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# Silica gel modified with lumogallion for aluminum determination by spectroscopic methods

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## Abstract

Simple, easy to use and selective method of Al(III) sorption–spectroscopic (SS) determination was proposed. For this purpose, silica modified with tridecyloctadecylammonium chloride(SGII) using adsorption technique and glass slide modified with thin silica–poly(dimethyldiallylammonium chloride) (SGI) composite film obtained by sol–gel technique were worked out. It was shown that lumogallion (LG) easily absorbs on SGI and SGII. Obtained sorbents SGIII and SGIV, respectively, were used for aluminum(III) determination by diffuse reflectance and spectrophotometric methods. The ranges of determination were (mg L$^{-1}$): (0.08–0.54), $s_r \leq 0.13$, $n = 4$ for SGIII and (0.05–2.0), $s_r \leq 0.11$, $n = 4$ for SGIV. The detection limits (blank + 3$\sigma$) for aluminum were 70 and 30 μg L$^{-1}$ using SGIII and SGIV, respectively, where $\sigma$ is the standard deviation of blank estimation. The accuracy of the developed spectrophotometric method was examined by the determination of standard addition of aluminum in alcohol-free beverages. The relative error did not exceed 9%. SGIII can be regenerated by 0.05 M EDTANa$_2$H$_2$ solution and reused. SGIV was shown to be perspective for determination of aluminum in solution in the range of 0.01–0.13 mg L$^{-1}$ by solid phase luminescent technique.

*Keywords:* Silica; Sol–gel; Lumogallion; Aluminum; Sorption–spectroscopic determination

## 1. Introduction

One of the elements that needs precise control in the environment is aluminum. High concentration of Al(III) in water can cause serious health problems [1]. The correlation between uptake of aluminum from drinking water and Alzheimer's disease was shown [2]. The development of simple, easy to use and selective methods of detection of this element at the trace level in environmental and biological samples is of great importance today. Several sorption–spectrophotometric (SS) and sorption–luminescent (SL) methods using organic anion-exchangers and membrane filters were proposed for this purpose [3–10].

Chrome azurol S and eriochrome cyanine R as chromophorous reagents were widely used for SS determination of aluminum [3–6]. An optical sensor based on eriochrome cyanine R immobilized on XAD-2 resin was proposed for determination of ≥10 μmol L$^{-1}$ aluminum in aqueous environment using diffuse reflectance spectroscopy (DRS) [6]. More sensitive and selective fluorimetric technique of Al(III) detection in tap water in the concentration range 0.2–14 μg L$^{-1}$ is based on adsorption of its complex with salicyliden-*o*-aminophenol onto dextran-type cation-exchange gel [7]. Besides luminescent-optic sensors using 8-oxyquinoline sulfonate and morin immobilized on an ion-exchange resin Amberlite CG-400 or bio-membrane

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were reported [8–10]. Modified membranes must be replaced within two days. Manganese(II), iron(III) and copper(II) interfered Al(III) detection.

Among other sensitive reagents 2,2″,4′-trioxy-5-chloro-(1-azo-1′)-benzene-3-sulfonic acid (lumogallion or LG) was proposed for fluorimetric determination of Al (III) in solution [11]. A flow injection method of aluminum determination with LG in natural water was described. The detection limit (DL) was ($\mu g\,L^{-1}$): 0.1 and 0.05 after preconcentration of the metal ion on the column modified with 8-oxyquinoline [11–13]. As far as we know, no application of immobilized LG for Al(III) sorption–spectroscopic determination was reported.

Mesoporous silica gels are characterized by significant active surface area and are widely used in analytical chemistry for preconcentration of microelements [14–17]. Obtained modified sorbents can be successfully applied as active element of optical chemical sensors.

It was previously described that silica gel (SG) modified with high molecular weight quaternary ammonium salts (QAS) possessed anion-exchange properties and was used for preconcentration and determination of metal ions and organic anions in environmental objects by spectroscopic methods [18–20]. The advantage of SG modified with QAS compared to organic ion-exchangers is its chemical and mechanical stability, high rate of sorption equilibrium, homogeneous and small size of the particles.

Another perspective and simple way of silica modification is low temperature sol–gel technology [21]. Recent research has demonstrated that silicate glasses or thin films obtained by sol–gel method can be a promising host matrix for immobilized analytical reagents. Incorporation of poly(dimethyldiallyl-ammonium chloride)(I) causes formation of a composite silica film (SGI) with anion-exchange properties [22]. Electrostatic immobilization of the dye molecule onto SGI composite film platform can be a perspective way of preparation of sensitive element of optical sensor.

In the present paper, sorption of LG onto SG powder modified by adsorption with tridecyloctadecylammonium iodide (SGII) and thin SGI film obtained by sol–gel technique on the glass slide surface is investigated. Analytical application of obtained modified sorbents for traces of aluminum detection is examined.

## 2. Experimental

### 2.1. Reagents and solutions

All reagents were of analytical grade. Metal ions solution were prepared by dissolving of analytical grade salts in deionized water with addition of hydrochloric acid. Lumogallion (Merck), tridecyloctadecylammonium chloride(II), 99% purity obtained from [24] was used to prepare $1 \times 10^{-2}\,mol\,L^{-1}$ solution in hexane:toluene (1:2). Acetic buffer (pH 5.0); silica gel (Chemapol L 40/100) were used in the work. Tetraethyloxysilane (TEOS), poly(dimethyldiallyl-ammonium chloride)(I), (MW 240,000), were purchased from Aldrich Chemicals. Bidistilled water was used for preparation of all solutions.

Glassware was acid washed. Microscopic glass slides 1 cm × 1 cm were used as support for silica sol–gel composite film.

### 2.2. Apparatus

UV–vis and diffuse reflectance spectra were recorded on Specord M-40 (Carl Zeiss), pH meter, pH 340 was used in the work. Sorption was developed by magnetic stirrers.

The photoluminescence (PL) spectra were measured at room temperature using an optical multichannel analyzer as the detector at excitation by the pulse nitrogen $N_2$ laser ($\lambda$ = 0.34 $\mu$m, $t_p = 5 \times 10^{-9}$ s, $E = 10^{-5}$ J) [23].

### 2.3. Procedures

#### 2.3.1. Sol–gel procedure

Silica was obtained by hydrolysis and polycondensation reactions of TEOS in the presence of I according to the previously described procedure [21,22]. Thin films were prepared from freshly formulated sol–gel stock solution containing polyelectrolyte by dropping 2–10 $\mu$L of solution onto microscopic glass using microsyringe. The film was dried in the air overnight. Obtained composite film (SGI) was characterized by high mechanical and chemical stability and transparency. The average thickness of the film was estimated by optical interference method [25].

#### 2.3.2. Modification of SG with II

One gram of SG was stirred with 20 mL of $1 \times 10^{-2}\,mol\,L^{-1}$ solution of II for 30 min using magnetic stirrer, filtered and dried for 40 min at 60 ± 5 °C. The modified sorbent (SGII) obtained in such way contained $1 \times 10^{-4}\,mol\,g^{-1}$ of II on the surface. Anion-exchange properties of SGII were described earlier [24].

#### 2.3.3. Immobilization of LG onto silica modified with I and II

The batch procedure was applied for sorption of LG onto modified silica. The residue of LG in solution after contact with SGI and SGII was detected spectrophotometrically using calibration graph. Then the amount of LG adsorbed on SGI and SGII was calculated.

*Modification of SGI*: 10 pieces of the glass slides modified with composite film (SGI) were immersed into 10 mL of $1 \times 10^{-3}\,mol\,L^{-1}$ solution of LG for 30 min at pH 4.3 (acetic buffer), washed with water and dried in the air for 30 min. SGIII was obtained in such way.

*Modification of SGII*: 0.500 g of the sorbent was stirred by magnetic stirrer with 12.0 mL of $5 \times 10^{-4}\,mol\,L^{-1}$ aqueous solution of LG at pH 4.3 (acetic buffer) for 40 min.

The modified sorbent was filtered through the paper filter, washed with water and dried for 40 min at 60 ± 5 °C. Thus, SGIV was obtained with the content of LG on the surface 10 μmol $g^{-1}$.

### *2.3.4. Sorption of metal ions*

The batch procedure was applied for sorption of the metal ions.

*2.3.4.1. Sorption onto SGIII.* Ten to twenty-five milliliters of the water sample at pH 1.0 containing 1–10 μmol $L^{-1}$ standard aqueous solutions of aluminum(III), copper(II) and iron(III) was adjusted to pH 5.0 by addition of 5 mL of acetic buffer. SGIII was immersed into solution which was then thermostated at $T = 323 \pm 3$ K for 5–60 min. Then the slide was taken out and washed with distilled water. The absorbance spectra of the complex formed on SGIII was measured by spectrophotometer using as a blank SGIII which was treated by the same way after contact with bidistilled water adjusted to pH 5.0.

For determination of Al(III) in alcohol-free beverage, the sample of the beverage was acidified with HCl to pH 1.0 and heated for 10 min at 343 ± 3 K using water bath. Then the above described procedure was applied.

*2.3.4.2. Sorption onto SGIV.* Water sample (10–50 mL) containing 2–80 μmol $L^{-1}$ standard aqueous solution of aluminum(III), copper(II) and iron(III) at pH 1.0 was adjusted to pH 5.0 by addition of acetic buffer. SGIV (0.100–0.200 g) was placed into the mixture which was then thermostated at $T = 343 \pm 3$ K and stirred for 5–40 min by magnetic stirrer. The sorbent was filtered through the porous filter and dried for 40 min at 60 ± 5 °C. Diffuse reflectance and luminescence spectra of the dry SGIV were measured. Sorbent which was treated by the same way after contact with bidistilled water adjusted to pH 5.0 was used as a blank for DRS. The luminescence of sorbent was measured using the quartz cell put at the angle 45° towards falling light beam.

## 3. Results and discussion

### *3.1. Sorption of LG onto SGI and SGII*

Selected QAS easily adsorbed onto SGI and SGII and were not washed from the surface by water and 0.1 mol $L^{-1}$ solutions of inorganic and short chain organic electrolytes.

LG adsorbed on SGI and SGII surfaces contrary to non-modified silica. Thus, SGIII and SGIV were obtained. Adsorbed dye was not washed from SGIII and SGIV surfaces by ≤0.1 mol $L^{-1}$ aqueous solutions of $Na_2SO_4$, $NaNO_3$, $NaHCO_3$ and sodium acetate. Sodium chloride solution at concentration ≥0.1 mol $L^{-1}$ eluated LG from the surface of SGIII contrary to SGIV powder. The optimal pH of the LG sorption onto both sorbents was 4.0–5.0 when $H_3L^-$ form of the reagent prevailed in solution [26]. The sorption equilibrium was reached within 30 min under optimal conditions. Diffuse reflectance spectra of SGIV and absorbance spectra of LG in solution at different pH are presented in Fig. 1 (curves 1, 2 and 5). The absorbance spectrum of monoanion (pH 4.3) of LG in solution has maximum at λ = 425 nm. The maximum of the absorbance spectrum of LG immobilized on the surface at the same pH is $\lambda_{max} = 450$ nm. Such bathochromic shift in the spectrum may indicate the formation of ion associate between LG and immobilized QAS. The same results were observed for SGIII film.

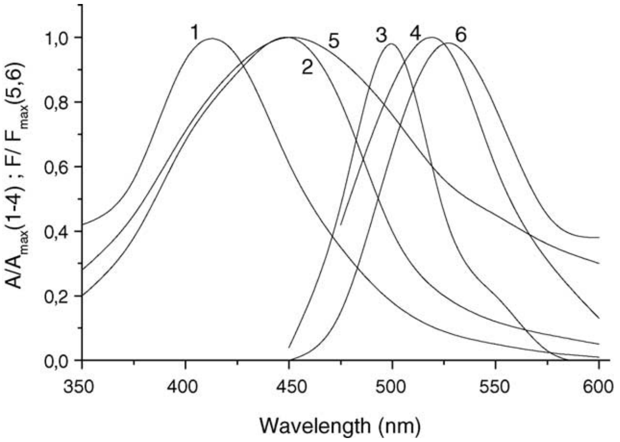

Fig. 1. Standardized absorbance spectra of LG (curves 1 and 2) and its complex with Al(III) (curve 3) in solution and on SGIII (curve 4) and diffuse reflectance spectra of SGIV before (curve 5) and after (curve 6) contact with solution of Al(III). pH 4.3 (curves 1 and 5), 5.0 (curves 3, 4 and 6) and 6.5 (curve 2). For LG: $pK_2 = 5.64$ and $pK_3 = 7.20$ [26].

Isotherms of LG adsorption onto SGI and SGII are presented in Fig. 2 (curves 1 and 3). They may be characterized by L-type. The adsorption capacity of SGII was $9 \times 10^{-5}$ mol $g^{-1}$ of LG for $1.0 \times 10^{-4}$ mol $g^{-1}$ of QAS. It confirms the fact of formation of ion associate with the ratio LG:II = 1:1.

The content of anion-exchange groups on the surface of SGI composite film was not known. It was shown earlier that

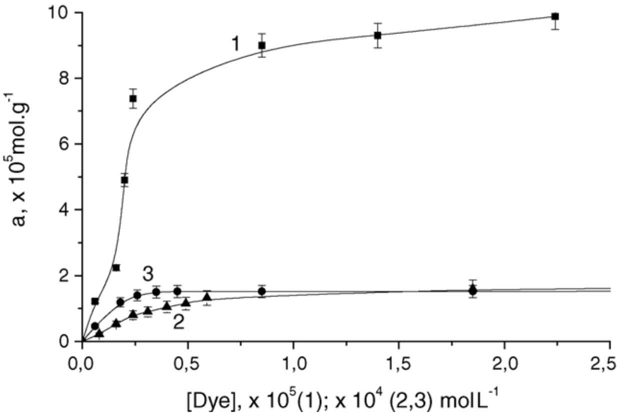

Fig. 2. Isotherms of LG adsorption onto SGII (curve 1) and SGI (curve 2), $a_{II} = 1 \times 10^{-4}$ mol $g^{-1}$; mass of the sorbent (g): 0.020 (SGII) and 0.002 (SGI), $V = 10$ mL.

methyl orange (MO) as monoanion formed with II immobilized on SG ion associate with the ratio MO:II = 1:1 [19]. To understand better the mechanism of LG immobilization onto SGI sorption of MO as a model compound was studied and compared. Isotherms of LG and MO adsorption at pH 5.0 are presented in Fig. 2 (curves 2 and 3). It is seen that maximum absorption capacity is 15.5 and 16.0 $\mu$mol $g^{-1}$ for LG and MO, respectively. It can be made a conclusion that LG as well as MO formed the same ion associate with immobilized QAS onto SGI surface.

### 3.2. *Aluminum interaction with immobilized LG*

Aluminum reacts with immobilized LG which is accompanied by the changes in spectroscopic characteristics of the sorbents (Fig. 1, curves 4 and 6). This fact testifies that immobilized LG retains its complex formation ability and grafting of LG on SGI and SGII surface may be a result of interaction between sulfuric group of the reagent and quaternary nitrogen of QAS. The optimal pH of complex formation on SGIII and SGIV is 5.0 compared to 5.5 in solution. The complex formed was not washed from the surface by water.

The heating of the mixture at $T = 343 \pm 3$ K for SGIV and $323 \pm 3$ K for SGIII thin film for 15 min accelerates the process of complex formation. The dependence of the coefficient of diffuse reflectance of SGIV and absorbance of SGIII film on the time of their contact with Al(III) solution are presented in Fig. 3. It is seen that equilibrium of sorption is reached within 15–20 min for both the sorbents. The optimal film thickness for SGIII composite film was $1.0 \pm 0.2$ $\mu$m. The time of the sorption equilibrium increased with increasing of the film thickness. Thinner films possessed less stability.

It can be seen that maximum of the spectra of the complex Al–LG formed on the surface is more red shifted compared to absorbance spectra of this complex in solution (Fig. 1). It may be a result of binding of LG with immobilized QAS. This effect is more noticeable for SGIV powder than for SGIII film.

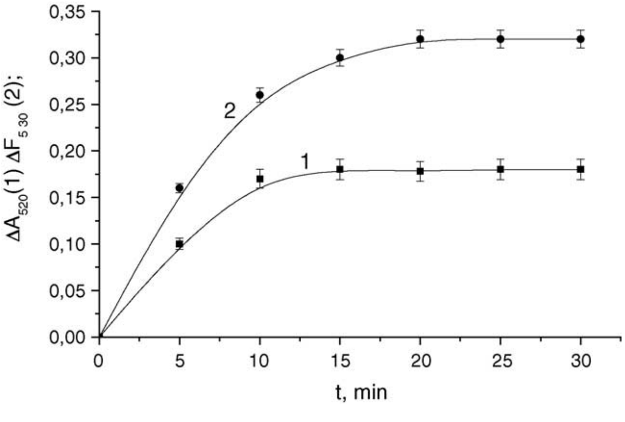

Fig. 3. The absorbance of SGIII (curve 1) and the coefficient of diffuse reflectance of SGIV (curve 2) as a function of time of the sorbents contact with Al(III) solution. $C_{Al} = 0.40$ mg $L^{-1}$; $T = 323$ K (curve 1) and 343 K (curve 2); pH 5.0.

### 3.3. *Interferences*

The influence of metal ions presented in natural water at the levels comparable with aluminum was investigated [27]. It was shown that Ca(II), Mg(II), Zn(II), $NO_3^-$, $SO_4^{2-}$, $HCO_3^-$ and $CH_3COO^-$ did not influence the results of Al(III) sorption–spectroscopic detection. Fe(III) and Cu(II) formed complexes with immobilized LG and, thus, interfered aluminum determination. Their influence can be removed by addition of 1,10-phenanthroline in solution. The comparable with Al(III) amounts of $F^-$ interfere determination.

### 3.4. *Sorption–spectroscopic determination of aluminum*

#### 3.4.1. *Diffuse reflectance spectroscopic method of aluminum determination in water using SGIV*

Water sample (10 mL) containing 0.08–1.5 mg $L^{-1}$of Al(III) was placed into 50 mL glass. It was acidified with HCl to pH 1.0. Then 5.0 mL of acetic buffer solution (pH 5.0), 1.0 mL of 0.2% 1,10-phenanthroline and 0.200 g of SGIV were added to solution. The resulting mixture was thermostated at $343 \pm 3$ K and stirred for 20 min. Then the sorbent was filtered through the porous filter, dried at $343 \pm 3$ K for 30 min and examined by diffuse reflectance spectroscopy. Sorbent which was treated by the same way after contact with bidistilled water adjusted to pH 5.0 was used as a blank. The concentration of Al(III) in the sample was detected using calibration graph obtained by the same procedure from standard solution of Al(III). The equation of calibration graph is: $\Delta F_{530} = (0.010 \pm 0.004) + (0.39 \pm 0.05)C$ (mg $L^{-1}$). The graph is linear in the range of 0.05–2.0 mg $L^{-1}$ Al(III). DL is 30 $\mu$g $L^{-1}$ for the sample volume 10 mL that is 1/8 of maximum contaminant level (MCL) of Al(III) in the tap water [27]. The DL can be decreased five times by increasing sample volume up to 50 mL.

#### 3.4.2. *Sorption–spectrophotometric method of Al(III) determination in natural water and alcohol-free beverage using SGIII*

The sample of the water (10 mL) containing 0.10–0.50 mg $L^{-1}$ of aluminum was acidified with HCl to pH 1.0. Then the solution was adjusted to pH 5.0 by 5 mL of acetic buffer and mixed with 1 mL of 0.2% 1,10-phenanthroline. The modified glass slide was placed into solution. The mixture was thermostated at $323 \pm 3$ K for 15 min. The glass was taken out and rinsed with water. The absorption of the film was measured at $\lambda = 520$ nm by spectrophotometer using a blank modified glass slide which was treated by the same way after contact with bidistilled water adjusted to pH 5.0. The amount of Al(III) was calculated using calibration graph prepared by the same procedure from standard Al(III) solution. The equation of calibration graph is: $\Delta A_{520} = (0.020 \pm 0.008) + (0.36 \pm 0.03)C$ (mg $L^{-1}$). It is linear in the range of Al(III) content 0.08–0.54 mg $L^{-1}$. DL is 70 $\mu$g $L^{-1}$ which is less than 1/3 MCL of this element in water [27].

Table 1
Results of aluminum determination in distilled water (1), model solution containing (mg $L^{-1}$): 1.0 Cu(II) and 0.5 Fe(III) and 1 mmol $L^{-1}$ of 1,10-phenanthroline (2), and in alcohol-free beverage (3) using SGIII (*A*) and SGIV (*B*) ($n = 4$; $P = 0.95$)

| Sample | *A*, Al(III) (mg $L^{-1}$) | | $s_r$ | *B*, Al(III) (mg $L^{-1}$) | | $s_r$ |
|---|---|---|---|---|---|---|
| | Added | Found ($x \pm \Delta x$) | | Added | Found ($x \pm \Delta x$) | |
| 1 | 0.30 | $0.30 \pm 0.03$ | 0.06 | 0.11 | $0.11 \pm 0.02$ | 0.09 |
| 1 | 0.19[a] | $0.18 \pm 0.02$ | 0.07 | 0.27 | $0.28 \pm 0.02$ | 0.05 |
| 2 | 0.19[a] | $0.20 \pm 0.03$ | 0.09 | 0.27[b] | $0.52 \pm 0.06$ | 0.07 |
| 2 | 0.30[b] | $0.47 \pm 0.05$ | 0.07 | 0.27 | $0.26 \pm 0.03$ | 0.07 |
| 2 | 0.30 | $0.28 \pm 0.03$ | 0.07 | 0.38 | $0.37 \pm 0.03$ | 0.04 |
| 3 | – | $0.07 \pm 0.02$ | 0.13 | – | – | – |
| 3 | 0.11 | $0.19 \pm 0.03$ | 0.08 | – | – | – |
| 3 | 0.19 | $0.25 \pm 0.03$ | 0.07 | – | – | – |

[a] The same silica film was used after regeneration with 0.05 M $EDTANa_2H_2$ for four times.
[b] The samples without addition of 1,10-phenanthroline.

*3.4.2.1. Determination of Al(III) in alcohol-free beverage.* Fifteen milliliters of the sample was acidified by HCl to pH 1.0 and heated for 10 min at 343 ± 3 K. Then the pH of solution was adjusted to pH 5.0 with 5 mL of acetic buffer, 1 mL of 0.2% 1,10-phenanthroline was added and procedure described above was applied. The accuracy of the developed spectrophotometric method using SGIII was controlled by standard addition of aluminum into alcohol-free beverages. For this purpose, known amount of standard solution of aluminum was added into the sample and procedure described above was applied. The error of determination did not exceed 9%.

The results of Al(III) sorption–spectroscopic determination using SGIII and SGIV are presented in Table 1. It is seen that data obtained for SGIV are characterized by some higher precision than those obtained for SGIII. But the determination of Al(III) using SGIII is more simple and express than one using SGIV. It does not need procedures of filtration and drying of the sorbent. The frequency of Al(III) detection using SGIII by batch procedure is 4 determinations/h. The developed method can be used only in solutions with low ionic strength (natural, tap but not sea water) because of partial removing of LG from the sorbent surface especially from SGIII in solution with high ionic strength.

The regeneration of the sorbents was attempted by soaking them into 0.1 M solutions of NaCl or HCl or 0.05 M $EDTANa_2H_2$. The best result was reached for $EDTANa_2H_2$ solution. Unfortunately, SGIV cannot be used repeatedly because of loosing its complex formation ability. Thin silica composite film can be used repeatedly for four times without signal degradation. The time needed for film regeneration is 10 min.

### *3.4.3. Sorption luminescent determination of Al(III)*

LG is known to be one of the best reagent for fluorimetric determination of Al(III) in solution [10–12]. Thus, luminescent properties of Al–LG complex on the surface were examined using pulse photo luminescent technique [23]. SGIV after its contact with Al(III) solution was characterized by higher luminescent intensity compared to SGIII. That is why further luminescent measurements were made using SGIV.

The pulse luminescent spectra of SGIV before and after contact with solution of Al(III) and spectra of the complex in solution with the molar ratio Al:LG = 1:1 are presented in Fig. 4. The similarity of the spectra in solution and on the surface testifies that the same complex prevails on SGIV surface under optimal conditions.

It is seen that immobilized LG possessed very low luminescence intensity compared to its complex with Al(III). This fact is important for reducing the signal of the blank. The intensity of the pulse peaks noticeable increased with increasing of Al(III) concentration in solution in the range of 0.1–2.0 mg $L^{-1}$. At higher Al(III) concentration, saturation of PL intensity was observed. The equation of calibration graph is: $I_{575} = (-60 \pm 9) + (2.18 \pm 0.08)C$ (μg $L^{-1}$).

The amount of aluminum(III) in the range of 10–130 μg $L^{-1}$ can be detected using integral luminescence intensity ($I_{\text{integral}}$) of the complex formed on SGIV surface. The equation of calibration graph for determination of aluminum in this range is: $I_{\text{integral}} = (18 \pm 5) + (2.07 \pm 0.06)C_{\text{Al}}$ (μg $L^{-1}$), DL is 8 μg $L^{-1}$ for the sample volume 10 mL. The sensitivity of the sorbent is enough for determination of this metal ion in the water samples.

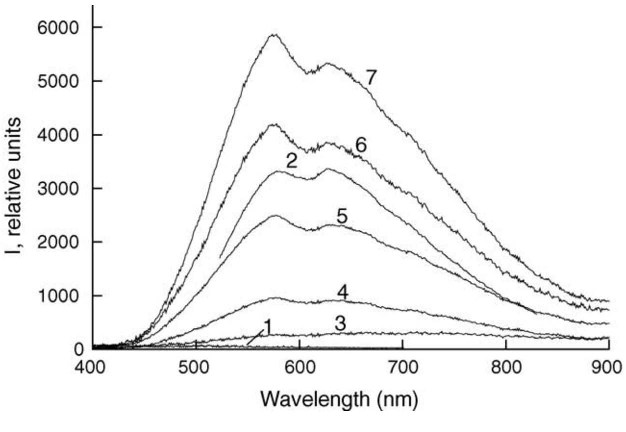

Fig. 4. Pulse luminescent spectra of LG (curve 1) and its complex with Al(III) (curve 2) in solution, PL (*I*, 10), and SGIV before (curve 3) and after (curves 4–7) its contact with solution of Al(III). Concentration of Al(III) ($10^{-5}$ mol $L^{-1}$): 1 (curve 2); 2 (curve 4); 4 (curve 5); 8 (curve 6); 20 (curve 7); $C_{LG} = 1 \times 10^{-5}$ mol $L^{-1}$; pH 5.5 (curves 1 and 2) and 5.0 (curves 3–7).

Table 2
Comparative characteristic of sorption–spectroscopic methods of aluminum determination

| *N* | Sorbent | Modifying agent | Method of detection | DL ($\mu$g L$^{--}$) (sample volume, mL) | Ref. |
|---|---|---|---|---|---|
| 1 | XAD resin | Eriochrome cyanine R | DRS | $\geq$270 | 5 |
| 2 | Silica-QAS (SGIV) | Lumogallion | DRS | 30 (10) | Proposed |
| 3 | Membrane filter | Al(III)–chrome azurol S and zephiramine | SS | 5 (20) | 2 |
| 4 | Dextran-type anion-exchangers | Al(III)–chrome azurol S | SS | 0.6 (500) | 3 |
| 5 | Dextran-type anion-exchangers | Al(III)–eriochrome cyanine R | SS | 0.02 (1000) | 4 |
| 6 | Silica-QAS (SGIII) thin film | Lumogallion | S | 70 (10) | Proposed |
| 7 | Dextran-type cation-exchange gel | Al(III)–salicyliden-*o*-aminophenol | SL | 0.2 (500) | 6 |
| 8 | Amberlite CG-400 | 8-Oxyquinoline sulfonate | SL | 27 | 7 |
| 9 | Cellulose powder or bio-membrane | Morin | SL | 27 | 8, 9 |
| 10 | Silica-QAS (SGIV) | Lumogallion | SPL | 8 (10) | Proposed |

Diffusion reflectance spectroscopy (DRS); spectrophotometric (S), sorption–spectrophotometric (SS), sorption–luminescent (SL), sorption pulse luminescent (SPL).

The comparisons of some chemical–analytical characteristics of the developed and known earlier methods of sorption–spectroscopic determination of aluminum are presented in Table 2. It is seen that proposed DRS method is 10 times more sensitive than the method using eriochrome cyanine R. Proposed luminescent method possesses similar sensitivity compared to developed earlier methods at equal sample volume. All developed methods do not need addition of the reagent into solution. Spectrophotometric method using SGIII is simple and has enough sensitivity for detection of Al(III) in water at its MCL [27].

## 4. Conclusion

Thus, obtained sorbents based on silica modified with QAS and LG (SGIII and SGIV) in comparison with other modified sorbents were demonstrated to be perspective analytical forms for sorption–spectrophotometric and sorption–luminescent determination of traces of Al(III) in water and alcohol-free beverage. SGIII can be regenerated four times and reused. Proposed methods are simple, express, sensitive and do not need addition of the reagent into reaction mixture which is important for the development of active element of optic sensor.

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