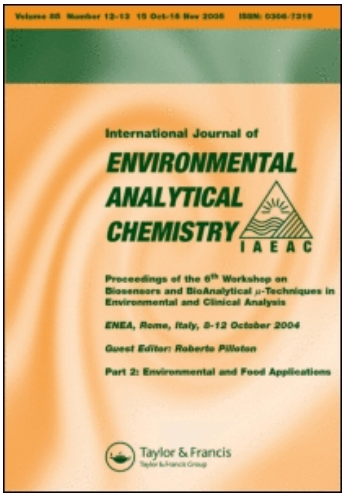

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Silica Gel and Cellulose Loaded with Bis-Quaternary Ammonium Salts as Sensitive Reagents for Iron, Bismuth and Anionic Surfactants Determination in Water

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SILICA GEL AND CELLULOSE LOADED WITH BIS-QUATERNARY AMMONIUM SALTS AS SENSITIVE REAGENTS FOR IRON, BISMUTH AND ANIONIC SURFACTANTS DETERMINATION IN WATER

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Sorption of some high molecular weight bis-quaternary ammonium salts (QAS) on silica gel and cellulose was investigated. It was shown that QAS were not washed practically from the sorbents surface at pH= 1 – 9. Sorption of bismuth tetraiodide and iron (III) thiocyanate complexes and anionic dye – picric acid (Picr) onto silica gel modified with QAS was studied. The solid-phase reagents for bismuth(III) and iron (III) spectroscopic and visual test determination in natural water were worked out. Detection limits of Bi (III) and Fe (III) determination were 3 and 2 $\mu g.l^{-1}$, respectively. Indicator paper for Fe(III) determination in different types of water was obtained. Silica gel modified with QAS and Picrate was used for determination of anionic surfactants in natural and waste waters using spectrophotometric and visual test methods. The detection limit was 0.05 $\mu g.l^{-1}$

Keywords: Sorption; modified silica gel; cellulose; quaternary ammonium salts; visual test method; water analysis

INTRODUCTION

As inorganic and organic pollutants increase in the environment the necessity of their control grows. Sorption methods are widely used for preconcentration and determination of trace elements [1,2]. Silica gels (SG) and cellulose immobilized by adsorption and impregnation of chromophorous, luminescent and chemiluminescent reagents are known to be effective modified sorbents for pollutants determina-

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tion in the environment using diffuse reflectance spectroscopy and visual test methods [3,4]. The preparation of such loaded silica gels is rather simple but their properties do not yield the properties of chemically modified silica gels [5].

Quaternary ammonium salts (QAS) are effectively adsorbed on different porous sorbents, SG in particular [3]. Such modified sorbents possess anion-exchange properties and can be used repeatedly for different types of anion determination [6]. The adsorption of amino ammonium salt didecylaminoethyl-β-tridecylammonium iodide (I) onto silica gel was successfully used for the preparation of solid phase reagents for Zn(II), Cu(II), Co(II) and Bi (III) sorption-spectroscopic and visual test determination [6,7]. But the application of I-SG is limited in weakly acid medium because of reagent washing from the surface at pH<3. Therefore, the use of chelating reagents to prevent metal ions hydrolysis at pH> 3 is necessary. I-SG modified by Methyl Orange (MO) was used for anionic surfactants determination only at pH 3–7 [8], but at these conditions humic and fulvic acids interfered. It is known that high molecular weight QAS are not usually dissolved in acids. Thus, they will be more effective modified reagents at pH<3. The modification of cellulose by high molecular weight QAS will give the possibility to obtain effective indicator paper with ion exchange properties for the detection of trace pollutants in the environment.

In the present work we investigate the sorption of high molecular weight bis-quaternary ammonium salts N-methyl-N,N,N′,N′,N′-pentadecylethyldiammonium diiodide (II), and N,N,N,N′,N′,N′-hexadecylhexamethylenediammonium diiodide (III) onto silica gel and cellulose. The possibility of applying the modified II-III silica gels and cellulose to Bi(III), Fe (III) and anionic surfactants determination and screening in natural, tap waters and sewage has been tested.

EXPERIMENTAL

Reagents

All reagents were of analytical grade. Water was purified according to ref. 9. Standard metal solutions, 0.01 mol.l^{-1}, potassium iodide and sodium thiocyanate solutions, 1.0 mol.l^{-1}were used. Picrate (Picr) (5.0 mmol.l^{-1}) and dodecyl sulfate (DDS) (1.0 mmol.l^{-1}) solutions were prepared by dissolving the appropriate sodium salts (Merck). II and III solutions (0.01 mol.l^{-1}) were obtained by dissolving the appropriate salts (Chemical Dept. of Minsk University, Belarus [10]) in a mixture of hexane:toluene (1:1). SG (Chemapol L 40/100) was digested in nitric or hydrochloric acid, washed with purified water and dried at 80 °C for a

day. Chromatographic paper "Filtrak FN-18" (thickness 0.51 mm, density 27 $mg.cm^{-2}$) was digested in 1 $mol.l^{-1}$ hydrochloric acid, washed with water and dried at 80 °C.

Apparatus

The absorbance of solutions and the coefficient of diffuse reflectance (R_λ) of sorbents were registered with an UV/Vis spectrophotometer Specord M-40 (Carl Zeiss, Germany). A potentiometer model EV-74 with glass electrode (Gomel, Belarus) was used for pH measurements.

Procedure

The immobilization of II and III onto SG was made according to [6]. SG with QAS content 0.12 $mmol.g^{-1}$ (II-SG, III-SG) was used in the work. The batch technique has been applied to study the adsorption of compounds onto sorbents. For this purpose modified SG (0.2 g) was stirred mechanically for 10–60 min with aqueous solutions (10–250 ml) with appropriate pH, containing a known amount of Fe(III) or Bi(III) and thiocyanate or iodide ions, respectively. Then, the sorbent was filtered through a dry filter paper and dried at room temperature. Fe(III) and Bi(III) residues in solutions were controlled spectrophotometrically by the absorbance of iodide and thiocyanate complexes, respectively. Sorbents with metal ions adsorbed were analyzed using diffuse reflection spectroscopy (DRS).

For the preparation of indicator paper the chromatographic paper was impregnated with solutions of I or II and dried at 60 °C for a day. The dynamic technique has been used for the investigation of metal complexes adsorption onto the paper. The sample solution (50–100 ml) containing a known amount of the investigated ions and appropriate complexing ligands at optimal pH was percolated through the special cartridge (20 mm diameter) with the indicator paper disc at a flow rate of 10 $ml.min^{-1}$. The adsorption value was controlled by measuring the metal ions residues in solutions. The color of the disk was measured by DRS.

The modification of II-SG with Picr was made according to ref. 8. Silica gel with a Picr content of 5. 10^{-5} $mol.g^{-1}$ was used.

The desorption of Picr from the surface of II-SG using a batch method was studied. II-SG modified with Picr (0.05 g) was stirred mechanically with 50 ml of 0.01 – 0.1 $mmol.l^{-1}$ DDS aqueous solutions at appropriate pH for 10–60 min and centrifuged. The amount of the dye removed by DDS from the surface into solution was controlled spectrophotometrically by its own absorbance at $\lambda = 364$ nm.

RESULTS AND DISCUSSION

The dependences of the adsorption value (a, $mol \cdot g^{-1}$) of II and III onto SG on their concentration in solutions was studied. The isotherms obtained were formally described by a Langmuir equation at QAS concentration over 0.03 $mmol.l^{-1}$ and linearized in the coordinates [C]/a -[C] (where a is the value of QAS adsorption and [C] is their equilibrium concentration in solution) with conditional constant $k = 2.5 \cdot 10^4$ $l.mol^{-1}$. The maximum value of QAS adsorption was 0.2 $mmol \cdot g^{-1}$. It was found that QAS were adsorbed almost completely (a>0 when [C] = 0) from their dilute solutions. Such type of isotherms testified the strong QAS connection with the adsorbent.

The experiments showed that II-SG and III-SG were stable at pH 1–9 and can be used for anionic compounds preconcentration from acid medium. The adsorption of the iodide complex of bismuth (III) and thiocyanate complex of iron (III) onto II-SG and III-SG was studied at optimal conditions of these complexes formation (pH = 0 – 2). The kinetic curves of metal complexes adsorption are shown in Figure 1. The equilibrium of complexes adsorption from aqueous solutions was reached in 10 min after a start of mixing. The optimal concentrations of iodide and thiocyanate experimentally obtained were 0.1 and 0.5 $mol.l^{-1}$, respectively, at metal ion concentration $\leq 10^{-4}$ $mol.l^{-1}$. The effect of pH on Bi (III) and Fe (III) adsorption onto II-SG is represented in Figure 2. Since QAS-SG was not stable in water solutions at pH<1 and both metal ions hydrolyzed at pH> 2.5, the optimal range for their adsorption was pH =1.0–2.5.

Under optimal conditions the metal complexes were adsorbed almost completely (a>0 when [C] = 0) from their dilute solutions. The isotherms (Figure 3) were formally described by a Langmuir equation at concentration over 0.12 (Bi) and 0.30 (Fe) $mmol.l^{-1}$ with conditional constant k, 10^4 $l \cdot mol^{-1}$: 5.7 (Bi), 4.3 (Fe). The maximum chelating capacity of QAS -SG was 0.24 (Bi) and 0.12 (Fe) $mmol \cdot g^{-1}$ for 0.12 $mmol \cdot g^{-1}$QAS. It was shown that complexes *QAS Bi* (1 : 2) and QAS : Fe (1 : 1) prevailed on the surface under optimal conditions. The obtained results were used for preparation of solid-phase reagents for Bi (III) and Fe (III) determination.

DRS and visual test methods for these metal ions determination were developed (Table I). The equations of calibration graphs for their determination were $R_{480} = 5.2.10^{-3}$. $C(\mu g.l^{-1}) - 2.29.10^{-3}$ (Fe) and $R_{510} = 5.3.10^{-3}.C(\mu g \cdot l^{-1})$ (Bi). The colour scales for Fe(III) control were prepared by adsorption of Fe thiocyanate complex onto II-SG and II-IP from its standard solutions containing 0.5, 2.5, 5.0,

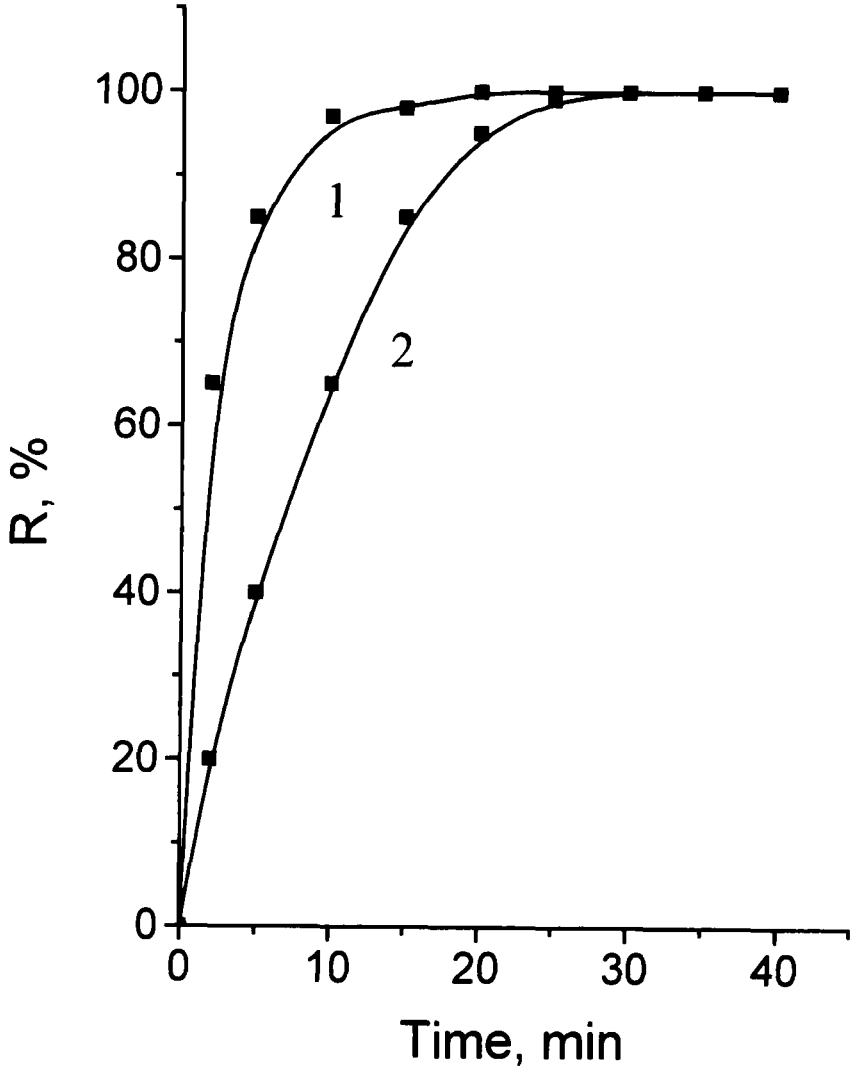

FIGURE 1 Kinetic curves of Bi(III) iodide (1) and Fe(III) thiocyanate (2) complexes adsorption on II-SG. Sample volume 250 ml (1) and 50 ml (2), m= 0.1 g

7.5, 10 and 20 and 1.0, 2.0, 4.0, 8.0 and 10 μg of iron, respectively. The scales were stable for more than 3 months. The visual test scales for Bi(III) determination were prepared by adsorption of Bi iodide complex at optimal conditions onto II-SG and II-IP from standard solutions containing, respectively, 1, 5, 10, 20

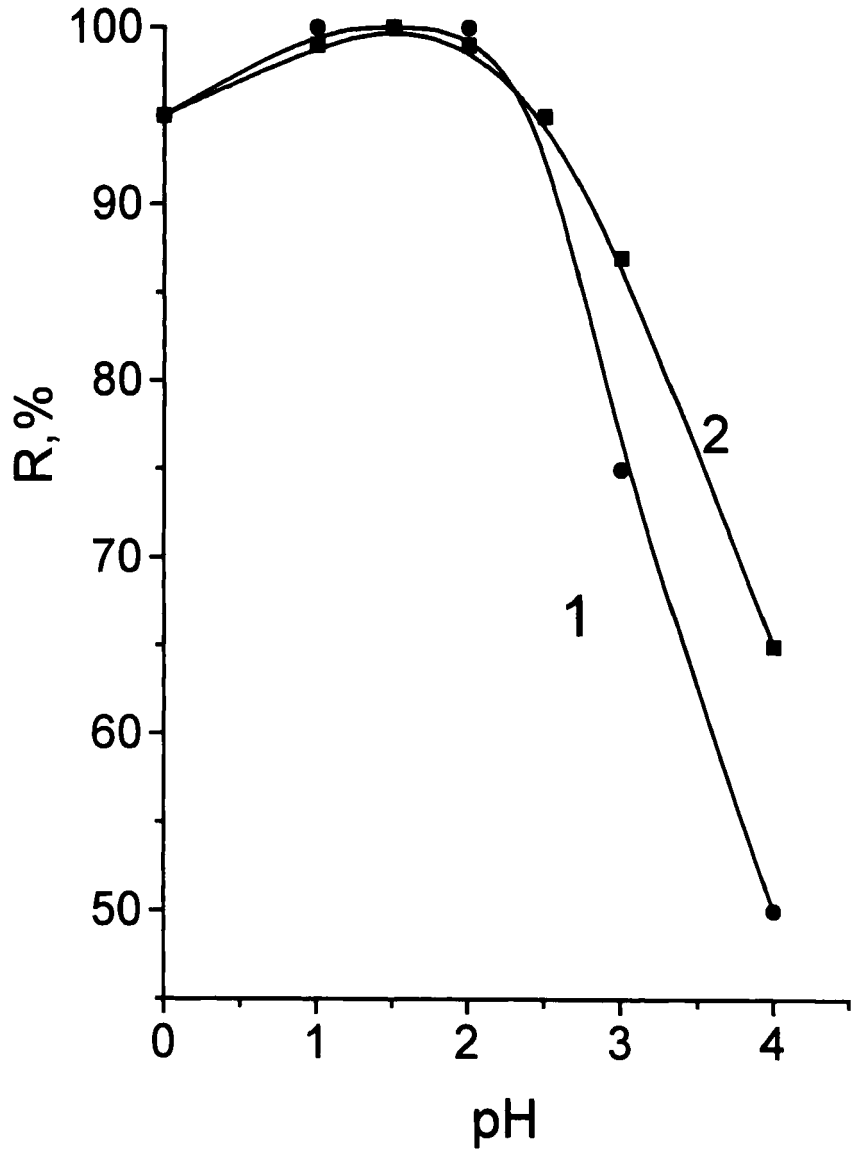

FIGURE 2 Effect of pH on Bi(1) and Fe(2) complexes adsorption onto II-SG

and 40 and 2.0, 4.0, 6.0, 8.0 and 10 μg of bismuth. The scales were stable for more than 6 months. The maximal error of visual test metal ions determination did not exceed 50 %.

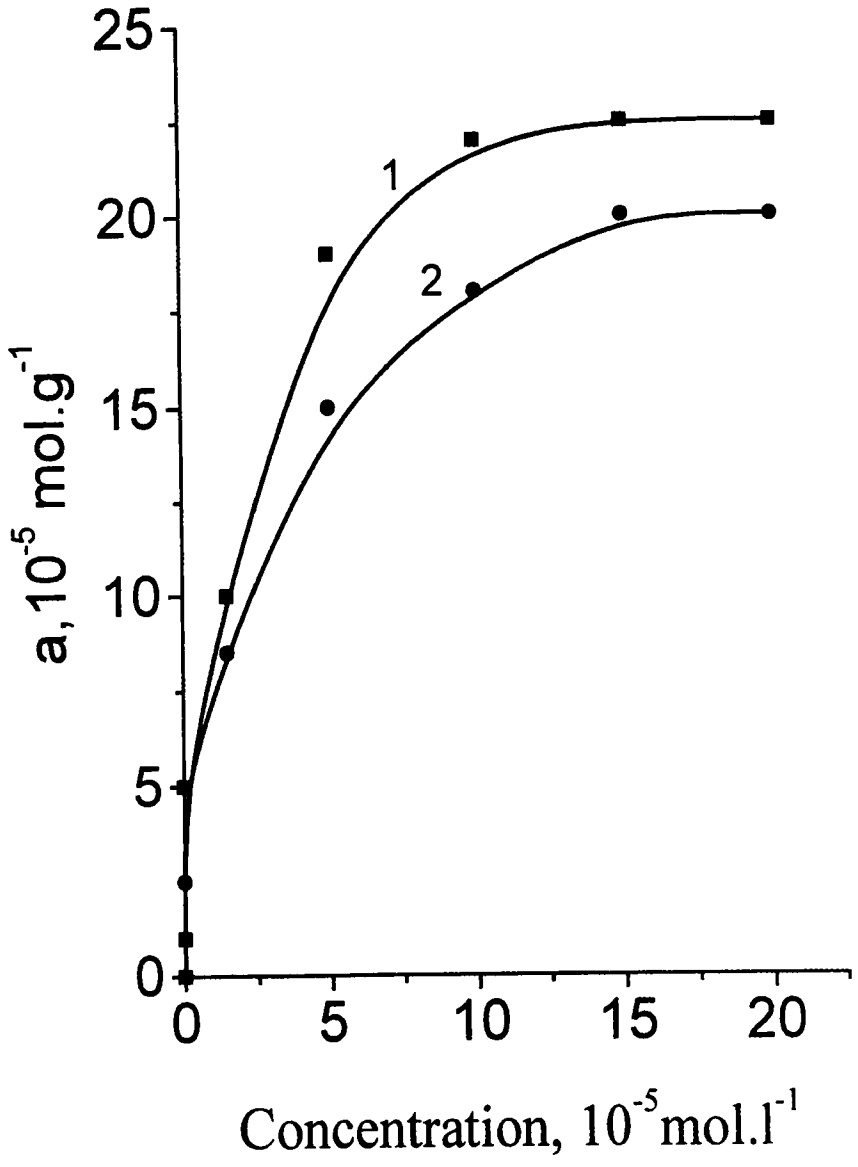

FIGURE 3 Isotherms of Bi(III) iodide (1) and Fe(III) thiocyanate (2) adsorption on II-SG. Sample volume 50 ml, m= 0.1 g, pH=2, T=294.0 ± 0.5

TABLE I The some chemical-analytical characteristics of methods developed. Sample volume 50, 100* (Fe), 250 (Bi) ml

Metal ion	*DRS*		*Visual test*			
			II-SG		*II-IP*	
	Detection limit, $\mu g \cdot l^{-1}$	*Range of graph linearity,* μg/ *sample*	*Minimum detected,* μg	*Range of colour scale,* μg/*sample*	*Minimum detected,* μg	*Range of colour scale,* μg/ *sample*
Fe	2	0.3–30	0.5	0.5–10	0.5*	1–10
Bi	3	1–40	1	1–40	2	2–10

The influence of foreign ions

Metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}) and inorganic anions (Cl^-, SO_4^{2-}, CO_3^{2-}, NO_3^-) did not influence on Fe (III) and Bi(III) determination at their MAC level in water. Cu (II) and PO_4^{3-} did not affect at concentrations lower than 50 $\mu g.l^{-1}$and 2 $mg.l^{-1}$, respectively. Bismuth did not interfere Fe (III) because of its content ($\mu g.l^{-1}$) in natural and tap waters. Bi (III) can be determined in the presence of Fe(III) in 2 % ascorbic acid medium.

The obtained reagents were applied to natural and tap water analysis. The results obtained using II-SG and II-IP are represented in Tables II and III. All data showed satisfactory reproductivity and accuracy for metal ions detection.

TABLE II The results of Fe(III) determination in natural (1), tap(2) and distilled (3) waters using II-SG and II-IP by DRS and visual test methods. The volume of sample – 10 (1,2) and 50 (3) ml. n= 4, P=0.95

Water type	*Fe concentration, µg/sample*			
	added	*found,* $\times \pm \Delta x$		
		DRS II-SG	*Test II-SG*	*Test II-IP*
1	0	1.8 ± 0.2	1.5 ± 0.5	2.0 ± 0.5
1	1.2	2.9 ± 0.2	3.5 ± 0.5	3.0 ± 0.5
1	2.4	4.5 ± 0.3	4 ± 1	4 ± 1
2	0	2.4 ± 0.3	2.0 ± 0.5	2.0 ± 0.5
2	2.5	5.0 ± 0.5	5 ± 1	4 ± 1
3	0	1.5 ± 0.1	2.0 ± 0.5	1.5 ± 0.5
3	1	2.6 ± 0.4	2.5 ± 0.5	3 ± 1

TABLE III The results of Bi (III) determination in sewage after purification (1) and tap water(2), using II-SG by DRS and visual test methods. Sample volume: 250 ml. n=5, P=0.95

Water type	*Bi concentration, µg/sample*		
	added	*found,* $\times \pm \Delta x$	
		DRS	*Test*
1	0	7.5 ± 0.9	5 ± 2
1	15	21 ± 1	20 ± 5
2	4	4.2 ± 0.3	4 ± 1
2	10	10.3 ± 0.4	10 ± 3

Anionic dye – Picr was effectively adsorbed on II-SG. The maximal value of its adsorption was 0.2 mmol.l^{-1}. The associate II : Picr (1:2) formed on the surface of modified SG.

The reaction $\mathrm{Picr-II-SG} + \mathrm{An}^{n-} \rightarrow \mathrm{An-II-SG} + n\,\mathrm{Picr}^{-}$ was studied. The obtained data showed that Picr was practically not removed from II-SG surface by short chain organic and inorganic ions except thiocyanate ions at concentrations higher than 1 mmol.l^{-1}. The maximum effect of replacement was observed for long chain organic ions, especially for anionic surfactants. Thus, the possibility of II-SG modified with Picr for anionic surfactants determination in acid medium in the presence of humic acids at contents higher than 0.5 mg·$l^{-1}$and fulvic acids higher than 10 mg·l^{-1} was studied. It is known that these compounds do not dissociate at pH<2.5 [11] so they will not interfere the DDS determination.

The kinetics of Picr removal by DDS (Figure 4) demonstrates that the equilibrium was reached in 40 min after starting the components mixing (50 ml sample volume). The blank values were stable under the studied conditions.

The range of DDS determination was 0.1 – 4.0 mg·$l^{-1}$with a detection limit of 0.05 mg·l^{-1}. The results of DDS determination in model solutions and natural water are represented in Table IV. The method can be applied to DDS determination in natural water with fulvic acids content up to 150 mg.l^{-1}. Humic acids did not interfere at this conditions.

TABLE IV The results of DDS determination in model solution(1,2) and natural water (3) by DRS (I) and visual test (II) methods using Picr-II-SG. Concentration: Cl^-, NO_3^-, SO_4^{2-},CO_3^{2-}-1 mmol.l^{-1}, humic acid – 10 mg·l^{-1} and fulvic acid – 150 mg·l^{-1}(1), Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}- 1.0 mmol.l^{-1}, cationic Surf- 1.10^{-3} mmol.l^{-1}, non ionic Surf- 1.10^{-2} mmol.l^{-1}(2). Sample volume 50 ml, m= 0.05g, pH= 2. n= 4, P=0.95

Sample	*Method*	*DDS, mg·l^{-1}*	
		added	*found* $\bar{x} \pm \Delta x$
1	I	0.20	0.21 ± 0.03
1	I	0.50	0.52 ± 0.04
1	II	1.2	1.5 ± 0.5
2	I	0.27	0.25 ± 0.06
2	II	1.36	1.4 ± 0.4
3	I	0	0.51 ± 0.03
3	I	0.50	1.04 ± 0.08
3	II	1.0	1.5 ± 0.5

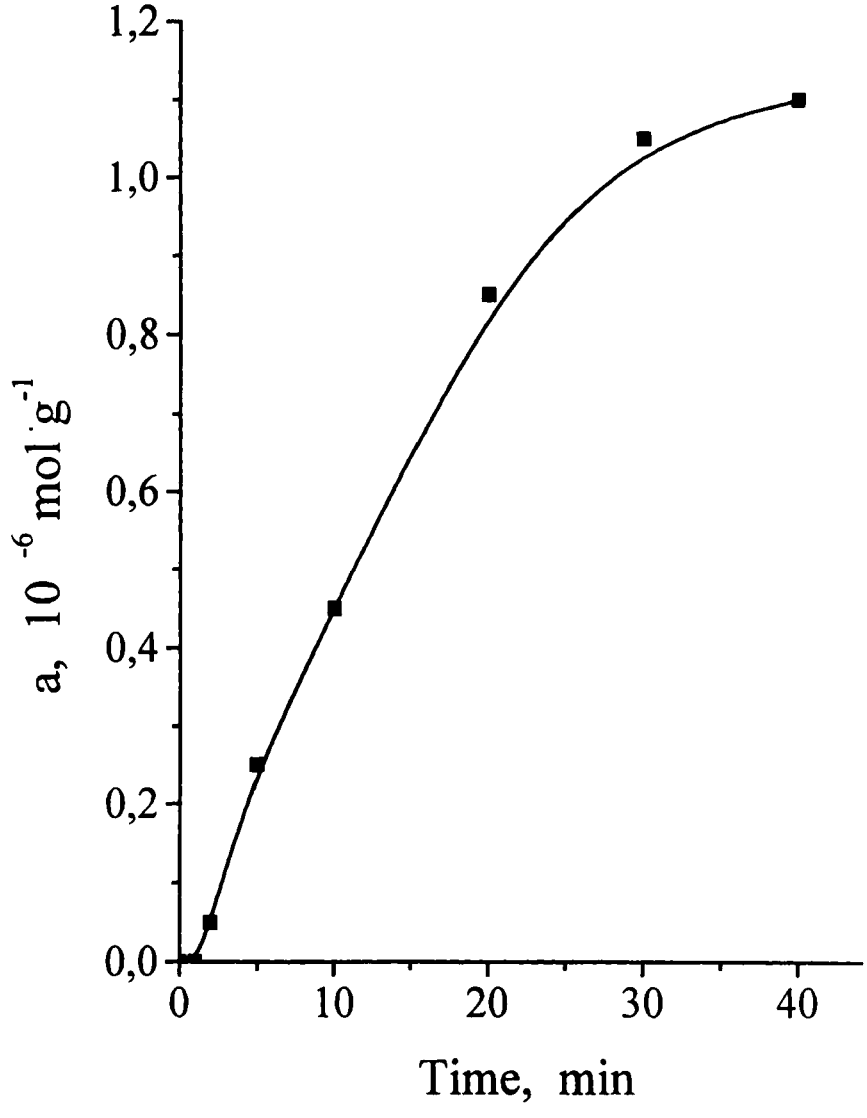

FIGURE 4 The kinetics of Picr removal from Il-SG surface by DDS. Concentration of DDS : 2.10^{-5} mol.l^{-1}. a, 10^{-5}mol.g^{-1}: 10 (Il) and 5 (Picr), pH= 2, sample volume 50 ml

CONCLUSIONS

The adsorption of high molecular weight quaternary ammonium salts onto silica gel and cellulose was shown to be successful for preparation of solid phase reagents and indicator paper for preconcentration and determination of bismuth (III) and iron (III) acid complexes in natural water at $\mu g \cdot l^{-1}$ levels using diffuse reflectance and visual test methods. Sorption of Picr on SG modified with QAS was studied. The new solid- phase reagent was used for anionic surfactants determination in natural water by diffuse reflectance spectroscopy and visual test methods. The detection limit was 0.05 $mg.l^{-1}$. Fulvic acids at contents up to 150 $mg.l^{-1}$ and humic acids did not interfere the anionic surfactants determination.

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