hydrogen peroxide. Determinations of ascorbic acid, salicylic acid and its derivatives, polyphenols, hydroxamic acids, hydrogen peroxide, naphthols, and esters after derivatization are based on heterogeneous complexation reactions with immobilized metal ions [1–3, 5, 11–20]. Cobalt(III)-doped xerogels were used to determine naphthols after nitrosation [1, 11]; and iron(III)-doped xerogels were employed to determine hydroxamic acids and esters after hydroxamation [1, 12]. Complex formation of titanium(IV) incorporated in silica–titania xerogels form the basis for determination of hydrogen peroxide, polyphenols, salicylic acid, and its derivatives [13–16]. Silica–titania xerogels modified with PCV were used to determine CPC [20]. Iron(III)-doped silica–titania xerogel in the presence of 1,10-phenanthroline was proposed as a sensing material for SPS determination of the total content of polyphenols in beverages. The determination is based on the reduction of iron(III) to iron(II) in the xerogel phase in the presence of polyphenols and the subsequent formation of intensely colored complexes in the modified xerogel phase [5].

Study of the effect of content of the immobilized metal ions in modified xerogels, conditions of analytical reactions, and method of detection of the analytic signal resulted in the development of SPS, visual, and IT determination procedures. The analytes, sensor materials, and the analytic signal detection methods are summarized in Table 9 [1–3, 5, 11–16].

Table 8. Application of xerogels with immobilized ligands as sensor materials [1–3, 6–10, 21–23]

Analyte	Material (additional compounds)	Method, analytical range
Ag	SCPAR–Si	SPS, 0.5–8.0 mg/L
Cd	BBT–Si	SPS, 0.02–0.20 mg/L Visual, 0.001–0.050 mg/L IT, 0.1–3.0 mg/L
Mn	PAN–Si	SPS, 0.07–2.00 mg/L Visual, 0.5–5.0 mg/L
Mo(IV)	LG–Si	SPS, 0.2–6.0 mg/L
Pb	CP1–Si (iodide ions)	SPS, 0.01–4.0 mg/L
Ni	PAN–CPC–Si	SPS, 0.1–2.0 mg/L IT, 0.1–30.0 mg/L
Zn	PAR–CPC–Si	SPS, 0.1–4.5 mg/L
Fe	XO–Si CAZ–CPC–Si	IT, 0.05–0.5; 0.5–5.0; 5–50 mg/L SPS, 0.08–5.00 mg/L Visual, 0.1–4.0 mg/L IT, 0.3–25.0; 0.2–20.0 mg/L
	Phen–Si	IVA, detection limit: 0.02 mg/L, preconcentration for 60 s
Cu	CAZ–CPC–Si BBT–Si PAN–Si ZNC–CPC–Si ECC+CPC–Si	Visual, 0.05–4.00 mg/L Visual, 0.004–1.50 mg/L IT, 0.1–3.0; 3–30; 30–65 mg/L IT, 0.2–10.0 mg/L IT, 0.6–5.0; 0.3–3.0 mg/L
Co(II)	PAR–CPC–Si	IT, 0.1–10.0 mg/L
Chloride ions	DPCon–Si (mercury(II))	SPS, 1.0–30.0 mg/L Visual, 3–20 mg/L IT, 20.0–200.0 mg/L
Fluoride ions	XO–Si (zirconium(IV))	SPS, 0.5–10.0 mg/L Visual, 1–10 mg/L

Determination of anions. Anions were determined using xerogels doped with analytical reagents and silica–titania xerogels [1–3, 7, 17, 18].

Studies of the effect of the content of analytical reagent in sensor materials, concentration of metal ions in the solution (fluoride ion–zirconium(IV)–XO–Si, chloride ion–mercury(II)–DPCon–Si systems), and solution acidity resulted in the development of procedures for the solid phase spectrophotometric and visual determination of chloride and fluoride ions (Table 8) [1–3, 7].

Conditions for the degradation of colored complexes of xerogel-immobilized titanium(IV) were adjusted for the development of procedures for determination of fluoride and oxalate ions (Table 9) [3, 17, 18].

Xerogels modified with polyphenols were used to determine high concentrations of fluoride ions [17], and PCV-modified xerogels served for determination of low concentrations of fluoride ions [18].

Intensely-colored silica–titania xerogels modified with eriochrome cyanine Si–Ti/ECC are bleached in the presence of oxalate ions due to the formation of non-colored complexes of oxalate ions with titanium(IV) incorporated in sensor materials. Conditions for the solid-phase spectrophotometric determination of oxalate ions in vegetables and herbs were selected [19].

Table 9. Application of xerogels with immobilized metal ions as sensor materials [1–3, 5, 11–20]

Analyte	Material	Method, analytical range
Naphthols	Co(III)–Si	SPS, 0.1–4.0 mg/L
Esters	Fe(III)–Si	SPS, 17–450 mg/L
Salicylhydroxamic acid	Fe(III)–Si	SPS, (2.7–150) × 10^{-5} M
Hydrogen peroxide	Si–Ti	SPS, 0.6–15.0 mg/L IT, 2–37, 10–60, 16–110 mg/L
Ascorbic acid	Si–Ti	SPS, 6–110 mg/L
Gallic acid	Si–Ti	SPS, 3–150 mg/L
	Fe(III)–Si/Phen	SPS, (1.6–50) × 10^{-5} M
Caffeic acid	Si–Ti	SPS, 0.2–50.0 mg/L
Rutin	Si–Ti	SPS, 36–500 mg/L
Quercetine	Si–Ti	SPS, 63–300 mg/L
Dihydroquercetine	Si–Ti	SPS, 1.2–200.0 mg/L
Catechol	Si–Ti	SPS, 1.5–330.0 mg/L
Dopamine	Si–Ti	SPS, 1–150 mg/L
Propyl gallate	Si–Ti	SPS, 2.1–38.2 mg/L
Salicylate	Si–Ti	SPS, 14–685 mg/L
Salicylamide	Si–Ti	SPS, 68–1370 mg/L
Methylsalicylate	Si–Ti	SPS, 8–714 mg/L
Cat. surfactant (in CPC equivalents)	Si–Ti/PCV	SPS, 0.01–0.56 mM
Fluoride ions	Si–Ti/CA Si–Ti/Cat Si–Ti/PCV	SPS, 50–200 mg/L SPS, 100–500 mg/L SPS, 0.05–1.0; 5.0–90.0 mg/L
Oxalate ions	Si–Ti/ECC	SPS, 35–900 mg/L

The results of application of the developed procedures for determination of metal ions, inorganic and organic compounds in biological fluids, pharmaceuticals, disinfectants and hygiene agents, food products, environmental media, and industrial solutions are summarized in Table 10. The determination procedures were validated by comparing the results of analysis of real samples with the results obtained using other methods and by the spike/recovery method [1–3, 5–22].

CONCLUSIONS

By studying the complex formation in the modified xerogel phase, conditions for the occurrence of 87 heterogeneous complexation reactions and the light absorption maxima of the complexes formed in the modified xerogels were determined. An approach for determination of compositions of complexes formed in modified xerogels and the equilibrium constants of heterogeneous reactions was developed. The potential of this approach was demonstrated by the data on complexation in 61 systems containing either immobilized ligands or immobilized metal ions. The systems that tend to form 1 : 1 and 1 : 2 complexes in solution were found to form complexes of the same composition in the immobilized state in modified xerogels. In those cases where formation of 1 : 3 and 1 : 4 complexes is inherent in solutions, the number of ligands coordinated around the central atom in the modified xerogel phases decreased. It was demonstrated that modified xerogels are promising as sensor materials

Table 10. Examples of application of modified xerogels in analysis of biological fluids, pharmaceuticals, disinfectants and hygiene agents, food products, environmental media, and industrial solutions [1–3, 5–22]

Analyte	Sensing material (method)	Object of analysis	Found	
			sensing material	independent method
Biological fluids				
Salicylate ions	Si–Ti (SPS)	Blood serum, mM	0.97 ± 0.15	1.03 ± 0.05[a]
		Urine, mM	0.46 ± 0.07	0.42 ± 0.01[a]
Salicylhydroxamic acid	Fe(III)–Si(SPS)	Urine, mM	0.49 ± 0.04	0.05[b]
Fluoride ions	Si–Ti/PCV(SPS)	Saliva, mg/L	0.21 ± 0.06	0.2[b]
Pharmaceuticals, disinfectants and sanitizers				
Acetylsalicylic acid	Si–Ti (SPS)	Tablets, mg/tab.	510 ± 20	500[c]
Ascorbic acid	Si–Ti (SPS)	Tablets, mg/tab.	264 ± 44	300[c]
Dopamine	Si–Ti (SPS)	Solution, mg/L	4.8 ± 0.5	5.0
Methyl salicylate	Si–Ti (SPS)	Ointment, mg/g	123 ± 8	128[c]
Dihydroquercetin	Si–Ti (SPS)	Tablets, mg/tab.	28.9 ± 0.4	25[c]
Hydrogen peroxide	Si–Ti (IT)	Disinfecting solution, g/L	50 ± 1	50[c]
Cat. surfactant (in CPC equivalents)	Si–Ti/PCV(SPS)	Disinfecting solution, %	0.050 ± 0.009	0.05[c]
Fluoride ions	Si–Ti/CA(SPS)	Toothpaste,%	0.11 ± 0.01	0.1[c]
		Mouth rinse, %	0.030 ± 0.001	0.03[c]
Food products				
Antioxidant activity (gallic acid equiv.)	Fe(III)–Si–Ti/Phen (SPS)	Black tea, mM	0.16 ± 0.02	0.15 ± 0.01[a]
Propyl gallate	Si–Ti (SPS)	Sunflower oil, mg/kg	183 ± 9	190 ± 3[d]
		Cookie, mg/kg fat	46 ± 15	44 ± 2[d]
Oxalate ions	Si–Ti/PCV(SPS)	Sorrel, mg/100 g	1079 ± 158	995 ± 24[d]
		Parsley, mg/100 g	782 ± 80	835 ± 17[d]
Fe(III)	XO–Si (IT)	Milk, mg/L	5.1 ± 0.4	4.7[a]
	CAZ–CPC–Si (IT)	Water, mg/L	0.20 ± 0.02	0.21[a]
Cu	ZNC–CPC–Si (IT)	Grapes, mg/kg	5.0 ± 0.5	4.4[e]
Zn	PAR–CPC–Si (SPS)	Pea, mg/kg	33 ± 2	35.7[e]
		Beef, mg/kg	60 ± 4	60.0[e]
Environmental media, industrial solutions				
Ni	PAN–CPC–Si (SPS)	Industrial solution, %	62 ± 3	65[e]
Zn	PAR–CPC–Si (SPS)	Soil, mg/kg	55 ± 2	53[f]
Fe(III)	XO–Si (SPS)	Natural water, mg/L	5.1 ± 0.4	4.7[e]
Cu	PAN–Si (SPS)	Fertilizer, mg/L	50 ± 5	54[e]

[a] Found by spectrophotometry, [b] spike/recovery method, [c] indicated by the manufacturer, [d] found using HPLC, [e] found by flame atomic absorption spectroscopy, [f] found by inversion voltammetry.

for determination of metal ions, inorganic and organic compounds in biological fluids, pharmaceuticals, disinfectants and hygiene agents, food products, environmental media, and industrial solutions.

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