Solid-phase extraction of trace gallium(III) and indium(III) prior to their determination by diffuse reflectance spectroscopy

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A sensitive and selective method for the solid-phase extraction preconcentration and diffuse reflectance determination of Ga(III) and In(III) was developed. A new adsorbent based on dimethylchlorosilane aerosil impregnated with acetone or ethanol as a pseudomembrane for solid phase extraction of gallium(III) and indium(III) was proposed. The optimal pH value for Ga(III) and In(III) adsorption is 2.7 and 4.0, respectively. Xylenol orange forms (1:1) complexes with the ions of these metals on the surface. The calibration graphs for determining Ga(III) and In(III) by diffuse reflectance spectroscopy are linear in the concentration range $0.020 \div 5.5$ and $0.018 \div 5.2$ mg L^{-1}, respectively. The proposed method was successfully tested in determining Ga(III) and In(III) in water samples with RSD of not more than 3.7%.

Keywords: diffuse reflectance spectroscopy, gallium, indium, solid-phase extraction.

INTODUCTION

Gallium and indium are economically significant elements due to their widespread use in various industries. Gallium and its compounds are used to create components of electronics, optoelectronic materials, fusible alloys, as well as in medicine as anti-cancer and tumor-scanning agents [1, 2]. High-purity indium and its compounds are used to create semiconductor materials, liquid crystal displays and infrared photodetectors [1]. At the same time, the content of gallium and indium in the Earth's crust is low, and these elements are found in trace amounts in bauxite and some zinc ores [1]. It should also be noted that these elements can have a negative impact on human health and the environment. The compounds of Ga(III) and In(III) produce pulmonary toxicity, and In(III) compounds also induce nephrotoxicity and hepatotoxicity [3]. Thus, the determination of these elements is an important task from the standpoint of health and economy.

Various methods for determining gallium(III) and indium(III) have been proposed. For example, there are spectrophotometry and derivate spectrophotometry [4, 5], voltammetry [6], flame atomic absorption spectrometry (FAAS) [7-9], graphite furnace atomic absorption spectrometry (GFAAS) [10, 11] and inductively coupled plasma optical emission spectrometry (ICP-OES) [12].

Regardless of the method used to detect the analytical signal, preconcentration of the trace quantities of gallium(III) and indium(III) should precede their determination. For preconcentration of these elements are offered liquid-liquid extraction [13, 14], cloud-point extraction [7, 15] and ion exchange [16] techniques. A special place among preconcentration techniques takes solid phase extraction [9, 17, 18]. The most interesting adsorbents are functionalized silicas because they allow to effectively combine solid phase extraction, complexation with chromogenic reagents such as Xylenol orange [19-21], 4-(2-pyridylazo)-resorcinol or 1-(2-pyridylazo)-2-naphtol [22] and detection *via* diffuse reflectance spectroscopy.

In continuation of our previous studies [23-25] on the solid-phase extraction preconcentration of trace amounts of analytes on modified and unmodified silica and similar adsorbents, this manuscript is devoted to the development of a method for aluminium(III), gallium(III) and indium(III) separation. The current study is aimed at developing a solid-phase extraction procedure for separation and preconcentration of gallium(III) and indium(III) as neutral monomeric hydroxoforms using dimethylchlorosilane aerosil (DMClSA) impregnated with acetone or ethanol as a pseudomembrane prior to their determination by diffuse reflectance spectroscopy with Xylenol orange.

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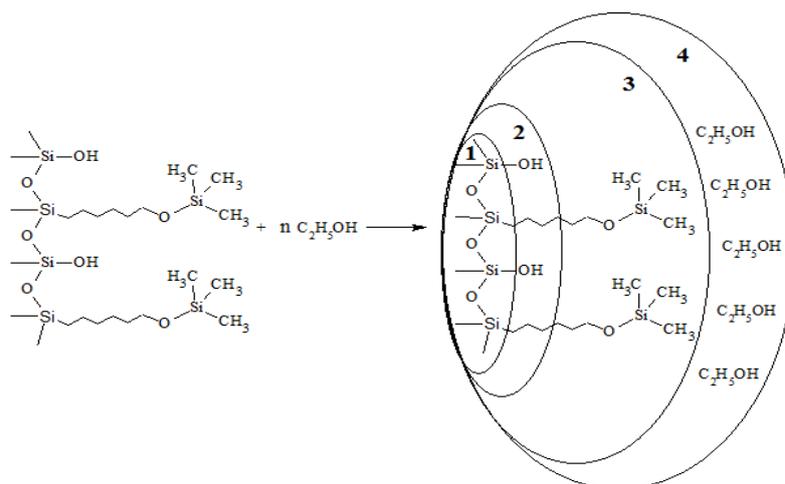
Fig. 1. The DMClSA-Solv surface: 1 - silica matrix; 2 - residual silanol groups; 3 - bonded fragments of dimethylchlorosilane; 4 - organic solvent (ethanol or acetone) impregnated due to hydrophobic interactions.

EXPERIMENTAL

Reagents. As an adsorbent, the dimethyl-chlorosilane aerosil (Ukraine) impregnated with acetone or ethanol as a pseudomembrane (DMClSA-Solv) was used. Based on our previous works [25], the surface of this sorbent is depicted in Fig. 1.

All solutions were prepared with double distilled water. A stock $1 \cdot 10^{-3}$ mol L^{-1} solution of Xylenol orange was prepared by dissolving an appropriate weight of the chromogenic reagent in water. A solution of Ga(III) and In(III) $1 \cdot 10^{-2}$ mol dm^{-3} was prepared by dissolving a sample of gallium(III) oxide and indium(III) oxide in concentrated nitric acid and dilution up to 100 mL with water. In standard solutions, the concentration of nitric acid is 1 mol dm^{-3}. Solutions with lower concentrations were prepared by appropriate dilutions. The reagents used in the work were not lower than analytical reagent grade.

Apparatus. Electronic absorption spectra and diffuse reflectance spectra were recorded on a spectrophotometer SF-56 (OKB "LOMO-Spectrum", Russia) in the wavelength range 380 ÷ 780 nm. The medium acidity was monitored by means of a glass electrode ESL-63-07 paired with a silver chloride reference electrode EVL-1M3 on an ionometer I-160 (ZIP, Belarus). Solid-phase extraction was studied in a static mode and mixing was performed with a shaker Elpan type 357 (Elpin+, Poland) with a frequency of 150 cycles min^{-1}. The Optima 2100 DV spectrometer (Perkin Elmer, USA) was used for ICP-OES determination of Ga(III) and In(III).

General procedure. Weights of 0.5 g of DMClSA were placed in 100 mL conical flasks and 6 mL of acetone (DMClSA-Ac) or 6 mL of ethanol (DMClSA-EtOH) was added to hydrophilize the surface of the silica matrix (to obtain a pseudomembrane on the surface). It should be noted that without solvent impregnation, the adsorbent is not wetted with water and is not suitable for the extraction of Ga(III) and In(III). 25 mL of the test solution containing Al(III), Ga(III), In(III) was added to 50-mL beakers, and pH was adjusted to 2.7 with 0.1 mol dm^{-3} sulfuric acid and 0.1 mol dm^{-3} sodium hydroxide solutions. The obtained solutions were quantitatively transferred to flasks with DMClSA-Ac and stirred for 60 min. The concentrate containing Ga(III) was separated from the solution by filtration through a blue ribbon filter. In the remaining solution containing Al(III) and In(III) the pH was adjusted to 4.0 and adsorption was carried out in static mode for 60 min by using DMClSA-EtOH as a sorbent. Concentrates were processed by 2 mL of 0.1% solution of Xylenol orange with pH 2.7 and 4.0, respectively, were air-dried, then diffuse reflection spectra were registered and the values of the Gurevich-Kubelka-Munk function ($\Delta F(R)$) were determined:

$$\Delta F(R) = \frac{(1-R)^2}{2R} = \frac{\varepsilon_\lambda C}{S}$$

where, R – diffuse reflectance; S – scattering coefficient; C – concentration; ε_λ – molar absorptivity.

The diffuse reflectance coefficient of the concentrates does not change at least during the day.

The proposed procedure was applied to the analysis of model solutions and water samples without any special treatment.

RESULTS AND DISCUSSION

To clarify the nature of the interactions of Ga(III) and In(III) with Xylenol orange on the surface of DMClSA-Solv a comparative analysis was made of the absorption spectra of aqueous Xylenol Orange solutions and of its Ga(III) and In(III) complexes with the diffuse reflection spectra of DMClSA-Solv impregnated by Xylenol orange and its complexes with the investigated elements (Fig. 2).
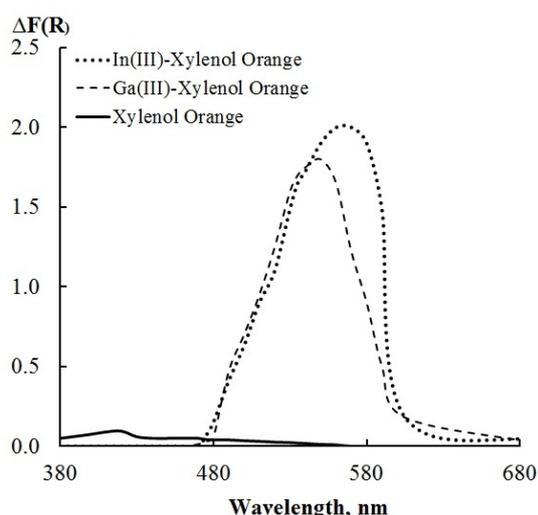

Fig. 2. Diffuse reflectance spectra of Xylenol orange and its complexes with Ga(III) and In(III) on the DMClSA-Solv surface.

As you can see on Fig. 2, the reflection maximum of Xylenol orange on the DMClSA-Solv surface is observed at 430 nm. It should be noted that Xylenol orange isn't practically sorbed by DMClSA-Solv because the reagent, unlike its Ga(III) and In(III) complexes, is not soluble in acetone and ethanol which form a pseudo-membrane on the surface of the sorbent. The formation of complexes of Xylenol orange with Ga(III) and In(III) on the silica surface is accompanied by a bathochromic shift of the main absorption band to 550 and 560 nm, respectively.

To optimize the conditions of Ga(III) and In(III) interaction with Xylenol orange on the surface of DMClSA-Solv the dependence of $\Delta F(R)$ on the solution pH, the volume and concentration of reagent was studied (Fig. 3a, b).

Fig. 3a shows that the pH of the medium in the range of pH 1-8 does not practically affect the value of the function of Gurevich-Kubelka-Munk sorbates of Xylenol orange, and the optimal acidity interval for interaction with Ga(III) is 2-4 and with In(III) 4-6. The obtained data on the complex formation of Xylenol orange with Ga(III) and In(III) in the solid phase are consistent with the data on the flow of these reactions in solutions. In [29] it is generalized that in aqueous solutions at pH ≈ 3 for Ga(III) and at pH ≈ 4 for In(III) red complexes are formed with Xylenol orange with a molar ratio M:R = 1:1 with maximal absorption at λ 550 and 560 nm, accordingly. The study of the influence of volume and concentration of reagent applied to concentrates Ga(III) and In(III), showed that for quantitative formation of a complex a two-fold excess of reagent is necessary (Fig. 3b). Therefore, in the further the concentrates were processed with 2.0 ml of 0.1% Xylenol orange solution with pH 2.7 and 4.0, respectively, for Ga(III) and In(III) because in these conditions the maximum values of the Gurevich-Kubelka-Munk function of the corresponding complexes on a surface of a solid phase were achieved (Fig. 3a, b).
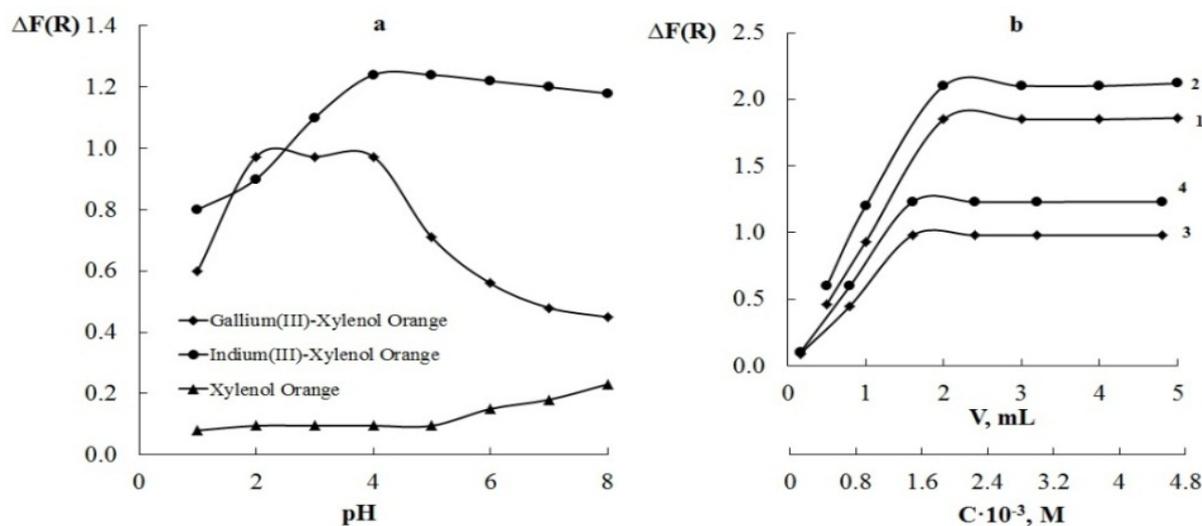
Fig. 3. Dependence of the Gurevich-Kubelka-Munk function on: **a** – acidity for Xylenol orange (λ = 430 nm) and its Ga(III) (560 nm) and In(III) complexes (λ = 550 nm) on the DMClSA-Solv surface; **b** – volume of 0.1% solution of chromogenic reagent (1, 2) and its concentration (3.4) for the complexes of Ga(III) (1, 3) and In(III) (2, 4), respectively.

Complex formation proceeds instantaneously and further increase of contact time of the concentrates with reagent does not noticeably change optical characteristics. The colored solid samples were air dried and diffuse reflection spectra were recorded using DMClSA-Solv passed through the entire course of analysis as a blank.

The composition of the complexes was established by the method of molar relations (Fig. 4).
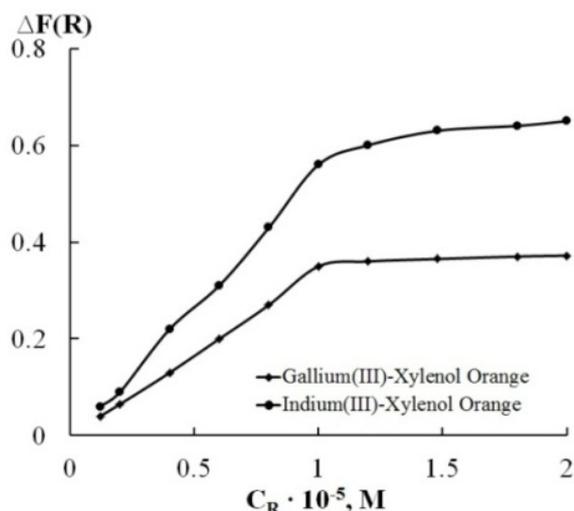

Fig. 4. Xylenol orange saturation curve for concentrates on the surface of DMClSA-Solv (Cm = $1 \cdot 10^{-5}$ mol L).

From Fig. 4 it is visible that on the DMClSA-Solv surface Xylenol orange forms complexes with Ga(III) and In(III) with a molar ratio of 1:1. Taking into account the condition of the chromogenic reagent and metal ions, it is possible to assume that the complex formation in the solid-phase system, as well as in the solution, is carried out due to substitution of hydrogen ions of carboxyl groups and coordination with nitrogen to formation of two cycles. The values of the molar absorptivity (ε_λ) of the Xylenol orange complexes with Ga(III) and In(III), which are equal to 34900 and 36400 L mol^{-1} cm^{-1}, respectively, and their stability constants ($6.0 \cdot 10^8$ and $1.0 \cdot 10^9$) were calculated by processing the saturation curve (Fig. 4) by the equilibrium shift method. It should be noted that the stability of the complexes on the surface of DMClSA-Solv increases in comparison with aqueous solutions ($2.0 \cdot 10^8$ and $1.7 \cdot 10^8$). The similar effect is observed for Xylenol orange complexes with Ga(III) and In(III) in aqueous-organic solutions [19].

Analytical figures of merit and interference study

The analytical signal dependence from Ga(III) and In(III) concentration was studied in the concentration range of 0.01÷10 mg L^{-1}. The maximum in the diffuse reflection spectra of fixed complexes does not depend on the metals concentration, and the F(R) function linearly increases with the increase of the initial Ga(III) and In(III) concentration of the investigated solutions. Calibration graphs $\Delta F(R) = f(C_0)$ are linear in a wide range of concentrations and are described by the equations given in Table. 1. It was established that the signals of Ga(III) and In(III) are not affected by a 100-fold excess of Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Sn (IV), Cu^{2+}, Mn^{2+}.

Table 1. Analytical figures of merit (n = 5; P = 0.95).

Analyte	Linear regression equation	pH	λ_{max}, nm	Linearity, mg L^{-1}
Ga(III)	y = 0.358x + 0.007 $R^2 = 0.997$	2.7	550	0.020÷5.5
In(III)	y = 0.395x + 0.017 $R^2 = 0.996$	4.0	560	0.018÷5.2

Table 2. Intra-day and inter-day accuracy and precision data for the proposed procedure for determination of Ga(III) and In(III) after solid-phase extraction preconcentration (n=5, P=0.95)

Spiked (µg L^{-1})	Intra-day					
	Found (µg L^{-1})		RSD(%)		R(%)	
	Ga(III)	In(III)	Ga(III)	In(III)	Ga(III)	In(III)
25	24.2±0.7	25.4±0.8	2.3	2.5	96.8	101.6
75	76.1±2.5	76.5±2.6	2.6	2.7	101.5	102.0
Spiked (µg L^{-1})	Inter-day					
	Found (µg L^{-1})		RSD(%)		R(%)	
	Ga(III)	In(III)	Ga(III)	In(III)	Ga(III)	In(III)
25	25.4±0.9	25.8±1.1	2.8	3.4	101.6	103.2
75	76.7±3.3	76.3±3.5	3.5	3.7	102.3	101.7

The influence of Bi^{3+} and Ti(IV), which are also adsorbed by DMClSA-Solv, can possibly be eliminated with the introduction of an additional stage of their adsorption removal from the solutions at pH = 1.0. The interfering effect of Fe^{3+} is eliminated by masking it with 1 cm^3 of 5% solution of NaF or with 1 cm^3 of freshly prepared 1% solutions of ascorbic or tartaric acid. The limits of detection (LOD), defined as $3s_a/b$, were 6.0 and 5.4 $\mu g\ L^{-1}$ for Ga(III) and In(III), respectively. The limits of quantification (LOQ, $10s_a/b$) for Ga(III) and In(III) were 20 $\mu g\ L^{-1}$ and 18 $\mu g\ L^{-1}$, respectively. The precision of the proposed method for the solid-phase extraction and diffuse reflectance spectroscopic determination technique were checked by performing 5 measurements at two concentration levels (25 and 75.0 $\mu g\ L^{-1}$) of Ga(III) and In(III) over two consecutive days and are summarized in Table 2.

Analytical application of the proposed technique

The proposed method was successfully applied to the determination of Ga(III) and In(III) in binary model solutions and water samples (Table 3).

Table 3. Determination of Ga(III) and In(III) trace quantities after their preconcentration by solid-phase extraction on DMClSA-Solv (n=5; P=0.95)

Sample		Spiked, mg L^{-1}	Found, mg L^{-1}	RSD, %	R, %	Found*, mg L^{-1}	RSD, %	R, %
Binary model solutions	Ga(III)	0.5 5.0	0.489±0.015 4.906±0.073	2.4 1.2	97.8 98.1	0.511±0.02 4.956±0.23	3.6 3.7	102.2 99.1
	In(III)	0.5 5.0	0.483±0.019 4.864±0.181	3.1 3.0	96.6 97.3	0.498±0.02 5.016±0.24	3.5 3.9	99.6 100.3
Water sample**	Ga(III)	- 0.5	0.852±0.024 1.353±0.045	2.3 2.7	- 100.2	0.891±0.04 1.375±0.06	3.4 3.7	- 96.8
	In(III)	- 0.5	0.231±0.009 0.728±0.032	3.3 3.5	- 99.4	0.254±0.01 0.749±0.04	3.6 3.8	- 99.0

RSD – relative standard deviation, %; R – recovery, %. * determined by ICP-OES according to ISO 11885:2007.
** circulating water in Bayer process which contains the following ions: Bi^{3+}, Ti^{4+}, Fe^{3+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Sn^{4+}, Cu^{2+}, Mn^{2+}

Table 4. Comparison with some literature studies

Analyte	Separation method	Detection technique	LOD, $\mu g\ L^{-1}$	Ref.
Ga	Amberlite XAD-4/5-phenylazo-8-quinolinol	XRF	81.0	26
	Polyurethane foam	FAAS	6.00	27
	Amberlite XAD-2/1-(2-pyridylazo)-2-naphthol	GFAAS	2.1	28
	Amberlite XAD-4/HMPN	FAAS	3.42	29
	Amberlite XAD-4/BTAHN	SF	3.1	30
In	Naphthalene/1-(2-pyridylazo)-2-naphtol	Differential pulse polarography	200	31
	Naphthalene/morpholine-4-dithiocarbamate	Differential pulse polarography	100	32
Ga; In	CPE using Gallic acid as chelating agent and Triton X-144 as surfactant	FAAS	3.50; 1.25	7
	Sorption on amino silica gel modified by gallic acid	FAAS	5.80; 1.82	9
	Solid phase extraction using DAPCH loaded on Duolite C20 as a sorbent	FAAS	30; 13	33
	Amino silica modified with HBAAS	FAAS	4.10; 1.55	17
Ga	Dimethylchlorosilane aerosil impregnated with acetone or ethanol / Xylenol orange	Diffuse reflectance spectroscopy	6.0	This work
In	Dimethylchlorosilane aerosil impregnated with acetone or ethanol / Xylenol orange	Diffuse reflectance spectroscopy	5.4	This work

XRF – X-ray fluorescence spectroscopy; FAAS – flame atomic absorption spectroscopy; GFAAS – graphite furnace atomic absorption spectroscopy; SF – spectrophotometry; HMPN – 1{[(6-{[(E)-1-(2-hydroxy-1-naphthyl)methylidene]amino}-2-pyridyl)imino]methyl}-2-naphthol; BTAHN – 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid; DAPCH – 1-(3,4-dihydroxybenzaldehyde)-2-acetylpyridiniumchloride hydrazone; HBAAS – 2-hydroxy-5-(2-hydroxybenzylideneamino)benzoic acid.

High recoveries (96.6-100.2 %) indicated that the proposed method was accurate, reliable and can be used for the preconcentration and determination of Ga(III) and In(III) traces *via* diffuse reflectance spectroscopy. The similarity of the results obtained by an alternative method also indicates the correctness of the proposed technique for Ga(III) and In(III) preconcentration and quantification.

Comparison of the present method with some other reported methods

A comparison of the proposed method with some analytical procedures for Ga(III) and In(III) determination, reported in the literature, is shown in Table 4. By comparing the data in Table 4, it is obvious that the sensitivity of the proposed technique is comparable with that of other spectrophotometric methods for the determination of Ga(III) and In(III).

CONCLUSION

This study presents a new adsorbent based on dimethylchlorosilane aerosil impregnated with acetone or ethanol as a pseudomembrane for solid phase extraction of gallium(III) and indium(III) and their determination by diffuse reflectance spectroscopy with Xylenol orange. The proposed method is simple, precise and accurate. The detection and quantification limits were 6.0 and 5.4 $\mu g\ L^{-1}$; 20 and 18 $\mu g\ L^{-1}$ for Ga(III) and In(III), respectively. The developed method was successfully applied to the trace level determination of gallium(III) and indium(III) in water samples.

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