=================== **ARTICLES** ===================

Inorganic Oxides with Immobilized Ferrozine and Ferene for the Sorption–Spectroscopic Determination of Iron(II)

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Abstract—Sorbents based on inorganic oxides sequentially modified with polyhexamethylene guanidine, ferrozine, and ferene S are proposed for the preconcentration and determination of iron(II). Upon sorption from solutions with pH 2.5–7.0, colored iron(II) complexes with ferrozine and ferene S, having broad bands with maxima at 560 and 600 nm in the diffuse reflectance spectrum, respectively, formed on the sorbent surface. Procedures for the sorption–photometric determination of iron(II) using diffuse reflectance spectroscopy were developed. The limits of detection for iron(II), calculated by the 3s criterion were 0.005 and 0.006 µg per 0.1 g for sorbents based on silica with immobilized ferrozine and ferene S, respectively. The linearity of calibration curves remains up to 5 and 10 µg per 0.1 g for sorbents based on silicon and aluminum oxides, respectively. The procedures were tested in the determination of the total iron concentration in bottled drinking waters and alcoholic drinks.

Iron is a necessary element for normal functioning of living bodies, including human beings, animals, and plants. Iron deficiency results in anemia and its high level in a human body increases the risk of tumor growth and cardiovascular and endocrine diseases [1]. Iron enters a human body through foods, drinking water, and beverages. The concentration of iron in natural and drinking waters in Russia is regulated by sanitary rules and regulations *SanPiN 2.1.4.559-96* [2] and *GN 2.1.5.1315-03* [3] and, in the European Union, by *Directive 98/83/EU* [4]. The development of procedures for the rapid and reliable determination of iron in environmental samples and food products is a topical problem.

One of cost-effective, simple, and quite sensitive methods for the determination of iron is photometry. To increase the sensitivity and selectivity of the photometric determination of iron, it is preconcentrated [5, 6] using sorbents based on different polymer matrices [7–9], resins [10, 11], and silicon dioxide [12, 13] with ion exchangers and complexing functional groups.

For the selective preconcentration of Fe(III) and Fe(II), it is most promising to use sorbents with immobilized organic analytical reagents selective to the determined iron ion. For the photometric determination of iron(II) *N*-heterocyclic bases, such as 1,10-phenathroline, 2,2'-dipyridyl, pyridyltriazine, and their derivatives,

are widely used as organic reagents [14]. The use of pyridyltriazine derivatives as reagents allows one to achieve lower limits of detection for iron(II) [14]. The reagents 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine and 2,4,6-tris(2'-pyridyl)-1,3,5-triazine, and the like are poorly soluble in water; therefore, organic solvents are used for the determination of iron(II) with these reagents [15–17]. The pyridyltriazine sulfo derivatives, 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4',4"-disulfoacid (ferrozine) and 3-(2-pyridyl)-5,6-di(2-furyl)-1,2,4-triazine-5',5"-disulfoacid (ferene S), are highly soluble in water, which allows one to determine iron(II) in aqueous solutions [18–20].

Ferrozine   Ferene S
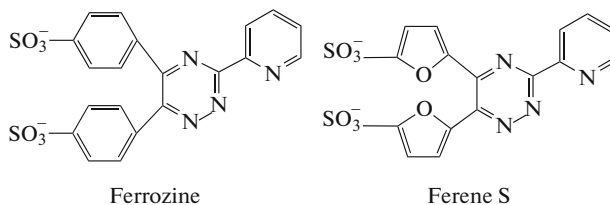
Preconcentration of iron(II) complexes with pyridyltriazine derivatives have been used for its sorption–photometric determination in blood serum, plants, and natural and drinking waters [17–20] with the application of different-nature sorbents.

As sorbent matrices for the sorption–photometric determination of iron, it is reasonable to use inorganic oxides (SiO_2, Al_2O_3, ZrO_2, and TiO_2) having no own

color. Ferrozine and ferene S can be immobilized only onto the surface of inorganic oxides premodified with polyhexamethylene guanidine [21].

The aim of the present work was to develop procedures for the sorption–photometric determination of iron(II) in drinking waters and alcoholic drinks using sorbents based on silica and alumina with immobilized ferrozine and ferene S.

EXPERIMENTAL

Reagents. A standard solution of iron(II) with a concentration of 200 mg/L was prepared by dissolving a weighed portion of chemically pure $FeSO_4 \cdot 7H_2O$ in 0.1 M H_2SO_4. Solutions with lower concentrations of iron(II) were prepared by dilutions of stock solutions with deionized water immediately prior to experimentation. To prevent the oxidation of iron(II) to iron(III), a 0.1 M solution of hydroxylamine in deionized water was used as a reductant.

The matrix for the preparation of sorbents was Silochrome C-120 (0.1–0.2 mm fraction with a specific surface area of ~120 m^2/g and a mean pore size of ~45 nm) and Al_2O_3 (Merck) (0.063–0.1 mm fraction with a specific surface area of ~256 m^2/g and a pore diameter of 8–15 nm). A 7% solution of polyhexamethylene guanidine (PHMG) was prepared dissolving a weighed portion of BIOPAG-D (Institute of Environmental Technological Problems, Moscow) in deionized water. Starting 1.5 mM solutions of ferrozine (Fz) and ferene S (FS) were prepared by dissolving a weighed portion of the sample purchased from Merck in deionized water. Reagent solutions with lower concentrations were prepared by dilutions of stock solutions with deionized water.

The required pH was adjusted adding HCl and high-purity NaOH, as well as acetate (pH 4.0–6.3), acetate-ammonium (pH 6.5–7.5) and ammonium (pH 8.0) buffers.

Apparatus. Diffuse reflectance spectra (**DRS**) on the coordinates of the Gurevich–Kubelka–Munk function $F(R) = (1 - R)^2/2R$–wavelength (nm), where R is the diffuse reflectance of sorbents, in a range of 380–720 nm were recorded on a Pulsar spectrophotocolorimeter (Khimavtomatika, Russia). Absorption spectra and absorbances of solutions were recorded on a Cary 100 spectrophotometer (Varian, Australia). The concentration of iron in solutions was determined by inductively coupled plasma atomic emission spectrometry (ICP–AES) on an Optima 5300 spectrometer (Perkin-Elmer, United States), the analytical line was 239.562 nm. pH of solutions was measured using a SevenEasy S20 potentiometer (Mettler-Toledo, Spain) with an InLabExpertPro combined electrode. Deionized water (18.1 MOhm) was obtained on an E-pure D4642-33 device (Barnstead International, United States).

Experimental procedure. The surfaces of silica and aluminum oxide were modified with polyhexamethylene guanidine to obtain SiO_2–PHMG and Al_2O_3–PHMG sorbents according to the procedure described in [21]. To study regularities of fixation of Fz and FS on the surface of SiO_2–PHMG and Al_2O_3–PHMG sorbents, a 0.2×10^{-7}–1×10^{-3} M solution of the reagent, NaOH and a buffer solution to adjust pH, and water (q.s. to 10 mL) were placed to a 20-mL volumetric tube with a ground stopper. The SiO_2–PHMG or Al_2O_3–PHMG sorbent (0.1 g) was added and the mixture stirred for 1–10 min. The resulting sorbents (SiO_2–PHMG–Fz, SiO_2–PHMG–FS, Al_2O_3–PHMG–Fz, and Al_2O_3–PHMG–FS) were separated by decantation and washed twice with deionized water. The sorption of reagents was controlled by the photometric analysis of the water phase at 283 (Fz) and 303 nm (FS).

The sorption of iron(II) was studied under batch conditions. For this purpose, a solution of iron(II) (1 mL) with a concentration of 5 μg/mL was placed in a 20-mL volumetric tube with a ground stopper, a 0.1 M solution of hydroxylamine (1.0 mL) was added, the required pH was adjusted, and water (q.s. to 10 mL) was added. The studied sorbent (0.1 g) was added, the tube was stoppered, and the mixture was stirred for 1–20 min. Solutions were decanted, the sorbent was transferred to a fluoropolymer cell, water excesses were removed with a filter paper, and diffuse reflectance in a range of 380–720 nm was measured. The concentration of iron in a solution prior to and after sorption was determined by ICP–AES.

The geometric parameters of molecules were calculated by the PM3 semiempirical method implemented in the GAMESS software [22]. The areas of molecules were estimated for the most stable conformation based on the obtained geometrical parameters and van der Waals atomic radii.

RESULTS AND DISCUSSION

Immobilization of ferrozine and ferene S onto the surfaces of SiO_2–PHMG and Al_2O_3–PHMG. Fz or FS are recovered quantitatively (≥98%) in a pH range of 2.5–7.5. The time of sorption equilibration does not exceed 5 min. The sorbents remain colorless in the sorption of Fz and become light-yellow in the sorption of FS.

At almost identical molecular structures of the reagents, the sorption capacities in terms of Fz and FS differ two-fold on both SiO_2–PHMG and Al_2O_3–PHMG (Fig. 1). This effect is likely due to different arrangements of reagent molecules relative to the sorbent surface. The Fz anion is retained on the surface due to the electrostatic interaction between sulfo groups of the reagent and protonated amino groups of PHMG and seems to be arranged perpendicularly to the sorbent surface. The FS anion is likely arranged in
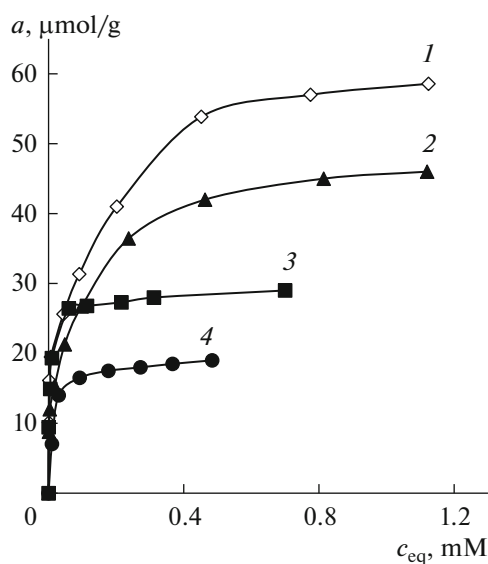
Fig. 1. Sorption isotherms of ferrozine (*1, 2*) and ferene S (*3, 4*) on SiO$_2$−PHMG (*1, 3*) and Al$_2$O$_3$−PHMG (*2, 4*) at pH 5.5.
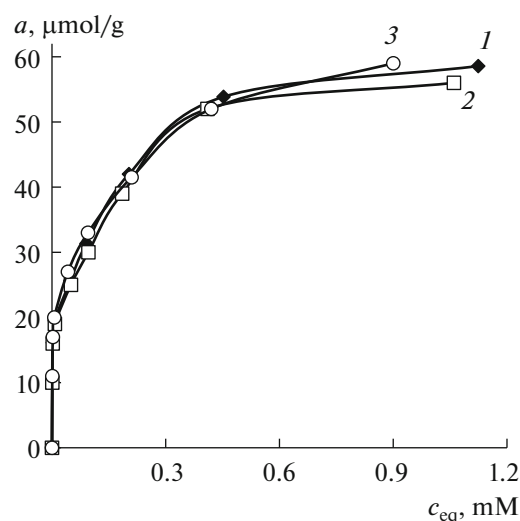
Fig. 2. Sorption isotherms of ferrozine on SiO$_2$−PHMG at pH 5.5: (*1*) is starting SiO$_2$−PHMG, (*2*) is SiO$_2$−PHMG after the first desorption, and (*3*) is SiO$_2$−PHMG after the second desorption with 2 M HCl.

parallel with the sorbent surface, being attached due to the electrostatic interaction and hydrogen bonding between the oxygen atoms of furyl rings and the amino groups of PHMG. According to quantum-chemical calculations, the projection of the Fz anion onto the sorbent surface is 0.67 nm^2 and that in the case of FS is 1.02 nm^2, which is due to different orientations of the reagent anions relative to the sorbent surface.

Acidic media or media with high saline backgrounds can have a significant effect on the fixation of Fz, FS, and PHMG onto the surface of inorganic oxides. The desorption of Fz with an increase in the concentration of acid and NaCl increases to a greater extent than that of FS (Table 1). A stronger fixation of FS is due to additional hydrogen bonding between the furyl oxygen atom of its molecule and the amino groups of PHMG.

The strength of PHMG fixation to the surface of inorganic oxides was estimated by the sorption isotherms of Fz (Fig. 2) obtained using a freshly prepared SiO$_2$−PHMG sorbent and sorbents after single and double desorption of reagents with 2 M HCl. As is shown in Fig. 2, the sorption isotherms of Fz obtained on the freshly prepared SiO$_2$−PHMG (curve *1*) and after single and double desorption of the reagent (curves *2* and *3*) coincide, which suggests a stronger fixation of the PHMG molecules on the surface of inorganic oxides.

Sorption preconcentration of iron(II). Sorption preconcentration of iron(II) was performed using SiO$_2$-based sorbents with a surface Fz and FS concentration of 20 μmol/g and Al$_2$O$_3$-based sorbents with a surface reagent concentration of 10 μmol/g corresponding to

Table 1. Desorption of ferrozine and ferrene S (%)

$c_{\text{desorp. sol}}$	SiO$_2$−PHMG−Fz	SiO$_2$−PHMG−FS	Al$_2$O$_3$−PHMG−Fz	Al$_2$O$_3$−PHMG−FS
	Desorbing solution—NaCl, g/L			
1	20	8	19	8
5	41	33	42	33
10	66	55	67	53
100	95	94	96	96
	Desorbing solution—HCl, mol/L			
0.01	26	16	27	17
0.1	63	44	63	45
1	91	88	93	90
2	97	92	97	92
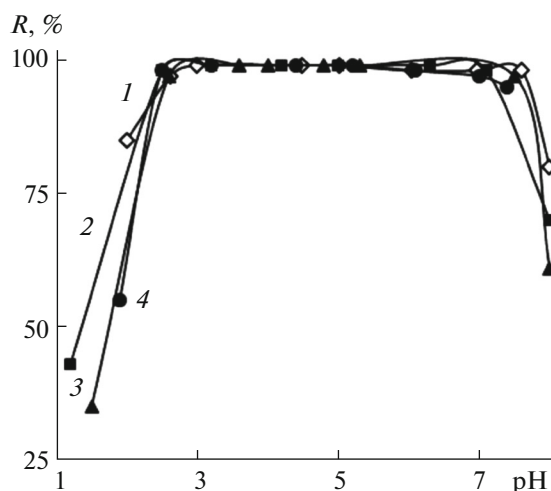
Fig. 3. Recovery rate of iron(II) as a function of pH onto SiO$_2$–PHMG–Fz (*1*), SiO$_2$–PHMG–FS (*2*), Al$_2$O$_3$–PHMG–Fz (*3*), and Al$_2$O$_3$–PHMG–FS (*4*): c_{Fe} = 0.5 µg/mL, 0.1 g of sorbent, V = 10 mL, and 0.01 M NH$_2$OH.

the range of their qualitative recovery. The time of sorption equilibration in the recovery of iron(II) using SiO$_2$-based sorbents from 10–20 mL of a solution does not exceed 5 min and that using Al$_2$O$_3$-based sorbents does not exceed 10 min. The quantitative (≥98%) recovery of iron(II) does not depend on the sorbent matrix and the reagent and is achieved in a range of pH 2.5–7.5 (Fig. 3). The sorption capacity of sorbents by iron(II) determined from horizontal regions of the sorption isotherms was 6.6 (SiO$_2$–PHMG–Fz), 6.3 (SiO$_2$–PHMG–FS), 3.4 (Al$_2$O$_3$–

PHMG–Fz), and 3.3 µmol/g (Al$_2$O$_3$–PHMG–FS). The comparison of the sorption capacities of sorbents with a surface concentration of reagents suggests the formation of surface complexes with the component ratio of Fe(II) : L = 1 : 3, i.e. the same as for iron(II) complexes with Fz and FS in aqueous solutions [23].

The equilibrium shift method in the version of diffuse reflectance spectroscopy was used to determine the Fe(II) : L ratio and to estimate the conditional stability constant (log β) by the dependence

$$\log(\Delta F(R)_i/(\Delta F(R)_{max} - \Delta F(R)_i)) - \log c_L,$$

where $\Delta F(R)_{max}$ is the difference between functions $F(R)$ for the maximum value and control experiment, $\Delta F(R)_i$ is the difference between the $F(R)$ values for the *i*-th and control experiment (Fig. 4). The log β value is numerically equal to the y-intercept. The stoichiometry of iron(II) complex with organic reagents equal to 1 : 3 was determined by the slope of straight line. The conditional stability constants for iron(II) complexes were log β = 17.3 ± 0.5 for Fe[Fz]$_3$ and log β = 16.5 ± 0.5 for Fe[FS]$_3$, which agrees with the data for these complexes in solutions [23].

In the sorption of iron(II), the surface of Fz-modified sorbents becomes lilac and that of FS-modified sorbents becomes blue. The maximum of DRS for the iron(II) surface complex with Fz is at 560 nm and that for the iron(II) complex with FS is at 600 nm (Fig. 5). The pattern of DRSs and the position of their maxima depend on the nature of SiO$_2$–PHMG or Al$_2$O$_3$–PHMG sorbent matrices. The highest color strength of the iron(II) surface complexes with Fz and FS remains in a range of pH 3.0–6.0 (Fig. 6). The silica-based sorbents differ in a more intense color; the $\Delta F(R)$ value of iron(II) surface complexes on the sor-
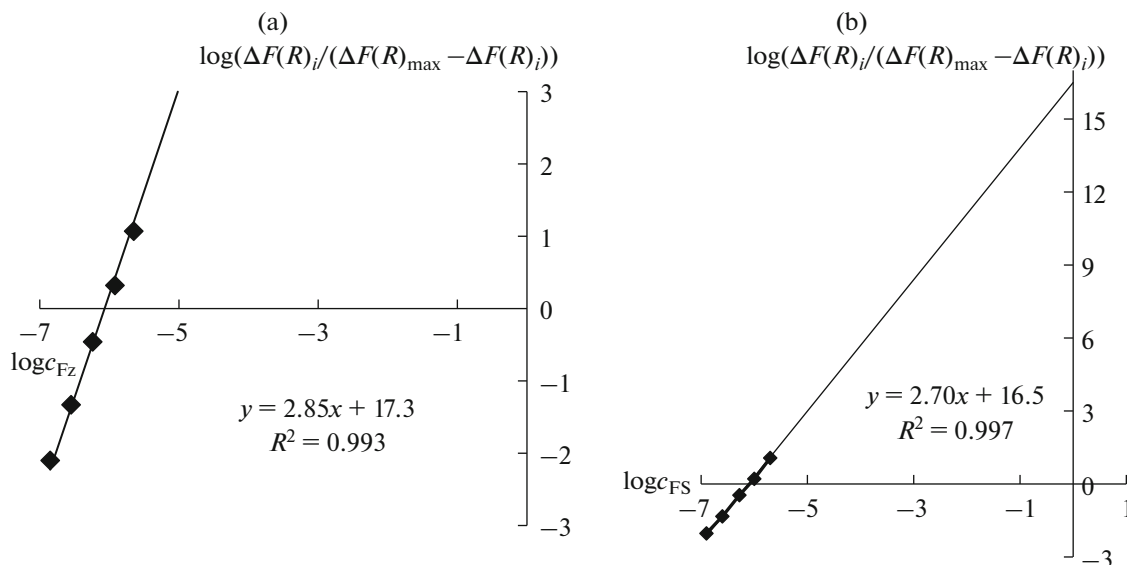

Fig. 4. Equilibrium shift method for the systems of iron(II) and SiO$_2$–PHMG–Fz (a) and iron(II) and SiO$_2$–PHMG–FS (b): c_{Fe} = 1 µg/0.1 g of sorbent, 0.01 M NH$_2$OH, pH 3.5.
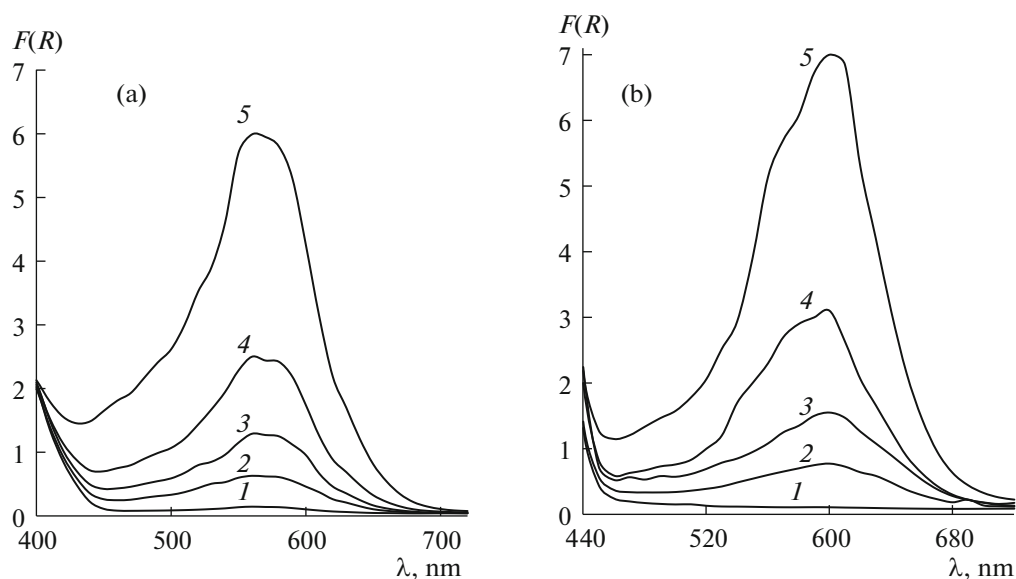
Fig. 5. Diffuse reflectance spectra for iron(II) surface complexes on Al_2O_3−PHMG−Fz (a) and Al_2O_3−PHMG−FS (b): $c_{Fe(II)}$, μg/0.1 g of sorbent: 0 (*1*), 0.5 (*2*), 1 (*3*), 2 (*4*), and 5 (*5*); V = 10 mL; $c_{reagent}$ = 10 μmol/g; pH 3.5; 0.01 M NH_2OH.

bents with the functional groups of FS being higher than that on the sorbents with the functional groups of Fz (Fig. 6).

The concentration of hydroxylamine in the solution in the range 0.005−0.1 M has no effect on the degree of iron(II) recovery and the color strength of its surface complexes.

Sorption−photometric determination of iron(II) using SiO_2−PHMG−Fz, SiO_2−PHMG−FS, Al_2O_3−PHMG−Fz, and Al_2O_3−PHMG−FS sorbents. The formation of intensely colored iron(II) surface complexes with Fz and FS was used in the development of procedures for the sorption−photometric determination of total iron as iron(II).

Plotting of calibration curves. Iron(II) (from 0.01 to 15 μg) as a solution in 0.1 M H_2SO_4, 0.1 M hydroxylamine (1 mL), NaOH (until pH 3.5), and deionized water (q.s. to 10 mL) were added to several 20-mL volumetric tubes with ground stoppers. The sorbent (0.1 g) was added, the tubes were stoppered, and the mixture was stirred for 10 min. The sorbent was separated from a solution by decantation, transferred to a fluoropolymer cell, water excesses were removed with a filter paper, and diffuse reflectance was measured at 560 nm for sorbents with the functional groups of Fz and 600 nm for sorbents with the functional groups of FS.

The performance characteristics of procedures for the sorption−photometric determination of iron(II) are given in Table 2.

The selectivity of sorption−photometric determination of iron(II) was studied in binary systems containing 0.05 μg/mL of iron(II) and from 0.05 to 50 μg/mL of other metal ions. The determination of 0.5 μg of iron(II) per 0.1 g of sorbents at pH 3.5 does

not interfere with multiple amounts of Ca(II), Mg(II), Sr(II), Al(III), Pb(II), Cd(II), Mn(II) (10^3), Zn(II) (10^2), Ni(II) (5) at a background salt content of 50 g/L by NaCl or Na_2SO_4. The interference of copper(II) up to 10-fold excesses was eliminated by masking with a 2% solution of thiourea.

Procedure for the determination of iron in bottled drinking waters using Al_2O_3-based sorbents. The analyzed water (10 mL), 0.1 M $NH_2OH \cdot HCl$ (1 mL), and NaOH (until pH 3.5) were placed in a volumetric tube
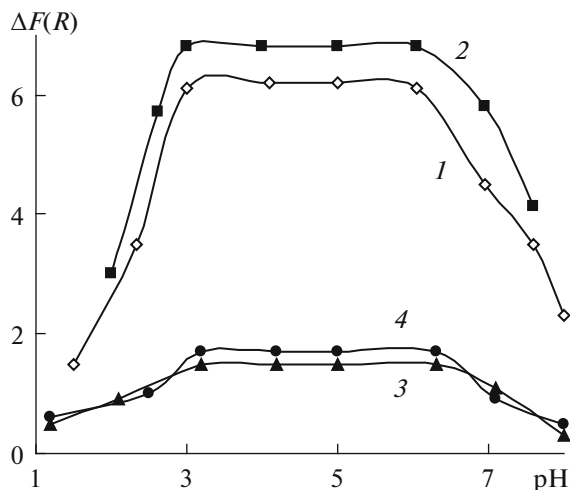

Fig. 6. $\Delta F(R)$ of iron(II) surface complexes as a function of pH on SiO_2−PHMG−Fz (*1*), SiO_2−PHMG−FS (*2*), Al_2O_3−PHMG−Fz (*3*), and Al_2O_3−PHMG−FS (*4*): c_{Fe} = 2.0 μg/0.1 g of sorbent (*1, 2*), c_{Fe} = 1.5 μg/0.1 g of sorbent (*3, 4*), V = 10 mL, 0.01 M NH_2OH.

Table 2. Performance characteristics of procedures for the sorption–photometric determination of iron(II) using sorbents with immobilized ferrozine and ferene S (0.1 g of sorbent, $V = 10$ mL, $n = 5$, $P = 0.95$)

Sorbent	Equation of calibration curve	RDC*, μg/0.1 g	Limit of detection, μg/0.1 g	RSD, %**
$SiO_2–PHMG–Fz$	$\Delta F(R) = 3.20 c_{Fe}$	0.03–5.0	0.005	7
$SiO_2–PHMG–FS$	$\Delta F(R) = 3.57 c_{Fe}$	0.03–5.0	0.006	7
$Al_2O_3–PHMG–Fz$	$\Delta F(R) = 1.25 c_{Fe}$	0.05–10.0	0.01	5
$Al_2O_3–PHMG–FS$	$\Delta F(R) = 1.33 c_{Fe}$	0.05–10.0	0.01	5

  * RDC is the range of determined concentrations.
** Upon determination of iron, it is 10-fold higher than the limit of detection.

with a ground stopper. The sorbent (0.1 g) was added and the mixture was stirred for 10 min. The sorbent was separated from a solution by decantation and transferred into a fluoropolymer cell, water excesses were removed with a filter paper, and the diffuse reflection factor was measured at 560 nm for sorbents with the functional groups of Fz and 600 nm for sorbents with the functional groups of FS. The concentration of iron was determined by calibration curves. The data of the determination of iron(II) in bottled drinking waters are given in Table 3. The validity of the

Table 3. Sorption–photometric determination of iron(II) in drinking and mineral waters using sorbents based on Al_2O_3 with immobilized ferrozine and ferene S (the sample volume was 10 mL, $n = 5$, $P = 0.95$)

Water sample	Added, μg	Found, μg
$Al_2O_3–PHMG–Fz$		
"Lel," natural drinking water	0	0.06 ± 0.01
	0.1	0.15 ± 0.02
	0.2	0.26 ± 0.01
"BonAqua," drinking water	0	0.09 ± 0.01
	0.1	0.20 ± 0.02
	0.2	0.29 ± 0.01
$Al_2O_3–PHMG–FS$		
"Baikal," mineral natural drinking water	0	0.05 ± 0.01
	0.1	0.16 ± 0.02
	0.2	0.25 ± 0.01
"Borjomi," mineral natural drinking water	0	0.36 ± 0.02
	0.1	0.47 ± 0.01
	0.2	0.56 ± 0.02

data obtained was confirmed by the added–found method.

Procedure for the determination of iron(II) in alcoholic drinks using sorbents based on SiO_2. The presence of iron in alcoholic drinks can result in their opacity due to precipitation of iron(II) and copper(II) titanates. The presence of iron in a cognac drink makes its green-olive at a concentration of 0.4–1.0 mg/L and black at concentrations more than 1 mg/L [24]. Iron is one of the standardized components of alcoholic drinks; according to *GOST R 33281-2015* and *GOST R 51145-98*, its concentration in whisky and cognacs should not exceed 1 mg/L [25, 26].

Whisky or cognac samples with a volume of 25 mL were prepared by dry mineralization in accordance with the requirements of *GOST 26929-94* [27]. After mineralization, the dry residue was dissolved in 2% HNO_3 (10 mL). An aliquot of the solution (2 mL) was placed in a graduated test tube with a ground stopper. 0.1 M $NH_2OH \cdot HCl$ (1 mL), a 10% solution of thiourea (2 mL), NaOH (until pH 3.5), and water (q.s. to 10 mL) were added. Sorbent (0.1 g) was added and then treated as described above.

The validity of data from the sorption–photometric determination of the iron(II) concentration was verified by flame atomic absorption spectrometry in accordance with the recommendations of [28]. The data of determination of iron(II) in alcoholic drinks are given in Table 4.

The developed procedures for the sorption–photometric determination of iron(II) allow one to obtain accurate and reproducible data (Tables 3 and 4). As it follows from the data given in Tables 2 and 5, the use of sorbents based on silica with the functional groups of Fz and FS allows a 10-fold decrease in the limits of detection of iron compared to those with the functional groups of bathophenanthroline [21] and the use of silica and alumina allows decreasing more than 2–5-fold the limits of detection of iron and expanding 2–3-fold the range of its determined concentrations

Table 4. Data (mg/L) of the iron(II) determination in alcoholic drinks using sorbents based on SiO_2 with immobilized ferrozine and ferene S ($n = 5$, $P = 0.95$)

Sample, sorbent	Sorption–photometric method	Atomic absorption method
"Jack Daniel's" whisky, SiO_2–PHMG–Fz	0.15 ± 0.02	0.16 ± 0.02
"Ararat" cognac, SiO_2–PHMG–FS	0.34 ± 0.03	0.33 ± 0.02

Table 5. Performance characteristics of procedures for the sorption–photometric determination of iron(II) using sorbents based on inorganic oxides with functional groups of bathophenanthroline, ferrozine, and ferene S, 0.1 g of sorbent, $V = 10$ mL, $n = 5$, $P = 0.95$)

Sorbent	RDC, µg/0.1 g	Limit of detection, µg/0.1 g	Reference
SiO_2–PHMG–Bathophen	0.06–6.0	0.02	[21]
Al_2O_3–PHMG–Bathophen	0.2–8.0	0.05	[21]
ZrO_2–PHMG–Fz	0.1–4.0	0.006	[29]
TiO_2–PHMG–Fz	0.1–3.5	0.05	[30]
ZrO_2–PHMG–FS	0.1–4.0	0.015	[29]
TiO_2–PHMG–FS	0.1–4.0	0.04	[30]

compared to the sorbents based on titanium and zirconium oxides with the functional groups of Fz and FS [29, 30].

ACKNOWLEDGMENTS

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